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Photochemical Nucleophile-Olefin, Combination Aromatic Substitution (Photo-NOCAS) Reaction: Methanol, Dienes, 1,4-Dicyanobenzene

by

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Submitted in partial fulfilment of the requirements
for the degree of Doctor of Philosophy

at

Dalhousie University
Halifax, Nova Scotia
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This thesis is dedicated to my mom and dad, and my gram and gramp
for all their love and encouragement.

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List of Abbreviations

A	electron acceptor
a	encounter distance
anal. calcd.	analysis calculated
Ar	4-cyanophenyl, unless otherwise noted
CIP	contact radical ion pair
Chrom W	chromasorb white
CTC	charge-transfer complex
D	electron donor
d	doublet
δ	dimensionless (nmr) scale
dc/fc	dry column/flash chromatography
dd	doublet of doublets
DEPT	distortionless enhanced polarization transfer
E	electrophile
e_o	elementary charge, 1.602×10^{-19} C
ϵ	dielectric constant
ϵ_o	permittivity of vacuum, 8.854×10^{-12} $C^2 \cdot N^{-1} \cdot m^{-2}$
$E_{0,0}$	electronic excitation energy
$E_{1/2}^{ox}$	oxidation potential of electron donor
$E_{1/2}^{red}$	reduction potential of electron acceptor
EA	electron affinity

esr	electron spin resonance
FFAP	free fatty acid phase
FRI	free radical ions
gc/fid	gas chromatography/flame ionization detector
gc/ms	gas chromatography/mass selective detector
HOMO	highest occupied molecular orbital
IP	ionization potential
ir	infrared spectrum
k	proportionality coefficient, $8.99 \times 10^9 \ \mathrm{N \cdot m^2 \cdot C^{-2}}$
LUMO	lowest occupied molecular orbital
m	multiplet
MM2	molecular mechanics program, second version
mplc	medium pressure liquid chromatography
m/z	mass-to-charge ratio
N	nucleophile
nmr	nuclear magnetic resonance
NOE	nuclear Overhauser enhancement
o	*ortho*
P	product
p	*para*
Ph	phenyl
photo-NOCAS	photochemical nucleophile-olefin, combination aromatic substitution

prep/gc	preparative/gas chromatography
Q	quencher
q	quartet
t	tert
t	triplet
tlc	thin layer chromatography
s	singlet
SCE	saturated calomel electrode
SE-30	100% methyl silicone gum
SSIP	solvent separated radical ion pair
uv(vis)	ultraviolet and visible spectrum
WCOT	wall coated open tubular

All other abbreviations are standard.

Abstract

Previous studies of the photo-NOCAS (photochemical nucleophile-olefin, combination aromatic substitution) reaction have focused upon monoalkenes, including prospective ring-opening alkenes. In this thesis, the study has been extended to conjugated dienes and unconjugated dienes (and their potential to undergo ring closure).

The unconjugated dienes studied were 1,5-hexadiene (**12**), 2-methyl-1,5-hexadiene (**13**) and 2,5-dimethyl-1,5-hexadiene (**14**). These dienes were irradiated in the presence of 1,4-dicyanobenzene in acetonitrile-methanol (3:1) solution. The three dienes behaved quite differently. Diene **12** gave cycloaddition to 1,4-dicyanobenzene and dienes **13** and **14** each gave normal acyclic photo-NOCAS products. Addition of the co-donor, biphenyl (**9**), to the irradiation mixture was found to increase the efficiency of the photo-NOCAS reaction for the latter two dienes. Only for the case of 2,5-dimethyl-1,5-hexadiene with biphenyl present were cyclized products observed. Both *cis*- and *trans*-4-(4-cyanophenyl)-1-methoxy-1,4-dimethylcyclohexane (**23** and **24**) were formed. The mechanism and limitations of the reaction are discussed.

The conjugated dienes studied were 1,3-butadiene (**37**), 2-methyl-1,3-butadiene (**38**), 2,3-dimethyl-1,3-butadiene (**39**) and 2,5-dimethyl-2,4-hexadiene (**36**). Dienes **37**, **38** and **39** were irradiated in the presence of 1,4-dicyanobenzene and biphenyl in acetonitrile-methanol (3:1) solution. Both 1,2- and 1,4-addition products were formed in an approximate equimolar ratio (total yields range from 50-60%). However, irradiation of 2,5-dimethyl-2,4-hexadiene, **1** and **9** in acetonitrile-methanol (3:1) solution yielded 86% 1,4-addition products; *trans*-2-(4-cyanophenyl)-5-methoxy-2,5-dimethyl-3-hexene (**35**,82%) and *trans*-2-(4-cyanophenyl)-2,2,5-trimethyl-3-hexenenitrile (**40**,4%). Irradiation of an acetonitrile solution containing **36** and **1** yielded 94% **40**. The mechanism of this reaction is discussed. Also, a probable explanation of the regio- and stereoselectivity of the photo-NOCAS reaction involving these conjugated dienes is given.

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General Introduction

One of the fundamental processes in chemistry is the transfer of an electron between two molecules. This process has been extensively studied in organic chemistry in general and more specifically, in organic photochemistry (1,2). When electron transfer occurs between two neutral species, bonds are neither formed nor broken, instead the new species formed are referred to as a radical cation and a radical anion. A radical cation is defined as a molecule that results from the removal of an electron from a neutral species; a radical anion is a molecule that results from the addition of an electron to a neutral species. The ease of formation of a radical cation or anion is dependent upon a molecule's ionization potential (IP) or electron affinity (EA) in the gas phase, or equivalently by its oxidation or reduction potential in solution. The lower the IP or oxidation potential, the more easily an electron is released; on the other hand, the higher the EA or reduction potential, the more easily an electron is accepted.

To identify a molecule that has a low IP or favorable oxidation potential, the highest occupied molecular orbital (HOMO) has to be examined. Electrons in low energy orbitals, such as those in sigma-bonds, are not as easily removed as those in higher energy orbitals such as pi-bonds or on heteroatoms with unshared pairs of electrons (3). To identify a molecule that has a high EA or favorable reduction potential, the lowest unoccupied molecular orbitals (LUMO) have to be examined. A LUMO of lower energy yields a higher EA; for instance, aromatic molecules with electron-donating groups have a higher energy LUMO than those aromatics with electron-withdrawing groups and thus, their affinity for electrons is lower (2).

The radical ions mentioned above can be produced in a variety of ways. Examples include the use of oxidants (3), such as concentrated sulfuric acid (4), Lewis acids (5) and halogens (6) (Scheme 1).

Concentrated Sulfuric Acid

$$\mathrm{ArH} + \mathrm{H_2SO_4} \rightleftarrows \mathrm{ArH_2^{+}} + \mathrm{HSO_4^{-}}$$

$$\mathrm{ArH} + \mathrm{ArH_2^{+}} \rightleftarrows \mathrm{ArH_2^{\bullet}} + \mathrm{ArH^{\bullet +}}$$

$$\underline{\mathrm{ArH_2^{\bullet}} + 2\mathrm{H_2SO_4} \quad \rightleftarrows \quad \mathrm{ArH^{\bullet +}} + 2\mathrm{H_2O} + \mathrm{HSO_4^{-}} + \mathrm{SO_2}}$$

$$2\mathrm{ArH} + 3\mathrm{H_2SO_4} \longrightarrow 2\mathrm{ArH^{\bullet +}} + 2\mathrm{H_2O} + \mathrm{SO_2} + 2\mathrm{HSO_4^{-}}$$

Lewis Acids

$$\mathrm{ArH} + \mathrm{SbCl_5} \longrightarrow \mathrm{ArH^{\bullet +}} + \mathrm{SbCl_5^{\bullet -}}$$

Halogens

$$2\mathrm{Ar_3N} + 3\mathrm{Br_2} \longrightarrow 2\mathrm{Ar_3N^{\bullet +}Br_3^{-}}$$

Scheme 1. Radical ions can be produced using a variety of oxidants.

Radical ions can also be formed electrochemically (7a) or by mass spectrometry (7b). More relevant to this work is the formation of radical ions via photoinduced electron transfer. This process involves both an electron-donor (D) (also referred to as a reducing agent) and an electron-acceptor (A) (also referred to as an oxidizing agent).

Photoinduced electron transfer has an advantage over other types of electron transfer. Photochemical excitation changes the oxidation and reduction potentials (in the gas phase: IP and EA) of the donor and acceptor, respectively (8-10), to facilitate electron transfer. If the donor is selectively excited, the electron is promoted to a higher energy orbital. As mentioned previously, the properties required for a lower IP and a favorable oxidation potential are HOMOs of high energy. Consequently, if one compares the ground state HOMO to the excited state HOMO, the excited state HOMO will give up an electron much more easily. If the acceptor is selectively excited, an electron is promoted to a higher energy orbital. As a result, there is a "hole" in the lower energy orbital (8) that accepts electrons much more easily than the vacant, higher energy orbital, of the ground state. Thus, a higher EA and more favorable reduction potential results from excitation. The effect of excitation on the IP and EA is shown in Figure 1; the effect of excitation on the oxidation and reduction potentials is shown in Figure 2.

The effect of excitation upon electron transfer has been described; now the pertinent effects of solvent upon electron transfer will be discussed. Electron transfer is much less complicated in the gas phase than in solution. In solution there are

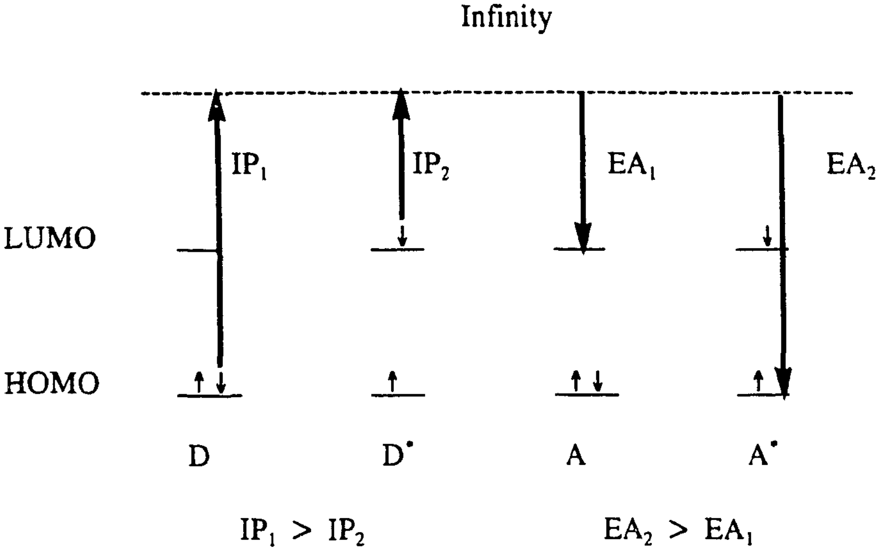


Figure 1. The effect of excitation upon IP and EA.

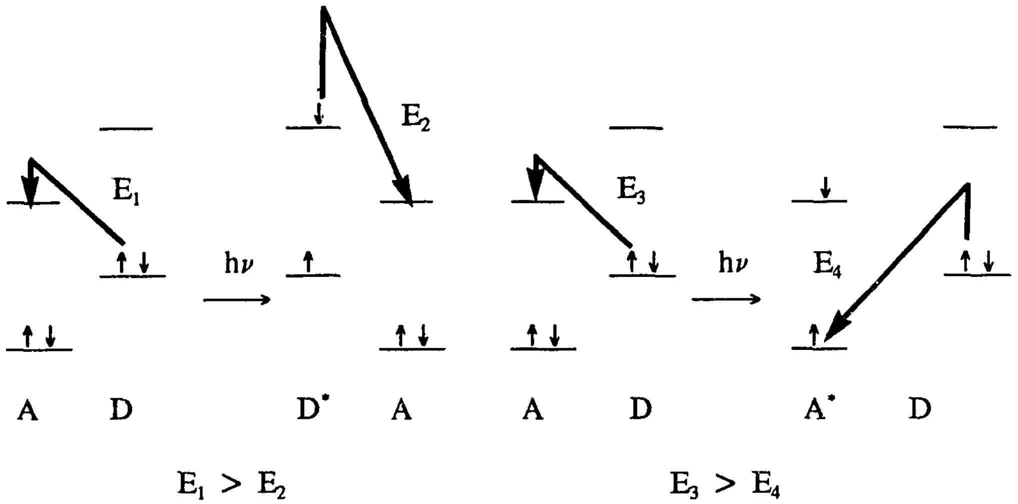


Figure 2. The effect of excitation upon oxidation and reduction potentials.

different degrees of solvation and dissociation of radical ions (11). Specifically, three major types of solvated radical ion pairs have been postulated (12). There are: contact radical ion pairs (CIP), solvent separated radical ion pairs (SSIP) and free solvated radical ions (FRI). The CIP is defined as a pair of radical ions, opposite in sign, in direct contact with one another and surrounded by solvent molecules (11). The SSIP is defined as a pair of radical ions opposite in sign, not in direct contact with one another and each radical ion is surrounded by solvent molecules (11). A pictorial representation is shown in Figure 3.

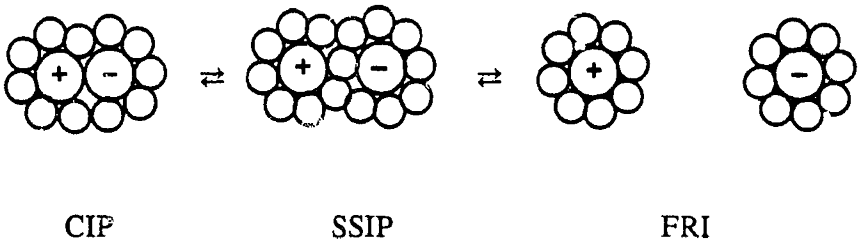
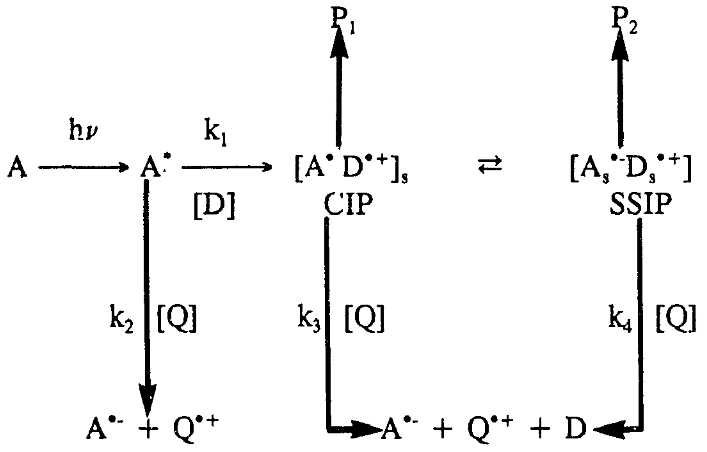


Figure 3. A representation of a CIP, SSIP, and FRI.

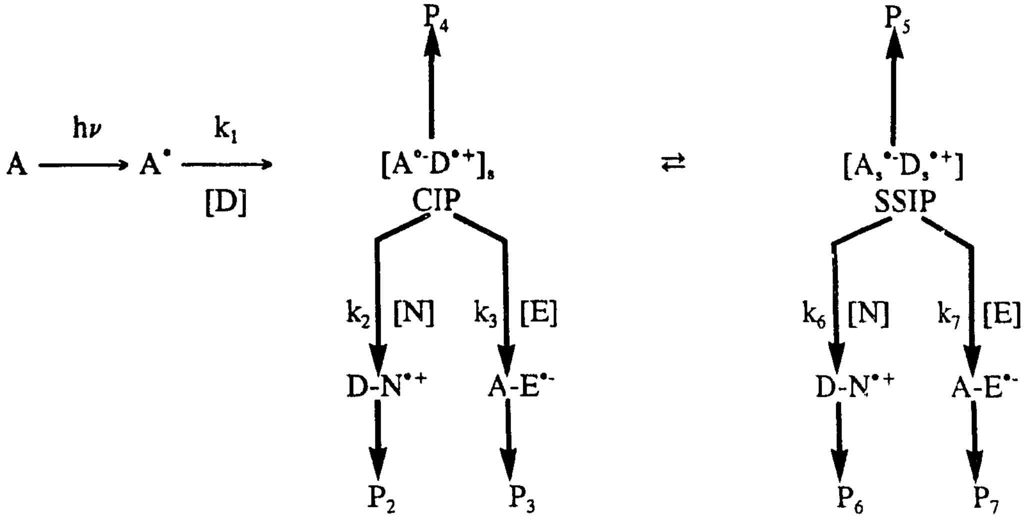
To prove the presence of these types of solvated radical ion pairs, a variety of spectroscopic evidence was used. In the beginning, identification of radical ion pairs was obtained by esr (13) but later other techniques, such as uv(vis) (14), ir (15) and nmr (16), were also used. More recently, nanosecond (17) and picosecond (18) flash photolysis have provided uv spectra of these short-lived radical ion species.

There are ways of obtaining evidence of radical ion pairs other than spectroscopically. If the idea is accepted that each type of CIP and SSIP should have different reactivities due to unequal solvation and dissociation of the radical ions, then scavengers such as electron transfer quenchers, nucleophiles and electrophiles should distinguish between the different types of species of radical ion pairs (11). A generalized example using a quencher is shown in Scheme 2.



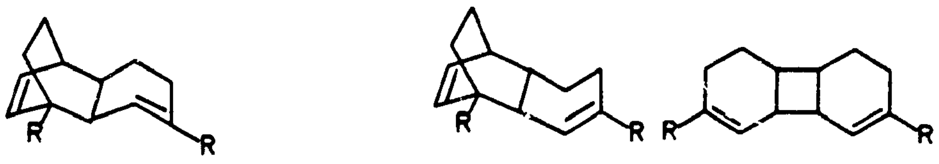
Scheme 2. A-electron acceptor, D-electron donor, Q-quencher, and P-products.

Scavenging by nucleophiles and electrophiles may also distinguish between the different types of CIP and SSIP (Scheme 3). The attack of nucleophiles and electrophiles should depend on the extent of solvation of the radical ion pairs.



Scheme 3. A-electron acceptor, D-electron donor, N-nucleophile, E-electrophile and P-products.

To illustrate this indirect way of proving the presence of different types of radical ion pairs, an example by Mattay *et al.* (19) is shown on the dimerization of 1,3-cyclohexadiene derivatives. Two products were observed (Figure 4). One was an *endo*-and the other was an *exo*-Diels-Alder adduct (also present was a cyclobutane adduct).



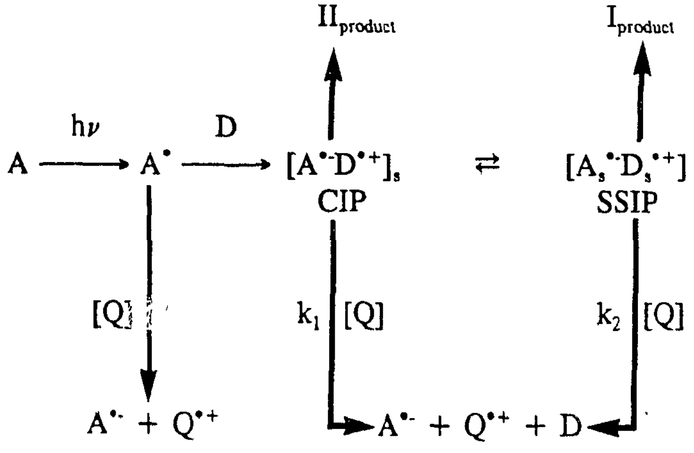
I

II

Figure 4. *Endo*- and *exo*-Diels-Alder adducts.

Using an electron transfer quencher, 1,2,4-trimethoxybenzene, and a nucleophilic scavenger, ethanol, quenching experiments were performed. 1,2,4-Trimethoxybenzene almost totally quenched formation of product I and showed some quenching of products II.

These experiments distinguished between the pathways for formation of products I and II since the electron transfer quencher will selectively quench SSIP (or FRI) over the CIP. This assumption is based on the extent of charge transfer within the radical ion pair. In the CIP, there is less electron transfer than in the SSIP (or FRI); thus, the electron transfer quencher reacts preferentially with the SSIP (or FRI) because oxidation of the donor is more favorable. Since the formation of product I was quenched more than that of products II, it was concluded that product I came from the SSIP (or FRI) and products II from the CIP (refer to Scheme 4).



$k_1 < k_2$

Scheme 4. A-electron acceptor, D-electron donor, Q-quencher and P-products.

Thus, evidence can be obtained for the various types of intermediate radical ion pairs without directly observing them spectroscopically.

Previously, definitions for CIP and SSIP were given. These definitions were not very specific due to the fact that there are several species that can fall under the category of each of these general types of radical ion pairs. For instance, other nomenclature has been used to be more specific about certain types of CIP. Weller (20) uses the term CIP when describing an exciplex and less specifically, refers to a SSIP as a radical ion pair. An excited charge-transfer complex can also fall under the category of CIP.

What is a charge-transfer complex (CTC) and an exciplex, and what is the difference between the two? A ground state CTC can be described using the following wavefunction (21) (Equation [1]):

[1] $$\Psi = a(D,A) + b(D^{\bullet +},A^{\bullet -})$$

where (D,A) is the electronic configuration of a non-bonding contributor and $(D^{\bullet +},A^{\bullet -})$ is a complete charge-transfer electronic configuration. A ground state CTC has the coefficient 'b' less than 'a', but in the excited state CTC, the coefficient 'a' is less than 'b'. Some of the first physical evidence for a CTC was provided by Mulliken (22). He observed uv(vis) absorption spectra unlike those of either the donor or acceptor (Reaction 2).

[2] $$D + A \overset{K}{\rightleftarrows} [D,A \leftrightarrow D^{\bullet +},A^{\bullet -}]^{CTC} \xrightarrow{h\nu} [D^{\bullet +},A^{\bullet -} \leftrightarrow D,A]^{*CTC}$$

Further experimentation with CTCs led Kainer, Isenberg and Eastman (23) to investigate the effect of solvent upon CTCs. They noted that varying degrees of electron transfer occurred depending upon the dielectric constant of the medium. For instance, when a solvent of low dielectric constant was used, CTCs existed; in solvents of high dielectric constant, CTCs were non-existent because complete electron transfer had occurred (the radical cation and anion were both detected by esr and uv absorption).

An exciplex can be simply described by using the following wavefunction (Equation [3]):

[3] $$\Psi^{*} = a(D^{*},A) + b(D^{\bullet +},A^{\bullet -}) \quad \text{or} \quad \Psi^{*} = a(D,A^{*}) + b(D^{\bullet +},A^{\bullet -})$$

where (D^{*},A) or (D,A^{*}) is an electronic configuration of a non-bonded excited state of a donor (acceptor) and an acceptor (donor), and $(D^{\bullet +},A^{\bullet -})$ a complete charge-transfer electronic configuration. The coefficients that describe an exciplex have 'b' greater than 'a' (24). The species initially discovered were termed excimers not exciplexes. An excited complex which is formed from a ground state molecule and an excited state molecule of the same species is referred to as an excimer. This type of complex formed from two different molecules is referred to as an exciplex. The excimer was first identified by Förster and Kasper (25). Using pyrene, they observed the fluorescence spectrum of pyrene decrease with increased pyrene concentration; moreover, they observed a new fluorescence emission at a longer wavelength than the pyrene monomer fluorescence band. Eight years later, Hochstrasser (26), as well as Leonhardt and Weller (27), observed the first exciplexes. Hochstrasser observed one with perylene-pyrene and Leonhardt and Weller observed one with perylene-N,N-dimethylaniline.

Both excited CTCs and exciplexes are known to fluoresce at longer wavelengths than either component molecule. This shift to longer wavelengths has been justified by postulating that these complexes are stabilized by some charge-transfer interaction (shown in Equations [1] and [3]). IP (oxidation potential) of donors, EA (reduction potential) of acceptors and polarity of solvents have been some of the factors used in supporting this postulate. For instance, a correlation between the emission maximum of an exciplex and the reduction potential of an acceptor was found by Weller and co-workers (28). They observed that the more easily the acceptor is reduced, the more stable is the exciplex (fluorescence shifts to longer wavelengths) and from this they concluded that charge-transfer was important for the existence of an exciplex. Also, CTCs will not form unless very good oxidizing and reducing agents are used such that partial ground state electron transfer can occur. Polarity of the solvent, as mentioned before when discussing the definition of a CTC, is very important in stabilizing the complex. For instance, as the polarity of the solvent is increased the CTC becomes more stable (absorption shifts to longer wavelength); of course, further polarity increase will cause complete electron transfer and thus, loss of the CTC. This effect holds true for exciplexes as well (29,30).

Following the above definitions of an exciplex and a CTC, one can conclude that photoinduced electron transfer can proceed via two main pathways:

1) A charge-transfer complex. Photoinduced electron transfer can occur by two

molecules undergoing partial charge-transfer in the ground state. The complex then absorbs a photon and becomes an excited state CTC (with charge-transfer being the greater contributor to the complex).

2) An exciplex. Photoinduced electron transfer can occur when an acceptor (donor) absorbs a photon and then complexes with a ground state donor (acceptor) molecule. This complex becomes stabilized by some charge-transfer interaction.

These pathways are outlined in Scheme 5:

$$(1)\quad A + D \overset{K}{\rightleftarrows} [A,D \leftrightarrow A^{\bullet -},D^{\bullet +}]^{CTC} \xrightarrow{h\nu} [A^{\bullet -},D^{\bullet +} \leftrightarrow A,D]^{*CTC} \longrightarrow A^{\bullet -}D^{\bullet +} \longrightarrow \text{Products}$$

$$(2)\quad A\ (D) \xrightarrow{h\nu} A^{*}\ (D^{*}) + D\ (A) \longrightarrow [A,D]^{*}_{\text{exciplex}} \longrightarrow A^{\bullet -}D^{\bullet +} \longrightarrow \text{Products}$$

Scheme 5. Pathways to formation of radical ions.

The potential for photoinduced electron transfer depends upon various conditions. In the gas phase (8), electron transfer depends upon the IP and EA of the donor and acceptor, respectively. Knowing the definitions of IP (energy required to remove an electron from a molecule) and EA (energy released on adding an electron to a molecule), the energy for ground state electron transfer between an acceptor and a donor can be written as:

[4] $\Delta E = IP - EA$

When photoinduced electron transfer occurs in the gas phase, the zero-zero electronic energy of an excited state, $E_{0,0}$, must be taken into account. If the donor absorbs a photon, the IP can be written as:

[5] $IP^{*} = IP - E_{0,0}$

The rationale for the above equation is illustrated in Figure 5.

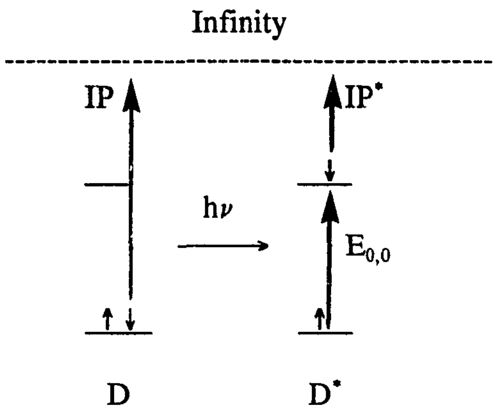


Figure 5. $IP^{*} = IP - E_{0,0}$

If the acceptor absorbs a photon, the EA can be written as:

[6] $EA^{*} = EA + E_{0,0}$

The rationale for the above equation is illustrated in Figure 6.

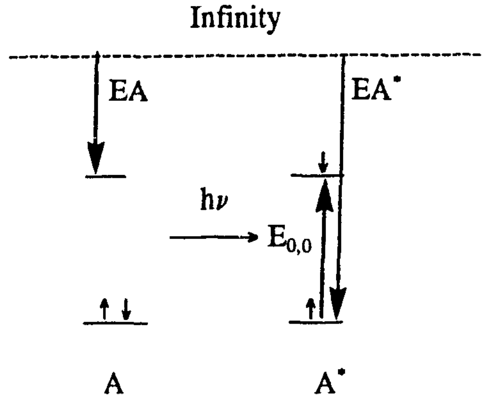


Figure 6. $EA^{*} = EA + E_{0,0}$

The overall energy involved when photoinduced electron transfer occurs between a donor and an acceptor is:

[7] $\Delta E = IP - EA - E_{0,0}$

This equation is applicable for excitation of either the donor or the acceptor.

[8] $\Delta E = IP^{*} - EA = IP - EA^{*}$

Equation 4 cannot be directly applied to photoinduced electron transfer in solution because it does not take into account solvent and coulombic interactions. The energy of production of radical ions via photoinduced electron transfer in solution can be predicted by the Rehm-Weller equation (31), Equation [9].

[9] $\Delta G = 96.47\,(E_{1/2}^{ox} - E_{1/2}^{red} - ke_o/\epsilon a) - E_{0,0}$ (kJ/mol)

$E_{1/2}^{ox}$: Oxidation potential of the electron donor.

$E_{1/2}^{red}$: Reduction potential of the electron acceptor.

$e_o/\epsilon a$: The free energy gained by bringing the two radical ions to encounter distance "a" in a solvent of dielectric constant ϵ (i.e. Coulombic attraction term).

$E_{0,0}$: Electronic excitation energy.

k : Proportionality coefficient in the Coulomb equation ($k = 1/4\epsilon_0\pi = 8.99 \times 10^9\ N \cdot m^2 \cdot C^{-2}$).

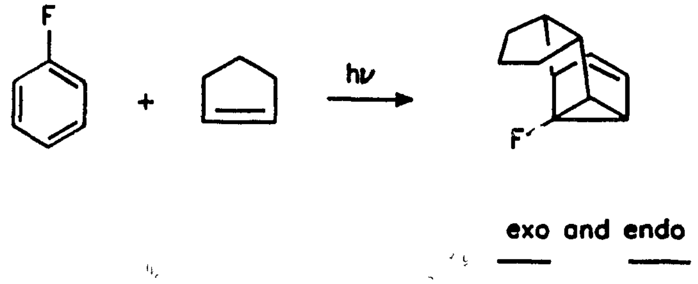
The Rehm-Weller equation takes into account the energy required in kJ/mol for electron transfer which is equivalent to 96.47 ($E_{1/2}^{ox} - E_{1/2}^{red}$) if the potentials are in volts. From this term is subtracted the energy that is available from the system : $E_{0,0}$ and the Coulombic attraction term. Consequently, photoinduced electron transfer in solution is influenced by the electronic properties of the substrates; the more easily the donor is oxidized and the more easily the acceptor is reduced, the more thermodynamically favored is electron transfer. Previously, it was mentioned that the polarity of the solvent had an effect on the extent of electron transfer that occurs. Polar solvents facilitate the formation of radical ions, whereas lower polarity may cause a decrease in the yield of radical ions and an increase in the efficiency of back electron transfer to yield the substrates in the ground state (1,9). In conclusion, the electronic properties of the substrates and the solvent effect can direct the photoinduced electron transfer reaction to be either thermodynamically favorable (ΔG negative, exergonic) or not (ΔG positive, endergonic).

The Rehm-Weller results demonstrated that the rate constant of photoinduced electron transfer was a function of the free energy (32). The rate constant for electron transfer proceeds at the diffusion-controlled rate if ΔG is less than -17 kJ/mol (-4 kcal/mol) and becomes slower when ΔG > 0 kJ/mol, perhaps requiring an activation energy. As the free energy for forward electron transfer becomes less exergonic, theory predicts the rate for back electron transfer will fall in the Marcus inverted region (32,33) (less exergonic, more energy stored in radical ion pair) and the rate constant of back electron transfer will revert to a lower value. When the free energy change for forward electron transfer is greater than zero, forward electron transfer becomes less important. However, exciplex formation may still be involved (1). In these cases, the reactions that usually occur between donors and acceptors of unsaturated systems yield cycloaddition products (1).

After electron transfer has taken place, there are basically two processes that can occur: the electron can be transferred back or the radical ions can undergo chemical reactions. Thus, back electron transfer is an important deactivating pathway for chemical reactions that occur via photoinduced electron transfer.

To compete with deactivating back electron transfer, other processes must be rapid. For instance, unsaturated systems may undergo cycloadditions to yield products (9,34) (Reaction [10]).

[10]



Other reactions include trapping of the radical cation by nucleophilic solvents (35,36) or by salt formation (special salt effect: the cation of an added salt may combine with the radical anion to form a complex which prevents back electron transfer (1); Reaction [11]).

[11] $$(A_s^{\bullet -}D_s^{\bullet +}) + Li_s^{+} \rightleftarrows (A^{\bullet -}Li^{+})_s + D_s^{\bullet +}$$

Another way of preventing back electron transfer is "electrostatic alteration of the redox pair" (9). Instead of excitation of a neutral species, an excited state of a carbanion (for example) is used. Carbanions are very good electron donors (37) which is a further advantage over excitation of neutral species. The major advantage, however, is that the radical and radical anion pair formed from photoinduced electron transfer are now not electrostatically attracted to one another, as they are when starting with the neutral species (Scheme 6).

$$A + D^{-} \overset{h\nu}{\rightleftarrows} A^{\bullet -} + D^{\bullet}$$

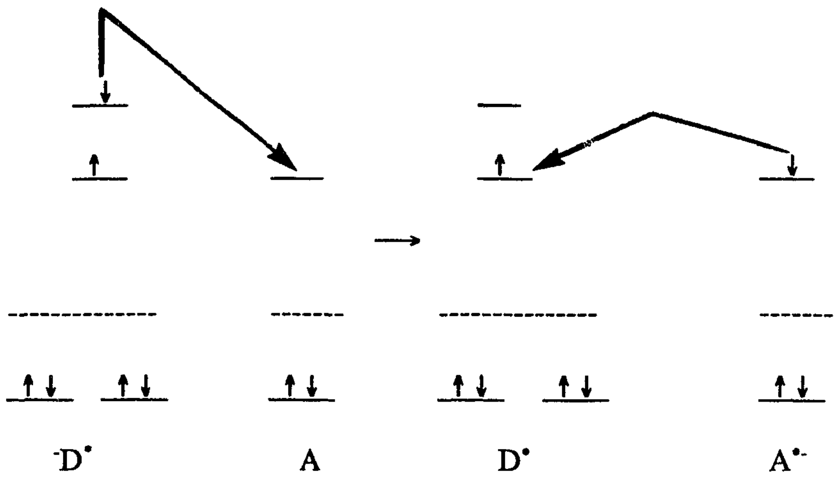
$$A + D \overset{h\nu}{\rightleftarrows} A^{\bullet -} + D^{\bullet +}$$

Scheme 6. Comparison of electron transfer between a neutral-carbanion species and a neutral-neutral species.

Since electrostatic attraction is eliminated, there is less chance of the redox pair coming together and undergoing back electron transfer and thus, more chance of dissociation to undergo further chemical reactions.

Another way of describing this process of electrostatic alteration of redox pairs, is to exhibit an energy diagram (of the carbanion case) with energies disfavoring back electron transfer (Figure 7).

Carbanion-Neutral Species



Neutral-Neutral Species

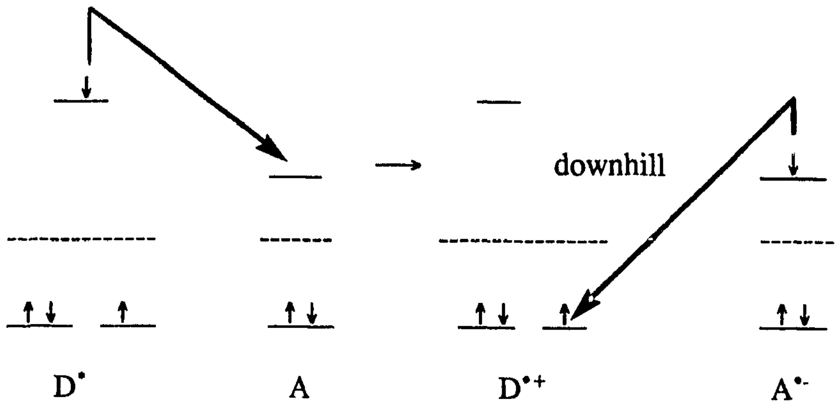
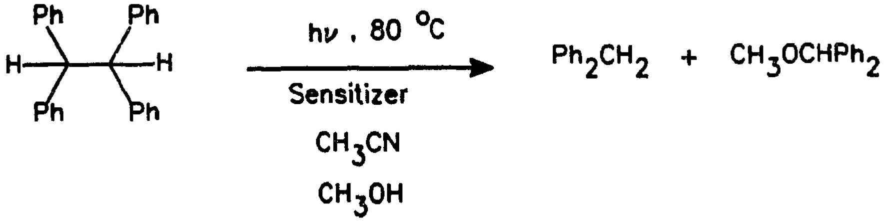


Figure 7. Electrostatic alteration of redox pairs.

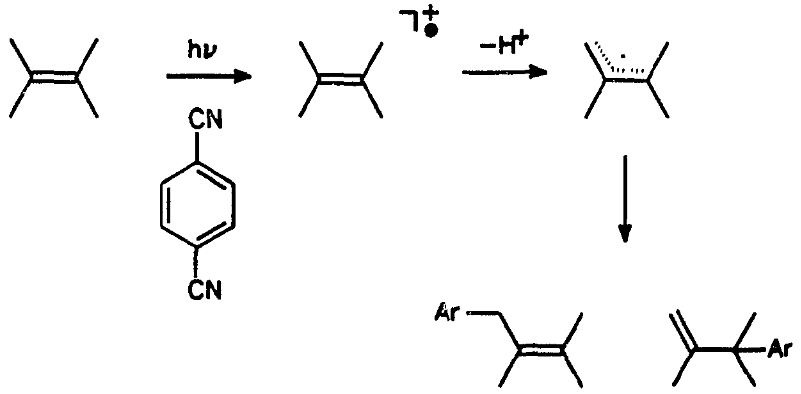
There are many more electron transfer reactions that can occur to prevent back electron transfer. Some of these will be outlined below, focusing mainly on olefin radical cations.

Fragmentation of bonds *β* to an aromatic system is competitive with back electron transfer. Arnold and co-workers (38) have studied the scope of photosensitized electron transfer carbon-carbon bond cleavage for various phenethyl derivatives (Reaction [12]).

[12]

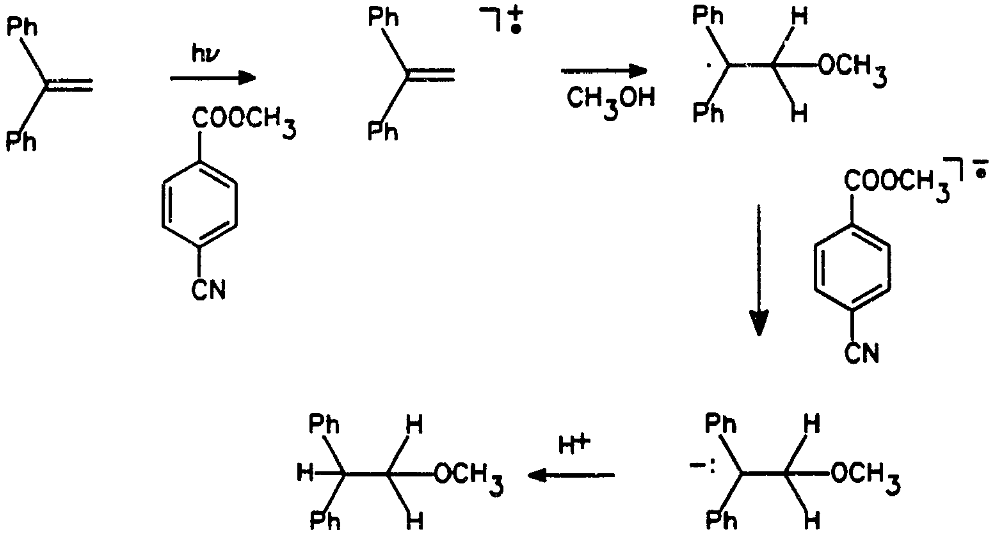


Another example of a chemical reaction competitive with back electron transfer is deprotonation of radical cations. This has been observed, for instance, using 2,3-dimethyl-2-butene and cyanoaromatics (36,39) (Scheme 7).



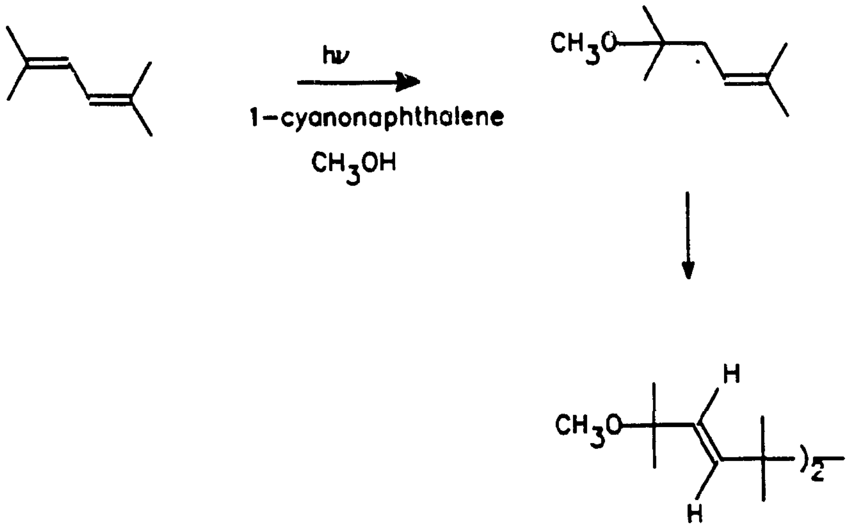
Scheme 7. Deprotonation of the 2,3-dimethyl-2-butene radical cation.

Nucleophilic addition reactions to radical cations have been a topic for electron transfer reactions. One of the first nucleophilic addition reactions involving electron transfer and an olefin was that reported by Arnold and co-workers (40). This reaction involved addition of methanol to 1,1-diphenylethylene using methyl *p*-cyanobenzoate as the electron acceptor (Scheme 8).



Scheme 8. Nucleophilic addition of methanol to 1,1-diphenylethylene.

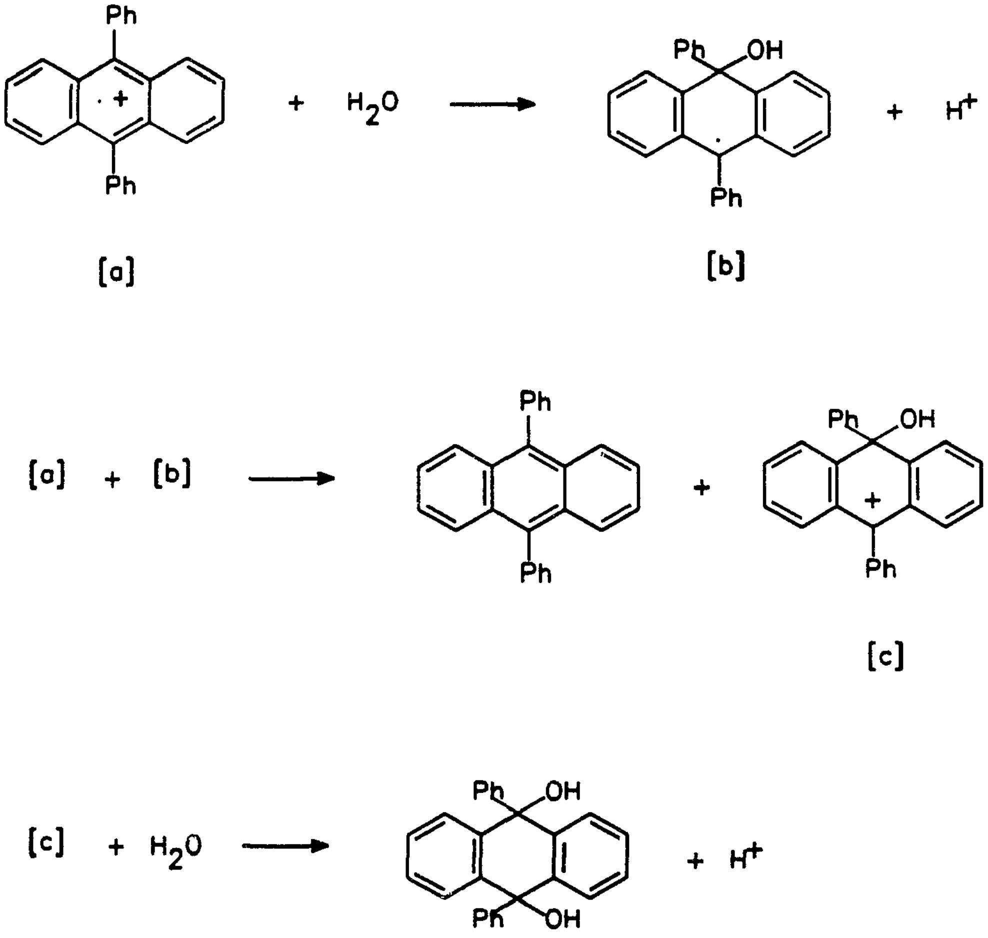
Another interesting example of a nucleophilic addition reaction involved addition of methanol to 2,5-dimethyl-2,4-hexadiene, followed by dimerization of the resulting radical (41) (Scheme 9).



Scheme 9. Nucleophilic addition of methanol to 2,5-dimethyl-2,4-hexadiene.

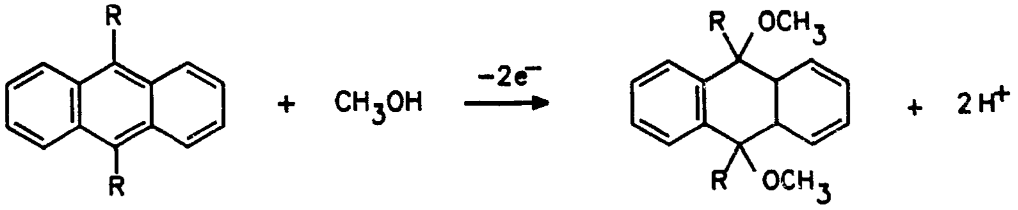
Examples of nucleophilic substitution reactions can be illustrated using 9,10-diphenylanthracene and water (42).

Water adds to the 9,10-diphenylanthracene radical cation (formed by anodic oxidation) to give the 9-hydroxy- 9,10-diphenylanthracene radical. The radical then undergoes electron transfer with the 9,10-diphenylanthracene radical to form the 9-hydroxy-9,10-diphenylanthracene cation and 9,10-diphenylanthracene. Finally, 9,10-dihydroxy- 9,10-diphenylanthracene cation reacts with water to form 9,10-dihydroxy-9,10-diphenylanthracene (42) (Scheme 10).



Scheme 10. Nucleophilic addition of water to 9,10-diphenylanthracene.

Anodic oxidation reactions in the presence of alcohols, such as methanol, are also common. For example, 9,10-substituted anthracenes in solution with methanol and sodium methoxide give a dimethoxy substituted derivative (43) (Reaction [13]).

[13] 

Nucleophilic reactions, without loss of aromaticity, have been extended to aromatics as well. Examples include $S_{RN}1$ (reductively initiated nucleophilic substitution, unimolecular) and $S_{ON}2$ (oxidatively initiated nucleophilic substitution, bimolecular) reactions. One of the first to discover the $S_{RN}1$ reaction was Bunnett in 1978 (44). The proposed mechanism is outlined in Scheme 11.

$$ArX + e^- \rightleftarrows ArX^{\bullet -}$$

$$ArX^{\bullet -} \rightarrow Ar^{\bullet} + X^-$$

$$Ar^{\bullet} + Nu^- \rightarrow ArNu^{\bullet -}$$

$$ArNu^{\bullet -} + ArX \rightarrow ArNu + ArX^{\bullet -}$$

Scheme 11. The mechanism of the $S_{RN}1$ reaction.

Another reaction involving a radical cation chain mechanism is referred to as a $S_{ON}2$ reaction (45,46). The mechanism is elaborated upon in Scheme 12.

$$ArX - e^- \rightarrow ArX^{\bullet +}$$

$$ArX^{\bullet +} + Nu^- \rightleftarrows ArXNu^{\bullet}$$

$$ArXNu^{\bullet} \rightarrow ArNu^{\bullet +} + X^-$$

$$ArNu^{\bullet +} + ArX \rightarrow ArNu + ArX^{\bullet +}$$

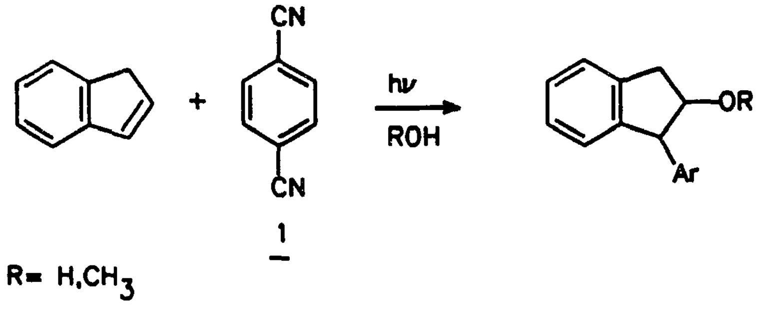
Scheme 12. The mechanism of the $S_{ON}2$ reaction.

A limitation to this reaction is that the leaving group must be difficult to oxidize; otherwise, the final step will be a termination step instead of a chain propagating one.

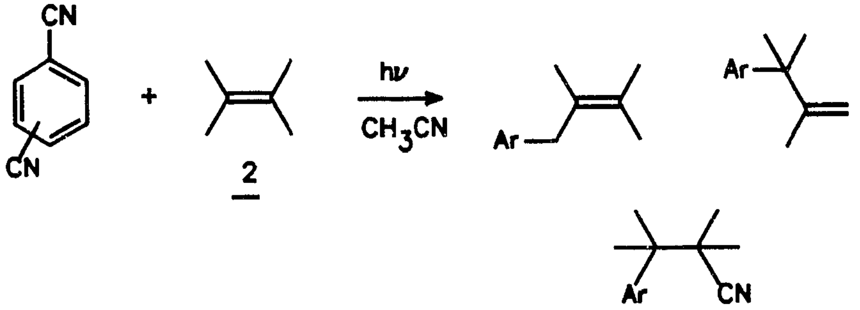
At approximately the same time these reactions were discovered, another type of electron transfer aromatic substitution was being investigated. The reaction included a selected olefin, an aromatic and a nucleophile producing a complex alkylation of an aromatic in a single step (35,36). This reaction is termed the photochemical nucleophile-olefin, combination aromatic substitution (Photo-NOCAS).

One of the first examples of the photo-NOCAS reaction was a reaction reported by Pac and co-workers (47). The olefin used was indene, the aromatic was 1,4-dicyanobenzene (1) and the nucleophile was water/alcohol. They observed a low yield of the photo-NOCAS adduct (Reaction [14]).

[14]



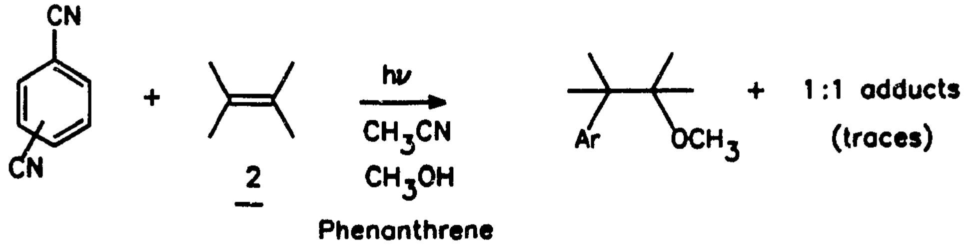
The photo-NOCAS reaction and mechanism was later examined in greater detail by Arnold and co-workers (35,36,48). Some of the first photo-NOCAS reactions were reported by Borg and Arnold (36). Various substituted dicyanobenzenes (*ortho-*,*meta-* and *para-*) and simple alkenes such as 2,3-dimethyl-2-butene (**2**), cyclohexene (**3**) and 2-methylpropene (**4**) were irradiated in acetonitrile to yield a number of substituted alkenes (Scheme 13).



Scheme 13. Reaction of a variety of substituted dicyanobenzenes with 2,3-dimethyl-2-butene.

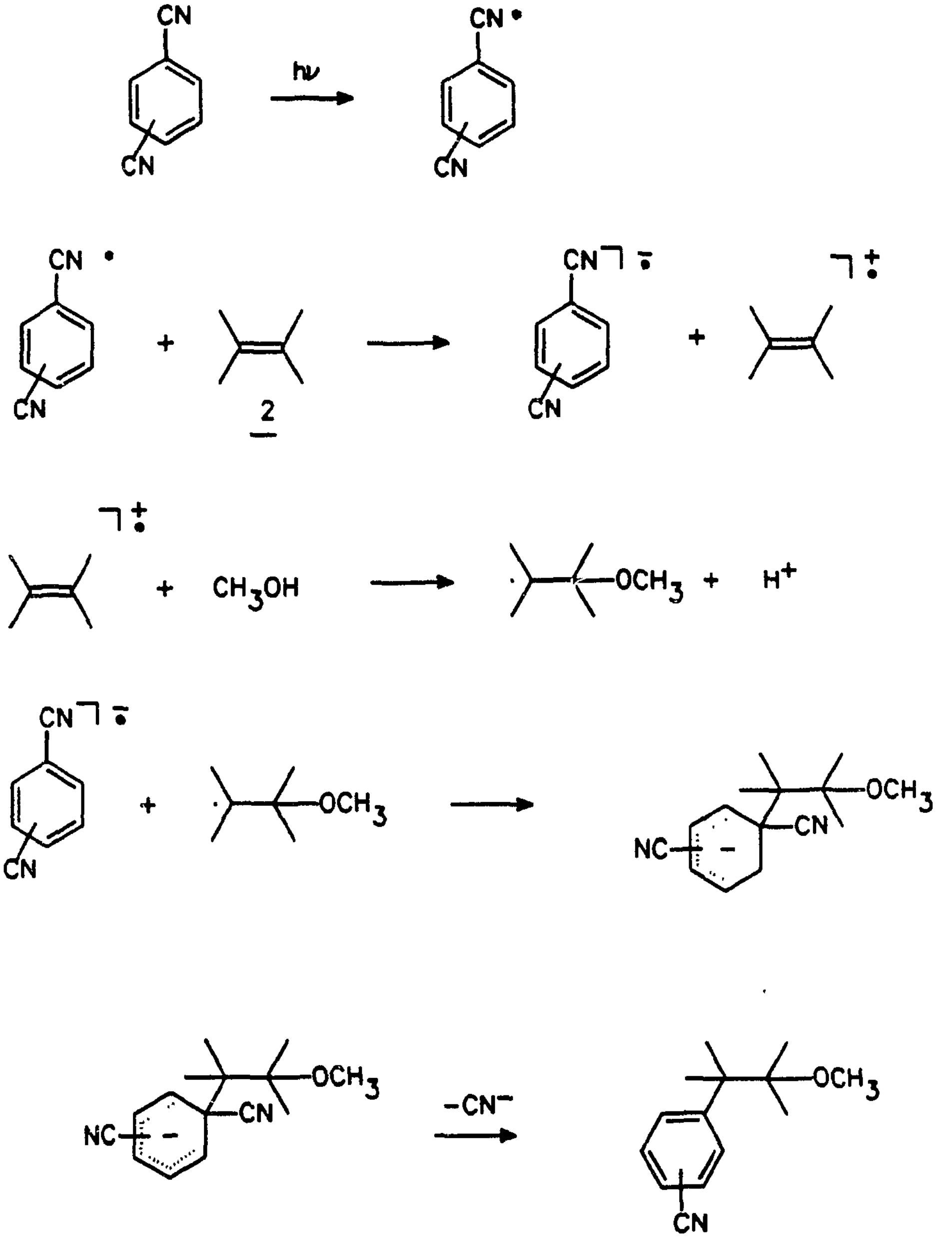
A mixture of acetonitrile and the more nucleophilic solvent, methanol, was then tried. The result was both an increase in the efficiency of the reaction and the formation of different products. The major products were 1:1:1 adducts of methanol: olefin: aromatic (Reaction [15]). Phenanthrene (**5**), when used as a sensitizer, appeared to further increase the efficiency of this reaction.

[15]



The first step in the proposed mechanism of the photo-NOCAS reaction (Scheme 14, (36)) is preferential absorption of light by 1,4-dicyanobenzene (it absorbs at wavelengths slightly longer than the Pyrex cut-off of 280 nm). Using fluorescence lifetimes and Stern-Volmer plots, the first singlet excited state of 1,4-dicyanobenzene was found to be involved in the primary step of the mechanism; in acetonitrile, the fluorescence of dicyanobenzene was quenched by the olefin, at the diffusion-controlled rate. Subsequently, various pathways are available depending upon solvent polarity and the oxidation/reduction potential of the olefin. If the solvent is polar, such as acetonitrile, electron transfer between 1,4-dicyanobenzene and the olefin can follow one of two pathways: it can follow a pathway through an exciplex, or via a short-lived encounter complex (more favored in polar solvent). If the solvent is non-polar, such as benzene, formation of an exciplex is much more likely than a short-lived encounter complex. Solvent separation of the exciplex into ion pairs is less likely, so that formation of a stable exciplex is favored. Cycloadducts (1,49-51) are generally formed unless simple back electron transfer is highly competitive, as is the case when benzene was used and little or no reaction occurred with the various olefins (36).

For electron transfer products to be observed, the free energy change (calculated by using the Rehm-Weller (31) equation) should be negative (or less than 21 kJ/mol). The calculations for the various alkenes used by Borg and Arnold (36) suggested 2,3-dimethyl-2-butene and cyclohexene would show favorable electron



Scheme 14. The abbreviated mechanism proposed by Borg and Arnold (36) for the photo-NOCAS reaction.

transfer whereas 2-methylpropene would not. Moreover, 2-methylpropene, which had a calculated free energy value suggesting electron transfer was endergonic, did exhibit diffusion-controlled quenching and did not react with dicyanobenzene. This suggested that exciplex formation occurred with 2-methylpropene and dicyanobenzene and that the exciplex decayed to the ground state. (No exciplex emission was detected in acetonitrile, but weak emission was observed upon irradiation in hexanes.)

Once electron transfer occurs between dicyanobenzene and the olefin, the solvated radical cation of the olefin could undergo nucleophilic addition. A more efficient reaction resulted with a methanol/acetonitrile mixture than with just acetonitrile alone. This can be explained by assuming that attack of methanol upon the radical cation inhibits back electron transfer. The radical formed from attack of methanol upon the olefin radical cation then couples with the radical anion of dicyanobenzene resulting in substitution at the *ipso* position. What follows is rearomatization by loss of the cyanide anion.

A few factors are essential in order for this mechanism to occur. The radical resulting from attack of methanol on the olefin radical cation must have a reduction potential greater (more negative) than that of dicyanobenzene. Otherwise, the dicyanobenzene radical anion will reduce the radical to an anion and protonation will occur, resulting in ethers instead of aromatic substitution. In fact, ethers do form even when the β-alkoxy radicals have reduction potentials greater than that of the dicyanobenzene radical anion. They are hypothesized to result from disproportionation (52); the evidence is that these two ethers are observed in approximately equal amounts in the product mixture involving **2** (Figure 8).

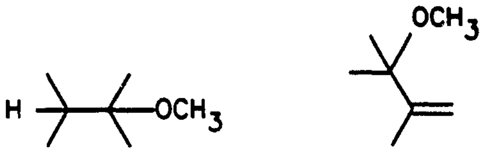


Figure 8. Disproportionation of β-alkoxy radicals.

To increase the efficiency (i.e. to reduce the irradiation time required and make more effective use of light) of the photo-NOCAS reaction, sensitizers were incorporated. The idea was that they would not only reduce the efficiency of back electron transfer but also have an effect on the regio- and stereoselectivity of the reaction. Aromatic hydrocarbons such as phenanthrene, naphthalene and anthracene were among the first sensitizers tried since these had been suggested to be effective sensitizers (53-55).

Phenanthrene was found to increase the efficiency of the photo-NOCAS reaction, naphthalene had apparently no effect and anthracene had an adverse effect; it quenched the reaction. These results can be explained by examining each sensitizer's wavelength of absorption and the oxidation potential of the olefins used. The absorbance spectrum of phenanthrene extends to 360 nm and naphthalene to 330 nm. Phenanthrene has a much higher extinction coefficient than naphthalene and thus, more energy is transferred to the system, resulting in more effective use of light in the reaction. Anthracene absorbs at a wavelength even longer than phenanthrene and, moreover, has a higher extinction coefficient than phenanthrene. Nevertheless, instead of further enhancing the efficiency, it resulted in quenching the reaction. This result is due to the olefins having oxidation potentials greater than that of anthracene, and as a result, no electron transfer could take place. Thus, choice of sensitizers was made by considering the delicate balance between absorption efficiency and oxidation potential.

The reaction using an effective sensitizer is thought to occur by excitation of the sensitizer followed by electron transfer to dicyanobenzene. The evidence for this was provided by fluorescence quenching of the sensitizers by dicyanobenzene at the diffusion-controlled rate (53). As well, the electron transfer was calculated to be exergonic and, consequently, electron transfer was favorable (53). Once the radical cation of the sensitizer was formed by electron transfer with dicyanobenzene, oxidation of the olefin followed. The olefin radical cation then reacted with methanol and carried on to products.

Irradiations using sensitizers do not always yield the same product mixtures as the corresponding reaction without sensitizers present. Sometimes products are formed from the sensitizer by incorporation of the cyanide anion. For example, 9-cyanophenanthrene and 9-cyano-9,10-dihydrophenanthrene were two products which resulted from incorporation of a cyano group (generated from rearomatization of the photo-NOCAS product) into phenanthrene. Methanol did not add to phenanthrene.

Further examples of the photo-NOCAS reaction were provided by Arnold and Snow (35). Studies with several types of olefins were required to further understand the regio- and stereoselectivity of the photo-NOCAS reaction and to better understand the mechanism. The olefins used were 2-methylpropene (**4**), cyclohexene (**3**), 1-methylcyclohexene (**6**), norbornene (**7**) and 2-methylnorbornene (**8**). All olefins were irradiated in the presence of 1,4-dicyanobenzene, for which the calculated free energy change is exergonic except with 2-methylpropene. This explained the low yield of photo-NOCAS products obtained with this olefin. Reaction with each olefin was regioselective and *anti*-Markovnikov[1] products were the result.

Sensitizers and co-donors[2] were once again utilized to try to increase the efficiency of the photo-NOCAS reaction and to examine their effect on the regio- and stereoselectivity of the reaction. Phenanthrene (**5**) and biphenyl (**9**) were the chosen sensitizer and co-donor. Biphenyl absorbs at a shorter wavelength, 290 nm, than phenanthrene. Dicyanobenzene is the major light absorbing species and favorable electron transfer occurs to it from biphenyl (ΔG = -79 kJ/mol). As a result, biphenyl is oxidized by the excited state of 1,4-dicyanobenzene and then reduced by the olefin. This latter process could be exergonic or even slightly endergonic; either way, addition of this co-donor seems to improve the efficiency of the reaction. For example, 2-methylpropene had an oxidation potential 79 kJ/mol higher than that of biphenyl and still the efficiency of the reaction was increased. Conversely,

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[1] The naming of adducts as Markovnikov and *anti*-Markovnikov is based upon the original definition. By the Markovnikov rule of orientation for the addition of hydrogen halides to olefins, the anion (methanol in this case) combines with the less hydrogenated of the ethenoid carbons (55b). No mechanistic information is implied.

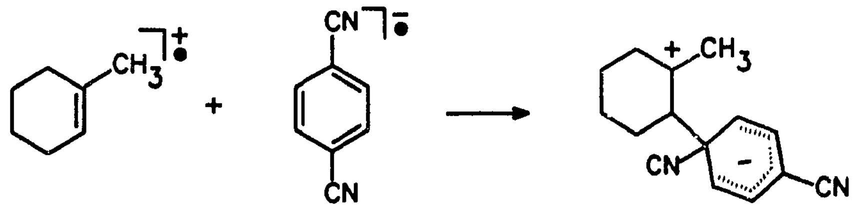
[2] The term co-donor refers to another donor present in the irradiation mixture besides the original donor (olefin). The term co-donor is used instead of sensitizer because it is not the major light absorbing species.

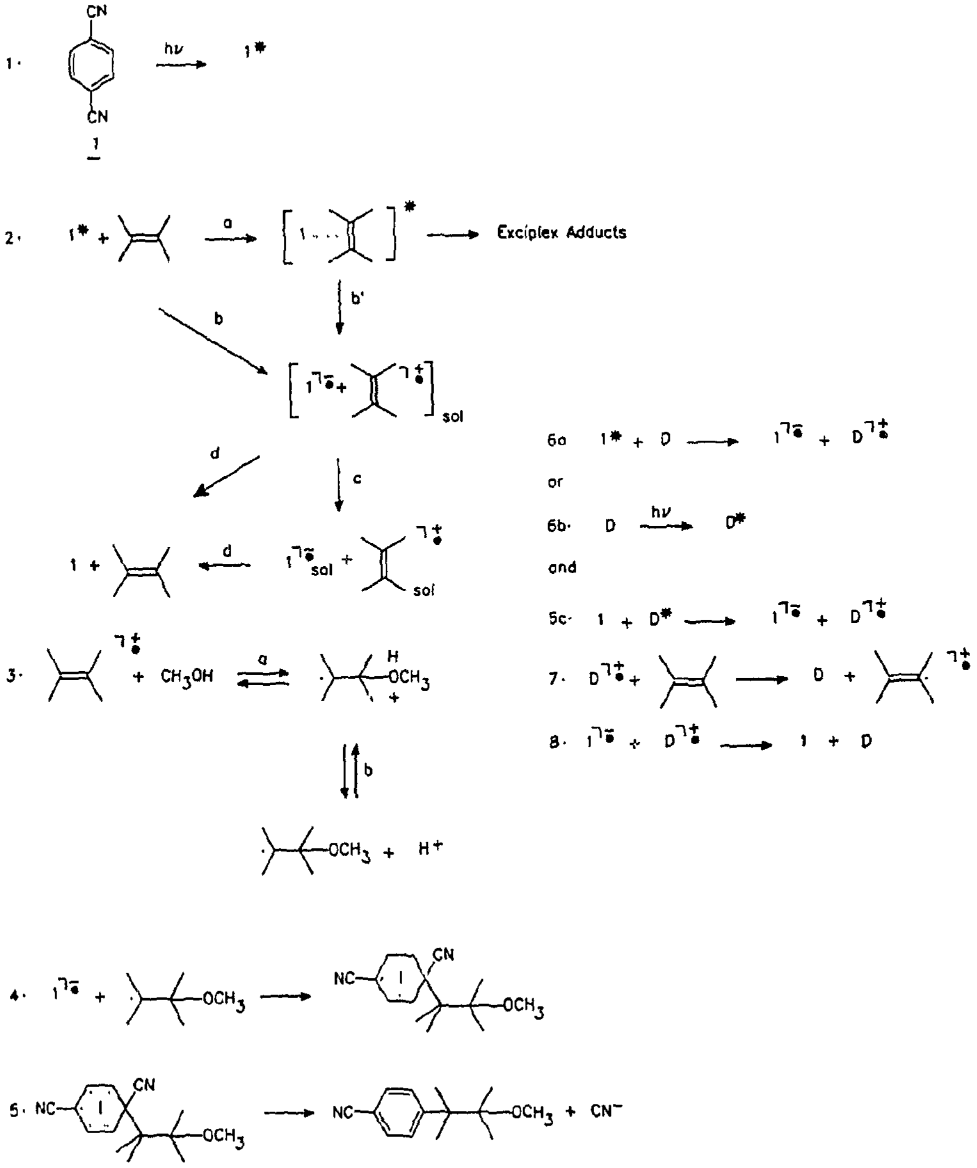
phenanthrene quenched this reaction; the potential difference was now 96 kJ/mol. The reaction with norbornene was efficient in the presence of phenanthrene; the oxidation potential of phenanthrene was 50 kJ/mol lower than norbornene. Biphenyl increased the efficiency of the reaction with cyclohexene (the potential difference was 46 kJ/mol), while phenanthrene decreased the efficiency of the reaction (the potential difference was 63 kJ/mol). This behavior suggested that simple electron transfer occurring from the sensitizer/co-donor to the olefin was unlikely. Consequently, a bimolecular radical cation complex of sensitizer-olefin or co-donor-olefin was postulated. These types of complexes are well known (56); for instance, the benzene-ethylene radical cation complex has been examined. Formation of this type of complex may decrease back electron transfer by keeping the olefin radical cation away from the dicyanobenzene radical anion. This may allow the olefin radical cation to become solvated by methanol more easily. As a result, the efficiency of the sensitized reaction increases.

Another explanation for the increased efficiency of the photo-NOCAS reaction by additions of sensitizer or co-donors was given by Farid and co-workers (33). The efficiency of the reaction depends upon the exergonicity of the forward electron transfer reaction. The less exergonic forward electron transfer is, the slower back electron transfer; the more exergonic forward electron transfer is, the faster back electron transfer occurs (Marcus inverted region). Since the free energy change for electron transfer from the alkene to dicyanobenzene is more exergonic than the free energy change for electron transfer from the co-donor or sensitizer to dicyanobenzene, the reaction is more efficient in the presence of the co-donor or sensitizer due to the decrease in the efficiency of back electron transfer. In our case, the forward electron transfer from the co-donor to dicyanobenzene is more exergonic than forward electron transfer from the alkene to dicyanobenzene. Thus, back electron transfer is faster for the co-donor-dicyanobenzene radical ion pair. Perhaps the solvent reorganization energy is larger for the olefin than for the co-donor and this would increase the rate of back electron transfer for the olefin-dicyanobenzene radical ion pair compared to the co-donor-dicyanobenzene.

The photo-NOCAS mechanism (Borg and Arnold (36)) was described in more detail by Arnold and Snow (35) (Scheme 15). For example, the regioselectivity of the reaction was postulated to result from different degrees of olefin radical cation-dicyanobenzene radical anion separation or sensitizer-olefin (co-donor-olefin) radical cation separation. If the olefin radical cation-dicyanobenzene radical anion pair remained coupled, a zwitterionic or diradical intermediate would form, and Markovnikov products would dominate the photo-NOCAS reaction. For instance, the radical cation of the olefin would be attacked by dicyanobenzene radical anion at the more hydrogenated carbon of the olefin, resulting in a zwitterion with a more stabilized cation (Reaction [16]).

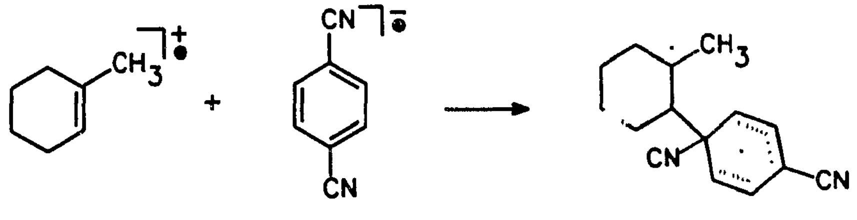
[16]





Scheme 15. The advanced mechanism proposed by Arnold and Snow (35) for the photo-NOCAS reaction. Sensitizers and co-donors, D in steps 6-8, are biphenyl and phenanthrene.

If a diradical intermediate formed, attack of the dicyanobenzene radical anion would occur at the more hydrogenated (less sterically hindered) carbon of the olefin radical cation as well, resulting in the more highly substituted radical (Reaction [17]).

[17] 

These intermediates cannot be formed in the photo-NOCAS reaction because *anti*-Markovnikov products are predominant. Therefore, the regioselectivity is determined by methanol first reacting with the radical cation of the olefin, followed by dicyanobenzene reacting with this radical.

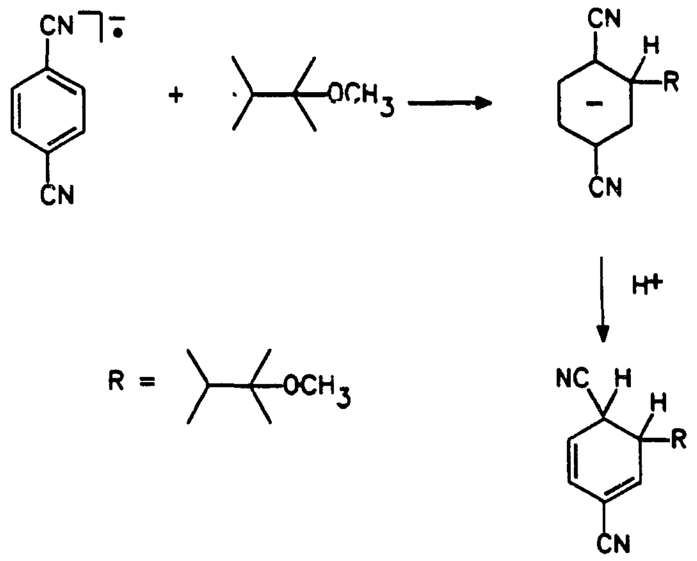
The regioselectivity of the reaction of alkenes is influenced by the number of hydrogens at the ends. For instance, methanol adds to diphenylethylene at the less substituted carbon because the radical formed is resonance stabilized. For 2-methylpropene, methanol adds preferably to the less substituted carbon as well, because the more highly substituted radical is formed. As well, and perhaps more importantly, there is less steric hindrance for attack of methanol at the terminal methylene.

A further complication in the mechanism is the attack by methanol on the radical cation. There are two possible modes of attack; either methanol can directly attack the radical cation or the radical cation can form an ion-dipole π-complex.

Furthermore, a competing process of deprotonation from methanol and attack of the 1,4-dicyanobenzene is possible. A termolecular reaction could occur involving methanol, the olefin radical cation and the 1,4-dicyanobenzene radical anion. Or, deprotonation could occur from the methanol-olefin distonic radical cation by attack of the 1,4-dicyanobenzene radical cation at the olefinic carbon.

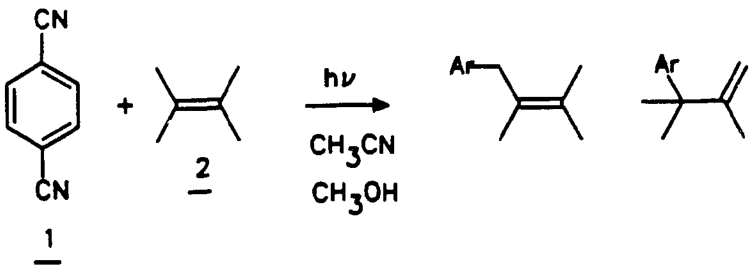
The regioselectivity of the photo-NOCAS reaction is thought to depend mostly on methanol reacting with the radical cation of the olefin first. Perhaps the methanol-olefin distonic radical cation intermediate may control the stereoselectivity of the reaction. Bridging is more important in the distonic radical cation which is present prior to deprotonation, and it is thought that this bridging accounts for the stereoselectivity of the photo-NOCAS reaction since *anti*-addition of the dicyanobenzene radical anion to the bridging distonic radical cation would be favored. The evidence for this reasoning was supplied by the results for addition to cyclohexene which yielded *trans* products. Coupling of the methoxy-olefin radical (bridging is unimportant in a radical) with the dicyanobenzene radical anion is less likely since this pathway would not be expected to result in stereoselective addition products.

As mentioned previously, coupling of the distonic radical cation or β-methoxy alkyl radical occurs at the *ipso* position of the dicyanobenzene radical anion (the spin density is highest at the *ipso* position). If substitution occurred at another carbon other than at the *ipso* position, then the anion would be protonated, and addition to instead of substitution on the aromatic ring would occur (Scheme 16).



Scheme 16. Addition of the β-alkoxy radical to the 1,4-dicyanobenzene radical anion.

Further studies of the photo-NOCAS reaction involved addition of salts (35) to the irradiation mixture. Salts are known to effect photosensitized electron transfer reactions significantly (57,58). The various salts incorporated were lithium perchlorate, tetrabutylammonium perchlorate and magnesium perchlorate. The yield of photo-NOCAS products were low compared to reactions in the absence of salts. The yields of ethers and allylic substitution products (Reaction [18]) increased and regioselectivity of the reaction favored *anti*-Markovnikov products.

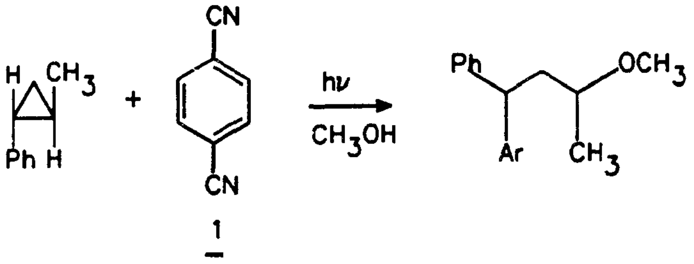
[18] 

The effect of salts on the photo-NOCAS reaction can be incorporated in the reaction mechanism as follows. In the case of magnesium perchlorate, the magnesium cation is thought to stabilize the dicyanobenzene radical anion. This is thought to be the reason for the increased regioselectivity of the reaction and for the decreased reactivity of the dicyanobenzene. This can be explained by looking at the alkene radical cation which would be kept away from the dicyanobenzene radical anion since the magnesium cation is complexed with the radical anion. Thus, there would be less back electron transfer and more selectivity in the addition of methanol to the alkene radical cation. This would imply that the dicyanobenzene radical anion plays a part in determining the regiochemistry of the reaction in the absence of magnesium perchlorate. For instance, Markovnikov and *anti*-Markovnikov products are formed in the photo-NOCAS reaction with the *anti*-Markovnikov products being favored. The formation of Markovnikov adducts is due to a termolecular reaction analogous to Ad_E3 (if it were due to coupling of the radicals or formation of a zwitterionic intermediate then Markovnikov adducts would be the major photo-NOCAS products). The Ad_E3 mechanism involves formation of a transition state of methanol, the olefin radical cation and the 1,4-dicyanobenzene radical anion. This transition state does not resemble the β-alkoxy radical and thus the stability of the radical or the steric hinderance of attack of methanol is unimportant and Markovnikov products form. In the presence of magnesium perchlorate, the dicyanobenzene radical anion is not involved with the coupling of the alkene radical cation and methanol because the magnesium cation keeps the dicyanobenzene away, and thus, the reaction proceeds via a bimolecular mechanism analogous to the Ad_E2 mechanism. The rate determining step involves coupling of methanol to the olefin radical cation; the reaction thus depends on the stability of β-alkoxy radical and on the steric hinderance of attack of methanol, thus Markovnikov adducts do not form. This step is also rate determining in the photo-NOCAS reaction in the absence of salts since *anti*-Markovnikov products are favored.

The lithium and tert-butyl ammonium perchlorate salts used had little effect upon the yield of photo-NOCAS adducts. In some cases, the lithium perchlorate salt was found to increase the yield of photo-NOCAS products incorporating methanol. Some trace amounts of photo-NOCAS products incorporating cyanide were found in the absence of salts, but in the presence of lithium perchlorate the yield of these cyano products decreased. This could be due to the association of the lithium cation with the cyanide anion allowing methanol incorporated photo-NOCAS products to be formed in higher yield.

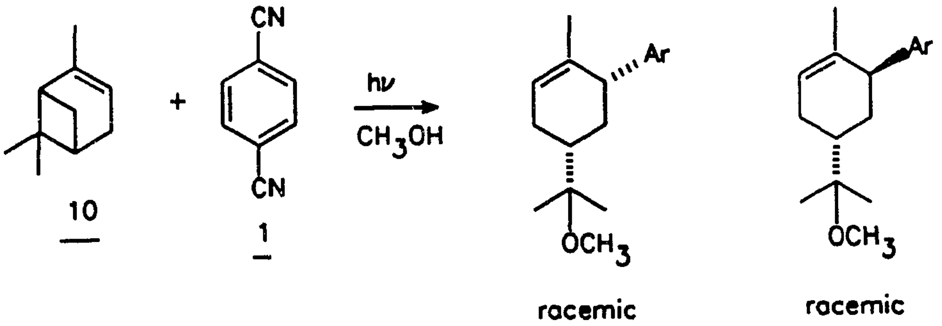
In conclusion, Arnold and co-workers (35,36) developed the ground work for the photo-NOCAS reaction by incorporating various olefins, sensitizers, co-donors and salts, and left further ideas involving the photo-NOCAS reaction to be explored. Recently, Arnold and Du (48) have discovered ring opened photo-NOCAS adducts using α- and β-pinene (**10**,**11**). This type of ring opening formation of 1:1:1 (nucleophile: saturated ring: aromatic) adducts was also reported by Rao and Hixson (59). They irradiated **1** and *trans*-1-methyl-2-phenylcyclopropane in methanol and obtained a 1:1:1 adduct that resulted in the opened cyclopropane ring (Reaction [19]).

[19]



Extension of this idea to α- and β-pinene by Arnold and Du (48) led to regioselective 4-membered ring cleavage to yield 1:1:1 adducts. The products were the result of selective formation of the tertiary cation and allylic radical (60) (Reaction [20]).

[20]



Since previous studies have been performed on monoalkenes and alkenes with the possibility of ring-opening, further work has been focused upon unconjugated dienes (and their potential to undergo ring closure) and conjugated dienes.

Section I

Introduction I

Using 1,1,1-trichlorotrifluoroethane and γ-irradiation to generate radical cations at low temperature (61), Williams and Guo (62) observed that the 1,5-hexadiene radical cation undergoes C1-C6 exergonic ring closure to the 1,4-cyclohexyl radical cation. These results prompted this project to see whether cyclized products from 1,5-hexadiene, and its homologues, will form using the photo-NOCAS procedure.

Previous studies involving the photo-NOCAS reaction have shown that alkylation of an aromatic can occur in a single step (35,36). Now possibly by using unconjugated acyclic dienes, cyclization of the radical cation of an unconjugated acyclic diene could result in substitution of an aromatic ring with a saturated ring system. The conjugated dienes chosen were 1,5-hexadiene (**12**), 2-methyl-1,5-hexadiene (**13**) and 2,5-dimethyl-1,5-hexadiene (**14**). These substituted alkenes were selected to obtain results on both the regio- and stereoselectivity of the reaction.

There are various factors that must be taken into account if cyclization is to succeed. For instance, if the photoinduced electron transfer between the acyclic diene and 1,4-dicyanobenzene (**1**) is exergonic or slightly endergonic, then the acyclic diene radical cation may cyclize to form the 1,4-cyclohexyl radical cation and then form photo-NOCAS products.

If the photoinduced electron transfer is endergonic for the acyclic diene and

1,4-dicyanobenzene, an exciplex could result. If the exciplex does not dissociate to give radical ions then it is possible for a reaction to take place within the exciplex. For example, work by Buchi (49) showed that [2+2] cycloaddition (within the exciplex) at the 1,2-positions of the benzene ring of benzonitrile by various alkenes resulted in adducts termed *ortho*-adducts. Cantrell (50) also reported this, as well as the addition of more electron-rich alkenes across the cyano group (azetine formation).

Further work in this area has been reported by Mattay (1). He noted that *para*-cycloaddition, even though seldom observed, can also occur within the exciplex. In some cases, *para*-cycloaddition results from *ortho*-adducts undergoing secondary photochemical processes.

If the exciplex is unable to dissociate into radical ions, another possible exciplex adduct may result. For instance, Cornelisse (51) reports mainly *meta*-cycloaddition of benzonitrile to cyclopentene with *ortho*-adducts constituting less than 10% of the products. Like Cantrell's example, this reaction occurs in non-polar solvent as a result of the lower tendency for exciplex dissociation to radical ions. Although solvent polarity is high in the usual photo-NOCAS procedure, perhaps with acyclic dienes having a high oxidation potential, both *ortho*- and *meta*-cycloaddition products could form.

Results I

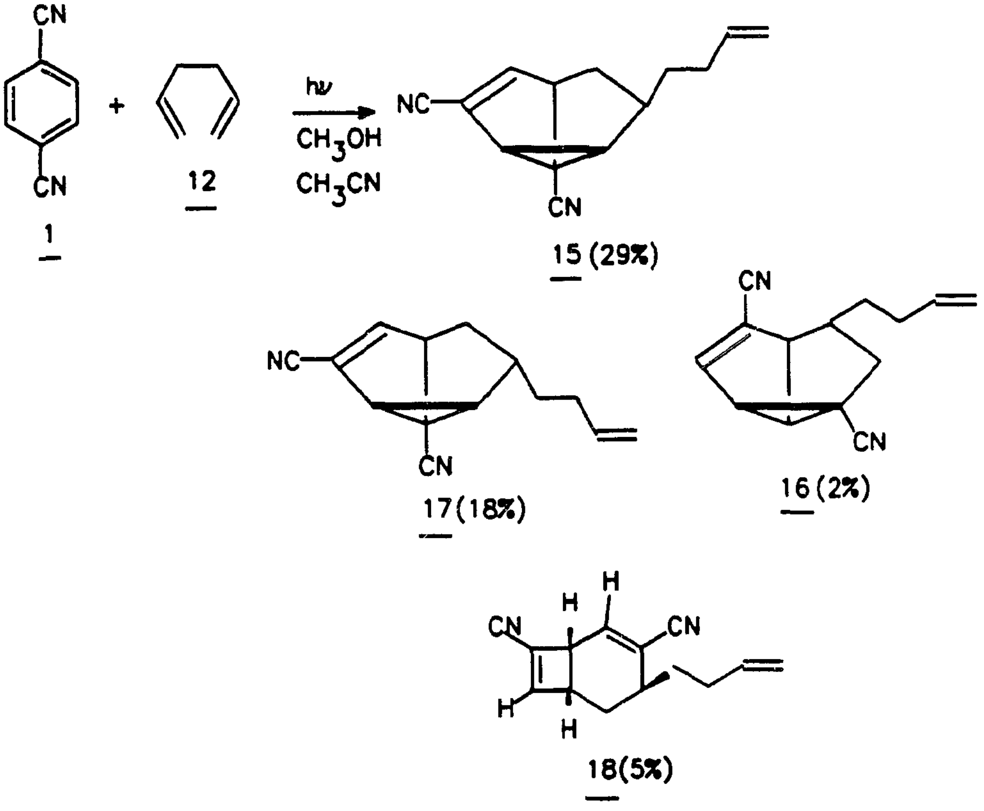
1,4-Dicyanobenzene (**1**) and an unconjugated diene were irradiated in an acetonitrile-methanol (3:1) solution. In some cases, the products included 1:1:1 (methanol: diene: **1**) adducts. The effect of the addition of co-donors or sensitizers, such as phenanthrene (**5**) or biphenyl (**9**), to the irradiation mixture was studied. The effect of added salt was examined using an acetonitrile-methanol (3:1) solution of magnesium perchlorate (0.3 M).

The product ratio of the reaction was monitored by a gas chromatograph equipped with a flame ionization detector (gc/fid). The first indication of the structure of the products was achieved using a gas chromatograph equipped with a mass selective detector (gc/ms). The photo-NOCAS products were isolated by column chromatography and the yields were based upon 1,4-dicyanobenzene as the limiting reagent. In cases where the photo-NOCAS products were difficult to separate, a total weight of the combined products was obtained, and the ratios of the isomers determined by gc/fid. In these cases, the ratio of products was not dependent upon the extent of 1,4-dicyanobenzene conversion; the product ratios remained constant. Structural assignments of the products were based primarily upon detailed analysis of ^{1}H and ^{13}C nmr spectra.

Irradiation of 1,5-hexadiene (**12**), in the absence of sensitizer or co-donor, yielded no photo-NOCAS products. Instead, cycloaddition (1,49-51) products **15**, **16**, **17**, and **18** from the exciplex were formed, in a combined yield of 54% (Reaction

[1.01]). The major cycloaddition products were *meta*-adducts.

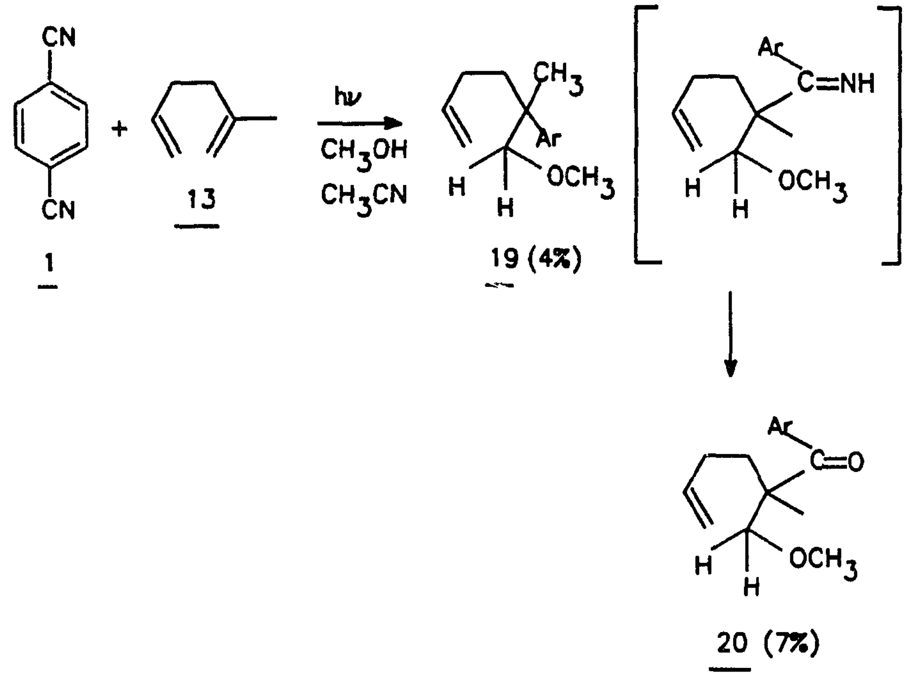
[1.01]



Addition of biphenyl yielded a small amount of cycloaddition products from the exciplex (9%) but no photo-NOCAS products. Phenanthrene was not effective as a sensitizer; no products resulted. Addition of magnesium perchlorate to reactions with and without co-donor or sensitizer present, also quenched the reaction; neither photo-NOCAS nor cycloaddition products were formed.

Irradiation of 2-methyl-1,5-hexadiene (**13**) and **1** in acetonitrile-methanol (3:1) yielded the *anti*-Markovnikov adduct **19** in low yield (4%). Also isolated from the reaction was a 4-cyanophenyl ketone (tentatively assigned) (**20**) in 7% yield. Examination of the initial irradiation mixture revealed no ketone (**20**) present (gc/ms retention times of the compounds in the irradiation mixture do not match the retention time of the ketone (**20**)). The ketone did not appear until after the irradiation mixture was chromatographed by medium pressure liquid chromatography (mplc). It was then hypothesized that an imine was formed in the irradiation mixture and was consequently hydrolyzed to the ketone once the irradiation mixture was placed on the mplc (Reaction [1.02]).

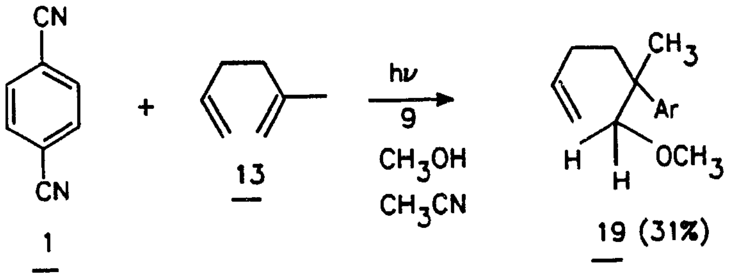
[1.02]



The only evidence found to prove the ketone forms from an imine was the mass spectrum. The mass spectra of the peaks from the gc/ms (of the irradiation mixture) do not exhibit a molecular ion for an imine, but one peak shows similar fragmentation patterns to that of the ketone (**20**) (mz: 55, 67, 68, 81, 101, 102, 128, 129 and 171). The only products isolated from the mplc were **19** and **20**; no imine was isolated.

Addition of the co-donor, **9**, to the irradiation mixture of **13** and **1** in acetonitrile-methanol (3:1) yields **19** in higher yield (31%). There was no ketone, **20**, (or imine) detected in this irradiation mixture (Reaction [1.03]).

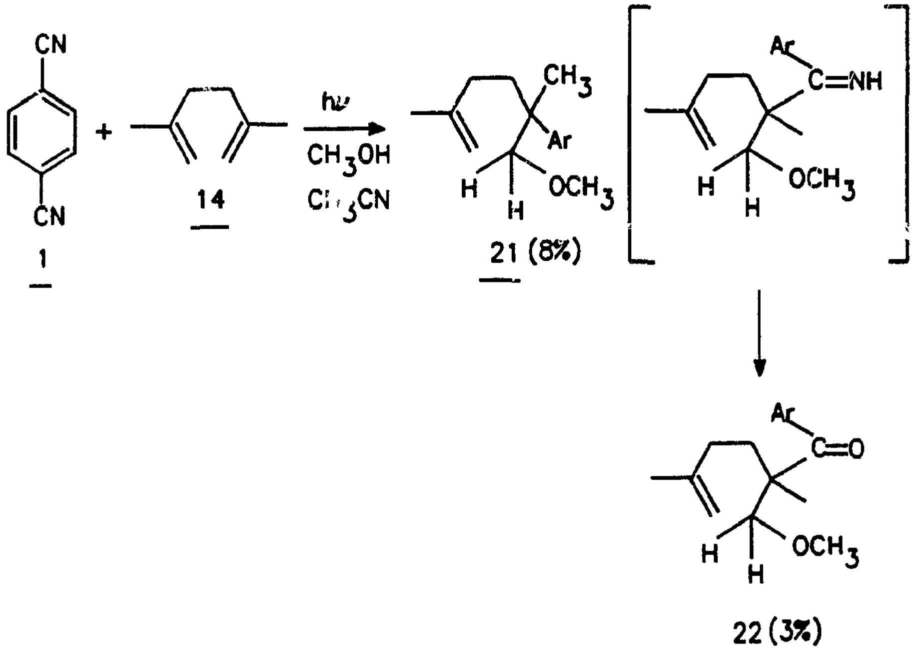
[1.03]



Phenanthrene was less efficient as a sensitizer and hindered formation of **19** (no ketone (**20**) or imine was present). With and without co-donor or sensitizer present, addition of magnesium perchlorate hindered the formation of **19**.

Irradiation of 2,5-dimethyl-1,5-hexadiene (**14**) and **1** yielded the *anti*-Markovnikov adduct **21** in low yield (8%). Also isolated from the reaction was a 4-cyanophenyl ketone (tentatively assigned) (**22**) in 3% yield. Examination of the irradiation mixture revealed no ketone (**22**) present (gc/ms retention times of the compounds from the irradiation mixture do not match the retention time of the ketone (22)}. The ketone did not appear until the irradiation mixture was chromatographed (mplc). These results are also consistent with the initial formation of an imine which is hydrolyzed to the ketone upon being placed on a mplc (Reaction [1.04]).

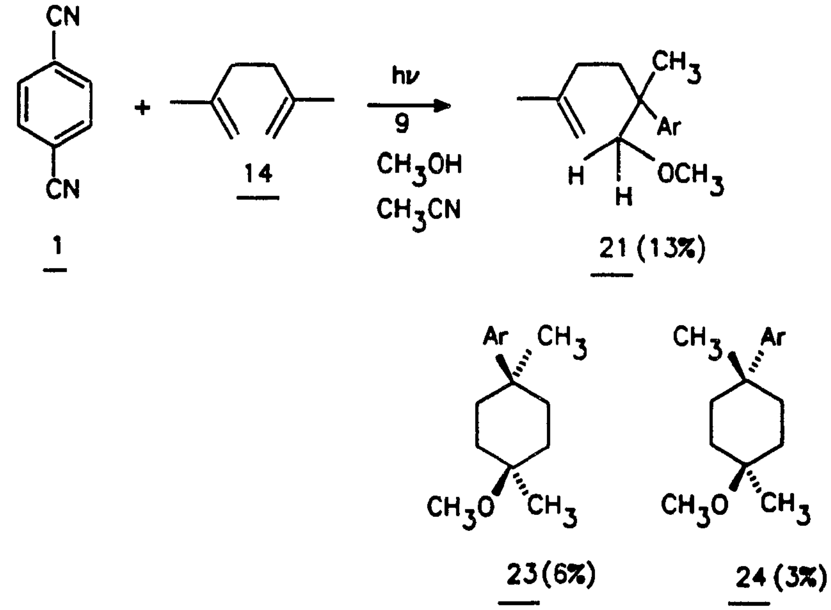
[1.04]



The only evidence found to prove the ketone forms from an imine was the mass spectrum. The mass spectra of the peaks from the gc/ms (of the irradiation mixture) do not exhibit a molecular ion for an imine but one peak shows similar fragmentation patterns to that of the ketone (**22**) (mz: 55, 67, 68, 85, 95, 102, 128, 129 and 171). The only products isolated from the mplc were **21** and **22**; no imine was isolated.

When **9** (biphenyl) was added to the irradiation mixture, **21** (13%) was formed as well as the *cis* and *trans* cyclization products (4-(4-cyanophenyl)-1-methoxy-1,4-dimethyl-cyclohexane; **23** and **24**) in a 2:1 ratio (Reaction [1.05]).

[1.05]



It was noted that when the irradiation was carried out without added biphenyl, no cyclization occurred, and the more biphenyl present the more efficient was the formation of cyclized products **23** and **24**. For instance, a ratio of (4:1) **14** to **9** was added to the solution of **1** and acetonitrile-methanol (3:1). The irradiation of this solution produced a ratio of *cis* adduct, **23**, to *anti*-Markovnikov adduct, **21**, that was

0.1:1 (determined by gc/fid after irradiating for 78 hrs). Another ratio of **14** to **9** used was 2:1, and the ratio of **23** to **21** was 0.4:1 (after irradiating for 76 hrs). Isolated yields were compared as well. A ratio of **14** to **9** used in a typical irradiation mixture was 1:4, and after irradiation for fifty-one hours the yield of the photo-NOCAS products was 16% **21**, 10% **23** and 4% **24** (**21**:(**23** and **24**); 1:0.9). Another irradiation using a ratio of 3:1 **14** to **9**, produced a yield of photo-NOCAS products as being 13% **21**, 6% **23** and 3% **24** (**21**:(**23** and **24**); 1:0.7). Isolated ratios of **21** to (**23** and **24**) show that cyclization increased with the ratio of biphenyl to alkene (**14**). This gives evidence that biphenyl plays an important role in formation of cyclized photo-NOCAS products.

Another important factor that controls the formation of cyclized photo-NOCAS products, is the concentration of methanol. It can be shown that cyclization increases with decreased methanol concentration (Tables 1.1 and 1.2; Figures 1.1 and 1.2). In very low concentrations of methanol, more side products resulted but cyclization also increased. At higher concentrations of methanol, the plot of the ratio of uncyclized to cyclized products versus methanol concentration becomes scattered but continues to incline (Figures 1.1 and 1.2). In these cases, accurate conclusions of the effect of methanol upon cyclization, at such high concentration, cannot be made. Thus, the conclusion that cyclization increases with decreased methanol is based primarily upon results obtained when the methanol concentration was less than 5.0 M.

Three side products were produced from irradiation of **14** and **9** in a typical irradiation mixture of **1** and acetonitrile-methanol (3:1). 2-Cyanobiphenyl (**25**), 4-

Table 1.1. The cyclization products, **23** and **24**, increase with decreased methanol when comparisons are made to the acyclic product, **21**.

$[CH_3OH]$ (M)	**21**/ **23**+**24** (gc/fid area ratios)
0.50	0.89 ± 0.06
1.00	1.14 ± 0.07
3.00	1.83 ± 0.07
5.00	1.87 ± 0.14
7.00	2.22 ± 0.08

Table 1.2. The cyclization products, **23** and **24**, increase with decreased methanol when comparisons are made to the acyclic product, **21**. Experiment repeated.

[CH_3OH] (M)	**21**/ **23**+**24** (gc/fid area ratios)
0.25	0.58 ± 0.04
0.50	0.77 ± 0.03
1.00	1.02 ± 0.03
1.50	1.20 ± 0.02
2.00	1.37 ± 0.02
2.50	1.41 ± 0.06
3.00	1.46 ± 0.06
5.00	1.62 ± 0.04
7.00	2.84 ± 0.11

Ratio of Uncyclized to Cyclized Products vs. Methanol Concentration

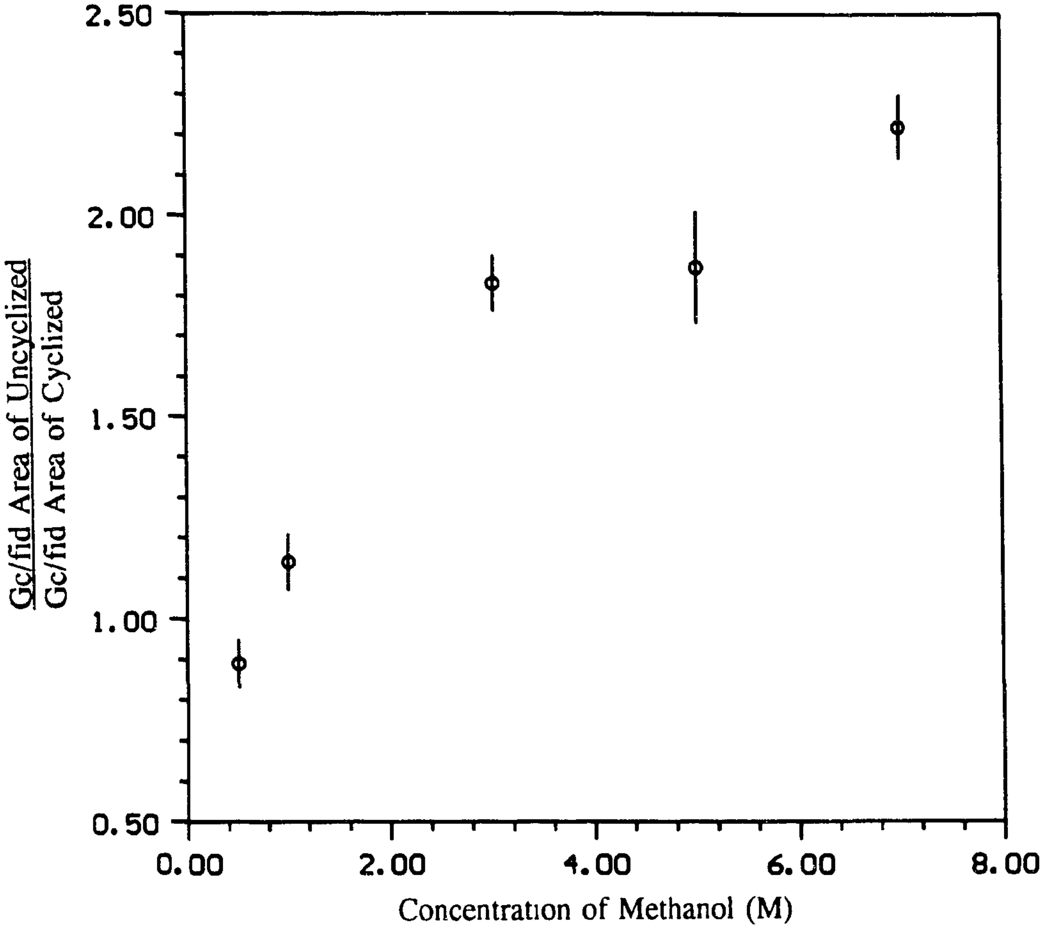


Figure 1.1. The plot illustrates the effect of methanol concentration upon yields of cyclized products. The data is found in Table 1.1.

Ratio of Uncyclized to Cyclized Products vs. Methanol Concentration

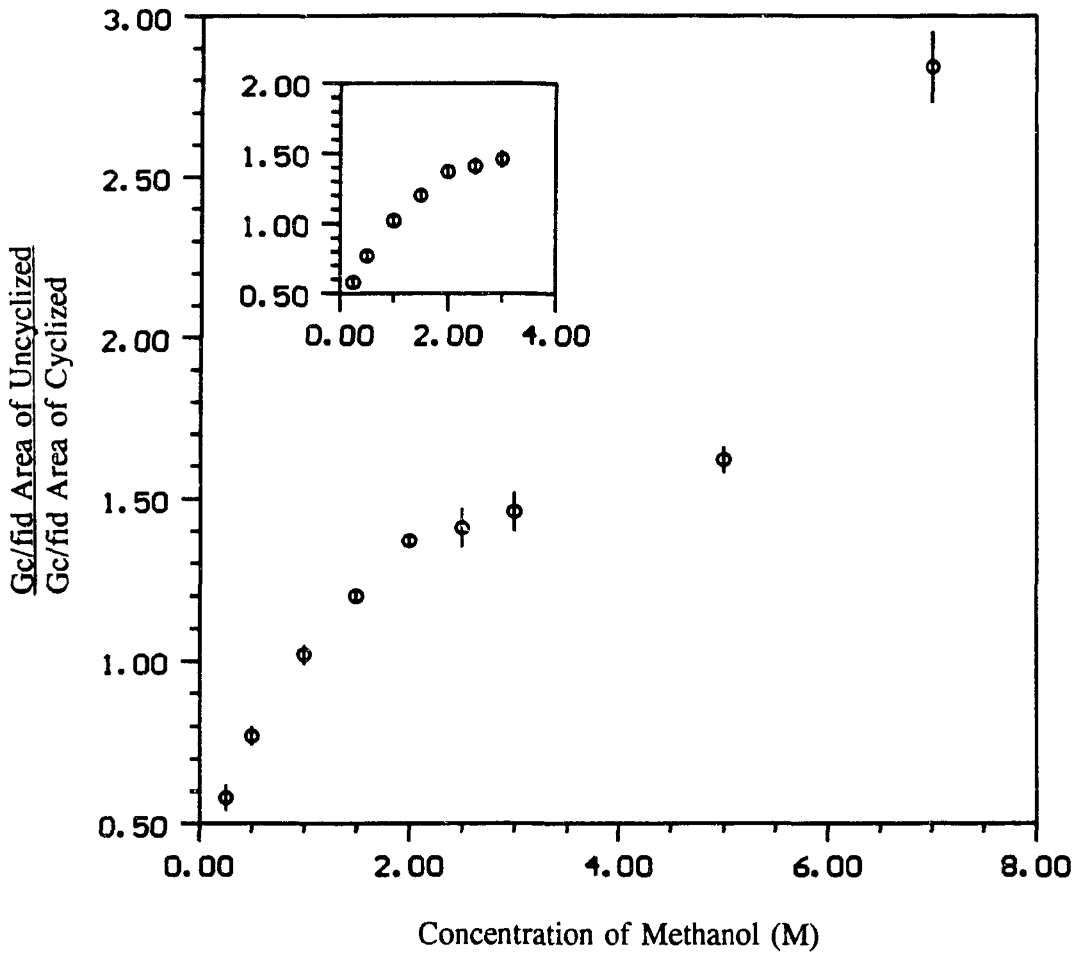


Figure 1.2. The plot illustrates the effect of methanol concentration upon yields of cyclized products. The data is found in Table 1.2.

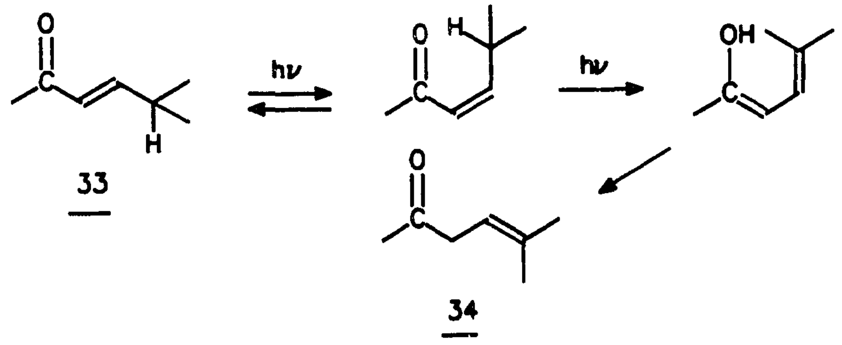
cyanobiphenyl (**26**) and 3,5-dimethoxy-4-phenylcyclohexanecarbonitrile (**27**) (Appendix) were formed.

Two other products, 4-(4-cyanophenyl)-5-methoxy-2,5-dimethyl-1-hexene and 5-(4-cyanophenyl)-4-methoxy-2,5-dimethyl-1-hexene, were formed; **28** and **29**, respectively. They were identified as products from the tautomer of **14**. This will be expanded upon shortly.

Addition of **5** to the irradiation mixture of **14**, **1** and acetonitrile-methanol (3:1) yielded methoxy- and cyano-substituted phenanthrene by-products, **30** and **31**; a small yield of **21** was also obtained (less than 3%).

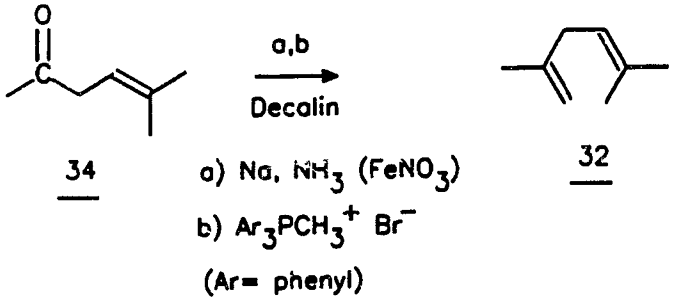
As mentioned, two other products (**28** and **29**) formed in the irradiation of **14**, **9** and **1**, were identified as products formed from a tautomer of **14**. The tautomer was identified as an impurity in **14** (Aldrich Chemical Co.; 90% pure). This was proven by obtaining Aldrich's 99% pure **14**, where **28** and **29** were produced in smaller amounts as compared to an irradiation with 90% pure **14**. The tautomer of **14** was recognized as 2,5-dimethyl-1,4-hexadiene (**32**) and was prepared to provide evidence that **28** and **29** came from it. Diene **32** was prepared by initially isomerizing 5-methyl-3-hexen-2-one (**33**) to its β,γ-isomer; 5-methyl-4-hexen-2-one (**34**) (Reaction [1.06]) (63).

[1.06]



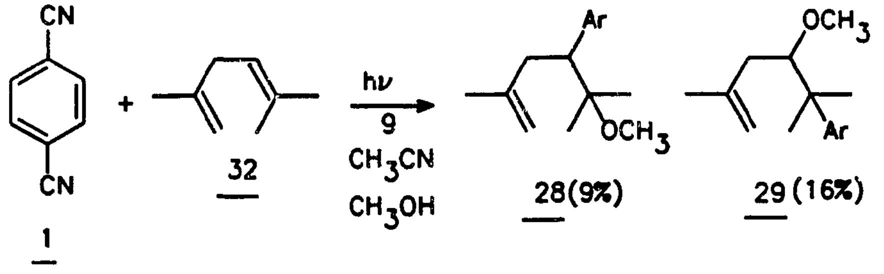
Once **34** was produced, a Wittig reaction (64) was completed to obtain **32** (Reaction [1.07]).

[1.07]



Irradiation of **32**, **9** and **1**, yielded both the Markovnikov and *anti*-Markovnikov adducts; 9% **28** and 16% **29**, respectively (Reaction [1.08]).

[1.08]



Another product from this reaction was *trans*-2-(4-cyanophenyl)-5-methoxy-2,5-dimethyl-3-hexene (**35**); another product formed from a tautomer. The tautomer was identified as 2,5-dimethyl-2,4-hexadiene (**36**) which actually forms from **32** upon irradiation. Gc/ms evidence shows that **36** is formed from **32** upon irradiation because there is no tautomer, **36**, present before irradiation.

The products and their yields obtained from the above photo-NOCAS reactions are summarized in Table 1.3.

Table 1.3. Summary of the products and yields[c] of the photo-NOCAS reaction involving unconjugated dienes.

Reaction	**Olefin**	**Product(s) (Yield)**
[1.01][b]	1,5-Hexadiene	**15**(29%), **16**(2%), **17**(18%), **18**(5%)
[1.02][b]	2-Methyl-1,5-hexadiene	**19**(4%), **20**(7%)
[1.03][a]	**13**	**19**(31%)
[1.04][b]	2,5-Dimethyl-1,5-hexadiene	**21**(8%), **22**(3%)
[1.05][a]	**14**	**21**(13%), **23**(6%), **24**(3%)
[1.08][a]	2,5-Dimethyl-1,4-hexadiene	**28**(9%), **29**(16%)

[a] Irradiations were carried out in (3:1) acetonitrile-methanol solution, with **1** and **9** present.

[b] Irradiations were carried out in (3:1) acetonitrile-methanol with **1** present.

[c] Yields based upon **1**. Yields were not optimized.

Structural Assignments

The structural assignments for the products obtained were based primarily upon ^{1}H and ^{13}C nmr spectra. Mass spectra (including exact mass determination), infrared spectra and elemental analyses (obtained in most cases) were also helpful.

The structural assignments for the cycloaddition products obtained from 1,5-hexadiene were based essentially upon analysis of their ^{1}H nmr spectra, and comparison to similar ^{1}H nmr spectra obtained from the literature (34).

As mentioned in Introduction I there are four types of possible cycloadducts: the *ortho-*, *meta-* and *para-* adducts, as well as the azetine adduct (addition across the cyano group) (Figure 1.3 and 1.4). The *ortho-*, *para-* and azetine adducts can be excluded. The ^{1}H nmr spectra of the cycloaddition products obtained from 1,5-hexadiene exhibit only four olefinic protons. The *ortho-* and *para-* adducts would each show six olefinic protons. Azetine adducts would show four protons in the aromatic region of the ^{1}H nmr spectrum (displaying an AA'XX' pattern), and three other protons in the olefinic region. Therefore, the above adducts were eliminated leaving the *meta*-adducts as the only possible products. There are twelve possible *meta*-adducts (34) and these are shown in Figure 1.4.

The ^{1}H nmr spectrum of the major cycloaddition product (7-*endo*-(3'-butenyl)-1,3-dicyanotricyclo[3.3.0.0^{2,8}]oct-3-ene (**15**); 29% yield) formed from the irradiation of 1,5-hexadiene, resembles group 1 compounds (Figure 1.4) rather than group 2 or 3 of the *meta*-adducts. The ^{1}H nmr spectrum of **15** shows a distinctive doublet (one proton) in the aliphatic region of the spectrum (coupling is ca. 13 Hz). According to

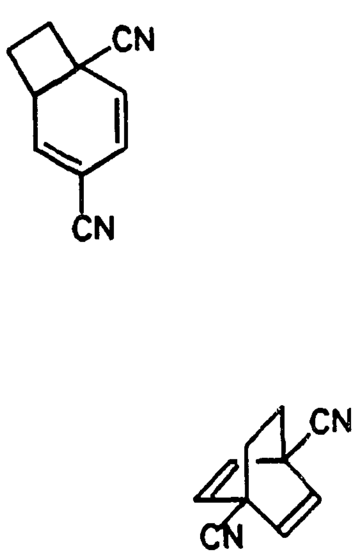


Figure 1.3. Structures of *ortho*-, *para*- and azetine cycloaddition products.

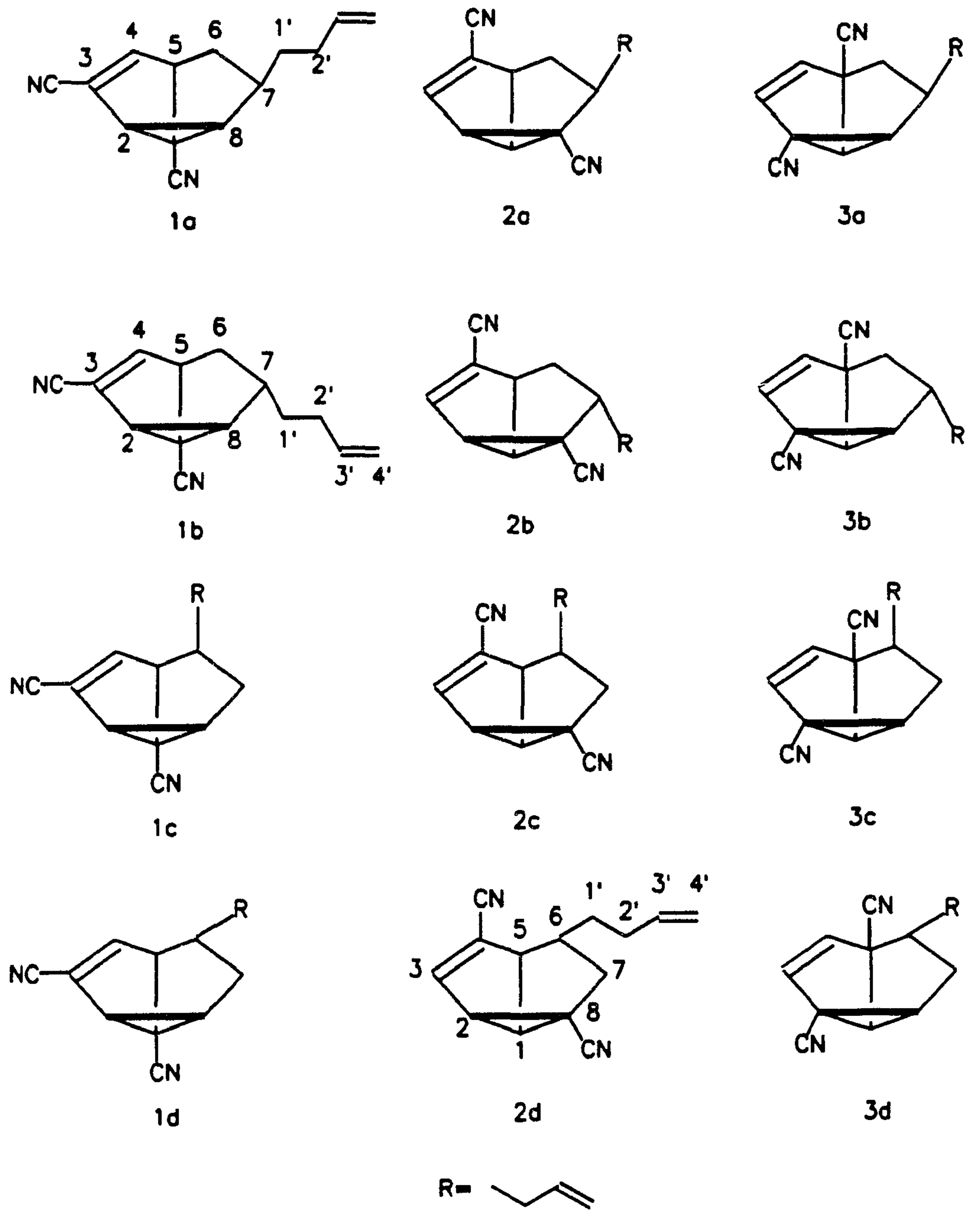


Figure 1.4. Structures of 12 possible *meta*-adducts.

the literature (34), this is typical for group 1 compounds. For group 2 and 3 compounds the largest coupling is typically 7 Hz (34).

Of the group 1 compounds, 1(a) and 1(b) would be the most likely candidates for the major cycloadduct. Using decoupling experiments, it was found that the 13 Hz doublet represents the proton on carbon 2 (1.80 ppm) adjacent to the alkene cyano substituent. This proton on carbon 2 is coupled to the proton on carbon 8 (2.69 ppm) adjacent to it, thus yielding the doublet of 13 Hz. Further decoupling experiments showed that the proton on carbon 8 is largely coupled to one other proton on carbon 7 (2.94 ppm); the coupling is 11.3 Hz.

Proof that leads to elimination of 1(c) and 1(d) as possibilities for compound **15**, was provided. The signal assigned to the proton on carbon 7 (2.94 ppm) integrates to one, thus one would expect it to be a methine proton; however, there is a possibility that the proton on carbon 7 is part of a non-equivalent methylene group. If this were true, the other methylene proton should have a chemical shift close to the proton on carbon 7. The chemical shift of the nearest protons to carbon 7 were looked at; the proton on carbon 8 was assigned, and the *exo* proton on carbon 6 (3.45 ppm) was too far downfield to be the other methylene proton. Consequently, the proton on carbon 7 is that of a methine group with a four-carbon chain attached; as in 1 (a) or 1(b).

Whether the four-carbon chain is *exo* or *endo* can be demonstrated by noting the large coupling of the proton on carbon 8 to the proton on carbon 7. The literature (34) indicates large coupling when the four-carbon chain is in the *endo* position.

Thus 1 (a) is the preferred structure.

The proton on carbon 8 shows unusual long range coupling (w-coupling) to a proton of a methylene group in the ring (*endo* proton on carbon 6); this coupling was not reported in the literature (34). (This type of coupling is possible since the molecule is rigid through the ring portion of the compound.) Further evidence of w-coupling is supported by decoupling the proton on carbon 8. This showed a change in the coupling pattern assigned to the *endo* proton on carbon 6 (3.50 ppm).

The *endo* proton on carbon 6 gives a multiplet. This is due to coupling to the *exo* proton on carbon 6, the proton on carbon 7 and the proton on carbon 8. The coupling constants are 5.8 Hz, 1.2 Hz and 5.5 Hz, respectively. The *exo* proton on carbon 6 shows a similar coupling pattern. It is coupled to the *endo* proton on carbon 6, the proton on carbon 7, and the proton on carbon 5 (2.62 ppm). The coupling constants are 5.8 Hz, 0.9 Hz and 6.6 Hz, respectively.

The literature (34) was used to determine which one of the protons on carbon 6 was *endo* or *exo*. The literature (34) supports the idea that only one of the methylene protons should be coupled to the proton on carbon 5 and this proton should be *exo*. Thus, the proton that showed coupling to the proton on carbon 5 in our molecule was assigned to the *exo* proton on carbon 6.

The proton on carbon 5 shows a distinct doublet of doublets with coupling to the *exo* proton on carbon 6, and to the alkene proton on carbon 4 (6.54 ppm), the coupling being 6.6 Hz and 2.0 Hz, respectively. The proton on carbon 4 exhibits a sharp doublet, 2.0 Hz.

Previously, it was reported that the proton on carbon 7 is coupled to the proton on carbon 8 and to the *exo* and *endo* protons on carbon 6. However, the proton on carbon 7 also shows coupling to the adjacent methylene group (unequivalent protons) of the four-carbon chain (carbon 1′, 1.61-1.71 ppm). The coupling constants are 11.3 Hz, 0.9 Hz, 1.2 Hz, 7.7 Hz and 7.7 Hz, respectively.

Consequently, the non-equivalent methylene protons on carbon 1′ are coupled to one another, to the proton on carbon 7, and to an allylic methylene group (carbon 2′, 2.15-2.22 ppm); 7.8 Hz, 7.7 Hz, 7.7 Hz, 7.5 Hz and 7.5 Hz, respectively.

The protons on carbon 2′ show typical coupling to the protons on carbon 1′, the vinyl proton on carbon 3′ (5.77 ppm) and to the terminal vinyl protons: the *cis* (5.03ppm) and *trans* (5.08 ppm) protons on carbon 4′. The coupling constants are 7.5 Hz, 7.5 Hz, 7.0 Hz, 1.2 Hz and 1.6 Hz, respectively.

The vinyl proton on carbon 3′ shows typical *cis* and *trans* coupling to protons on carbon 4′, and shows vicinal coupling to the protons on carbon 2′ (10.2 Hz, 17.1 Hz and 7.0 Hz, respectively).

The *cis* proton on carbon 4′ shows *cis* coupling to the proton on carbon 3′ (10.2 Hz) geminal coupling to the *trans* proton on carbon 4′ (1.6 Hz) and long range coupling to the allylic methylene protons on carbon 2′ (1.2 Hz). This similar coupling was observed for the terminal vinyl *trans* proton on carbon 4′; of course, the *trans* coupling was exhibited instead (17.1 Hz).

From the above information the ^1H nmr spectra supports the formation of compound 1(a), and this assignment is further supported by ^{13}C nmr spectra.

Additional evidence was obtained through ^{1}H nmr simulation; a spectrum similar to the observed spectrum was produced.

Another cycloaddition adduct from direct irradiation of 1,5-hexadiene was formed as a minor product and was identified as 6-*exo*-(3′-butenyl)-4,8-dicyano-tricyclo[3.3.0.0^{2,8}]oct-3-ene (**16**); 2%. The product is a *meta*-adduct. There are twelve possible *meta*-adducts and these are demonstrated in Figure 1.4. Group 2 compounds appear to be more likely than group 1 or 3 of the possible *meta*-adducts. The ^{1}H nmr spectrum does not exhibit a distinctive splitting pattern (ca. 13 Hz coupling) for vicinal protons on the cyclopropane ring of group 1 compounds. The ^{1}H nmr spectrum does not show *cis* coupling for the vinyl protons on the ring which is distinctive for group 3 compounds. Therefore, the compound must be one of the four possibilities of group 2.

Of group 2, compounds 2(c) and 2(d) would be the most probable. Compound **16** exhibits a bridgehead proton on carbon 5 (3.27 ppm), adjacent to a cyano group on the ring, coupled only to a proton at the apex of three bridgeheads (carbon 1, 3.29 ppm). Therefore, this evidence eliminates 2(a) and 2(b) as possibilities for compound **16** since the proton on carbon 5 in these cases would be coupled to a proton in an adjacent methylene group and to an apex proton.

It can easily be decided whether 2 (c) or 2(d) is compound **16**. Since the bridgehead proton on carbon 5 shows no coupling to adjacent protons, the four-carbon chain must be in the *exo* position; the literature (34) supports this assignment. Thus, if the four-carbon chain is in the *endo* position, sufficient coupling to the bridgehead proton would result. Thus, 2 (c) is eliminated and the preferred structure is 2(d).

The proton on carbon 1 exhibits coupling to the allylic proton on carbon 2 (2.74 ppm) and to the other bridgehead proton on carbon 5. The couplings to the proton on carbon 1 are 5.8 Hz and 5.7 Hz, respectively.

The proton on carbon 2 exhibits coupling to the vinyl proton on carbon 3, as well as to the apex proton on carbon 1. The couplings to the proton on carbon 2 are 2.5 Hz and 5.7 Hz, respectively. The vinyl proton on carbon 3 shows a sharp doublet (coupling is 2.5 Hz).

The methylene protons in the ring (*endo* and *exo* protons on carbon 7, 1.92-2.02 ppm) show distinctive coupling to each other and to the adjacent *endo* proton on carbon 6 (2.20-2.30 ppm). The couplings are 5.7 Hz and 4.6 Hz, respectively. Only one of the methylene protons exhibits measurable coupling to the *endo* proton on carbon 6, and according to the literature (34) it should be the *endo* proton on carbon 7.

The *endo* proton on carbon 6 displays coupling to one of the adjacent methylene protons (as previously discussed, it is coupled to the *endo* proton on carbon 7) and to an adjacent methylene group in the four-carbon chain (carbon 1′, 1.59 ppm). (If the methylene protons on the ring are decoupled, an overlapping doublet of doublets forms for the proton on carbon 6. This is due to coupling of the proton on carbon 6 to non-equivalent methylene protons in the four-carbon chain.) The coupling constants are 4.6 Hz, 6.8 Hz and 6.8 Hz, respectively.

The non-equivalent methylene protons on carbon 1′, as mentioned, are coupled to the proton on carbon 6, and they also show coupling to the allylic methylene protons on carbon 2′ (2.07-2.18 ppm) and to each other. The coupling constants are 6.8 Hz, 6.8 Hz, 7.1 Hz, 7.1 Hz and 5.5 Hz, respectively. The protons on carbon 1′, as well as the remaining vinyl protons, show coupling patterns that are very similar to those found in the major *meta*-adduct (**15**; 29%). The ^{13}C nmr spectra and ^{1}H nmr simulation support the structural assignment of this compound. As well, the infrared spectrum shows that two cyano groups are present in the molecule (two $C\equiv N$ stretching frequencies at 2229 and 2234 cm^{-1}).

Another cycloadduct (7-*exo*-(3′-butenyl)-1,3-dicyanotricyclo[3.3.0.0^{2,8}]oct-3-ene (**17**)) was observed in 18% yield; the structure was established from an analysis of the ^{13}C and ^{1}H nmr spectra of a 50/50 mixture of **15** and **17**. A ^{1}H nmr spectral simulation helped to construct the ^{1}H nmr spectrum of **17** to compare with the actual ^{1}H nmr spectrum of the mixture.

Most of the signals in the ^{1}H nmr spectrum of **17** were found to be quite similar to those of the ^{1}H nmr spectrum of **15**. As the spectrum of **17** was so similar to **15**, compound **17** could only be one of the three *meta*-adducts left in group 1 (Figure 1.4). Compound **17** is 1(b) and not 1(c) or 1(d) for the same reasons given for 1(a) being compound **15**; the proton on carbon 7 is part of a methine group, not a methylene group, because there are no other protons close enough in chemical shift to the proton on carbon 7 to allow a methylene group to be present.

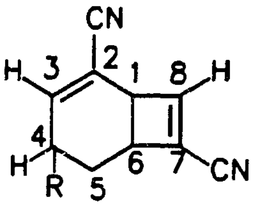
The only large difference between compound **15** and **17** was the coupling between the proton on carbon 7 and the proton on carbon 8. For **15**, the coupling was 11.3 Hz (indicative of an *exo*-hydrogen (34)). For **17**, the coupling was 3.2 Hz (indicative of an *endo*-hydrogen (34)). Thus, compound **17** is 1(b) with an *exo*-four-carbon chain.

In total there were four cycloadducts identified from the reaction of 1,5-hexadiene with **1** in acetonitrile-methanol (3:1). The fourth and final cycloadduct identified was *trans*-4-(3′-butenyl)-*cis*-3,8-dicyanobicyclo[4.2.0]octa-2,7-diene (**18**). The structure of this compound remained elusive (the spectra did not fit any of the mentioned cycloadducts) until a paper by Wagner and Nahm (65) identified an analogous compound as a photo-initiated *ortho*-cycloadduct (bicyclo[4.2.0]octa-2,4-diene) which underwent conversions to a bicyclo[4.2.0]octa-2,7-diene adduct. The substrates used in Wagner and Nahm's work were *o*- and *p*-alkenoxy phenyl ketones. Gilbert *et al.* (66) also reported *ortho*-adducts undergoing conversions. The substrates used in this case were benzonitrile derivatives.

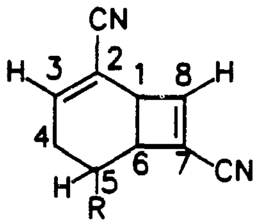
Using the ^{1}H nmr spectrum and x-ray data listed by Gilbert *et al.* (66), the structure of **18** was deduced as a bicyclo[4.2.0]octa-2,7-diene. The possible bicyclo[4.2.0]octa-2,7-dienes are listed in Figure 1.5 (only the gross structure is depicted; no stereochemistry is shown).

The vinyl protons were identified in the ^{1}H nmr spectrum of compound **18**. One vinyl proton is a doublet of doublets and the other is a doublet. Using this information, one of the four possible structures was identified as compound **18**.

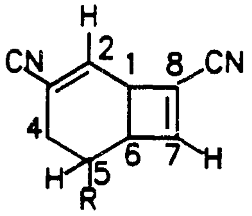
If structure 1 is compound **18**, the vinyl protons can be assigned in two ways. First, the vinyl proton on carbon 8 can be assigned the doublet (coupling: 1.2 Hz) and



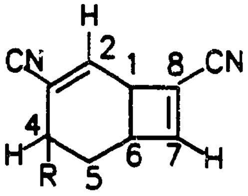
Structure 1



Structure 2



Structure 3



Structure 4

Figure 1.5. Structures of 4 possible bicyclo[4.2.0]octa-2,7-dienes.

the vinyl proton on carbon 3 can be assigned the doublet of doublets (couplings: 2.5 and 5.5 Hz). The bridgehead proton on carbon 1 would have to be a multiplet with couplings of 1.2, 3.3, 4.1 and 5.9 Hz. The bridgehead proton on carbon 6 would have to be a multiplet with 1.5, 4.1 and 5.5 Hz couplings. From this assignment, the proton on carbon 6 is coupled to the proton on carbon 3 and this would not be possible since this would be a five bond coupling of 5.5 Hz. The second way of assigning the vinyl protons, would be to assign the vinyl proton on carbon 8 as the doublet of doublets (couplings: 2.5 and 5.5 Hz) and the vinyl proton on carbon 3 as the doublet (coupling: 1.2 Hz). This would leave the bridgehead proton on carbon 1 to be assigned as a multiplet (couplings 1.5, 4.1 and 5.5 Hz) and the bridgehead proton on carbon 6 to be a multiplet (couplings: 1.2, 3.3, 4.1 and 5.9 Hz). Thus, the proton on carbon 6 is coupled to the proton on carbon 3 by 1.2 Hz which is five bonds away; making this assignment highly unlikely. Therefore, compound **18** cannot be structure 1.

Structure 2 is another possibility for compound **18**. If the vinyl proton on carbon 8 is assigned the doublet of 1.2 Hz, the bridgehead proton on carbon 1 would have to be assigned a multiplet of 1.2, 3.3, 4.1 and 5.9 Hz coupling. The protons on carbon 4 are each assigned as multiplets; one proton has coupling of 5.9, 10.3 and 13.5 Hz coupling and the other proton has 1.5, 3.3, 4.9 and 13.5 Hz coupling. The protons on carbon 4 show couplings to the proton on carbon 1 through five bonds; this is highly unlikely.

If the vinyl proton on carbon 8 is, instead, assigned a doublet of doublets (coupling: 2.5 and 5.5 Hz) in structure 2, then the bridgehead proton on carbon 1 would be a multiplet of 1.5, 4.1 and 5.5 Hz coupling. The proton on carbon 5 would have to be assigned as a multiplet of 2.5, 4.9 and 10.3 Hz. This would mean the proton on carbon 5 is coupled via five bonds to the vinyl proton on carbon 8. Thus, structure 2 is dismissed as a possibility for compound **18**.

Another structural possibility for compound **18** is structure **15**. If the vinylic proton on carbon 7 is assigned the doublet of 1.2 Hz, then the bridgehead proton on carbon 6 is a multiplet of 1.2, 3.3, 4.1 and 5.9 Hz coupling. If the vinylic proton on carbon 2 is assigned the doublet of doublets signal of 2.5 and 5.5 Hz coupling, then the bridgehead proton on carbon 1 is a multiplet of 1.5, 4.1 and 5.5 Hz coupling. The proton on carbon 5 is a multiplet of 2.5, 4.9 and 10.3 Hz coupling; showing coupling to the proton on carbon 2 of 2.5 Hz. This coupling is not possible since it represents coupling through five bonds. Thus, this assignment of the ^{1}H nmr spectrum fails.

If the vinylic proton on carbon 7 is assigned the doublet of doublets (coupling: 2.5 and 5.5 Hz), then the bridgehead proton on carbon 6 is a multiplet (couplings: 1.5, 4.1 and 5.5 Hz). The vinylic proton on carbon 2 is the doublet (coupling: 1.2 Hz) and is coupled to the bridgehead proton on carbon 1 which is represented by a multiplet (couplings: 1.2, 3.3, 4.1 and 5.9 Hz). Since the protons on carbon 4 show couplings of 3.3 and 5.9 Hz to the proton on carbon 1, this again is an impossible assignment since coupling through five bonds cannot exist here.

If we look at structure 4 and assign the doublet of doublets to the proton on carbon 7 (couplings: 2.5 and 5.5 Hz) and the bridgehead proton on carbon 6 to a multiplet (couplings: 1.5, 4.1 and 5.5 Hz), this leaves the proton on carbon 4 to be a multiplet with couplings 2.5, 4.9 and 10.3 Hz. The 2.5 Hz coupling of the proton on carbon 4 is due to coupling to the proton on carbon 7 (five bonds away); thus, this structure does not fit the ^{1}H nmr spectrum.

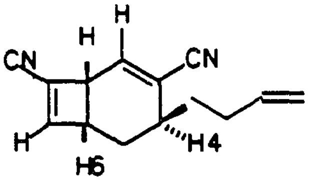
Consider structure 4 again but assign the doublet signal for the vinyl proton to the proton on carbon 7 (coupling: 1.2 Hz) and the bridgehead proton on carbon 6 to a multiplet (couplings: 1.2, 3.3, 4.1 and 5.9 Hz). The vinyl proton on carbon 2 would then have to be assigned the doublet of doublets signal (couplings: 2.5 and 5.5 Hz) and the adjacent bridgehead proton on carbon 1 would have to be a multiplet (couplings: 1.5, 4.1 and 5.5 Hz). The proton on carbon 4 is a multiplet consisting of couplings 2.5, 4.9 and 10.3 Hz; consistent with the allylic coupling to the proton on carbon 2; 2.5 Hz. The remaining assignments are listed in the experimental section and they all appear consistent with structure 4. (The ^{1}H nmr spectrum of **18** shows a similar pattern for the four-carbon chain as was previously shown in the *meta*-adducts.)

It seems that compound **18** has very similar coupling constants to that of the bicyclo compound (benzonitrile derivative) reported by Gilbert *et al.* (66). Although the ^{1}H nmr spectral shifts appear further downfield than that reported for Gilbert's compound, the overall couplings are uncannily similar. This further substantiates that compound **18** is structure 4.

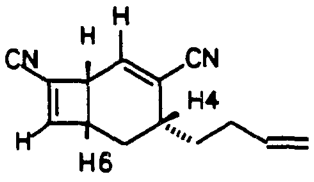
To determine whether the bridgehead had *cis* or *trans* configuration, the coupling constant between the two bridgehead protons was compared to the coupling between the bridgehead protons of the bicyclo[4.2.0]octa-2,7-diene structure reported by Gilbert *et al.* (66). According to x-ray data obtained by Gilbert *et al.* (66) for the bicyclo[4.2.0]octa-2,7-diene, the bridgehead junction is *cis*. They found the coupling constant between the two bridgehead protons to be 4.0 Hz. The coupling for compound **18** was 4.1 Hz. Thus, it was concluded that compound **18** has a *cis* junction as well due to the couplings being so similar between the two compounds.

There are now two diastereomers from which to choose (Figure 1.6). To determine whether the four-carbon chain was on the same side as the cyclobutene ring, a ^{1}H nuclear Overhauser enhancement (NOE) experiment was performed. The proton on carbon 6 was irradiated and the proton on carbon 4 was observed to see if any signal enhancement occurred. There was no NOE observed. This experiment does not yield much information because compound **18** could still be structure 18′ or 18 in Figure 1.6. Since no NOE was observed, it is possible structure 18′ prefers the proton on carbon 4 to be in its equatorial conformation. Structure 18 would still fit the NOE results whether or not the proton on carbon 4 was equatorial or axial.

P.C. Model calculations (67) were used to help identify whether the four-carbon chain was *cis* or *trans* to the cyclobutene ring. Coupling constants were calculated from P.C. Model (67) and optimized for the four-carbon chain being *cis* and *trans* to the cyclobutene ring. The calculated coupling are listed in Table 1.4, along with the actual couplings from compound **18**. The calculations support a four-carbon chain *trans* to the cyclobutene ring.



18



18'

Figure 1.6. Two possible diastereomers of structure 4 with a *cis* bridgehead junction (Figure 1.5).

Table 1.4. Calculations of couplings between protons by P.C. Model to determine whether the four-carbon chain is *cis* or *trans* to the cyclobutene ring.

Geometry of the Four-Carbon Chain With Respect to the Cyclobutene Ring	Couplings (Hz)			
	(4,5a)	(4,5b)	(5a,6)	(5b,6)
cis	5.1	1.7	4.6	2.3
trans	12.4	3.0	4.3	2.2
actual*	10.3	4.9	5.9	3.3

* actual corresponds to the experimental couplings obtained for compound **18**

^{1}H nmr spectral simulations were done to achieve confidence in the coupling constants and chemical shifts reported for the actual ^{1}H spectrum. From the combined evidence, compound **18** is *trans*-4-(3′-butenyl)-*cis*-3,8-dicyanobicyclo[4.2.0]octa-2,7-diene.

The photo-NOCAS product from the irradiation of 2-methyl-1,5-hexadiene, with and without co-donor present, was identified by ^{1}H and ^{13}C nmr spectra. The product is 5-(4-cyanophenyl)-6-methoxy-5-methyl-1-hexene (**19**). The structural information attained included: the aliphatic region of the ^{1}H nmr spectrum exhibits resonances corresponding to two adjacent methylene groups (carbons 3 and 4) and a singlet corresponding to a methyl group affixed to a quaternary centre. The ^{13}C nmr spectrum supports two methylenes and a methyl group.

A sharp singlet, in the ^{1}H nmr spectrum, at 3.29 ppm represents a methoxy group. A distinctive AB-type coupling pattern at 3.37 and 3.49 ppm supports a methoxy substituted methylene group adjacent to a chiral center; two sharp doublets are observed with equivalent coupling constants, 9.1 Hz. Concurrently, the ^{13}C nmr spectrum shows a triplet at 81.10 ppm which supports a methylene bonded to oxygen (the literature (35) supports this assignment), and a quartet at 59.34 ppm which indicates a methoxy group.

There are three vinyl protons present in **19** which exhibit coupling patterns similar to the vinyl protons in the cycloaddition products. This gives evidence for a terminal alkene.

The 4-cyanophenyl portion of the compound shows a distinctive AA′XX′

coupling pattern in the ^1H nmr spectrum which supports *para*-substitution. The 4-cyanophenyl and methyl group substitute the same carbon because the only methyl group in this compound has to be attached to a quaternary carbon. Thus, the ^1H and ^{13}C nmr spectra support the structural assignment of the *anti*-Markovnikov adduct **19**.

Another product formed from 2-methyl-1,5-hexadiene was a 4-cyanophenyl ketone; 1-(4-cyanophenyl)-2-methoxymethyl-2-methyl-5-hexen-1-one (**20**). This product appeared in the irradiation with no co-donor present. The structure of **20** was established by ^1H and ^{13}C nmr spectra, as well as by infrared spectra. The ^1H nmr spectrum appears very similar to the photo-NOCAS product, **19**. The same reasoning reported previously for compound **19** can be used to deduce the structure of compound **20**.

The proof of a carbonyl group being present was found in the infrared spectrum (a strong carbonyl stretch at 1687 cm^{-1}). It is known that conjugation with a phenyl group will lower the wavenumber of a ketone stretching frequency to 1666-1685 cm^{-1} (68). The observed frequency, 1687 cm^{-1}, is close enough to this range, and this helps to establish that the carbonyl group is in conjugation with the aryl group. The mass spectrum exhibited a molecular ion of 257 daltons and the exact mass indicates the molecular formula as $C_{16}H_{19}NO_2$. The ^{13}C nmr spectrum exhibits a singlet at 208.10 ppm, characteristic of a carbonyl group. Since the ^1H nmr spectrum of **20** exhibits very similar signals to compound **19**, the carbonyl group must be attached to the *para* position of the benzonitrile and to a quaternary centre. The structure deduced for **20** is consistent with these observations.

The adducts formed from 2,5-dimethyl-1,5-hexadiene without co-donor present were identified as 5-(4-cyanophenyl)-6-methoxy-2,5-dimethyl-1-hexene (**21**) and 1-(4-cyanophenyl)-2-methoxymethyl-2,5-dimethyl-5-hexen-1-one (**22**). The structural information attained for the *anti*-Markovnikov adduct, **21**, included: the aliphatic region of the ^{1}H nmr spectrum exhibits resonances corresponding to two adjacent methylene groups (carbons 3 and 4) and two singlets corresponding to two methyl groups affixed to a quaternary centre. The ^{13}C nmr spectrum indicates two methylenes and two methyl groups.

A sharp singlet, in the ^{1}H nmr spectrum, at 3.29 ppm represents a methoxy group and a distinctive AB-type coupling pattern at 3.38 and 3.49 ppm supports a methoxy substituted methylene group adjacent to a chiral center; two sharp doublets with equivalent coupling constants of 9.1 Hz are observed. Concurrently, the ^{13}C nmr spectrum shows a triplet at 81.23 ppm which supports a methylene bonded to an oxygen (literature (35) supports this assignment), and a quartet at 59.34 ppm which supports a methoxy group. This is very similar, as is expected, to the *anti*-Markovnikov adduct, **19**, from 2-methyl-1,5-hexadiene. The difference between the two adducts, **19** and **21**, is that **21** has two vinyl protons instead of three, thus the ^{1}H nmr spectrum exhibits the terminal vinyl protons as slightly broadened singlets. The 4-cyanophenyl substituted on the same quaternary carbon as the methyl shows the same evidence as the previous compound **19**.

The 4-cyanophenyl ketone (**22**) demonstrates very similar spectra to the photo-NOCAS product, **21**, and provides the same evidence for a ketone being present as was shown for ketone **20**. Spectra exhibit a carbonyl stretch in the infrared spectrum at 1688 cm^{-1}, an absorption at 208.54 ppm in the ^{13}C nmr spectrum and an increase in molecular ion by 26 daltons (compared to **21**) in the mass spectrum. Exact mass determination supports the molecular formula $C_{17}H_{21}NO_2$.

Irradiation involving the co-donor, **9**, and 2,5-dimethyl-1,5-hexadiene yielded the *anti*-Markovnikov product, **21**, and the *trans* and *cis* cyclized adducts **23** and **24**. Compound **21** was shown to be the *anti*-Markovnikov adduct, in the co-donor case, by comparing the mass spectrum and retention time with the compound identified in the irradiation without co-donor present.

The structure *cis*-1-(4-cyanophenyl)-4-methoxy-1,4-dimethylcyclohexane, **23**, was basically attained through ^1H and ^{13}C nmr spectral evidence. Since a 1,4-disubstituted cyclohexane ring is part of the gross structure of **23**, an ABCD-type coupling pattern should exist in the aliphatic region of the ^1H nmr spectrum. The result was an ABCD coupling pattern in the aliphatic region of the ^1H nmr spectrum, and two types of methylene groups in the ^{13}C nmr spectrum.

The 4-cyanophenyl portion of the compound shows a distinctive AA′XX′ coupling pattern in the ^1H nmr spectrum, thus supporting *para* substitution.

In the aliphatic region of the ^1H nmr spectrum, there are two singlets corresponding to two methyl groups; thus, the methyl groups are affixed to quaternary centres. A shift reagent was used to determine which methyl group was affixed to the same quaternary carbon as the methoxy group. The shift reagent chosen (europium (III) tris 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,5-octanedione) was known to complex to the methoxy group and, thus, selectively shift the methyl group attached to the same carbon as the methoxy group (69). The methyl signal at 1.00 ppm was found to correspond to this methyl group, and the methyl signal at 1.14 ppm corresponds to the methyl group occupying the same carbon as the 4-cyanophenyl group.

Further evidence for the methoxy and a methyl group substituting the same carbon is provided by the ^{13}C nmr spectrum. The ^{13}C nmr spectrum shows a singlet at 72.53 ppm (supporting a quaternary carbon bonded to an oxygen) and a quartet at 48.54 ppm (supporting a methoxy group).

The compound was designated as *cis* by using a NOE experiment. When the signal due to the high frequency methyl group was irradiated (1.14 ppm), an increase in the cyclohexane proton region was observed. This proves the high frequency methyl group is in the axial position because it showed 1,3-diaxial interactions with the protons on the cyclohexane ring. Thus the methyl group occupying the same carbon as the 4-cyanophenyl group is axial. The low frequency methyl signal (1.00 ppm) was irradiated and no change was observed in the cyclohexane proton region. Thus the methyl group occupying the same carbon as the methoxy group is equatorial. The accumulated evidence suggests the compound is the *cis* cycloadduct **23**.

The structure of *trans*-4-(4-cyanophenyl)-1-methoxy- 1,4-dimethylcyclohexane (**24**) was deduced, mainly, through structural information from ^{1}H and ^{13}C nmr spectra.

The ^{1}H nmr spectrum of the *trans* compound is quite similar to that of the *cis* compound. The aliphatic region appears a bit different, as would be expected. The result is still an ABCD coupling pattern, but the *trans*-cyclohexane protons are in a different environment than in the *cis* compound; both methyls will be either in the equatorial position or in the axial position. The compound was designated as *trans* by using the nuclear Overhauser enhancement experiment. When the methyl signal at 1.24 ppm was irradiated, no change in the cyclohexane proton region was observed. Thus the methyl group causing the signal at 1.24 ppm is in the equatorial position because it shows no 1,3-diaxial interactions with the protons on the cyclohexane ring. Consequently, the methyl group, occupying the same carbon atom as the 4-cyanophenyl group, is equatorial. The methyl signal at 1.18 ppm was irradiated and no change was observed in the cyclohexane proton region. Thus, the methyl group bonded to the same carbon atom as the methoxy group is equatorial. This evidence suggests the compound is the *trans* cycloadduct **24**.

As mentioned in the discussion of the results, there were two extra products (**28** and **29**) that resulted from irradiation of 2,5-dimethyl-1,5-hexadiene and **1** and **9**. These two products were identified as products resulting from an impurity in 2,5-dimethyl-1,5-hexadiene. This impurity was identified as 2,5-dimethyl-1,4-hexadiene (**32**). An irradiation involving **32**, **1** and **9** yields **28** and **29**.

Compound **28** was identified as 4-(4-cyanophenyl)-5-methoxy-2,5-dimethyl-1-hexene. The aliphatic region of the ^{1}H nmr spectrum exhibits three singlets assigned to methyl groups. There is support for a methylene group adjacent to a chiral methine centre. The methylene protons were designated as 2.50 and 2.64 ppm. The methine proton was designated as 2.95 ppm and this chemical shift is supported by typical reported shifts for this type of proton (ca. 2.8 ppm) (68). All three protons exhibit an ABX pattern quite nicely. The 2.50 and 2.95 ppm protons each show a four line pattern of a doublet of doublets and the 2.64 ppm proton exhibits a broad doublet. The ^{13}C nmr spectrum displays signals for three methyl groups, one methylene group and one methine group in the aliphatic region of the spectrum.

The ^{1}H nmr spectrum exhibits a sharp singlet at 3.22 ppm representing a methoxy group. The ^{13}C nmr spectrum shows a quartet at 49.22 ppm (methoxy group) and a singlet at 76.44 ppm which supports a methoxy substituted quaternary carbon (the literature (35) supports this assignment).

There are two vinyl protons. Their signals in the ^{1}H nmr spectrum are slightly broad singlets and in the ^{13}C nmr spectrum, they show up as doublets in the vinyl region of the spectrum.

The typical AA'XX' pattern for the 4-cyanophenyl group is present. Thus, all the evidence supports structure **28**.

Compound **29** was identified as 5-(4-cyanophenyl)-4-methoxy-2,5-dimethyl-1-hexene. The structural evidence is very similar to **28**. An AA'X pattern describes the methylene and methine protons instead of an ABX pattern that was described for **28**. This deceptively simple pattern exhibits a coupling only between the methine and the methylene protons; the coupling between the methylene protons cannot be obtained. Proof that the methoxy group is now affixed to a methine carbon is given by the ^{13}C nmr spectrum. A doublet at 87.98 ppm supports this fact. A singlet at

43.74 ppm provides evidence that the aryl group is now affixed to a quaternary carbon.

Another product obtained from the 2,5-dimethyl-1,4-hexadiene irradiation of **1** and **9** was **35**. Compound **35** was identified as *trans*-2-(4-cyanophenyl)-5-methoxy-2,5-dimethyl-3-hexene. This product actually comes from the tautomer 2,5-dimethyl-2,4-hexadiene (**36**), as reported earlier. The structural proof of compound **35** comes neatly from the ^{1}H nmr, ^{13}C nmr and infrared spectra. There are two singlets present in the aliphatic region of the ^{1}H nmr spectrum. Each singlet represents two chemically equivalent methyl groups. A singlet at 3.16 ppm indicates the presence of a methoxy group and an AA′XX′ pattern indicates the 4-cyanophenyl group. Two doublets appear in the vinyl region, each with a coupling of ca. 16 Hz (typical for *trans* geometry (68)).

In the ^{13}C nmr spectrum, there is a singlet at 40.73 ppm supporting a quaternary carbon substituted by a 4-cyanophenyl group. At 50.29 ppm, there is a quartet representing a methoxy group. This methoxy group is affixed to a quaternary carbon due to the fact that there is a singlet at 74.73 ppm.

The infrared spectrum shows a CH bend at 970 cm^{-1}; thus, further supporting the identification of a *trans* alkene.

In conclusion, all of the above mentioned adducts have been identified using several experimental procedures; not only ^{1}H and ^{13}C nmr spectra, but infrared spectra and mass spectra (including exact mass determination) and elemental analyses.

Discussion I

The mechanism (35,36) of the photo-NOCAS reaction has been described in some detail in the General Introduction. The behaviour of 1,5-hexadiene and its homologues appears to be consistent with the proposed mechanism.

Using the Rehm-Weller (31) equation, electron transfer between the olefin and 1,4-dicyanobenzene (**1**) has been calculated to be exergonic for 2,5-dimethyl-1,5-hexadiene (**14**), slightly endergonic for 2-methyl-1,5-hexadiene (**13**) and endergonic for 1,5-hexadiene (**12**). The oxidation potentials of these olefins and their free energies for electron transfer are reported in Table 1.5. From the Rehm-Weller (31) equation, the reaction pathway of 1,5-hexadiene can easily be predicted (70). Cycloaddition, resulting from an exciplex, will occur between 1,5-hexadiene and 1,4-dicyanobenzene. Due to the highly endergonic free energy value calculated, complete electron transfer will not occur and thus photo-NOCAS products will not be formed.

In the Introduction of Section I, examples were given to show that benzene derivatives can undergo *ortho*-, *para*- and *meta*-cycloadditions. Benzene derivatives containing the cyano group also undergo azetine formation with an olefin (1,49-51). Of the various possible cycloadducts, the *meta*-adduct is the most common (71).

A free energy correlation can be used to determine which mode of cycloaddition will be favored in a reaction (71). Cycloadditions to benzene were observed in alkenes of varying oxidation and reduction potentials. When $\Delta G > 135$-

Table 1.5. The calculated free energy change for the electron transfer process with the singlet excited state of 1,4-dicyanobenzene as the acceptor.

Olefin	$E_{1/2}^{ox}$(V)[a]	ΔG (kJ/mol)[b]
1,5-Hexadiene	>3.00	>35.7
2-Methyl-1,5-Hexadiene	2.70	6.81
2,5-Dimethyl-1,5-Hexadiene	2.60	-2.84
2,5-Dimethyl-1,4-Hexadiene	2.28	-33.7

[a] Oxidation potentials were measured at a platinum electrode relative to the saturated calomel electrode (SCE) using tetraethylammonium perchlorate (0.1 M TEAP) as the electrolyte in acetonitrile.

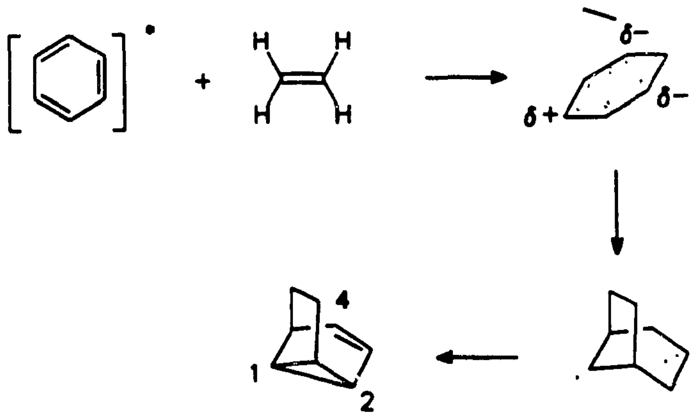
[b] Based upon the Rehm-Weller equation (31); $E_{0,0}$(1) 408.4 kJ/mol, $E_{1/2}^{red}$(1) -1.66 V, the Coulombic attraction term was taken to be 5.40 kJ/mol (36).

154 kJ/mol for electron transfer, *meta*-adducts are formed, while *ortho*-adducts form when 48 kJ/mol > ΔG > 135 kJ/mol. Cycloadditions with benzonitrile (71) resulting in azetine formation can be included in the various modes of cycloadditions. Azetine formation takes place when 0 kJ/mol < ΔG < 39 kJ/mol for electron transfer, *ortho*-adducts form if ΔG < 164 kJ/mol and *meta*-adducts if ΔG > 164 kJ/mol.

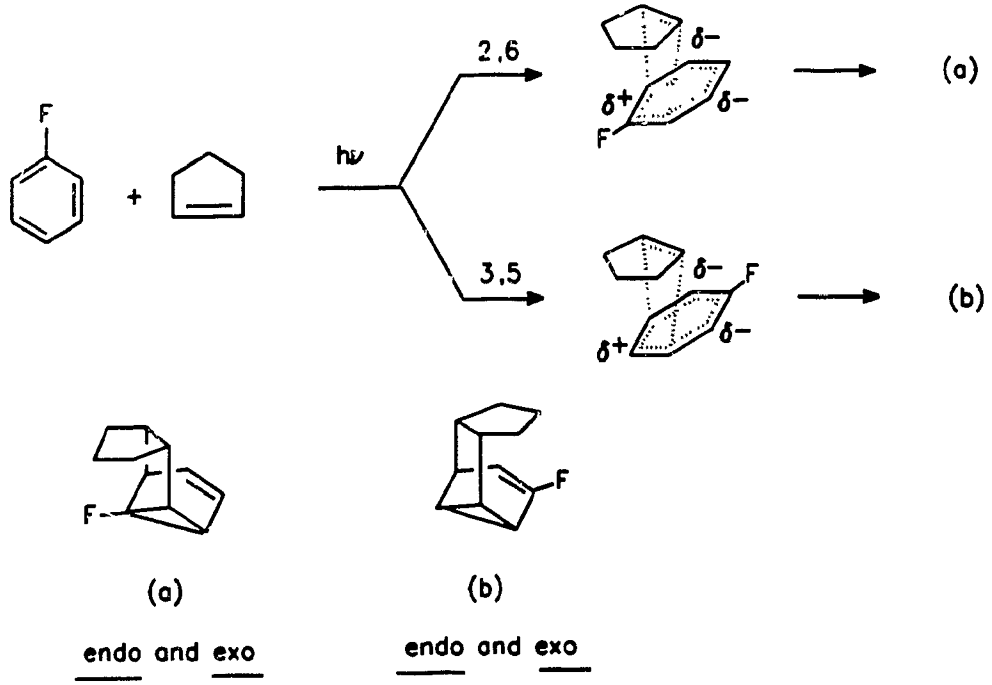
For 1,4-dicyanobenzene, the free energy correlation could be quite similar to benzonitrile. Using the Rehm-Weller (31) equation for the reaction of 1,5-hexadiene with 1,4-dicyanobenzene, the calculated free energy change was found to be greater than 36 kJ/mol. (The free energy change, 36 kJ/mol, is a lower limit because the electrochemical experiment could only measure an accurate oxidation potential up to 3.0 V, and the oxidation potential of 1,5-hexadiene was found to be greater than this.) If extrapolation from the results of benzonitrile to 1,4-dicyanobenzene is assumed to be reasonable, then the free energy should be greater than 164 kJ/mol since *meta*-adducts were formed as major products from 1,5-hexadiene and 1,4-dicyanobenzene. If this is a good estimate for 1,5-hexadiene then this would mean that the oxidation potential of 1,5-hexadiene is greater than 4 V!

The pathway for formation of *meta*-adducts was proposed by Morrison *et al.* (72), Cornelisse *et al.* (73), and Mattay *et al.* (74) to go via an exciplex intermediate. The actual mechanism for formation of the *meta*-adduct was proposed by Cornelisse (34) and is shown in Reaction [1.09].

[1.09]



Cornelisse established that there was a strong substituent effect controlling the reaction. The electron-withdrawing group on the arene directs the attack of the alkene onto the arene. For instance, fluorine has a strong electron-withdrawing inductive effect, as well as an electron-donating resonance effect. The resonance effect directs the addition of the alkene to the arene at carbon 2 and carbon 6 relative to fluorine, and the inductive effect directs the addition to carbon 3 and carbon 5 (Scheme 1.1).



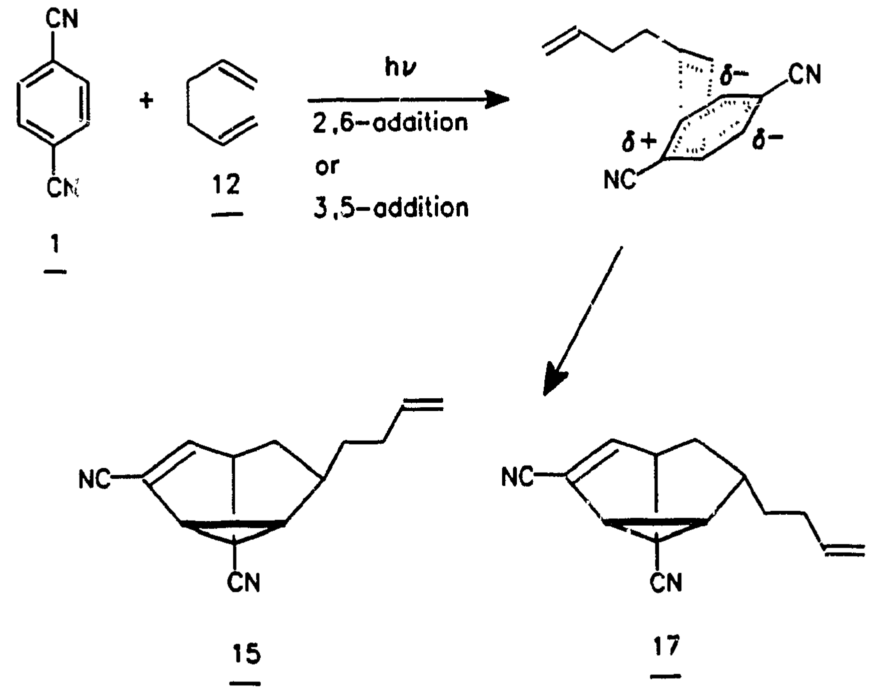
Scheme 1.1. The pathway to formation of the *meta*-adduct is strongly affected by the substituent on the aromatic ring.

The resonance effect stabilizes the partial positive charge at carbon 1 when addition of the olefin occurs at carbons 2 and 6. The inductive effect of fluorine can stabilize the adjacent partial negative charges when addition of the olefin occurs at carbons 3 and 5. The products from 2,6-addition made up 34% of the total yield and products from 3,5-addition made up 66% . Thus the inductive effect was dominant.

Irradiation of 1,5-Hexadiene and 1,4-Dicyanobenzene

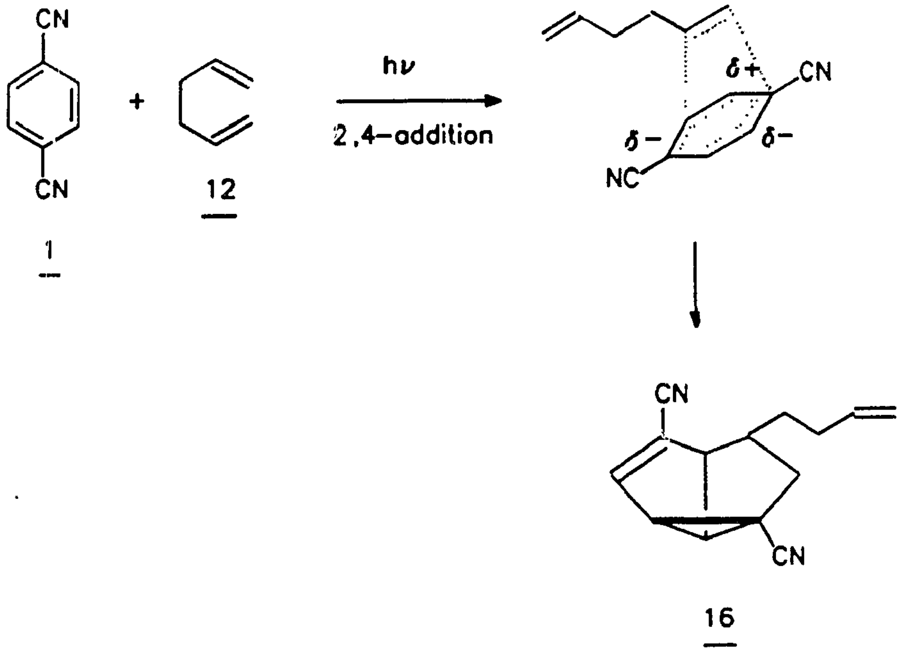
Reaction of 1,5-hexadiene with 1,4-dicyanobenzene resulted in 2,6-addition as the major product, which is equivalent to 3,5-addition in this disubstituted case (Reaction [1.10]).

[1.10]



This result agrees with the prediction which would have been made according to the arguments by Cornelisse (34) based on a combined resonance/inductive effect. Another product formed in the reaction of 1,5-hexadiene with 1,4-dicyanobenzene was the result of 2,4-addition of the alkene to the arene. This *meta*-adduct was produced in low yield (Reaction [1.11]).

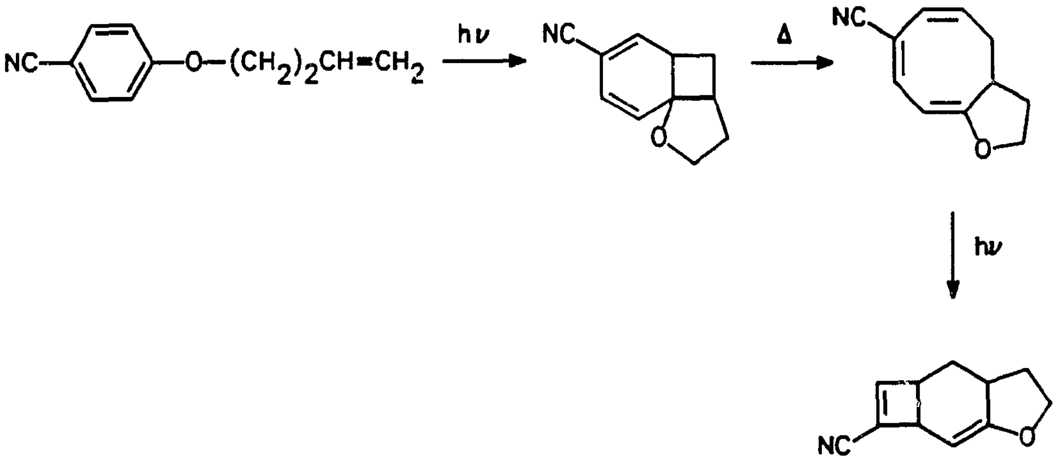
[1.11]



The inductive and resonance effects of the cyano group stabilize the partial negative charges in the 2,6≡3,5 *meta*-adduct. Conversely, the positive charge is highly destabilized by inductive effects but reasonable resonance structures can be drawn for the 2,4-addition *meta*-adduct. The inductive effect must be the most important effect since the 2,4-addition *meta*-adduct is the least favored adduct. Consequently, the combined resonance/inductive effect upon both partial positive and negative charges leads the 2,6≡3,5 addition to the arene to be the major product involving the irradiation of 1,5-hexadiene with 1,4-dicyanobenzene.

There were four products formed from the irradiation of 1,5-hexadiene with 1,4-dicyanobenzene. Three were identified as *meta*-adducts and the fourth product was identified as a bicyclo[4.2.0]octa-2,7-diene (**18**) adduct.

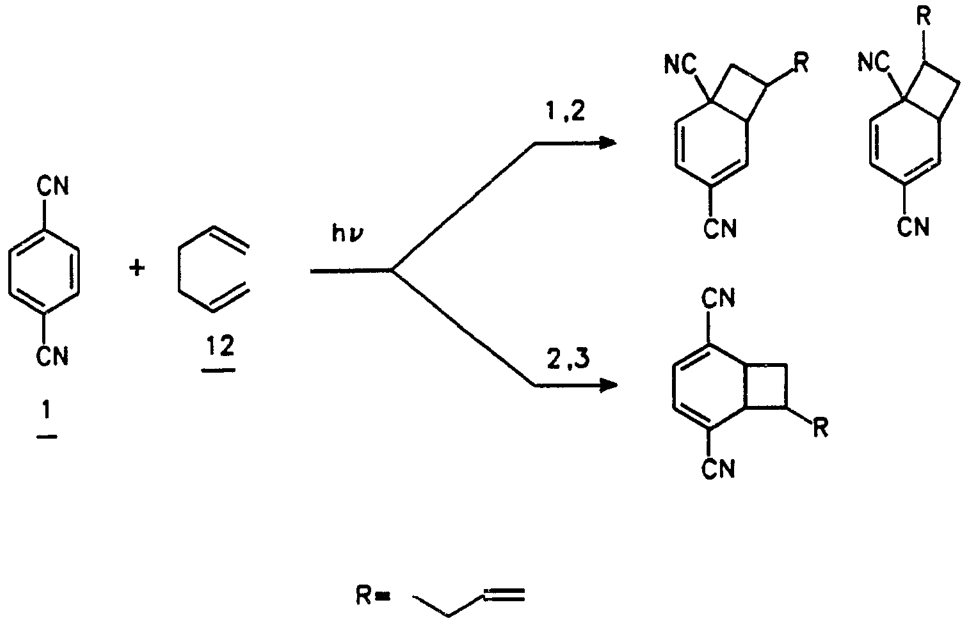
Both Wagner and Nahm (65) and Gilbert *et al.* (66) reported formation of compounds similar to **18**. They (65,66) agree upon a mechanism involving formation of a photo-initiated *ortho*-cycloadduct (bicyclo[4.2.0]octa-2,4-diene) which undergoes thermal conversions to *cis*-cyclooctatrienes followed by photochemical ring closure to a bicyclo[4.2.0]octa-2,7-diene adduct (Scheme 1.2 (66)).



Scheme 1.2. A proposed mechanism for the formation of bicyclo[4.2.0]octa-2,7-diene adduct.

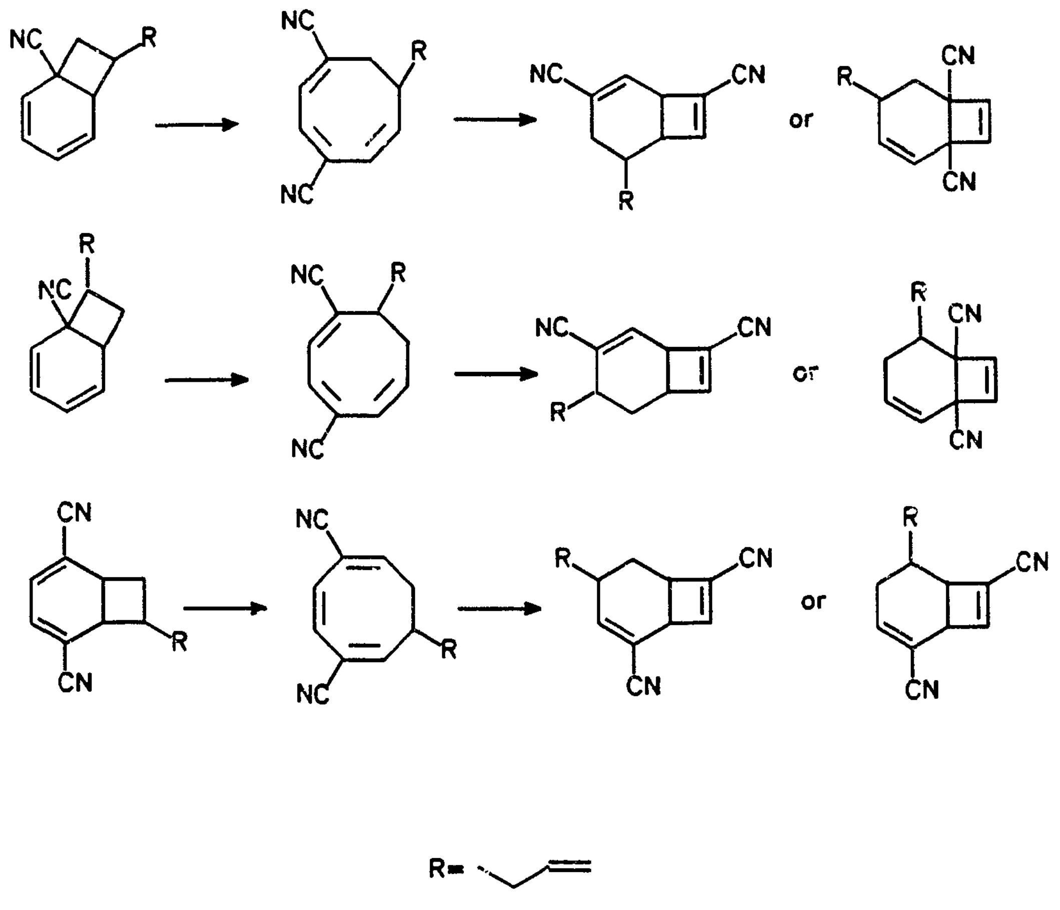
This same scheme can be invoked to explain the formation of the bicyclo[4.2.0]octa-2,7-diene (**18**).

There are two possible modes of *ortho*-addition to 1,4-dicyanobenzene. One involves attack of the olefin at carbons 1 and 2 of 1,4-dicyanobenzene and the other involves attack of the olefin at carbons 2 and 3 of 1,4-dicyanobenzene (Scheme 1.3).



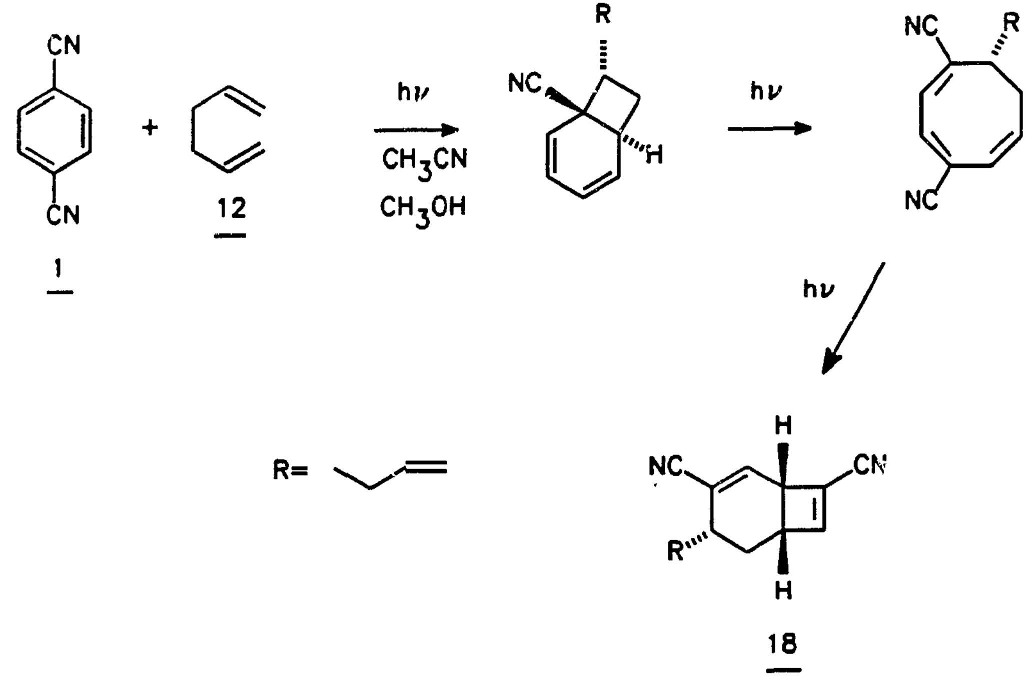
Scheme 1.3. Two possible modes of *ortho*-addition to 1,4-dicyanobenzene.

The concerted pathway that follows *ortho*-addition should be analogous to that occuring in the reactions reported by Wagner and Nahm (65) and Gilbert *et al.* (66). Scheme 1.4 outlines the reactions that follow *ortho*-addition (minus the stereochemistry).



Scheme 1.4. Possible reactions that could follow *ortho*-addition.

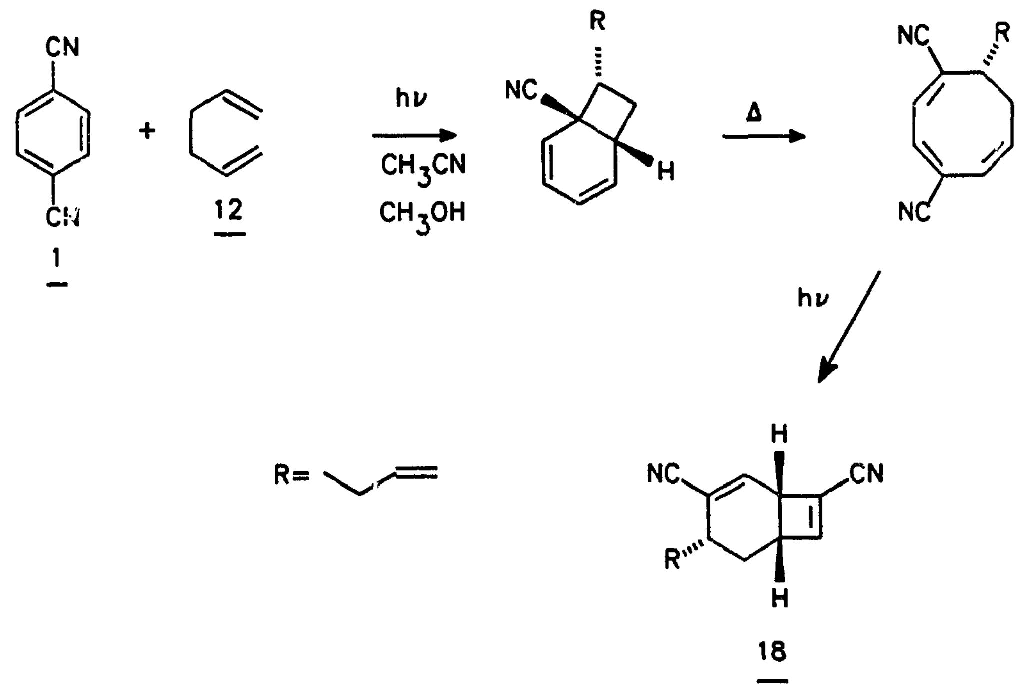
From all these possible products in Scheme 1.4, spectral analysis confirmed the identity of **18** as *trans*-4-(3′-butenyl)-*cis*-3,8-dicyanobicyclo[4.2.0]octa-2,7-diene. Thus, the reaction begins with 1,2-addition of 1,5-hexadiene to 1,4-dicyanobenzene to form the *ortho*-adduct. This step could be followed by photochemical ring-opening to *cis*-cyclooctatriene and finally photochemical ring-closure to form compound **18** (Scheme 1.5).



Scheme 1.5. A possible mechanism leading to formation of **18**.

Wagner and Nahm (65) and Gilbert *et al.* (66) both report a thermal ring-opening of the *ortho*-cycloadduct. Their evidence is based upon isolation of the *ortho*-cycloadduct following passage through a gc (columns ≥ 200°C). This produced a yellow compound identified as a *cis*-cyclooctatriene. Isolation of *cis*-cyclooctatrienes followed by irradiation yielded the bicyclo[4.2.0]octa-2,7-dienes. This demonstrated that the *cis*-cyclooctatriene could be formed thermally.

Since isolation of the cycloadducts that are precursors to **18** in the reaction of 1,5-hexadiene and 1,4-dicyanobenzene was not possible, proof for the thermal formation of the cyclooctatriene could not be obtained. Since the reactions were run at 10°C, thermal ring-opening seems less likely (Scheme 1.6), but there is no reason to rule out the possibility of photochemical ring-opening (Scheme 1.5).



Scheme 1.6. A possible mechanism leading to formation of **18** involving thermal ring-opening.

Addition of the co-donor, biphenyl (**9**), to the irradiation mixture of 1,5-hexadiene and 1,4-dicyanobenzene produced an 80% reduction in yield of cycloaddition products. The large difference in yield is due to biphenyl acting as a quencher of the reaction instead of as an efficient co-donor. This can be explained by looking at the mechanism of the reaction involving biphenyl.

The singlet excited state of 1,4-dicyanobenzene undergoes electron transfer with biphenyl to form the biphenyl radical cation and the 1,4-dicyanobenzene radical anion. The biphenyl radical cation could form a complex with 1,5-hexadiene which could then undergo electron transfer. However, the electron transfer step between 1,5-hexadiene and biphenyl is endergonic by 117 kJ/mol. Since the limiting value for electron transfer between biphenyl and an olefin is 79 kJ/mol, biphenyl is not an efficient co-donor in this case. Consequently, the only intermediates present in solution would be the biphenyl radical cation and 1,4-dicyanobenzene radical anion. No photo-NOCAS products are possible. The excited 1,4-dicyanobenzene will still form some cycloaddition products with 1,5-hexadiene but the majority of excited 1,4-dicyanobenzene will be quenched by biphenyl. This accounts for the low yield of cycloaddition products.

Addition of phenanthrene (**5**) was found to quench the reaction completely and no cycloaddition products were observed. This stems from the fact that now phenanthrene, and not 1,4-dicyanobenzene, is the excited species. Subsequently, phenanthrene undergoes electron transfer with 1,4-dicyanobenzene. Electron transfer will not occur between phenanthrene and the olefin because the free energy for this process is highly endergonic. Also, there will be very little excited state 1,4-dicyanobenzene to form cycloadducts with 1,5-hexadiene since phenanthrene is the major light absorbing species.

Irradiation with 1,5-hexadiene and 1,4-dicyanobenzene in benzene, instead of acetonitrile-methanol, was also tried. This resulted in exciplex product formation as expected. The reaction should perhaps have been more favorable in the non-polar solvent because polar solvents, like acetonitrile-methanol, prefer formation of free radical ions and thus shorten the lifetime of exciplexes. However, a very similar reaction mixture was obtained using benzene as the solvent and the reaction did not seem to be anymore efficient than in the polar solvent. The major product (by gc retention time and mass spectrum) was the same in both solvents.

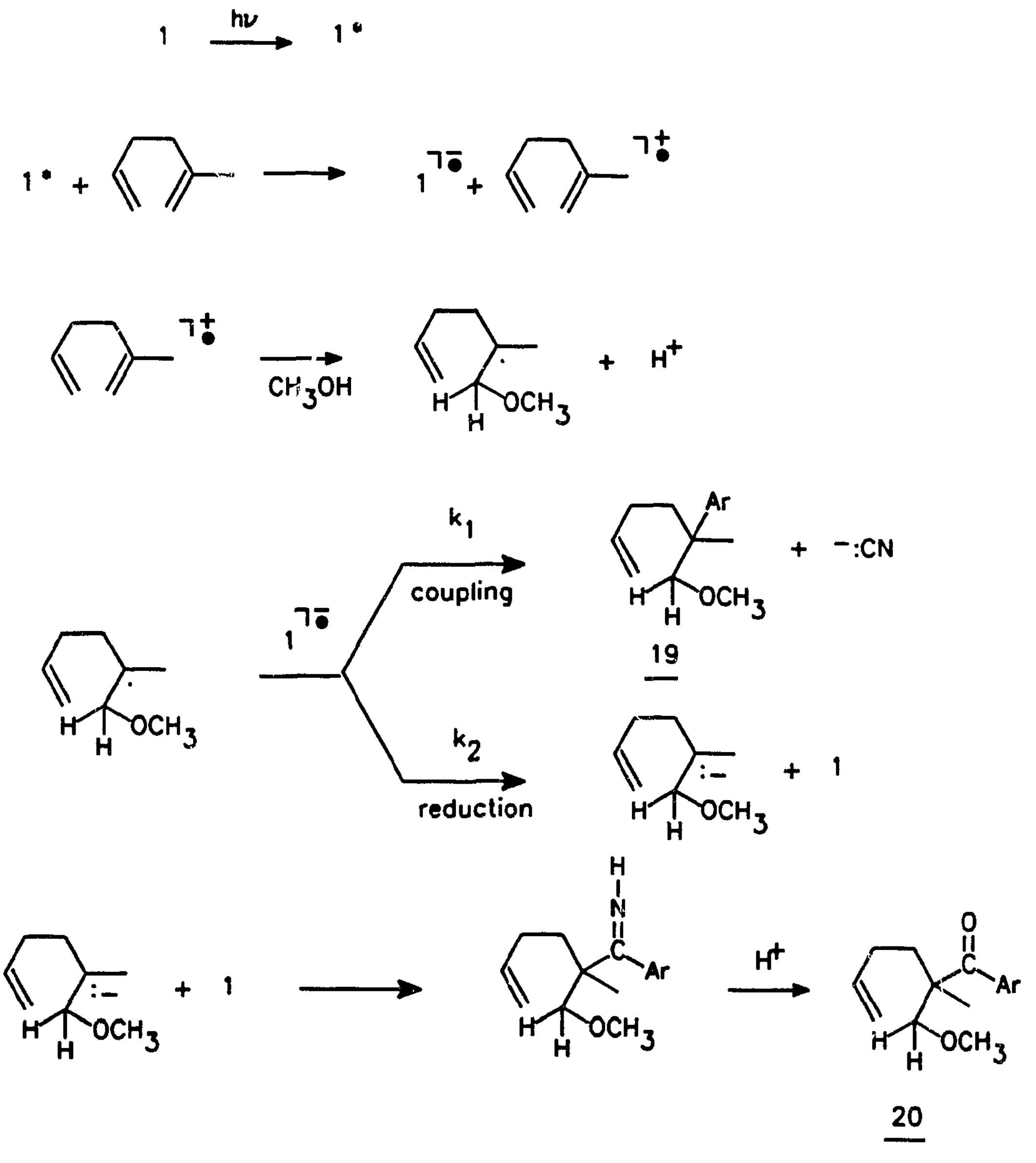
Irradiation of 2-Methyl-1,5-Hexadiene and 1,4-Dicyanobenzene

2-Methyl-1,5-hexadiene (**13**) and 1,4-dicyanobenzene were irradiated in a solution of acetonitrile-methanol (3:1). Using the Rehm-Weller (31) equation, step 2b (Scheme 15) was calculated to be slightly endergonic, and it is likely that either direct electron transfer via a short-lived encounter complex or electron transfer via the exciplex will occur. The products resulting from direct irradiation of 1,4-dicyanobenzene with 2-methyl-1,5-hexadiene were a photo-NOCAS product (*anti*-Markovnikov adduct; 5-(4-cyanophenyl)-6-methoxy-5-methyl-1-hexene (**19**)) and a 4-cyanophenyl ketone (**20**) (1-(4-cyanophenyl)-2-methoxymethyl-2-methyl-5-hexen-1-one; tentatively assigned) (Reaction [1.02] in Results I).

The photo-NOCAS product formed from 2-methyl-1,5-hexadiene is the *anti*-Markovnikov adduct (**19**). Attack of methanol occurs at the more substituted olefin. This is due to the oxidation potential being lower here due to the electron-donating ability of the methyl group. Once again the favored attack of methanol is at the less substituted end of the olefin, thus yielding the favored *anti*-Markovnikov adduct. The other product formed is the first of this type to be found in the photo-NOCAS reaction. Attack occurs at the cyano group on the aromatic, instead of at the *ipso* position. A possible mechanism for formation of this adduct has been proposed (Scheme 1.7). The mechanism entails the usual excitation of 1,4-dicyanobenzene followed by electron transfer from 2-methyl-1,5-hexadiene. Methanol attacks the olefin radical cation to yield the β-alkoxy radical. The β-alkoxy radical reacts by two different pathways: attack on the 1,4-dicyanobenzene radical anion at the *ipso* position or reduction by the 1,4-dicyanobenzene radical anion to give the carbanion. In order to form the 4-cyanophenyl ketone (**20**), reduction of the β-alkoxy radical must occur followed by attack of this anion at the cyano group of neutral 1,4-dicyanobenzene. Finally, hydrolysis on column chromatography gives the ketone (**20**).

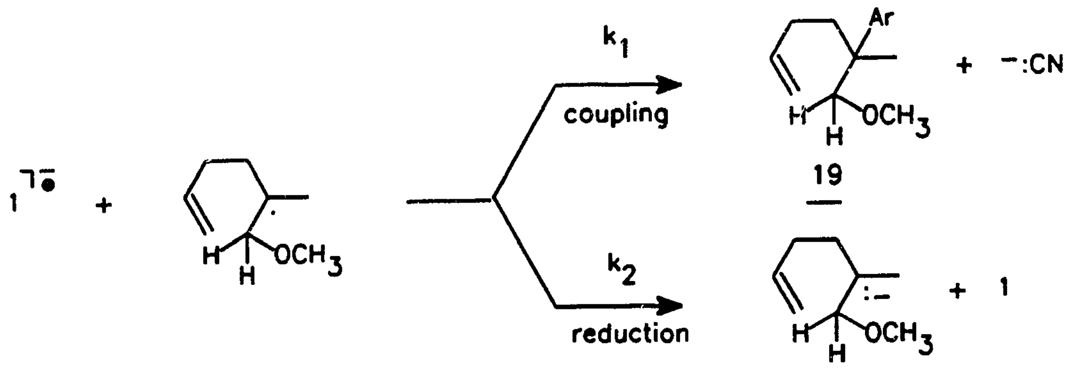
Several factors have to be examined to understand how this mechanism is plausible. The β-alkoxy radical formed is a tertiary radical which must be reduced by the 1,4-dicyanobenzene radical anion. The requirement for this is that the reduction potential of the tertiary radical must be lower than that of 1,4-dicyanobenzene. The known reduction potential of a *tert*-butyl radical of -1.60 V vs. SCE (75), should be comparable to the reduction potential of the β-alkoxy radical obtained from 2-methyl-1,5-hexadiene. If this is true, then reduction of the β-alkoxy radical is plausible since the reduction potential of 1,4-dicyanobenzene is -1.66 V. The β-alkoxy anion should proceed to attack the cyano group of the neutral 1,4-dicyanobenzene since ionic attack is known to occur at this position.

The rates of formation of the typical photo-NOCAS product and the 4-cyanophenyl ketone (**20**) must be explored. The two steps that determine the competition between the formation of the photo-NOCAS product and the 4-



Scheme 1.7. Mechanism proposed for formation of **20** from irradiation of **1** and **13**.

cyanophenyl ketone (**20**) are as follows (Scheme 1.8).



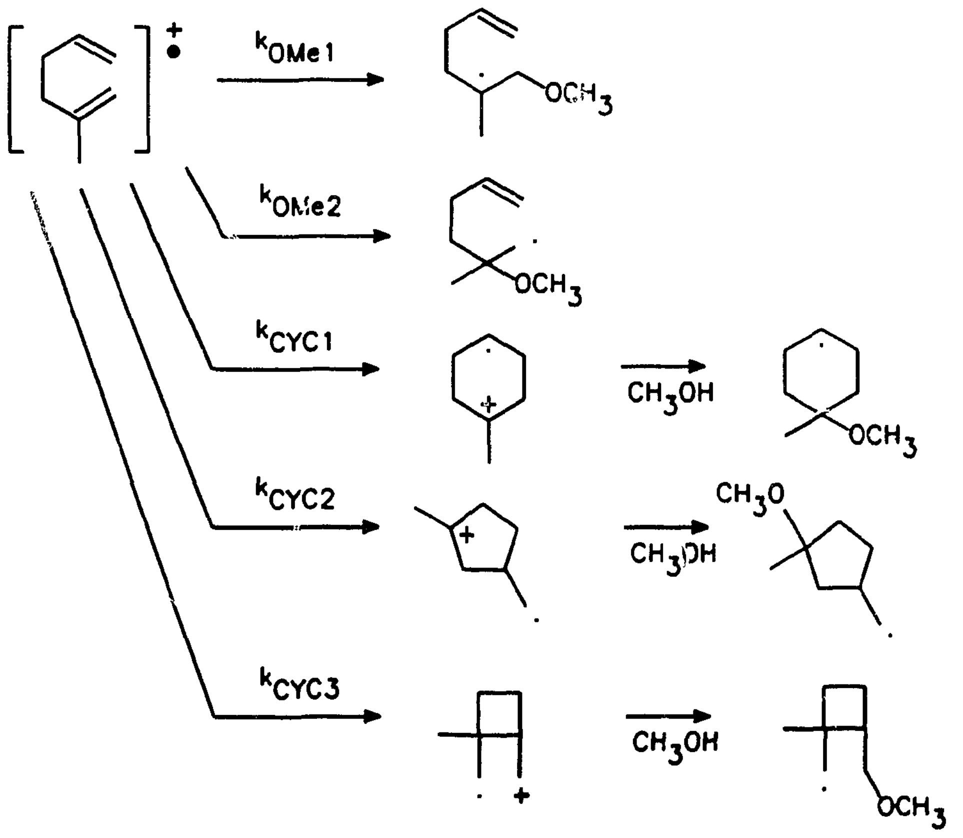
Scheme 1.8. Two competing pathways between the formation of the photo-NOCAS product and the 4-cyanophenyl ketone (**20**)

The yields of the photo-NOCAS product and the ketone (**20**) are 4% and 7%, respectively indicating that the activation energy must be slightly higher for coupling than for reduction.

Why this type of ketone (**20**) was observed here (also a ketone forms with 2,5-dimethyl-1,5-hexadiene) and not in any other photo-NOCAS reactions, remains a mystery. Perhaps the activation energy for reduction is higher in these other photo-NOCAS reactions or perhaps there is a competition between attack upon 1,4-dicyanobenzene by the β-alkoxy anion or hydrogen abstraction by the β-alkoxy anion to yield ethers. Perhaps the second process is much more favored in other photo-NOCAS reactions. (This could be true because very low yields of ethers are obtained in the reaction with 2-methyl-1,5-hexadiene).

When biphenyl was added to the irradiation mixture of 2-methyl-1,5-hexadiene and 1,4-dicyanobenzene, no ketone (**20**) was detected. A possible explanation for this cannot be given at this time.

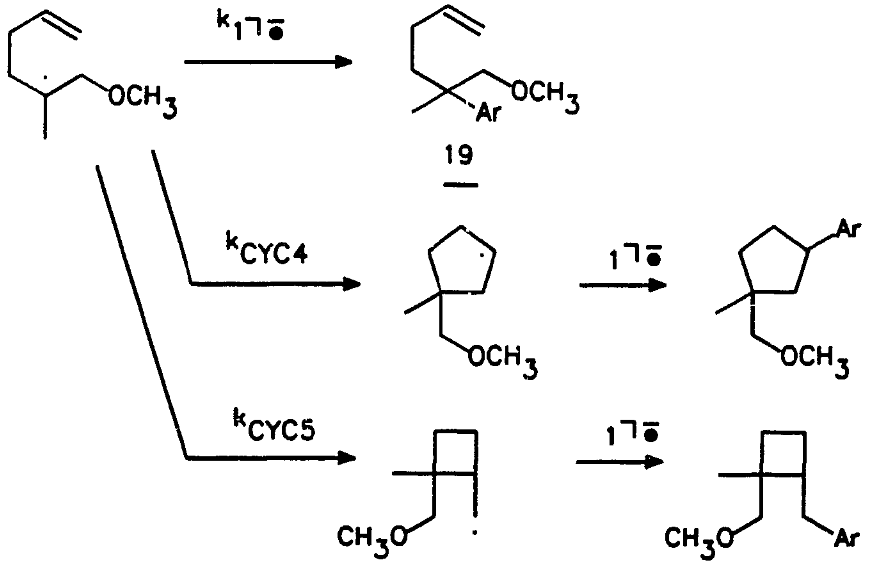
For the irradiation of 2-methyl-1,5-hexadiene and 1,4-dicyanobenzene, with and without co-donor present, no cyclized products resulted. Many competing reaction pathways leading to cyclized products are possible. (The pathway for formation of the ketone **20** will be ignored). These pathways for 2-methyl-1,5-hexadiene could, in principle, involve various competing reactions to form methanol substituted radicals (Scheme 1.9).



Scheme 1.9. Various competing reactions involving the radical cation of 2-methyl-1,5-hexadiene.

The positions of the radical and the cation in the cyclized products are limited to the most stable form of the radical cation in order to simplify the competing reaction scheme. The substrate radical cation depicted, represents various conformers. It was depicted this way to show the particular conformation that leads to cyclization. The rate constants represent average values from various conformers.

The *anti*-Markovnikov product **19** was the only photo-NOCAS product formed; hence, the uncyclized tertiary radical is preferred. There are neither cyclized products nor Markovnikov products formed; thus, the rate of formation of the tertiary radical (k_{OME1}) is much faster than the rate of formation of the other cyclized radical cations or radicals. Subsequent competing reactions, involving substitution of the 1,4-dicyanobenzene radical anion with the tertiary radical, are also possible (Scheme 1.10).



Scheme 1.10. Competing reactions involving substitution of 1,4-dicyanobenzene with the tertiary radical.

Apparently, attack of the dicyanobenzene radical anion occurred at a much faster rate than cyclization since none of these cyclized products were observed.

Biphenyl addition to the irradiation mixture of 2-methyl-1,5-hexadiene and 1,4-dicyanobenzene increases the efficiency of the reaction, resulting in a higher yield of *anti*-Markovnikov product and no 4-cyanophenyl ketone (**20**). When biphenyl is present, electron transfer occurs between biphenyl and the singlet excited state of 1,4-dicyanobenzene; this process is favorable (79 kJ/mol exergonic). The biphenyl radical cation forms a complex with 2-methyl-1,5-hexadiene and electron transfer occurs. The increased efficiency of the reaction is thought to be due to a lower efficiency of back electron transfer between the biphenyl radical cation and the 1,4-dicyanobenzene radical anion.

Compared to biphenyl, addition of phenanthrene had the opposite effect on the yield. When the complex forms between the phenanthrene radical cation and 2-methyl-1,5-hexadiene, electron transfer is less favorable. The energy gap between the two is too great for phenanthrene to perform as an efficient sensitizer. The result is a lower yield of the *anti*-Markovnikov product.

Irradiation of 2,5-Dimethyl-1,5-Hexadiene and 1,4-Dicyanobenzene

2,5-Dimethyl-1,5-hexadiene (**14**) and 1,4-dicyanobenzene were irradiated in a solution of acetonitrile-methanol (3:1). Using the Rehm-Weller (31) equation, step 2b

(Scheme 15) was calculated to be exergonic and thus 2,5-dimethyl-1,5-hexadiene should undergo electron transfer. The products resulting from direct irradiation (no co-donor or sensitizer present) of 2,5-dimethyl-1,5-hexadiene and 1,4-dicyanobenzene were a photo-NOCAS product (*anti*-Markovnikov adduct; 5-(4-cyanophenyl)-6-methoxy-2,5-dimethyl-1-hexene (**21**)) and a 4-cyanophenyl ketone (**22**) (1-(4-cyanophenyl)-2-methoxymethyl-2,5-dimethyl-5-hexen-1-one) (Reaction [1.04] in Results I).

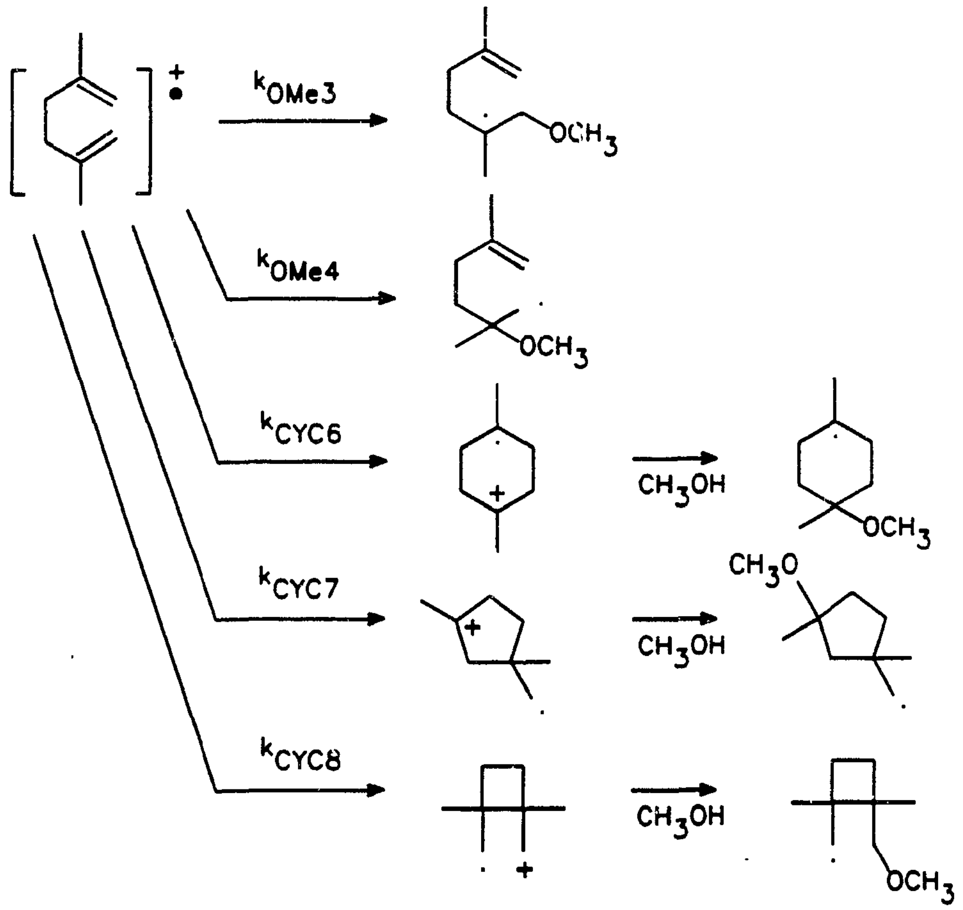
The photo-NOCAS product formed from 2,5-dimethyl-1,5-hexadiene is the *anti*-Markovnikov adduct (**21**). Attack of methanol occurs at the less substituted carbon yielding the more stable tertiary radical. The radical then couples with the 1,4-dicyanobenzene radical anion to yield the favored *anti*-Markovnikov adduct.

The other product formed from this photo-NOCAS reaction is the 4-cyanophenyl ketone (**22**). This is a similar compound to that obtained from 2-methyl-1,5-hexadiene. The same mechanism and explanation for formation of ketone **20** can be used to explain the formation of ketone **22**. However, in this case, coupling of the 1,4-dicyanobenzene radical anion to the β-alkoxy radical must have a slightly lower activation energy compared to reduction of the radical since the yields are 8% **21** and 3% **22**.

It was observed that by adding biphenyl to the irradiation of 2,5-dimethyl-1,5-hexadiene and 1,4-dicyanobenzene no ketone **22** resulted. This same result was found with 2-methyl-1,5-hexadiene. There is no obvious explanation for this effect of biphenyl upon the reaction.

When biphenyl was added to the irradiation mixture of 2,5-dimethyl-1,5-hexadiene, the *anti*-Markovnikov adduct (**21**) was formed along with two other products which were identified as cyclized products; *cis* and *trans*-4-(4-cyanophenyl)-1-methoxy-1,4-dimethylcyclohexane, **23** and **24**, respectively. It seems the more biphenyl present in this irradiation, the higher the yield of cyclized products. This provides some insight into how and why the cyclized products might be formed. The cyclized products were observed only when 2,5-dimethyl-1,5-hexadiene was irradiated in the presence of biphenyl. 2-Methyl-1,5-hexadiene gave no cyclized products with or without biphenyl. Thus, the combined effect of biphenyl and two methyl groups resulted in the formation of cyclized products.

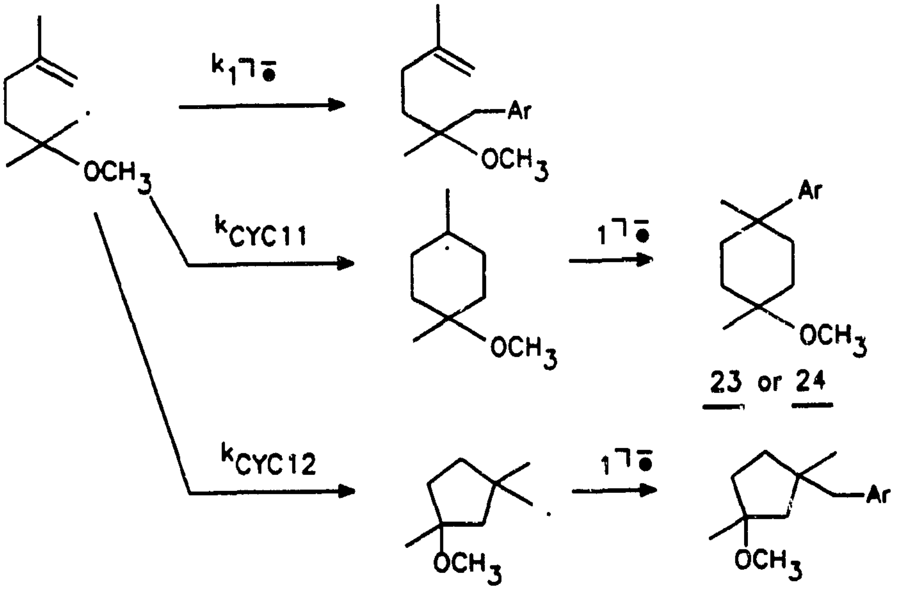
The possible pathways for formation of the cyclized products must involve various competing reactions of the radical cation of 2,5-dimethyl-1,5-hexadiene (Scheme 1.11).



Scheme 1.11. Various competing reactions involving the 2,5-dimethyl-1,5-hexadiene radical cation.

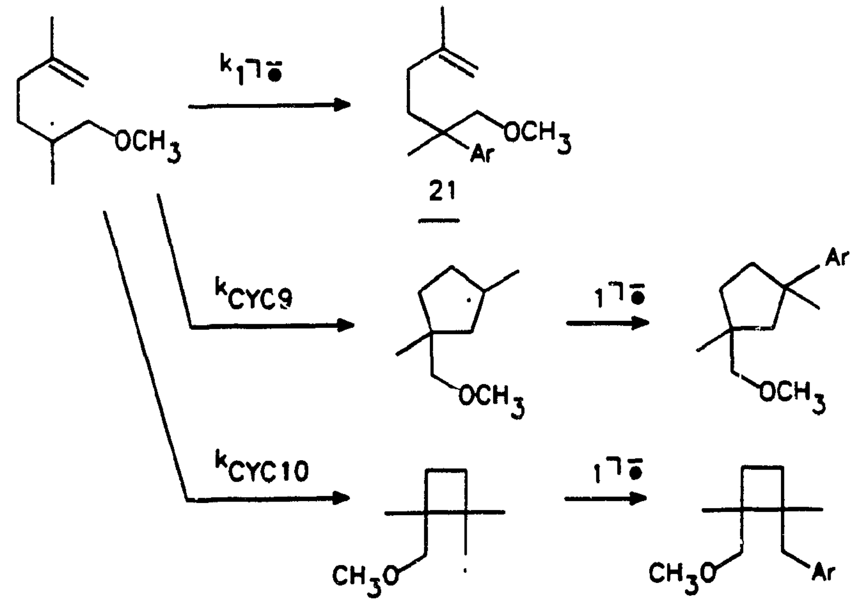
Again, the positions of the radical and the cation in the cyclized products are limited to the most stable form of the radical cation in order to simplify the competing reaction scheme. The substrate radical cation depicted, represents various conformers. It was depicted this way to show the particular conformation that leads to cyclization. The rate constants represent average values from various conformers.

In this reaction of 2,5-dimethyl-1,5-hexadiene, 1,4-dicyanobenzene and biphenyl, the *anti*-Markovnikov product **21** and the cyclohexane products **23** and **24** were the only products formed. Hence, it can be proposed that the uncyclized tertiary radical as well as the cyclohexyl radical cation are preferred (Scheme 1.11). The primary radical (Scheme 1.11) could also be an intermediate even though no Markovnikov products were formed since there is a possibility that the cyclohexane ring forms from this radical. If this is true then the rate of formation of the cyclohexane ring must be faster than the rate of formation of the Markovnikov uncyclized product. These competing reactions with the primary radical are shown in Scheme 1.12.



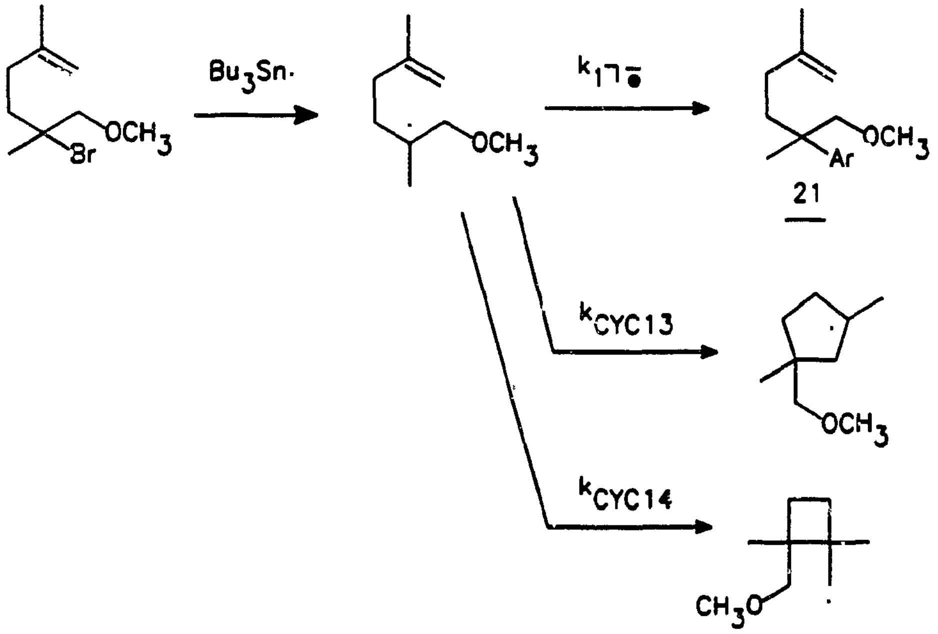
Scheme 1.12. Competing reactions involving the primary radical.

Furthermore, the tertiary radical could also have undergone other competing reactions (Scheme 1.13).



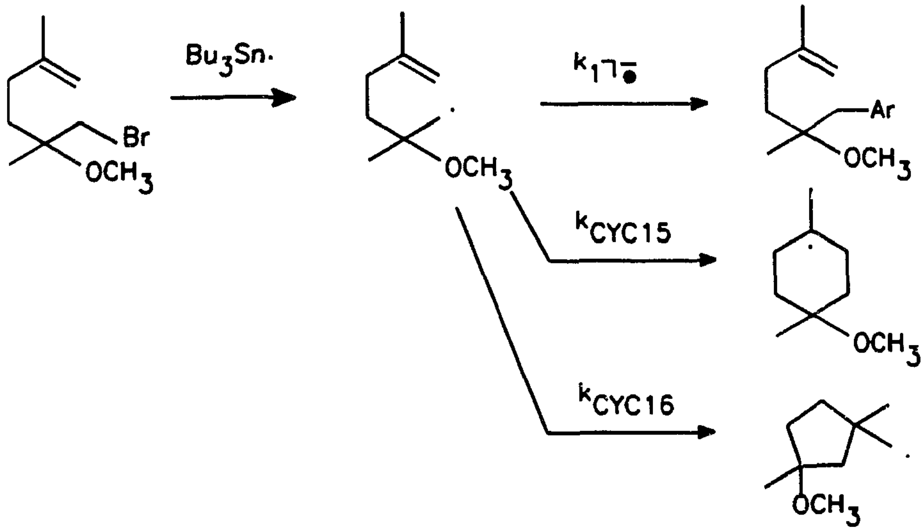
Scheme 1.13. Competing reactions involving the tertiary radical.

The rates of competing reactions can often be determined by using radical clocks (76-78). This is shown in Scheme 1.14.



Scheme 1.14. Possible radical clock.

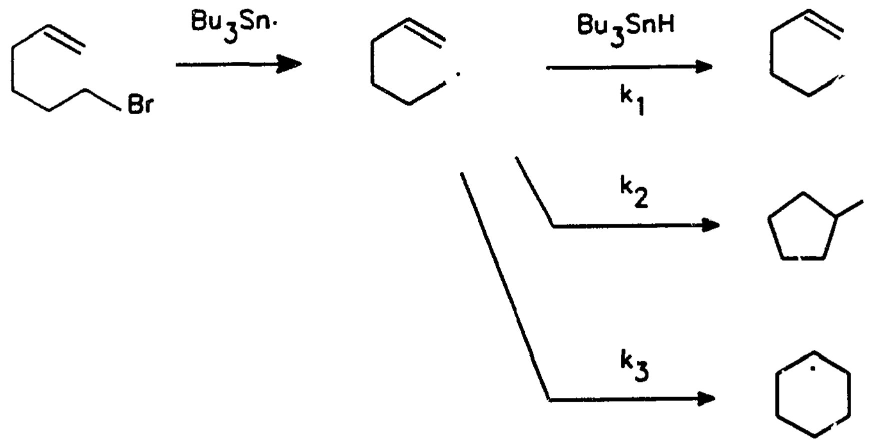
If similar reactions to these are known, then their rate constants could help strengthen the conclusion that cyclization to the 4- or 5-membered ring is less favored than coupling of the aryl group. Similarly, radical clocks could be useful for the rate of cyclization of a primary radical (Scheme 1.15).



Scheme 1.15. Possible radical clock to show rates of cyclization of a primary radical.

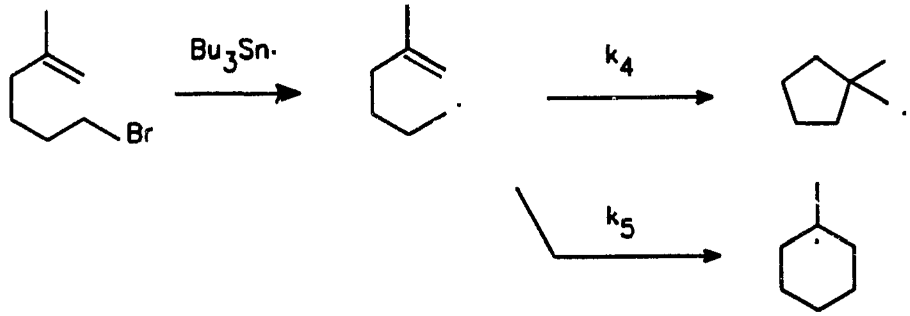
If similar reactions to these are known and coupling is found to be favored over cyclization, then this would provide evidence that the primary radical was not formed initially, since Markovnikov products were not found. Thus, cyclization to form the radical cation followed by methanol addition would provide the cyclohexane product.

The only known radical clocks that could be compared to these cyclizations are shown in Scheme 1.16 and 1.17.



Scheme 1.16. Known radical clocks for cyclization of the hexenyl primary radical.

The rate constants determined were: $k_1 = 1 \times 10^6\ M^{-1}s^{-1}$ (76), $k_2 = 1.1 \times 10^5\ s^{-1}$ (77) and $k_3 < 0.005 \times 10^5\ s^{-1}$ (77). (Beckwith *et al.* (78) also observed a preference for the 5-*exo-trig* cyclization).



Scheme 1.17. Known radical clocks for cyclization of the 2-methylhexenyl primary radical.

Here the values determined were: $k_4 = 0.9 \times 10^5\ s^{-1}$ (77) and $k_5 \leq 0.024 \times 10^5\ s^{-1}$ (77). Walling *et al.* (77) observed that methyl substitution at the double bond decreased the rate of formation of the 5-*exo-trig* product (compare Schemes 1.16 and 1.17) and increased the rate of 6-*endo-trig* cyclization. This was believed to be due to the increased stability of the radical formed which is now tertiary (Scheme 1.17). The conclusion that can be drawn from these literature results is that a primary radical cyclizes more rapidly to a five-membered than to a six-membered ring. This route to cyclization to form the six-membered ring photo-NOCAS products is therefore very unlikely.

There was also direct evidence in the photo-NOCAS reaction with 2,5-dimethyl-1,5-hexadiene to prove that cyclization to form cyclohexane adducts occurs before attack of methanol and not via the primary radical. This evidence was provided by two variations in the method: increased concentration of biphenyl in the irradiation mixture and decreased concentration of methanol.

Addition of more biphenyl caused less *anti*-Markovnikov adduct and more cyclohexane adduct to form. If the second step (coupling) was most important then cyclized product resulting from the tertiary radical (Scheme 1.13) should have occurred, there should now have been observable amounts of the cyclopentane adduct. However, there was still no cyclopentane adduct present in the irradiation mixture. From these results, the controlling factor for formation of the *anti*-Markovnikov adduct is formation of the tertiary radical from methanol attack upon the 2,5-dimethyl-1,5-hexadiene radical cation (Scheme 1.11). The role of biphenyl must have been to slow down the attack of methanol allowing further cyclization to occur to the 1,4-cyclohexyl radical cation (k_{CYC6}). The relatively lower yield of the tertiary radical decreases the amount of *anti*-Markovnikov adduct formed.

If formation of the primary alkoxy radical were the correct pathway to formation of the cyclohexane derivatives (Scheme 1.12), addition of biphenyl would hinder its formation since it would slow down attack of methanol (k_{OME4}) with respect to the other competing reactions. Thus, the yield of any cyclized product formed from the primary alkoxy radical would have been even less. The observation was the opposite; the cyclohexane derivative actually increased in yield. As well, there was no evidence of such products from direct irradiation (no biphenyl). Thus the primary radical can be excluded as an intermediate in both the direct and biphenyl irradiation mixtures.

The second variation that demonstrates the mechanism of cyclization in the photo-NOCAS reaction with 2,5-dimethyl-1,5-hexadiene is the methanol concentration. When a lower concentration of methanol was used, the reaction yielded a reduced amount of *anti*-Markovnikov product, **21**, and an increased amount of cyclized products, **23** and **24**. This reinforces the theory that cyclization to form the 1,4-cyclohexyl radical cation occurs before attack of methanol.

Proof for the existence of the 1,4-cyclohexyl radical cation is given by Williams and Guo (62,79), who reported spectroscopic evidence (esr) for its formation. Also, Miyashi *et al.* (80) report single electron transfer induced Cope rearrangement yielding the 1,4-cyclohexyl radical cation as an intermediate. The cyclized radical cation is a stable intermediate which was trapped by molecular oxygen. Subsequently, electron spin resonance studies by Kispert *et al.* (81) demonstrated the existence of a 1,4-dimethylcyclohexenyl radical cation from 2,5-dimethyl-1,5-hexadiene. Kispert *et al.* (81) compared their electron spin resonance spectrum of the 1,4-dimethylcyclohexenyl radical cation to William and Guo's (62,79) spectrum of the cyclohexenyl radical cation. They did not report any observation of the precursor to formation of the 1,4-dimethylcyclohexenyl radical cation. In contrast, William and Guo (62,79) reported a 1,4-cyclohexyl radical cation as the intermediate to the cyclohexenyl radical cation.

From our evidence and that of others, a reasonable mechanism that the photo-NOCAS reaction with 2,5-dimethyl-1,5-hexadiene yields the 1,4-cyclohexyl radical cation as an intermediate. This result provides a pioneering observation on the selectivity of cyclization of radical cations. Just as Baldwin (82) provided rules for anionic cyclizations, rules can be developed for radical cation cyclizations.

Obviously, the combination of lower methanol concentration, the two methyl groups in 2,5-dimethyl-1,5-hexadiene and the presence of biphenyl allows more efficient cyclization of the radical cation to occur in the photo-NOCAS reaction. Otherwise, irradiation of the mono-methylated diene with biphenyl present would have resulted in cyclization. The question raised is: why do two methyl groups in the diene make such a difference? A possibility is that the ground state of the dimethyl diene prefers the conformer with the two double bonds lined up for cyclization whereas the monomethyl case prefers this conformation less. For instance, the dimethyl diene is more sterically hindered than a hydrogen pointing towards the olefin in the monomethyl diene. Thus there would be a higher probability of the olefin pointing towards the other olefin in the dimethyl case than in the monomethyl case (Figure 1.7).

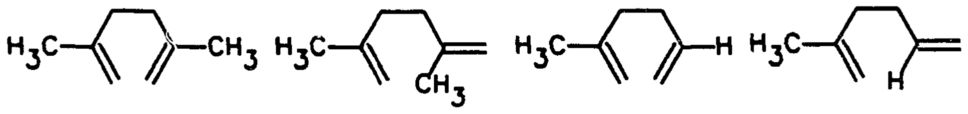


Figure 1.7. Some conformers of **13** and **14**.

If this is true then the population of the ground state conformer that leads to cyclization is higher in the dimethyl case than in the monomethyl case. The populations for the conformers of the radical cation should remain the same as before removal of an electron from the diene. Thus, there is a higher chance for cyclization since the conformer required for cyclization is more stable in the case of the dimethyl diene radical cation than in the monomethyl diene radical cation. Cyclization should have very little activation energy since there is documented evidence (82b) that attack of an olefin radical cation upon a neutral olefin is nearly diffusion-controlled. Thus the Curtin-Hammett (82c) postulate will not enter into this discussion. Methanol attack, from this particular conformation that leads to cyclization, will still compete with cyclization but to a lesser extent, so that cyclization predominates from this pathway. Overall, the other conformers leading to methanol addition make the pathway. Overall, the other conformers leading to methanol addition make the acyclic product dominate the reaction.

In the photo-NOCAS reaction involving 2,5-dimethyl-1,5-hexadiene, the *cis* cyclized product is preferred over the *trans* cyclized product. This stereochemistry can not be influenced by a bridging distonic radical cation (methanol-olefin) as it was in previous studies (35,36). The distance between the 1 and 4 positions of the ring must be too great for such bridging. The cyclohexane ring could have formed a boat conformation to narrow the distance for bridging but this must not have occurred since *trans* substitution of 1,4-dicyanobenzene would then have been favored.

The conformation of the 1,4-cyclohexyl derivatives was determined using a shift reagent, Eu(fod)$_3$, in combination with the nuclear Overhauser enhancement technique (this is explained in detail in Results I). From the nuclear Overhauser enhancement experiments, the *trans* cycloadduct was deduced to have an axial aryl and an axial methoxy group and the *cis* adduct to have an equatorial aryl and an axial methoxy group.

In the *cis* product (**23**), the aryl group prefers the equatorial position to the axial position. Since a methyl and an aryl group substitute the same carbon of the *cis*-isomer (**23**), the assumption that the aryl group might prefer the equatorial position is due to the idea that 1,3-diaxial interactions of the methyl group would be less than the 1,3-diaxial interactions of the aryl group. The conformational free energy difference between equatorial and axial positions for mono-substituted cyclohexanes is approximately 12 kJ/mol (83) for an aryl group and approximately 7 kJ/mol (84) for a methyl group. The conformational free energy shows more preference for the aryl group in the equatorial position than the methyl group.

The methoxy group in both the *cis* and *trans* isomers, **23** and **24**, prefers the axial position. The equatorial/axial conformational free energy difference for the methoxy group on a cyclohexane ring is 3.1 kJ/mol (85) and for the methyl group on a cyclohexane ring, it is 7.3 kJ/mol. From these values, the methyl group has a greater preference for the equatorial position on a cyclohexane ring than the methoxy group.

There is an error in concluding that the cyclized products of the photo-NOCAS reaction should be more stable with the aryl group in the equatorial position. The combined effect of having the methyl group and the aryl group on the same carbon atom has been ignored. Allinger and Tribble (86) have taken this factor into account in the calculation of the free energies of these types of compounds. Initially, they investigated four different chair conformations of phenylcyclohexane (Figure 1.8).

Equatorial Perpendicular Axial Perpendicular

Equatorial Parallel Axial Parallel

R= H,CH_3

Figure 1.8. Conformations of phenylcyclohexane and 1-methylphenylcylohexane.

The preferred conformation had the phenyl group occupying the equatorial position and lying parallel to the axial bond of the hydrogen attached at carbon 1 (equatorial-parallel conformation). When the phenyl is in the equatorial-perpendicular conformation, there are Van der Waals repulsions occurring between the *ortho* hydrogens on the phenyl ring and the equatorial hydrogens at carbon 2 and carbon 6 on the cyclohexane ring. In the axial position, the phenyl group is more stable in the perpendicular position because the unfavorable 1,3-diaxial interactions are smaller when compared to the parallel position. In the equatorial-parallel position, there are neither 1,3-diaxial interactions, nor are there any Van der Waals repulsions due to *ortho*-hydrogens. Thus this conformation is preferred.

When the hydrogen was replaced by a methyl group to give 1-methyl-1-phenylcyclohexane, the preferred conformation had the phenyl in the axial position, perpendicular to the equatorial methyl bond. The next preferred conformation had the phenyl in the equatorial position perpendicular to the axial methyl bond.

This preference for having the phenyl ring in the axial position can be rationalized by explaining why the other conformations are unfavorable. If the equatorial phenyl is parallel to the methyl bond, the *ortho* hydrogens from the phenyl will interact with the methyl hydrogens and cause Van der Waals repulsions. These repulsions will also occur, but to a lesser extent, when the phenyl is in the perpendicular position; the *ortho*-hydrogens repel the equatorial hydrogens at carbons 2 and 6 on the cyclohexane ring but this effect is smaller than the methyl repulsions when the phenyl is parallel. When the phenyl ring is axial-parallel, it causes 1,3-diaxial interactions and hence, this is the least preferred of the conformations. The axial-perpendicular phenyl has no 1,3-diaxial interactions and therefore this conformation is more stable than the equatorial-perpendicular phenyl, which has repulsions occurring between *ortho* hydrogens on the phenyl ring and equatorial hydrogens on the cyclohexane ring. The energy difference between a phenyl in the axial position and a methyl in the equatorial position compared to a phenyl in the equatorial position and a methyl in the axial position is 3.8 kJ/mol, which is enough to favor the axial-perpendicular phenyl conformation by approximately 80% at equilibrium (87).

From Allinger and Tribble's (86) work, one would expect the major cyclohexane adduct of the photo-NOCAS reaction to have the aryl group axial and the methyl group equatorial. Uebel *et al.* (88) report the conformational energy difference for the methoxy and methyl groups on the same carbon to be 1.25 kJ/mol in favor of an axial methoxy; the equilibrium would be 60-65% in favor of axial methoxy (87). From these observations, if the coupling of the dicyanobenzene radical anion and the cyclohexyl radical is controlled by the stability of the final conformation of the possible cyclohexanes then the major cyclohexane adduct of the photo-NOCAS reaction should be the *trans* compound (**24**); that is, the one with the axial phenyl and methoxy groups. Jensen's theory, involving torsional effects (89), also supports the idea that the *trans* cycloadduct is the more stable product in the photo-NOCAS reaction. The mechanism should proceed as follows: methanol would first attack the 1,4-cyclohexyl radical cation from the axial direction to yield the cyclohexyl radical. Axial attack by the 1,4-dicyanobenzene radical anion on the 1,4-cyclohexyl radical would then be preferred because, according to Jensen's theory, there would be less torsional effect if the aryl group attacked axially than if it attacked equatorially.

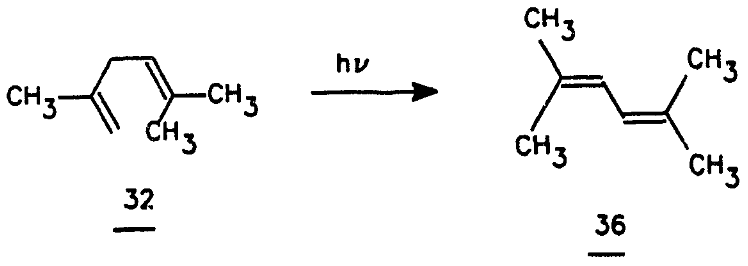
Despite all the theory mentioned above, a problem arises. The major cycloadduct in the reaction is the *cis*-cycloadduct not the *trans*-cycloadduct. The aryl group is equatorial and the methoxy group is axial. The product yields from the photo-NOCAS reaction are a result of kinetic preference and the transition state energy differences are not the same as in the products. There must be a slightly higher activation energy for coupling of the 1,4-dicyanobenzene radical anion with the cyclohexyl radical at the axial position than at the equatorial position to account for the small difference in yields of the *cis*- and *trans*-isomers; 6% and 3%, respectively. A difference in activation barriers as little as 2 kJ/mol is enough to account for this small difference in yields.

Addition of the sensitizer phenanthrene to the irradiation mixture of 2,5-dimethyl-1,5-hexadiene and 1,4-dicyanobenzene lowered the yield of the photo-NOCAS products. The main products formed were now by-products incorporating phenanthrene. One of these, not observed in previous studies (35,36), was the result of addition of methanol to phenanthrene. Another product was the *anti*-Markovnikov product **21** but the yield was lower than in previous reactions. This may be due to the fact that in direct irradiations (without sensitizer), 1,4-dicyanobenzene undergoes electron transfer directly with 2,5-dimethyl-1,5-hexadiene whereas, with phenanthrene present, the electron transfer occurs between phenanthrene and 1,4-dicyanobenzene. The phenanthrene radical cation then forms a complex with 2,5-dimethyl-1,5-hexadiene and then electron transfer results. If the energy gap for electron transfer between phenanthrene and 2,5-dimethyl-1,5-hexadiene is too great for phenanthrene to be an efficient sensitizer quenching of the reaction will result. Phenanthrene absorbs the light and undergoes electron transfer with 2,5-dimethyl-1,5-hexadiene very inefficiently; thus a lower yield of the *anti*-Markovnikov adduct **21** will result. Since addition of phenanthrene resulted in by-products, the phenanthrene is being consumed during the photolysis so that its ability as a sensitizer will slowly decrease.

None of the products formed in the reaction with phenanthrene, 2,5-dimethyl-1,5-hexadiene, and 1,4-dicyanobenzene were cyclized adducts. This could be due to the fact that the phenanthrene does not slow down the attack of methanol enough to prevent interception of the radical cation before cyclization occurs. As well, it could be due to the fact that the consumption of phenanthrene to give by-products results in less of it remaining available to participate in electron transfer with the olefin and protect it from attack by methanol.

As described in the Results I, two products formed from an impurity in the starting diene, 2,5-dimethyl-1,5-hexadiene. This impurity was identified as 2,5-dimethyl-1,4-hexadiene (**32**) and was synthesized. The pure diene (**32**), 1,4-dicyanobenzene and biphenyl were irradiated in acetonitrile-methanol (3:1) solution. Three products resulted and these were identified as 4-(4-cyanophenyl)-5-methoxy-2,5-dimethyl-1-hexene (**28**), 5-(4-cyanophenyl)-4-methoxy-2,5-dimethyl-1-hexene (**29**) and *trans*-2-(4-cyanophenyl)-5-methoxy-2,5-dimethyl-3-hexene (**35**). Compound **35** results after photochemical tautomerization of 2,5-dimethyl-1,4-hexadiene to 2,5-dimethyl-2,4-hexadiene (**36**) (Reaction [1.12]).

[1.12]



Diene **36** was obtained from the Aldrich Chemical Co. and the photo-NOCAS reaction was tried. The discussion of these results follows in Section II.

Compounds **28** and **29** result from olefin **32** and are produced due to selective oxidation of the more highly substituted olefin. No products were observed from oxidation of the less substituted olefin. The rate of removal of an electron from the more heavily substituted olefin must be much faster than from the less substituted olefin.

The products **28** and **29** are respectively the Markovnikov and *anti*-Markovnikov adducts. The *anti*-Markovnikov adduct was favored because the attack of methanol occurs preferentially at the less substituted carbon to yield the more stable radical. The Markovnikov adduct forms in this case as well because the radical formed is secondary compared to other photo-NOCAS reactions where the radical would have been primary.

Irradiation of the various dienes, **12**, **13** and **14**, in the presence of an added salt, magnesium perchlorate, was found to have an adverse effect on the yield of products. For instance, reaction of 1,5-hexadiene, 1,4-dicyanobenzene and magnesium perchlorate resulted in no products whether a co-donor was present or not. The salt appears to quench the formation of the exciplex. Similarily, addition of magnesium perchlorate to 2-methyl-1,5-hexadiene, both with and without co-donor, decreases the yield of the *anti*-Markovnikov product. This is not unusual since previous studies (35) have found that a decrease in yield of photo-NOCAS products resulted after addition of magnesium perchlorate to various olefins. Addition of magnesium perchlorate to the 2,5-dimethyl-1,5-hexadiene reaction, without co-donor, resulted in formation of the *anti*-Markovnikov product. When biphenyl was added to the mixture, the *anti*-Markovnikov product and possibly minor amounts of cyclized product formed. The suggested explanation is that the magnesium cation complexes with the 1,4-dicyanobenzene radical anion, allowing for increased regioselectivity and decreased reactivity of the 1,4-dicyanobenzene radical anion. Therefore, lower yields result. This reasoning can also be used to explain why there is a decrease in the yield of *anti*-Markovnikov and cyclized products. There is a slower attack by the 1,4-dicyanobenzene radical anion resulting in a less efficient reaction and a lower yield.

Section II

Introduction II

The conjugated dienes chosen for study were: 1,3-butadiene (**37**), 2-methyl-1,3-butadiene (**38**), 2,3-dimethyl-1,3-butadiene (**39**) and 2,5-dimethyl-2,4-hexadiene (**36**). These substituted dienes were chosen in order to examine the regio- and stereoselectivity of the reaction.

The addition of various reagents to 1,3-conjugated dienes has been studied (90-93). With hydrogen bromide or hydrogen chloride in the presence of diphenylamine, mainly 1,2-adducts were produced along with a minor amount of 1,4-adducts (90,91). This mechanism was recognized to proceed through a cationic intermediate leading to the favored Markovnikov adduct (1,2-adduct). Addition of peroxides to a similar reaction mixture, without diphenylamine, led to 1,4-adducts predominating. This reaction was found to proceed by a free radical mechanism and some *anti*-Markovnikov 1,2-adducts were formed as well.

Since knowledge of free radical chemistry has been known to be helpful in predicting the possible adducts formed from radical ion chemistry, free radical additions to conjugated dienes will be discussed in more detail. In general, free radical reagents tend to add to conjugated dienes to yield 1,4-adducts (90,91,94-98). The 1,2-adducts are known to be present in variable amounts also. For instance, trimethyltin hydride (97b) adds to 1,3-dienes to yield some 1,2-adducts. A reaction involving dichloroacetonitrile and 2-methyl-1,3-butadiene (isoprene) (**38**) yielded mainly 1,4-adducts along with minor amounts of 1,2-adducts (99). It has been suggested that the conformation of the allylic radical produced is crucial in determining whether or not 1,2- or 1,4-adducts form (Figure 2.1).

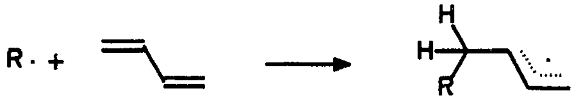


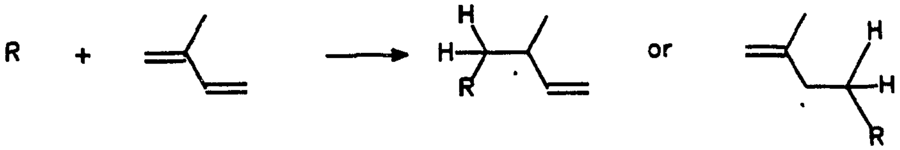
Figure 2.1. Planar conformation of the allylic radical.

If the radical formed cannot achieve the required planar geometry to allow allylic resonance, then the two double bonds will react as if they were isolated and no 1,4-adducts will form (100). This was shown to be a reasonable hypothesis by Huyser and co-workers (101). Addition of bromotrichloromethane to 2,3-di-*t*-butyl-1,3-butadiene, in both light- and benzoyl peroxide induced reactions, gave no product formation at all. They concluded that the *t*-butyl groups caused non-planarity and allylic resonance could not be achieved. (No 1,2-adducts were formed due to steric hindrance at position 2). Elimination of one of the *t*-butyl groups allows the molecule to become planar so that allylic resonance leads to 1,4-addition.

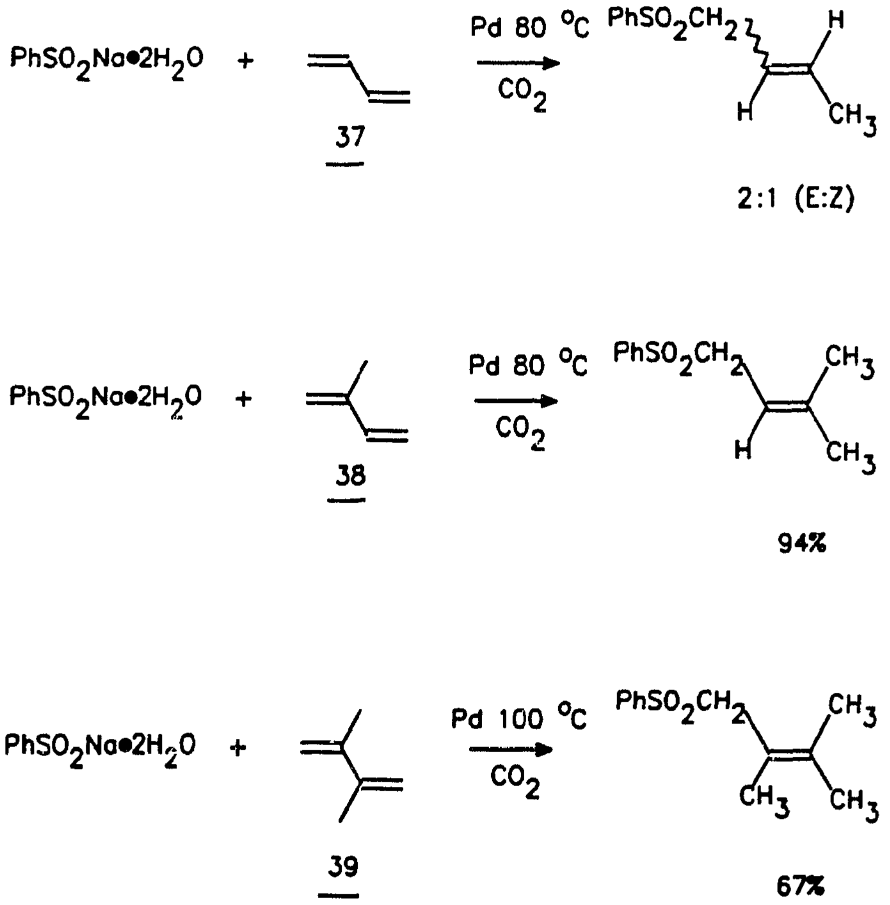
Reactions of 1,3-butadiene, 2-methyl-1,3-butadiene, and 2,3-dimethyl-1,3-butadiene with thiols have been shown to yield 1,4-adducts (102). 1,3-Butadiene yielded 95% *trans*-1,4-adducts, 2,3-dimethyl-1,3-butadiene gave both 1,4-adducts as well (stereochemistry unknown) and 2-methyl-1,3-butadiene gave 1,4-adducts and 4,1-

adducts (intermediates are shown in reaction [2.01]). 1,4-Adducts are favored over 4,1-adducts because the more stable allylic radical is formed preferentially (Reaction [2.01]).

[2.01]

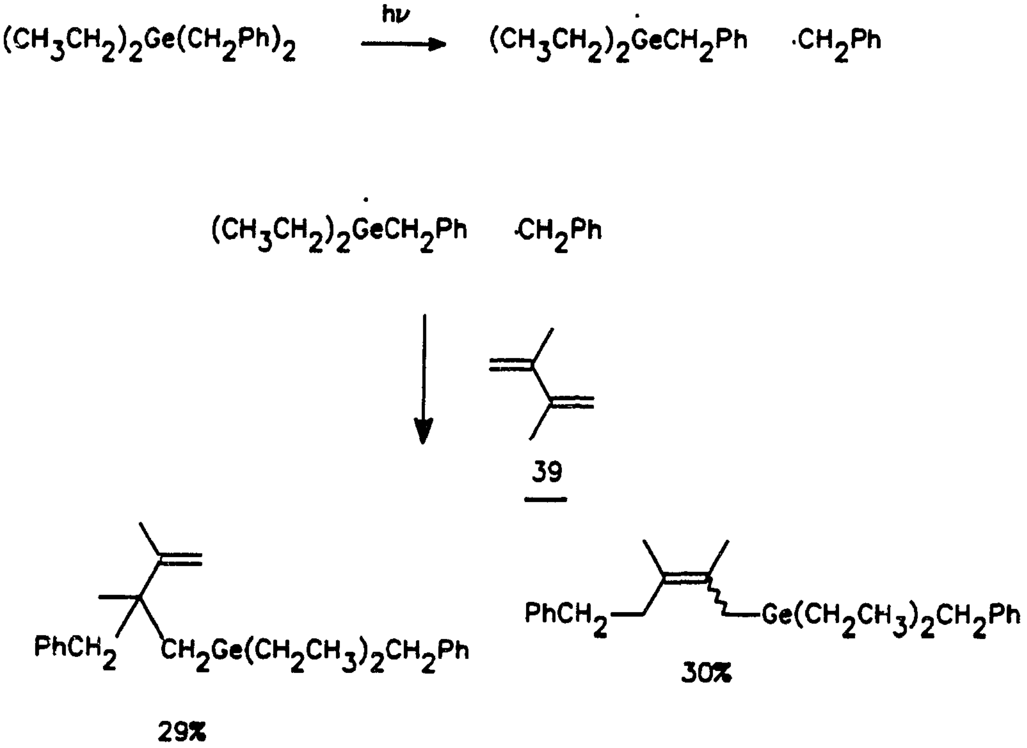


Reactions of the 1,3-butadiene homologues with other reagents have been studied. Reaction of sodium benzenesulfinate dihydrate, palladium and carbon dioxide with various dienes (103) gave the following products (Scheme 2.1).



Scheme 2.1. Reaction of sodium benzenesulfinate dihydrate, palladium and carbon dioxide with various dienes (103).

Photo-initiated free radical addition to the homologues has been studied. Photo-initiated reactions with diethyldibenzyl germane and 2,3-dimethyl-1,3-butadiene were observed to yield 1,2- and 1,4-adducts in similar molar ratios (104) (Scheme 2.2).



Scheme 2.2. Photochemical reactions with diethyldibenzyl germane and 2,3-dimethyl-1,3-butadiene.

Using benzyl germane, slightly more 1,4-adduct than 1,2-adduct formed (Reaction [2.02]).

[2.02]

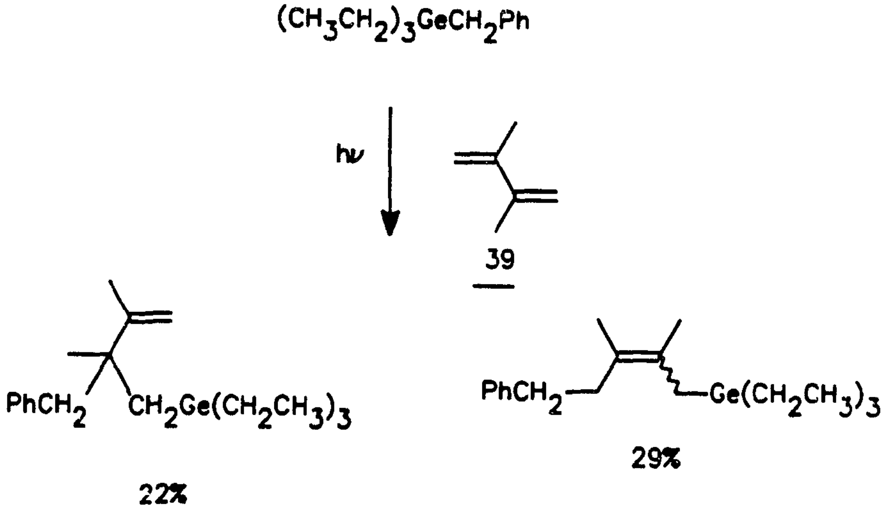
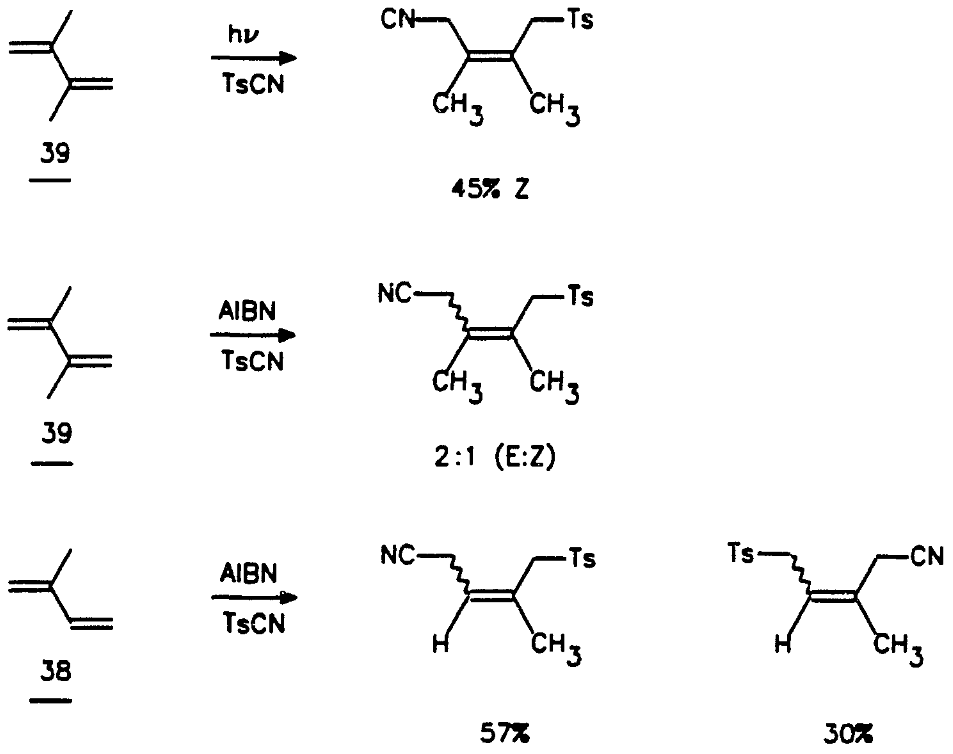


Photo- and azobisisobutyronitrile-initiated reactions involving toluene-*p*-sulfonyl cyanide, 2-methyl-1,3-butadiene and 2,3-dimethyl-1,3-butadiene were observed to yield only 1,4-adducts (105) (Scheme 2.3).



Scheme 2.3. Photochemical and radical azobisisobutyronitrile-initiated reactions involving toluene-*p*-sulfonyl cyanide, 2-methyl-1,3-butadiene and 2,3-dimethyl-1,3-butadiene.

Although free radical chemistry of conjugated 1,3-butadiene homologues has been extensively studied, radical ion chemistry involving conjugated 1,3-butadiene homologues is not nearly as well understood. Therefore, extension of 1,3-diene chemistry to the photo-NOCAS reaction would help increase this knowlege.

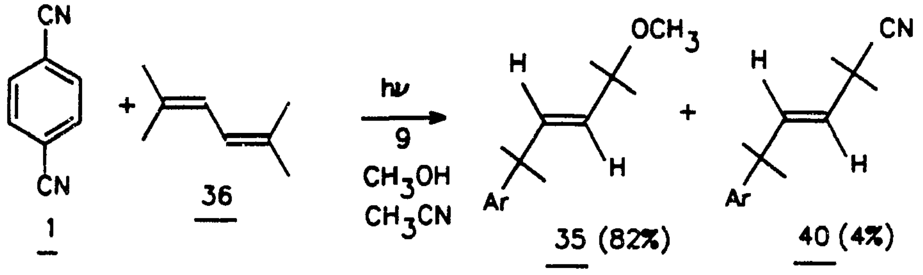
Results II

An acetonitrile-methanol (3:1) solution of 1,4-dicyanobenzene (**1**) and the conjugated diene were irradiated. The products formed were 1:1:1 (methanol: diene: **1**) adducts. The effect of the addition of the co-donor, biphenyl (**9**), to the irradiation mixture was studied.

The product ratio of the reaction was monitored by a gas chromatograph equipped with a flame ionization detector (gc/fid). The first indication of the structure of the products was achieved using a gas chromatograph equipped with a mass selective detector (gc/ms). The photo-NOCAS products were isolated by column chromatography and the yields were based upon 1,4-dicyanobenzene as the limiting reagent. In cases where the photo-NOCAS products were difficult to separate, a total weight of the combined products was obtained, and the ratios of the isomers determined by gc/fid. In these cases, the ratio of products was not dependent upon the extent of 1,4-dicyanobenzene conversion; the product ratios remained constant. Structural assignments of the products were based primarily upon detailed analysis of ^{1}H and ^{13}C nmr spectra.

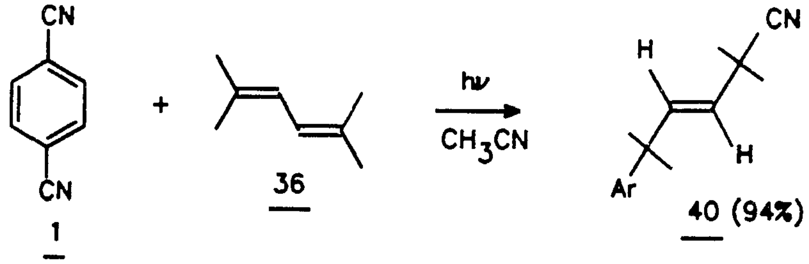
Irradiation of 2,5-dimethyl-2,4-hexadiene (**36**), **1** and **9** in acetonitrile-methanol (3:1) solution yielded two photo-NOCAS products: **35**(82%) and **40**(4%) (Reaction [2.03]). Compound **35** was identified as *trans*-2-(4-cyanophenyl)-5-methoxy-2,5-dimethyl-3-hexene. The other photo-NOCAS product, **40**, was not the typical photo-NOCAS product of methanol, olefin and **1**. Instead, it was a combination of cyanide, olefin and **1**. Compound **40** was identified as *trans*-5-(4-cyanophenyl)-2,2,5-trimethyl-3-hexenenitrile.

[2.03]



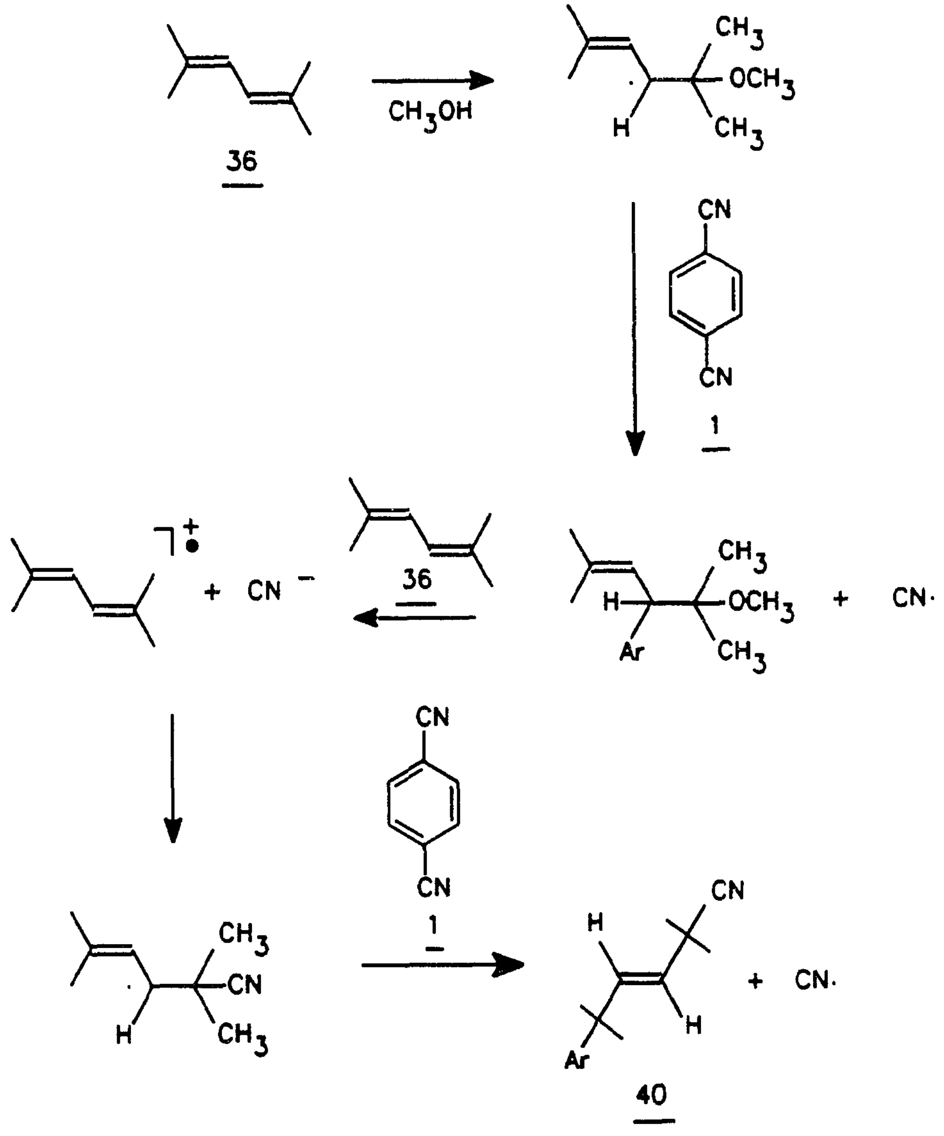
Another irradiation, involving **36** and **1** in acetonitrile solution (without added methanol), gave a 94% yield of **40** (reaction [2.02]). When **9** was added to the irradiation mixture, a similar yield was obtained and the reaction did not appear to go any more efficiently than the irradiation in absence of **9**.

[2.04]

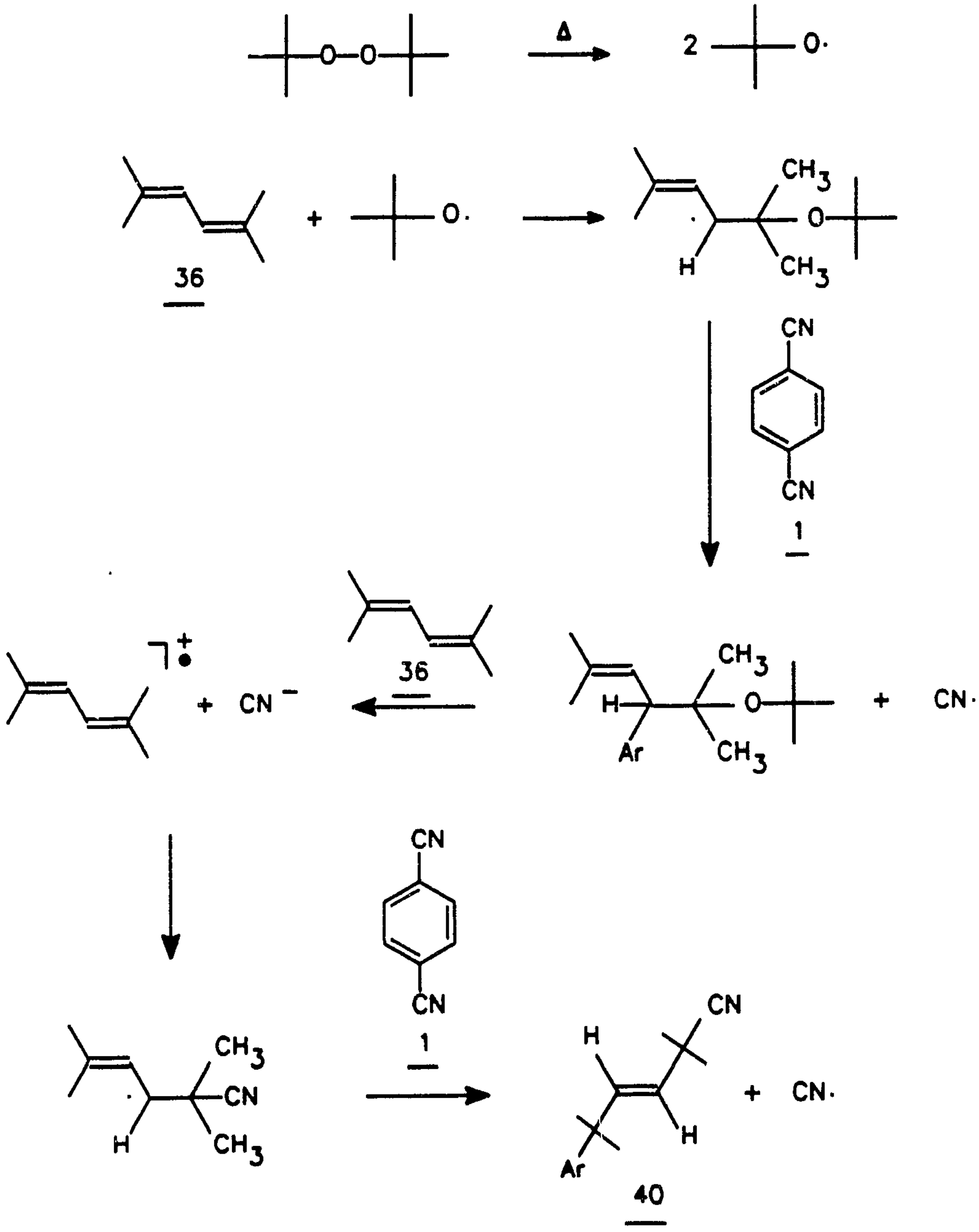


To determine the mechanism of the reaction involving formation of **40**, several experiments were tried. To determine whether or not **40** was produced from a radical mechanism (Scheme 2.4), *t*-butyl peroxide was added to the reaction and the reaction was then heated in the dark (proposed mechanism Scheme 2.5).

Using the Arrhenius equation (Equation [2.01]), the thermal reaction was estimated to be complete within 5 days.



Scheme 2.4. A possible radical mechanism for the formation of **40**.



Scheme 2.5. A possible mechanism for formation of **40** using *t*-butyl peroxide.

$$k = Ae^{-E_a/RT}$$

$$\ln k = \ln A - E_a/RT$$

[2.01] For a unimolecular reaction: $t_{1/2} = \ln 2/k$

$$\ln(\ln 2/t_{1/2}) = \ln A - E_a/RT$$

$$\ln(t_{1/2}) = E_a/RT + \ln(\ln 2/A)$$

$$t_{1/2} = e^{E_a/RT} + \ln 2/A$$

The values for the activation energy and pre-exponential factor used were 152.3 kJ/mol and $10^{15.33}$ s^{-1}, respectively (106). After 5 days of heating (110°C) the reaction mixture in the dark, no **40** was detected.

Another possible mechanism for the formation of 31 could involve a charge-transfer complex (CTC). To prove a CTC exists, an UV analysis of a standard concentration of **1** with varying amounts of **36** was examined in acetonitrile. Table 2.1 shows the concentrations used and the absorbances obtained. Figure 2.2 illustrates the UV-absorption spectrum and Figure 2.3 illustrates the absorbance of the CTC as a function of the olefin, **36**, concentration.

Since the CTC exists, it must now be proven that **40** comes from it. Filters were incorporated to selectively irradiate **1** or the CTC. Initially, selective irradiation of **1** was attempted. A filter absorbing up to 360 nm was used, along with a sensitizer; anthracene (**41**). Two reactions were carried out. One reaction involved the glass filter, **41**, **1** and **36** in acetonitrile-methanol (3:1). The other reaction consisted of the same components, except $K^{13}CN$ (99 atom%^{13}C) was added. Thus,

Table 2.1. CTC UV-absorption measurements taken using various concentrations of 2,5-dimethyl-2,4-hexadiene (**36**) in an acetonitrile solution of 0.06 M **1**.

[1](M)	[36](M)	**Absorbance of CTC**
0.06	0.000	0.00
0.06	0.050	0.24
0.06	0.075	0.33
0.06	0.100	0.43
0.06	0.125	0.54

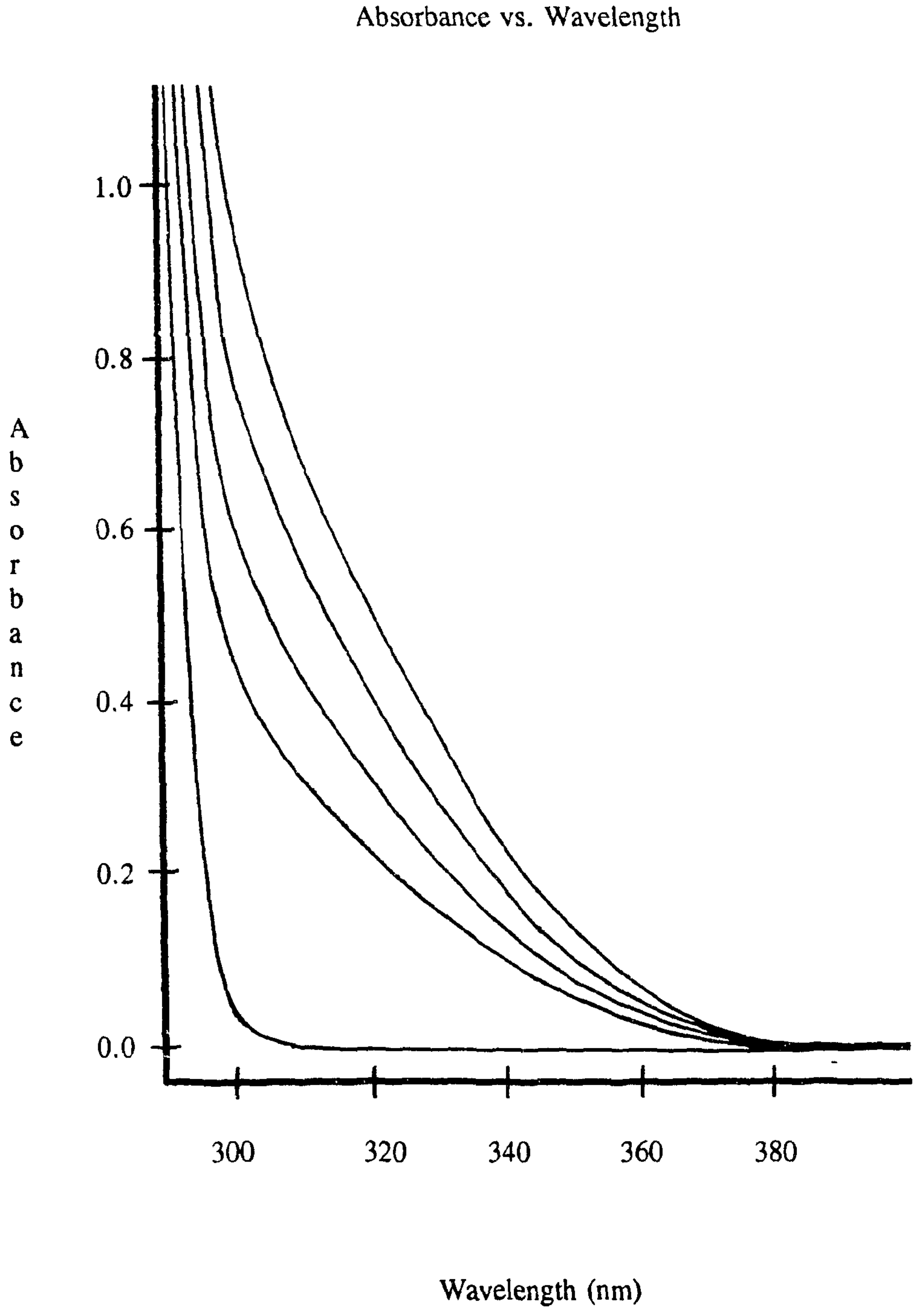


Figure 2.2. UV-absorption spectrum of **1**, in acetonitrile, during the formation of the CTC as a function of the concentration of **36**.

Absorbance vs. Concentration of **36**

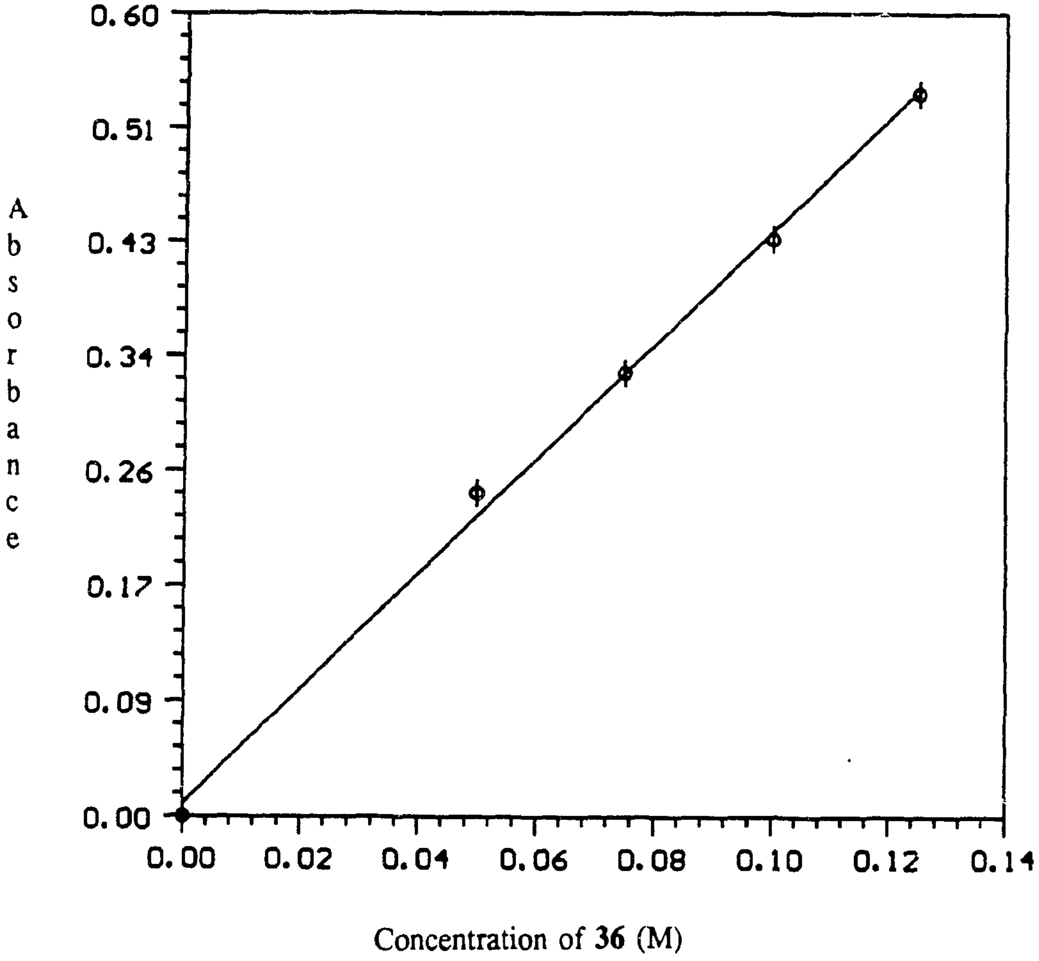


Figure 2.3. The plot illustrates the absorption of the CTC as a function of the concentration of 2,5-dimethyl-2,4-hexadiene (**36**). The correlation coefficient is 0.997.

41 and the filter allowed for selective initiation of **1**. The added KCN will, perhaps, tell whether or not cyanation occurs in or out-of-cage (within CIP or by SSIP(FRI)). The results observed were: formation of **40** in the first reaction and 13% incorporation of ^{13}C cyanide in the second reaction (the low incorporation of ^{13}C cyanide was most likely due to the low solubility of the salt, KCN, in acetonitrile solution).

A solution filter of **1** was chosen to selectively irradiate the CTC. The irradiation was done using a solution of **1** and **36** in acetonitrile-methanol (3:1) and placing it in a Pyrex tube with an outer Pyrex jacket. The outer jacket was then filled with a solution filter of **1**. Various concentrations of the filter were tried. The filter was working because **1** was consumed at a lower rate as the filter concentration increased. The rate of reaction was monitored by gc/fid. The areas of each peak on the gc were taken and ratios of the methoxy-adduct (**35**) and cyano-adduct (**40**) to **1** were measured. To monitor the formation of **40**, a ratio of areas of the methoxyadduct (**35**) to cyanoadduct (**40**) was taken. The ratios of the above adducts are listed in Table 2.2. From these limited results it was concluded that **40** was decreasing with increased filter concentration.

To provide further evidence to the above result, another experiment, using a selective wavelength instrument, was attempted. It was decided that if selectively irradiating **1**, using the instrument, yielded products (it was proven above by using **41** and a filter that photo-NOCAS adducts were produced from **1**), then it would be correct to proceed by selectively irradiating the CTC with the instrument.

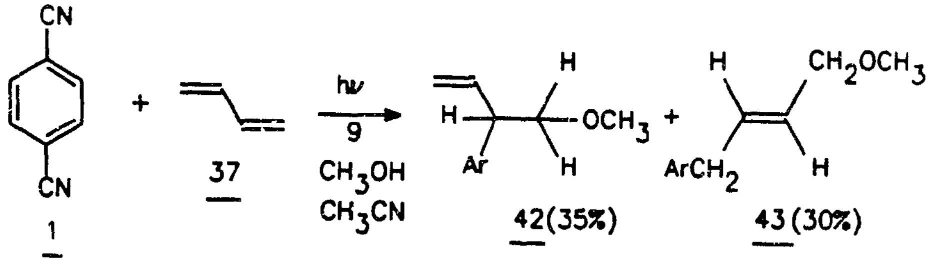
Table 2.2. Using various concentrations of a solution filter of **1**, the ratios of **35** to **40** were observed to see if **40** increased. To prove the solution filter was working, a ratio of **35** and **40** to **1** was taken to ensure **1** was being consumed at a lower efficiency as the filter concentration increased. Ratios are from gc/fid areas.

[1](M) of Filter	**35/40**	**35+40/1**
0.00	24.5	6.8
0.03	27.2	3.8
0.06	27.4	2.4
0.09	27.7	2.5

Unfortunately, the irradiation of **1** for several weeks led to no product formation; thus, the experiment was not conducted to selectively irradiate the CTC. In conclusion, **40** does form from irradiating **1** but formation of **40**, also, through irradiation of the CTC cannot be ruled out.

Irradiation of 1,3-butadiene (**37**), **1**, and **9** in acetonitrile-methanol (3:1) yielded 35% **42** and 30% **43** (Reaction [2.05]).

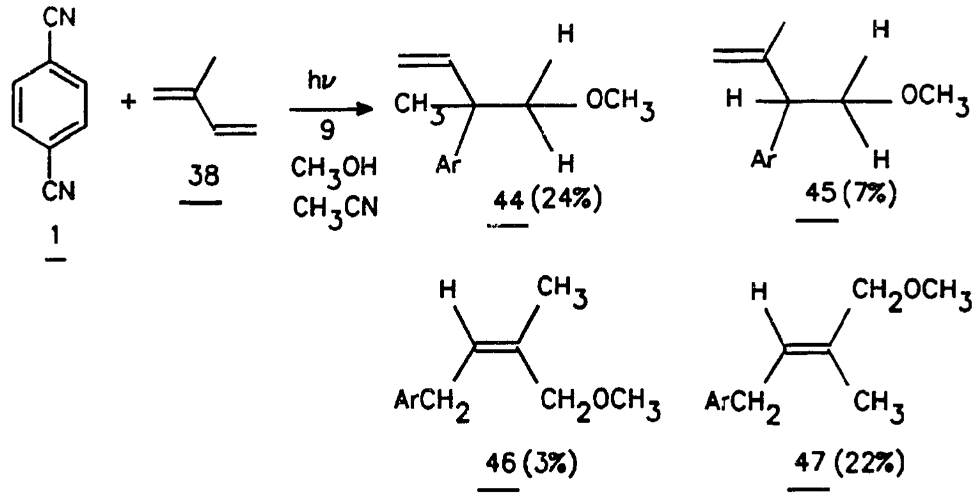
[2.05]



Compound **42** is a 1,2-addition product 3-(4-cyanophenyl)-4-methoxybutene, whereas, compound **43** is a 1,4-addition product *trans*-1-(4-cyanophenyl)-4-methoxy-2-butene.

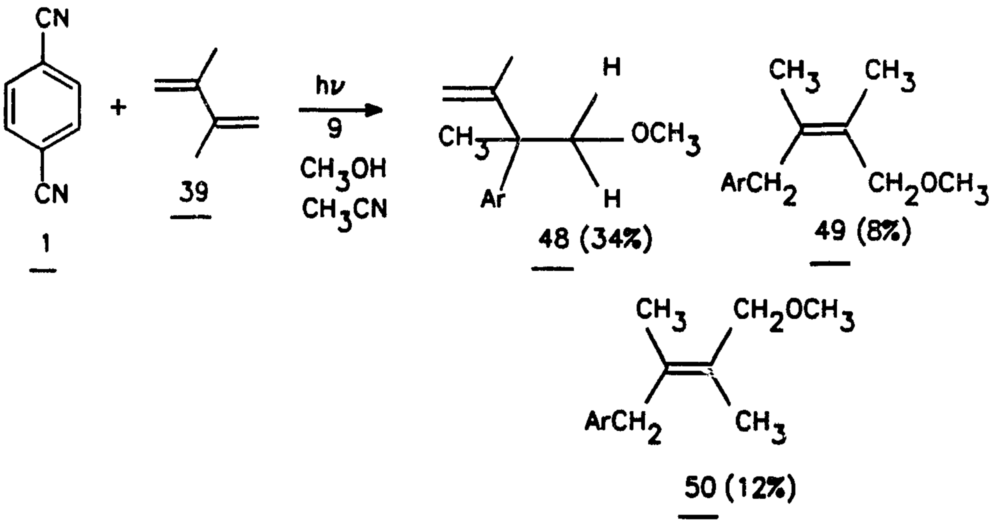
Four photo-NOCAS products were produced upon irradiation of a solution of 2-methyl-1,3-butadiene (**38**), **1**, **9** in acetonitrile-methanol (3:1). The yields of the products are: 24% **44**, 7% **45**, 3% **46** and 22% **47** (Reaction [2.06]). Compounds **44** and **45** are 1,2-addition products whose combined yield makes this the major addition mode. Compounds **46** and **47** are 1,4-addition products with the E-isomer, **47**, being the major of the two. Of the four products, **44** is the major adduct; the 1,2-addition product favoring addition at the more highly substituted olefin.

[2.06]



A solution of 2,3-dimethyl-1,3-butadiene (**39**), **1**, **9** and acetonitrile-methanol (3:1) were irradiated and three major photo-NOCAS adducts: 34% **48**, 8% **49** and 12% **50** were formed (Reaction [2.07]). The 1,2-addition product (**48**) is the major of the three adducts and is also the favored addition mode (34% 1,2-addition and 20% 1,4-addition).

[2.07]



No cyano-adducts were found in any of the above reactions with conjugated dienes **37**, **38** and **39**. Furthermore, when the irradiations were run in acetonitrile alone (without added methanol), there were no cyano-adducts produced.

The products and the yields obtained from the above photo-NOCAS reactions are summarized in Table 2.3.

Structural Assignments

The structural assignments for the products obtained were based primarily upon ^{1}H and ^{13}C nmr spectra. Mass and infrared spectra and elemental analyses (obtained in most cases) were helpful also.

Irradiations with 2,5-dimethyl-2,4-hexadiene (**36**) yield **35** and **40**. Compound **35** was identified as *trans*-2-(4-cyanophenyl)-5-methoxy-2,5-dimethyl-3-hexene. This structure was fully described in the Results of Section I when formation of this product from the tautomer of **32** was reported. In the reaction with **36**, identification of **35** was achieved by comparing the mass spectrum and the retention time to the product obtained from the irradiation of **32**.

Compound **40** was identified as *trans*-5-(4-cyanophenyl)-2,2,5-trimethyl-3-hexenenitrile. The aliphatic region of the ^{1}H nmr spectrum exhibits two singlets. Each singlet represents two chemically equivalent methyl groups. Two doublets appear in the vinyl region each with a coupling constant of ca. 16 Hz, which is typical for *trans* coupling (68). An AA′XX′ pattern in the aromatic region indicates

Table 2.3. Summary of the products and yields[c] of the photo-NOCAS reaction involving conjugated dienes.

Reaction	**Olefin**	**Product(s) (Yield)**
[2.03][a]	2,5-Dimethyl-2,4-hexadiene	**35**(82%), **40**(4%)
[2.04][b]	**36**	**40**(94%)
[2.05][a]	1,3-Butadiene	**42**(35%), **43**(30%)
[2.06][a]	2-Methyl-1,3-butadiene	**44**(24%), **45**(7%), **46**(3%), **47**(22%)
[2.07][a]	2,3-Dimethyl-1,3-butadiene	**48**(34%), **49**(8%), **50**(12%)

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[a] Irradiations were carried out in (3:1) acetonitrile-methanol solution, with **1** and **9** present.

[b] Irradiations were carried out in acetonitrile with **1** present.

[c] Yields based upon **1**. Yields were not optimized.

the presence of a 4-cyanophenyl group. Note: there is no signal due to a methoxy group in the ^{1}H nmr spectrum.

In the ^{13}C nmr spectrum, there is a singlet of 40.64 ppm, supporting a quaternary carbon substituted by a 4-cyanophenyl group. There are two cyano groups present in the molecule: carbon resonances at 118.90 and 123.52 ppm. Both cyano groups are affixed to quaternary centres. One signal at 34.56 ppm, representing an alkyl quaternary carbon substituted by a cyano group, and the other at 109.99 ppm, representing an aryl quaternary carbon substituted by a cyano group.

The infrared spectrum shows a CH bending frequency at 964 cm^{-1} further supporting a *trans* alkene. The elemental analysis is consistent with the molecular formula of the structure.

Irradiation of **36** in acetonitrile, without added methanol, yielded **40**. The retention time and mass spectrum were similar to that of the compound obtained from **36** with methanol present.

Irradiation of 1,3-butadiene (**37**) yielded compounds **42** and **43**. Compound **42** was identified as 3-(4-cyanophenyl)-4-methoxybutene. The ^{1}H and ^{13}C nmr spectra provide good evidence for the structure of this *anti*-Markovnikov adduct. A singlet in the ^{1}H nmr spectrum at 3.33 ppm is indicative of a methoxy group. A multiplet at 3.70 ppm represents a methylene and a methine group. The multiplet is then an ABC second-order pattern. The presence of a terminal olefin is supported by two doublets and a multiplet (proton on carbon 2) in the vinyl region. The proton on carbon 2 exhibits *cis*, *trans* and allylic coupling. The typical AA'XX' pattern in the aromatic region of the ^{1}H nmr spectrum, again, supports the presence of the 4-cyanophenyl group.

Even though the methylene and methine group could not be easily identified in the ^{1}H nmr spectrum, they were obvious in the ^{13}C nmr spectrum. The methine group appears at 49.63 ppm and is aryl substituted. The methylene group appears at 75.40 ppm as a triplet indicative of a methoxy substituted methylene. The terminal olefin is supported by methylene and methine signals appearing in the vinyl region of the ^{13}C nmr spectrum which exhibit the proper splitting patterns.

Compound **43** was identified as *trans*-1-(4-cyanophenyl)-4-methoxy-2-butene. The ^{1}H nmr spectrum exhibits a singlet at 3.33 ppm indicative of a methoxy group. Two doublets at 3.45 and at 3.90 ppm represent a methylene group aryl and methoxy substituted, respectively. The higher frequency shift is designated a methoxy substituted methylene rather than the aryl substituted methylene because the calculated shift for the methoxy substituted methylene (68) is higher. Two doublets of triplets appear in the vinyl region of the ^{1}H nmr spectrum, each representing a vinyl proton adjacent to a methylene group. The vinyl coupling constant is 15.4 Hz, supporting a *trans* configuration. An AA'XX' pattern in the aromatic region of the ^{1}H nmr is indicative of a 4-cyanophenyl group.

In the ^{13}C nmr spectrum, there is a triplet at 38.68 ppm which indicates a methylene group substituted by a 4-cyanophenyl group. There is a quartet at 58.00 ppm consistent with a methoxy group and a triplet at 76.62 ppm supporting a methoxy group affixed to a methylene centre. Two vinyl methine groups are present, one at 129.05 ppm and the other at 132.20 ppm. The infrared spectrum shows a CH bending frequency at 953 cm^{-1}; thus, further supporting a *trans* alkene. The elemental analysis is consistent with the molecular formula of this structure.

Irradiation of 2-methyl-1,3-butadiene (**38**), **1** and **9** in an acetonitrile-methanol (3:1) solution, led to four products: **44**, **45**, **46** and **47**.

Adduct **44** was identified as 3-(4-cyanophenyl)-4-methoxy-3-methyl butene. The aliphatic region of the ^{1}H nmr spectrum exhibits a singlet that indicates a methyl group. At 3.31 ppm, a singlet appears representing a methoxy group. A methylene group shows up as two doublets which is consistent with a methylene group adjacent to a chiral centre. In the vinyl region, the ^{1}H nmr spectrum exhibits signals that suggest a terminal olefin, as in compound **42**. Again, an AA'XX' pattern in the aromatic region of the ^{1}H nmr spectrum is present, thus supporting the presence of a 4-cyanophenyl group.

In the ^{13}C nmr spectrum, a quaternary carbon (aryl substituted) is observed at 46.11 ppm. At 59.29 ppm, there is a quartet representing a methoxy group. A triplet appears at 79.68 ppm, evidence that a methylene group substituted with a methoxy group is present. Since the aryl group is on a quaternary carbon, the only possible conclusion is that the methylene group, substituted with a methoxy group, is adjacent to it, thus, yielding two non-equivalent methylene protons. The existence of a terminal olefin is supported by methylene and methine patterns appearing in the vinyl region of the ^{13}C nmr spectrum.

Compound **45** was identified as the 1,2-addition product resulting from attack at the less substituted alkene. This product is 3-(4-cyanophenyl)-4-methoxy-2-methylbutene. The aliphatic region of the ^{1}H nmr spectrum shows a singlet at 1.62 ppm representing a methyl group. At 3.34 ppm, a methoxy group is present. Between 3.59 and 3.76 ppm, an AMX system of adjacent methylene and methine groups is present. Two terminal vinyl protons appear as singlets in the vinylic region of the spectrum. The typical AA'XX' pattern in the ^{1}H nmr spectrum, for the aryl group, is present.

The ^{13}C nmr spectrum exhibits a methine group, aryl substituted, at 52.39 ppm and a methylene group, methoxy substituted, at 74.14 ppm. A terminal vinyl methylene shows a triplet at 112.59 ppm and the quaternary vinyl carbon shows a singlet at 144.02 ppm.

Compound **46** was identified as a 1,4-addition product exhibiting (Z) geometry. **46** is (Z)-4-(4-cyanophenyl)-1-methoxy-2-methyl-2-butene. The aliphatic region of the ^{1}H nmr spectrum exhibits a singlet corresponding to a methyl group and a singlet at higher frequency appears for a methoxy group. A doublet appears at 3.48 ppm, representing an aryl substituted methylene group and a singlet appears at 3.99 ppm representing a methoxy substituted methylene group. These methylene signals were assigned on the basis of calculations (68).

A vinyl proton appears as a triplet at 5.50 ppm and exhibits coupling (7.4 Hz) to the methylene group at 3.48 ppm. Therefore, the aryl substituted methylene group is allylic to the vinyl proton. Since only one vinyl proton is present, the methyl and methoxy substituted methylene groups must be the other substituents on the alkene.

The ^{13}C nmr spectrum provides further evidence of structure **46**. A triplet at 34.04 ppm indicates an aryl substituted methylene group. A triplet at 70.96 ppm shows a methoxy substituted methylene group. A vinyl methine group is reported at 125.72 ppm and a vinyl quaternary carbon at 134.74 ppm.

The decision in favor of (Z) geometry was based upon the ^{1}H NOE. The methylene groups were irradiated and the NOE recorded. When the methoxy substituted methylene group was irradiated, an NOE was observed for a methyl, methoxy and aryl substituted methylene group. This shows the methoxy substituted methylene group is *syn* to the aryl substituted methylene group. Further proof of the (Z) geometry was provided by irradiating the aryl substituted methylene group. An NOE was seen for the methoxy substituted methylene group, the vinyl proton and the aryl protons. Thus, (Z) geometry is favored.

Compound **47** is (E)-4-(4-cyanophenyl)-1-methoxy-2-methyl-2-butene. The ^{1}H and ^{13}C nmr spectra show similar characteristic patterns to compound **46**. The (E) geometry was assigned by using ^{1}H NOE. Again, the methylene groups were irradiated and a NOE recorded. When the methoxy substituted methylene group was irradiated, an NOE was seen for the methyl group and the methoxy group. When the aryl substituted methylene group was irradiated, an NOE was seen for the methyl group and the aryl hydrogens. This information supports (E) geometry.

When 2,3-dimethyl-1,3-butadiene (**39**) was irradiated in an acetonitrile-methanol (3:1) solution containing **1** and **9**, compounds **48**, **49** and **50** were produced.

Compound **48** was identified as an *anti*-Markovnikov 1,2-addition product, 3-

(4-cyanophenyl)-4-methoxy-2,3-dimethylbutene. The ^1H and ^{13}C nmr spectra were similar to compound **44**. The only difference was that there is one additional methyl group which is identified in the ^1H nmr spectrum as a singlet and in the ^{13}C nmr spectrum as a quartet. Unlike **44**, there are only two vinyl protons instead of three and they appear as singlets in the vinyl region of the ^1H nmr spectrum; this is evidence for a terminal vinyl methylene. In the ^{13}C nmr spectrum, there is a vinyl quaternary carbon at 148.13 ppm and a vinyl methylene at 112.19 ppm.

Compound **49** was identified as a 1,4-addition product with (Z) geometry. Compound **49** is (Z)-1-(4-cyanophenyl)-4-methoxy-2,3-dimethyl-2-butene. The ^1H and ^{13}C nmr spectra are quite similar to compound **46**. The difference is one additional methyl group which shows up as a singlet in the ^1H nmr spectrum and a quartet in the ^{13}C nmr spectrum. The ^1H nmr spectrum, also, exhibits no vinyl protons but two vinyl quaternary carbons are identified in the ^{13}C nmr spectrum.

To determine the (Z) geometry of **49**, ^1H NOE was used. Again, the methylene groups were irradiated. The methoxy substituted methylene group was irradiated and an NOE was observed for one methyl group and an aryl substituted methylene group. The aryl substituted methylene group was irradiated and an NOE was observed for one methyl group and the methoxy substituted methylene group. This information supports the methylene groups appearing *syn* to one another. Thus, **49** has (Z) geometry.

Compound **50** was identified as a 1,4-addition product as well, but instead has (E) geometry. Compound **50** is (E)-1-(4-cyanophenyl)-4-methoxy-2,3-dimethyl-2-

butene. The ^{1}H and ^{13}C nmr spectra exhibit similar characteristic patterns to that of compound **49**. The (E) geometry was assigned by ^{1}H NOE. The methoxy substituted methylene group was irradiated and an NOE was observed for two methyl groups and a methoxy group. When the aryl substituted methylene group was irradiated, an NOE was observed for two methyl groups. This information supports a *trans* arrangement of the methylene groups. Thus, **50** has (E) geometry.

In conclusion, all of the above mentioned adducts have been identified using several experimental procedures; not only ^{1}H and ^{13}C nmr spectra, but infrared spectra, exact mass, mass spectra and elemental analyses.

Discussion II

Using the Rehm-Weller equation (31), electron transfer between the chosen 1,3-dienes and 1,4-dicyanobenzene (**1**) has been calculated to be exergonic. The oxidation potentials and free energy changes are listed in Table 2.4. Knowing that electron transfer would occur with 1,3-butadiene (**37**) and its homologues, the photo-NOCAS reaction was attempted.

The literature contains a vast amount of chemistry of 1,3-butadiene and its homologues. There have been many studies of additions to these particular 1,3-dienes but very few have involved the radical cation as the intermediate (107-109). The few examples involving radical cations will be outlined here in order to see if a similar trend in regiochemistry is obtained for the photo-NOCAS reaction.

Anodic oxidation of isoprene (**38**), in methanol or acetic acid, brought about 1,4-addition of the solvent to the diene (107). Anodic oxidation of 1,3-dienes, in the presence of sodium halides as the supporting electrolyte, led to 1,2-adducts selectively (108). Oxidative fluorination of 1,3-butadiene (**37**), in an amine-HF mixture, led to 1,4- and 1,2-difluoro-adducts in a ratio of 2:1 (109). Based on these observations, there is clearly competition between the two possible addition modes, with 1,4-addition being somewhat preferred.

The photo-NOCAS reaction involving 1,3-butadiene and its homologues yields both the 1,2- and 1,4-adducts with the 1,2-adduct slightly predominating. Specifically, 1,3-butadiene yields 1,2- and 1,4-adducts with the 1,2-adduct being

Table 2.4. The calculated free energy change for the electron transfer process with the singlet excited state of 1,4-dicyanobenzene as the acceptor.

Olefin	$E_{1/2}^{ox}$(V)	ΔG (kJ/mol)[b]
1,3-Butadiene	2.37[c]	-25.0
2-Methyl-1,3-Butadiene	2.25[a]	-36.6
2,3-Dimethyl-1,3-Butadiene	2.16[a]	-45.3
2,5-Dimethyl-2,4-Hexadiene	1.24[a]	-1.34×10^2

[a] Oxidation potentials were measured at a platinum electrode relative to the saturated calomel electrode (SCE) using tetraethylammonium perchlorate (0.1 M TEAP) as the electrolyte in acetonitrile.

[b] Based upon the Rehm-Weller equation (31); $E_{0,0}(1)$ 408.4 kJ/mol, $E_{1/2}^{red}(1)$ -1.66 V, the Coulombic attraction term was taken to be 5.40 kJ/mol (36).

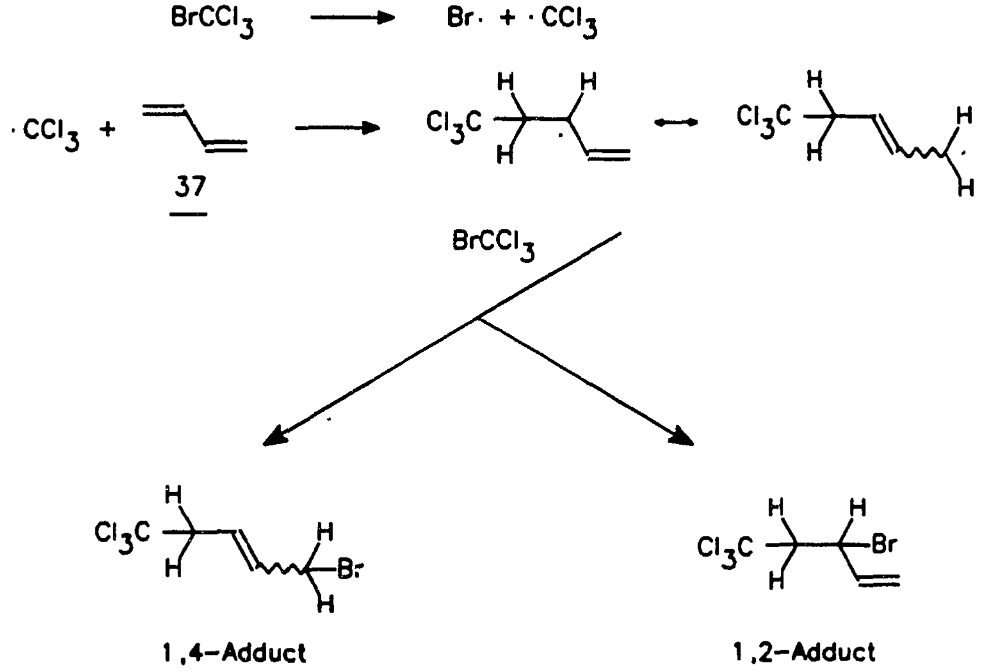
[c] W.C. Neikam and M.M. Desmond. J. Am. Chem. Soc. **86**, 4811 (1964). The potential reported in this paper was versus the silver/silver ion (Ag/0.1N Ag^+) and was related to the SCE by adding 0.34 V.

favored by only 5%. With an extra methyl group in isoprene, 1,2- and 1,4-adducts were formed in approximately equimolar amounts, the 1,2-adducts are favored by 6%. Even with addition of two methyl groups to 1,3-butadiene (2,3-dimethyl-1,3-butadiene, **39**), 1,2- and 1,4-adducts were still formed with 1,2-adducts being favored by 14%. Thus using as examples the very few radical cation reactions from the literature, accurate predictions would not have been made for the types of photo-NOCAS products formed from 1,3-butadiene and its homologues.

Previously, in the Introduction of Section II, free radical reactions were discussed. 1,4-Addition to 1,3-dienes tended to predominate in free radical reactions (90,91,94-98) as it did in the radical ion reactions (107-109). Moreover, there are several free radical reactions (97b,99,110-119), as well as photochemically initiated reactions (96a,104,120), which yield 1,2-adducts as minor or major adducts.

In general, the regioselectivity of free radical additions is dependent upon a variety of factors: strength of the bond formed, steric hindrance, polar effects and stability of the radical formed (121). There is an additional factor to take into account when 1,3-dienes are involved; the conformation of the allylic radical produced. If planar geometry to allow allylic resonance cannot be achieved readily then each double bond will act as if it were isolated from the other and no 1,4-adducts will form (100,101).

Most of the free radical and radical ion reactions with the 1,3-dienes mentioned, yield 1,4-adducts as major products. The major difference between these reactions and the reactions that yield 1,2-adducts as major products (or 1,2-adducts approximately equimolar with 1,4-adducts) is the step following formation of the allylic radical. In the mechanism of free radical and radical ion reactions with 1,3-dienes that give 1,4-adducts as major products (90,91,94-98,107-109), an allylic radical is formed which then has to abstract either hydrogen or halogen from the substrate. For instance, reactions involving bromotrichloromethane and 1,3-butadiene (96a) (Scheme 2.6).

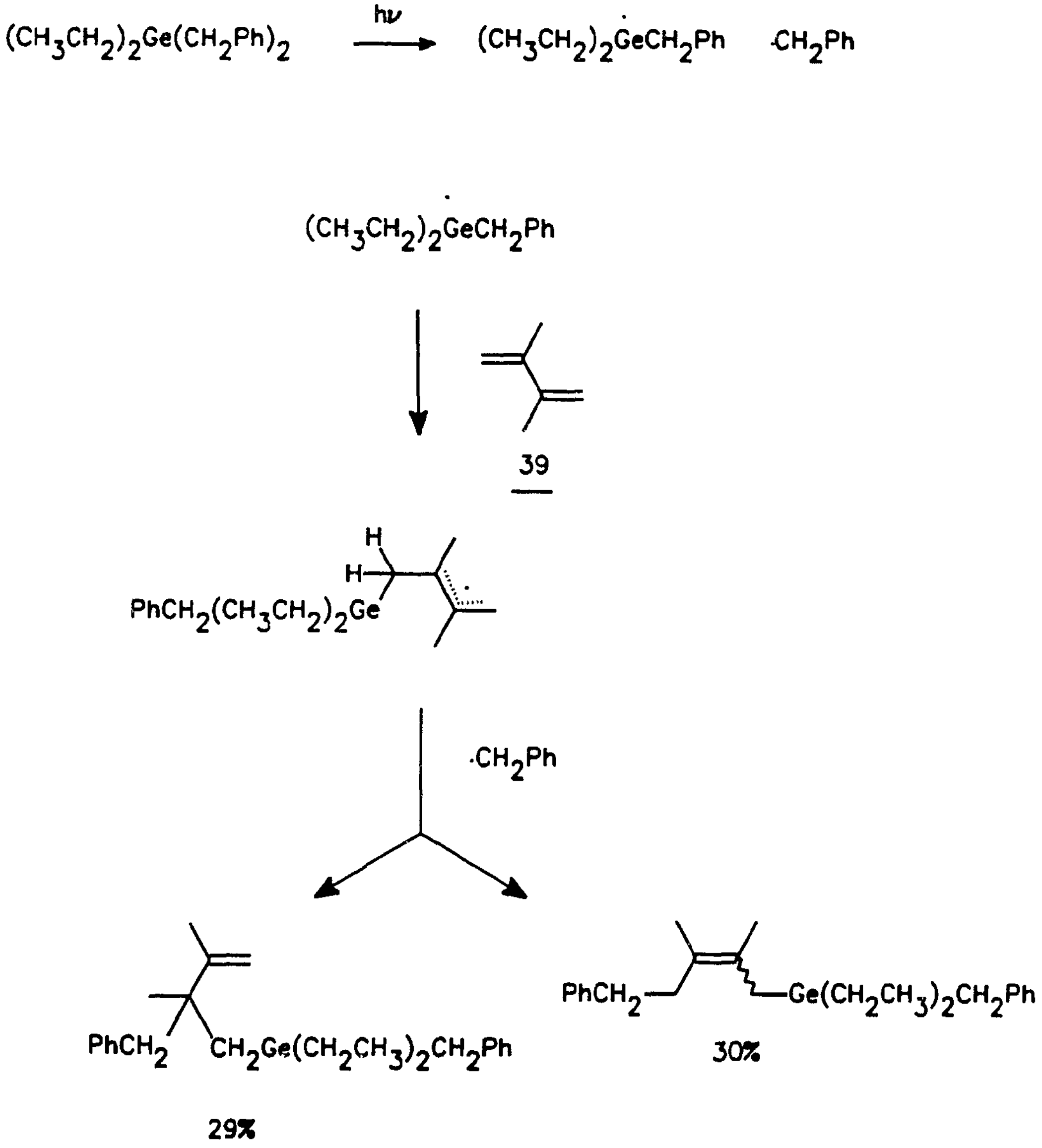


(In peroxide and light-initiated reactions (122,123), approximately 75% 1,4-addition and 25% 1,2-addition is obtained).

Scheme 2.6. Mechanistic scheme involving bromotrichloromethane and 1,3-butadiene.

These reactions involve an activation energy for hydrogen or halogen abstraction where steric hindrance is the major controlling factor (124). (The transition state will resemble the olefinic radical). There will be more steric hinderance at the more substituted end of the allylic radical (higher activation energy) when abstraction occurs, thus abstraction occurs at the primary end of the allylic radical producing 1,4-adducts.

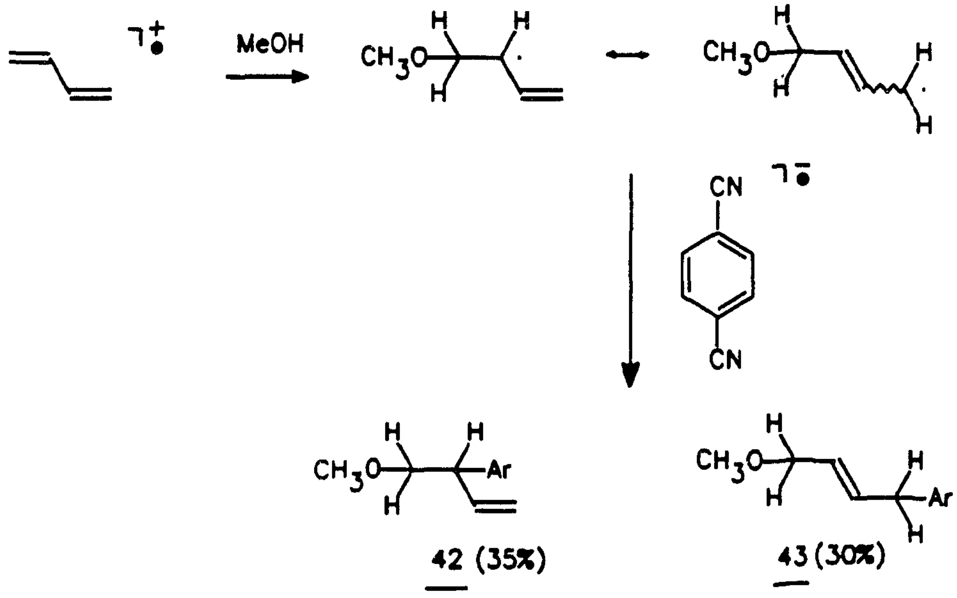
In the mechanism of free radical (104,112-114) and radical ion (108) reactions which give 1,2-adducts as major products (or approximately equimolar 1,2- and 1,4-adducts), an allylic radical couples with another radical; no abstraction occurs. An example is the reaction of diethyldibenzylgermane with 2,3-dimethyl-1,3-butadiene (104) (Scheme 2.7).



Scheme 2.7. Mechanistic scheme involving diethyldibenzylgermane and 2,3-dimethyl-1,3-butadiene.

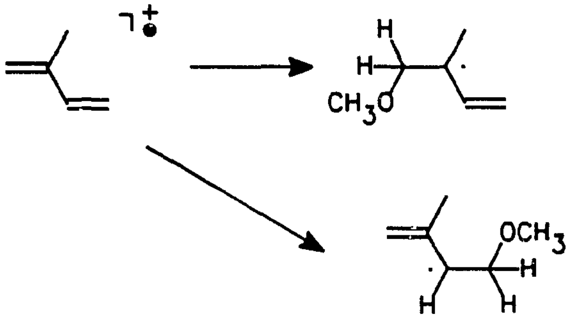
Coupling requires little or no activation energy, thus selectivity of attack of the benzyl radical is less since the transition state is early. The product distribution depends very little on the stability of the allylic radical or on the steric hindrance of attack of the benzyl radical.

From the examples above, conclusions can be drawn about the regioselectivity of the photo-NOCAS reaction involving 1,3-butadiene and its homologues. 1,3-Butadiene yields approximately equimolar amounts of 1,2- and 1,4-adducts. Methanol adds to the 1,3-butadiene radical cation at the less substituted end yielding the more stable allylic radical. (Since *anti*-Markovnikov adducts are dominant in the photo-NOCAS reaction, this selectivity of methanol attack comes as no surprise). Coupling of the allylic radical with the 1,4-dicyanobenzene radical anion is the step that follows and it is this step that determines the 1,2- versus 1,4-regioselectivity of the reaction. Since this process is kinetically controlled (coupling is irreversible) and since there must be little or no activation energy for coupling at either carbon 2 or carbon 4, the transition state resembles the allylic radical and the selectivity of coupling doesn't depend on the preference for reaction at either the primary or secondary carbon of the allylic radical. Consequently, equimolar amounts of 1,2- and 1,4-adducts are formed with 1,3-butadiene (Scheme 2.8).



Scheme 2.8. Equimolar 1,2- and 1,4-adducts formed from 1,3-butadiene.

2-Methyl-1,3-butadiene also yields approximately equimolar amounts of 1,2- and 1,4-adducts. However, there are two types of 1,2-adducts formed, one from attack of methanol at the more highly substituted olefin and the other from attack at the less substituted olefin (Scheme 2.9).



Scheme 2.9. Two types of 1,2-adducts formed from 2-methyl-1,3-butadiene.

1,2-Adducts, from attack of methanol at the more highly substituted olefin, are probably favored because there is greater positive charge on the more highly substituted alkene in the radical ion of the diene. Once again methanol attacks preferentially at the least hindered carbon to yield the more stable allylic radical. This is another factor which may cause preference of attack by methanol at the more highly substituted olefin since the tertiary-allylic radical is more stable than the secondary-allylic radical formed from attack at the other olefin. This same reasoning was used by Ito and co-workers to explain free radical attack of thiols upon isoprene (102).

After methanol has added to carbon 1 (the more substituted olefin) of isoprene, 1,4-and 1,2-adducts were again formed in an equimolar ratio. Again the regioselectivity of addition to isoprene could be due to little or no activation barrier for coupling of the 1,4-dicyanobenzene radical anion at either carbon 2 or carbon 4. Thus selectivity doesn't depend on the stability of the radical or steric hindrance of attack by the 1,4-dicyanobenzene radical anion.

When methanol has added to carbon 4 of isoprene, only 1,2-adducts and no 1,4-adducts were detected. (Perhaps there is 1% undetected 1,4-adduct present). A slight activation barrier to formation of these 1,4-adducts could exist as compared to the 1,2-adduct. This barrier difference could be as low as a few kJ/mol and still result in this difference since the yield of the 1,2-adduct is only 7%.

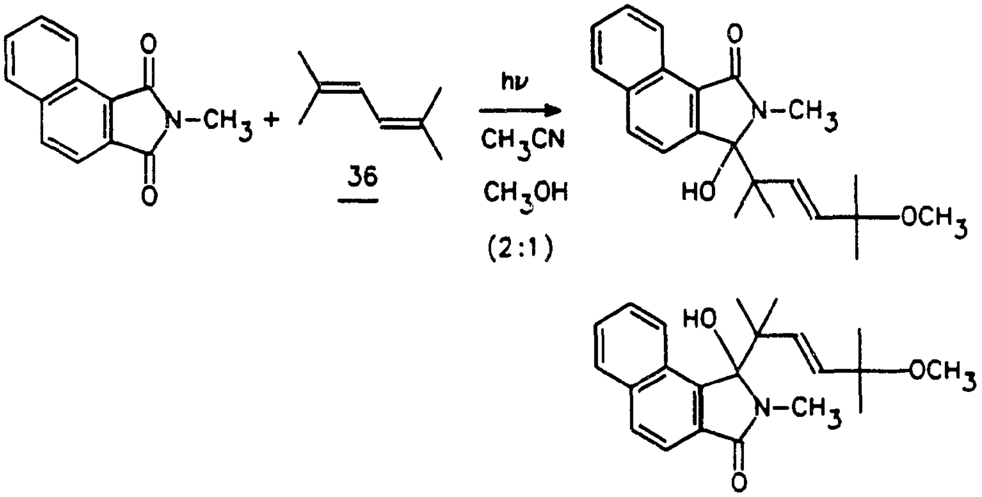
The reaction involving 2,3-dimethyl-1,3-butadiene favors 1,2-adducts over 1,4-adducts by approximately 14%. Methanol adds to the 2,3-dimethyl-1,3-butadiene radical cation at the less substituted end (carbon 1) yielding the stable allylic radical (*anti*-Markovnikov adducts are dominant in the photo-NOCAS reaction). Coupling of the allylic radical to the 1,4-dicyanobenzene radical anion determines the regioselectivity of this reaction. There must be a small difference in activation energy between coupling at carbon 2 compared to coupling at carbon 4 to account for the higher yield of the 1,2-adducts. Again, this barrier difference could be as small as 0.5-2 kJ/mol to account for the 14% difference in yield.

The reaction involving 2,5-dimethyl-2,4-hexadiene (**36**) results in 1,4-addition products only. The adducts obtained were 2-(4-cyanophenyl)-5-methoxy-2,5-dimethyl-3-hexene (**35**) and 5-(4-cyanophenyl)-2,2,5-trimethyl-3-hexenenitrile (**40**).

The cyanide adduct, **40**, was formed from cyanide anion produced by rearomatization after coupling of the 1,4-dicyanobenzene radical anion.

Attack on 2,5-dimethyl-2,4-hexadiene is known to occur at the tertiary carbon (41a,97c,125) (Reaction [2.08]) during free radical addition reactions but there are some examples of attack at the secondary carbon (carbon 2) (126).

[2.08]



In the photo-NOCAS reaction, the reason that methanol attacks the 2,5-dimethyl-2,4-hexadiene radical cation exclusively at the tertiary carbon results from the fact that the positive charge in the delocalized species is higher at this position (Figure 2.4).

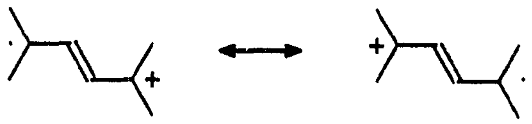


Figure 2.4. The most stable contributors of the **36** radical cation.

This step is followed by coupling of the 1,4-dicyanobenzene radical anion at the tertiary carbon of the allylic radical due to steric factors. For instance, if the radical anion attacked the radical formed at carbon 2 it would encounter strong steric interactions whereas, attack at carbon 4 would not. The steric hindrance at carbon 2 can be compared to an S_N2 reaction where α-substituents affect the attack of the incoming nucleophile much less than β-substituents (87) subsequently, attack at carbon 2 is hindered due to the two β-methyl groups and the one β-methoxy group. This β hindrance is absent when attack occurs at carbon 4. The regiospecificity of this reaction is then based on the charge distribution of the radical cation and on the steric hindrance of the radical.

The regioselectivity of addition of methanol to these 1,3-dienes seems to depend on either the charge distribution in the radical cation, the steric hindrance to attack of methanol at the radical cation, or both. The reactions of 1,3-butadiene and 2,3-dimethyl-1,3-butadiene probably depend mainly on the steric hindrance of attack by methanol upon the radical cation since the charge distribution in the radical cation is fairly similar at both carbons 1 and 2. The reaction of isoprene prefers attack of methanol at carbon 1 due to both steric hindrance and charge distribution being higher at the more substituted alkene. With 2,5-dimethyl-2,4-hexadiene, charge distribution in the radical cation must be more important than steric hindrance of attack of methanol on the radical cation. There are two equivalent resonance contributors for 2,5-dimethyl-2,4-hexadiene which have energy much lower than that of the other contributors. These two important resonance contributors control the regioselectivity of attack by methanol in this reaction.

The regioselectivity of the coupling with the 1,4-dicyanobenzene radical anion probably depends on steric hindrance. The reactions of 1,3-butadiene, isoprene and 2,3-dimethyl-1,3-butadiene involve a radical at either carbon 2 or carbon 4 where coupling is neither dominated by steric hindrance nor stability of the radical. However, with 2,5-dimethyl-2,4-hexadiene the radical formed at carbon 2 depends upon steric hindrance of attack by the 1,4-dicyanobenzene radical anion whereas, the radical at carbon 4 does not. Thus, attack is preferred at carbon 4 exclusively. Steric hindrance is relatively unimportant with 1,3-butadiene, 2-methyl-1,3-butadiene and 2,3-dimethyl-1,3-butadiene since there is only a slight interaction of a β-methoxy group to carbon 2 of these dienes which makes little difference.

Now that some possible explanations have been given for the regioselectivity of addition to these 1,3-dienes, some explanation will be given for the stereoselectivity of the 1,4-addition products.

Walling *et al.* (127) showed that free radical chlorination of *cis* or *trans* 2-butene produced only the respective *cis* or *trans* 1-chloro-2-butenes. This implied that the allylic radicals produced during chlorination were capable of maintaining their original geometry (116). Smith and Massingill (116), knowing this, were then able to estimate the s-*cis* and s-*trans* composition of a 1,3-diene substrate from direct measurements of the products from 1,3-dienes. Using the above idea that the stereoselectivity of 1,3-diene addition reactions is based upon the substrate's original conformation, an explanation may be given for the stereoselectivity of the photo-

NOCAS reaction involving the aforementioned 1,3-dienes. (The assumption used in this interpretation is that the reactions of the intermediate radical cations or allylic radicals are faster than any conformational change).

From the ratio of the yields of the *cis*/*trans* products obtained by 1,4-addition to 1,3-butadiene, isoprene and 2,3-dimethylbutadiene in the photo-NOCAS reaction, the substrate conformations should favor s-*trans* (1,3-butadiene-100% s-*trans*, isoprene-88% s-*trans* and 2,3-dimethyl-1,3-butadiene-60% s-*trans*). There are several references supporting s-*trans* predominance for 1,3-butadiene (128,129) and isoprene (128,130). At room temperature, actual s-*cis*/s-*trans* conformations for 1,3-butadiene and isoprene have been determined by spectroscopic and thermodynamic methods by Compton *et al.* (128). These values for the s-*trans* percentage in 1,3-butadiene and isoprene are very similar to the calculated s-*trans* percentages from product ratios of the photo-NOCAS reaction obtained here. Compton *et al.* (128) reported 97% s-*trans* for butadiene (compared to 100% s-*trans* calculated from the photo-NOCAS reaction) and 89% s-*trans* for isoprene (compared to 88% s-*trans* calculated from the photo-NOCAS reaction). If 97% s-*trans* is present initially in 1,3-butadiene and 30% yield of *trans* product was obtained from the photo-NOCAS reaction, then by a calculation using 97% s-*trans* to 3% s-*cis* in the substrate, approximately 1% *cis* product should be present. This 1% *cis* product could be present but detection or isolation would be difficult to accomplish.

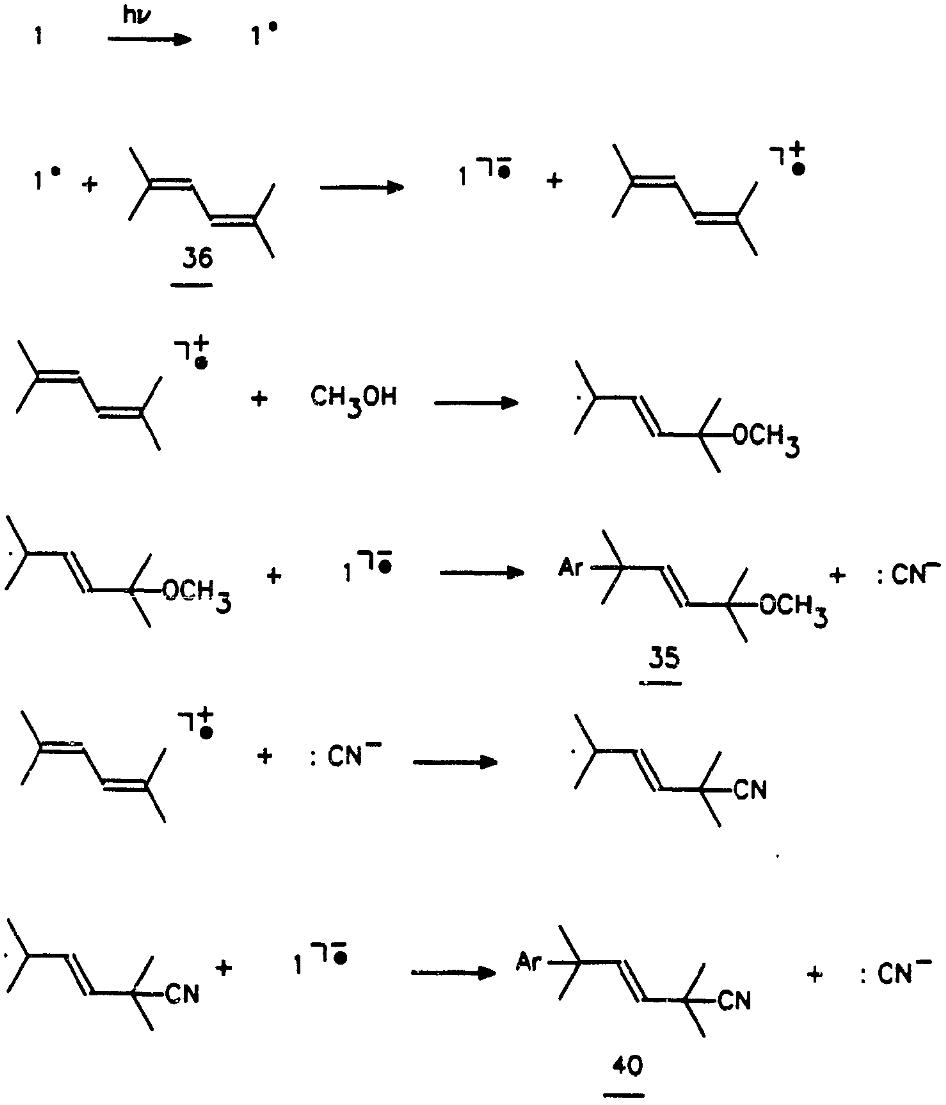
Although Compton's data fits the product yields from 1,3-butadiene and isoprene, other determinations (131-133) of s-*cis* and s-*trans* equilibrium percentages differ. For isoprene, 5% s-*cis* and 95% s-*trans* conformational equilibrium was reported. Mui *et al.* (131) concluded that 2,3-dimethyl-1,3-butadiene had a 5% s-*cis* and 95% s-*trans* conformational equilibrium which is very different from the 40% s-*cis* and 60% s-*trans* conformational equilibrium obtained from the photo-NOCAS product ratio. The results obtained from the photo-NOCAS reaction support Compton's results.

Allinger and Tai (134) calculated energies relative to the most stable conformation of some 1,3-dienes using MM2. In each case the s-*cis* conformer was calculated to be less stable than the s-*trans*. The differences were 11.0 kJ/mol for 1,3-butadiene; 9.5 kJ/mol for isoprene; and 3.3 kJ/mol for 2,3-dimethyl-1,3-butadiene. From these results, the percentage of the s-*cis* conformation increases with methylation at carbons 2 and 3 of 1,3-butadiene due to increased steric interaction of the methyl group on carbon 2 with the hydrogen on carbon 4. Qualitatively, this also rationalizes the increased *cis* to *trans* ratio of photo-NOCAS products on going from 1,3-butadiene to 2,3-dimethyl-1,3-butadiene.

The stereoselectivity of the photo-NOCAS reaction of 2,5-dimethyl-2,4-hexadiene can easily be explained by the assumption that the substrate conformation favors s-*trans* almost entirely. This is obviously due to the unfavorable steric interaction of the methyl groups on carbon 2 and 5 of s-*cis* 2,5-dimethyl-2,4-hexadiene. (Several free radical and radical ion addition reactions also yield *trans*-1,4-adducts exclusively (97c,114,125)).

2,5-Dimethyl-2,4-hexadiene was found to give the usual 1,4-adduct with methanol as well as a 1,4-adduct incorporating cyanide anion. This adduct involving the cyanide anion is not the first to be reported in a photo-NOCAS reaction. Borg and Arnold (36) found a trace amount of a 1:1:1 adduct (cyanide adduct) involving 1,4-dicyanobenzene and 2,3-dimethyl-2-butene in an acetonitrile solution. Consequently, cyanide is known to add to the sensitizer and co-donor in a photo-NOCAS reaction (35,36). The yield of the 1,4-cyanide adduct (**40**) was increased by an irradiation of 2,5-dimethyl-2,4-hexadiene in acetonitrile alone. (This was done to remove competition between methanol and cyanide anion attack). This resulted in a 94% yield of **40**. (Initial cyanide anion formation was probably due to the small amount of water present in acetonitrile which formed the 1:1:1 (water:diene:aromatic) adduct to release cyanide anion).

A proposed mechanism for the formation of **40** is shown in Scheme 2.10. To confirm this mechanism several experiments were performed. (These are outlined in the Results Section II and Experimental Section). One of the first mechanisms suggested was a radical mechanism as shown in Figure 2.4 (Results II). However, attempts to substantiate this possibility using *t*-butyl peroxide (Scheme 2.5, Results II) resulted in no products being formed. Another mechanism proposed involved a CTC between 1,4-dicyanobenzene and 2,5-dimethyl-2,4-hexadiene. It was concluded that a CTC existed but it was also proven that **40** does not come exclusively from the CTC. It seemed that **40** came, at least mainly, from direct irradiation of 1,4-dicyanobenzene alone (Scheme 2.10). Whether or not cyanation occurred within the initially formed CIP or through a SSIP (FRI) was another factor that was of interest. This possibility was tested by addition of ^{13}C cyanide to the reaction mixture. The observation of 13% incorporation of ^{13}C cyanide seemed sufficient to conclude that cyanation occurred through a SSIP (FRI).



Scheme 2.10. The proposed mechanism for photo-NOCAS cyanation of 2,5-dimethyl-2,4-hexadiene.

Experimental

General Information

^{1}H and ^{13}C nmr spectra were obtained from a Bruker 300 MSL spectrometer or a Nicolet 360 NB nmr spectrometer. Spectra were recorded in parts per million and frequencies are relative to tetramethylsilane.

Computer simulations (^{1}H nmr) were accomplished using a program modified by R. Dickson, R. Wasylishen and T.P. Forrest (Dalhousie University).

Infrared spectra (ir) were recorded on an air-purged Perkin-Elmer 180 grating spectrometer and are reported in wavenumbers (cm^{-1}) relative to the 1601.4 cm^{-1} absorption band of polystyrene film.

Elemental analyses were performed by Canadian Microanalytical Service Ltd., B.C. Exact mass determinations were performed by the staff of the Institute of Marine Biosciences using a ZAB-E spectrometer. Melting points were determined using a Cybron Corporation Thermolyne apparatus with a digital thermocouple (all melting points are corrected).

Ultraviolet (uv) absorbance spectra were recorded using a Cary Varian 219 spectrometer and are reported in nanometers. X-ray data was collected using an Enrauf-Nonius CAD4 diffractometer and the structure was solved using SHELXS; calculations were done using SHELX-76 (see Appendix).

Product determination was achieved using a Hewlett- Packard (HP) 5890 gas chromatograph (gc) with a DB-1701 fused silica WCOT column (30 m x 0.25 mm, 0.25-μm film thickness) and a flame ionization detector (fid). A HP 3392A integrator was interfaced with the gc/fid to obtain peak listings as well as peak areas. This software was designed at the Department of Chemistry, Dalhousie University using a Commodore PC-II. A HP 5890 gc with a 5% phenyl methyl silicone fused silica WCOT column (25 m x 0.20 mm, 0.33-μm film thickness) and an HP 5970 mass selective detector was also used for product analyses. Mass spectra were recorded and reported as m/z (relative intensity).

Separation of product mixtures was carried out using preparative medium pressure liquid chromatography (mplc). The mplc consists of a 2.5 cm x 1 m column packed with tlc (thin layer chromatography) grade silica gel (without binder) (cat. no. 7747 Merck) at a pressure of 15 psi using helium (1psi= 6 kPa) (the pressure is 15psi unless otherwise stated in the experimental procedure). Connected to the mplc is an uv spectrophotometer-fraction collector that collects ca. 10 ml fractions. Another method used for product separation was flash chromatography on a 35 mm x 160 mm column (Column "A") or a 30 mm x 180 mm column (Column "B"). The columns were packed with silica gel that was 230-400 mesh, 60 Å (Aldrich), under 3 psi of nitrogen. Fraction sizes were ca. 5 mls each. Preparative-GC (prep/gc) was also utilized, and it was carried out using a Varian Aerograph A700 or 920, fitted with either 10% FFAP on Chromasorb W 60/80 or 40% SE-30 Chromasorb W 60/80 columns.

A recently discovered method of separation was utilized. It is referred to as the "dry column" flash chromatography method (dc/fc) (135). The column was packed with tlc (thin layer chromatography) grade silica gel (without binder) (cat. no. 7747 Merck).

Materials

Acetonitrile (Fisher ACS grade) was distilled from sodium hydride followed by phosphorus pentoxide. It was then passed through a column of basic alumina and refluxed over calcium hydride for 24 h (under a nitrogen atmosphere). The acetonitrile was then fractionally distilled under nitrogen and stored over molecular sieves (3 Å) (60). Methanol was distilled and stored over molecular sieves (4 Å). 1,4-Dicyanobenzene (**1**) (Aldrich) was purified by dissolving it in methylene chloride and Norite, and recrystallizing it from 95% ethanol. Tetraethylammonium perchlorate (TEAP) (Aldrich) was recrystallized three times with water and dried in a vacuum oven for 15 h, 70 °C, 0.25 Torr (1 Torr= 133.3 Pa). 1,5-Hexadiene, 98% (**12**), 2-methyl-1,5-hexadiene, 99% (**13**), 2,5-dimethyl-1,5-hexadiene, 90% and 99% (**14**), 5-methyl-3-hexen-2-one, 80% (**33**), 1,3-butadiene, 99% (**37**), 2-methyl-1,3-butadiene, 99% (**38**), 2,3-dimethyl-1,3-butadiene, 98% (**39**) and 2,5-dimethyl-2,4-hexadiene, 99% (**36**) were obtained from the Aldrich Chemical Co..

Irradiations

Irradiations were carried out with a solution of acetonitrile-methanol (3:1), or acetonitrile alone, with 1,4-dicyanobenzene, olefin and the option of a sensitizer/co-donor. Solutions were either placed in a 2 cm i.d. Pyrex tube or a 5 mm Pyrex nmr tube and were degassed with nitrogen. The samples were irradiated at 10°C using a CGE 1-kW or a Hanovia 450-W medium-pressure mercury vapor lamp contained in a water cooled quartz immersion well.

Cyclic Voltammetric Measurements

Cyclic voltammetry was used to obtain the oxidation potential of the substrate olefins. The apparatus used has been described by Arnold and Wayner (136). The working electrode was a platinum sphere (1 mm diameter) and the counter electrode was a platinum wire. The reference electrode was a saturated calomel electrode (SCE) which was placed in a solution of TEAP (0.1M, electrolyte/acetonitrile) using a Luggin capillary. The olefins were purified by preparative gc using a 0.95 cm x 350 cm aluminum column packed with 40% SE-30 on Chromosorb W 60/80 NAW. The olefin concentration used for measurement of the oxidation potentials was ca. 0.005 M. Since the anodic wave was irreversible, the half-wave potential was taken as 0.028 V before the anodic peak potential (137).

Yield of Photo-NOCAS Products

Yields were based upon 1,4-dicyanobenzene as the limiting reagent. The weight of 1,4-dicyanobenzene used during the reaction was determined by separation of it, by column chromatography, from the reaction mixture. The weight of each separate photo-NOCAS product was determined by column chromatography as well, but in cases where the products were difficult to separate from each other, a total weight was obtained of the combined products and the proportions of each isomer were determined using gc/fid.

Formation of the 1,5-Hexadiene Adducts

A solution of 6.4 g (0.078 mol) 1,5-hexadiene (**12**) and 2.5 g (0.020 mol) 1,4-dicyanobenzene (**1**) in 270 ml of acetonitrile-methanol (3:1) was degassed with nitrogen for 15 min and irradiated for 67 h. The solvent was removed by rotary evaporation and yielded a dark brown mixture (5.0 g). To the mixture was added methylene chloride to precipitate out **1**. The mixture was suction filtered to remove some excess **1**. 0.3 g of the mixture was chromatographed by mplc using a gradient of hexanes versus 75% diethyl ether/ 25% hexanes.

Fraction no. 136-137: 11.3 mg of **15** and **16** products.

Fraction no. 138-139: 35.7 mg of **15**, **16** and **17** products.

Fraction no. 140-150: 95.3 mg of **15**, **17** and **18** products

An additional 0.5 g was chromatographed by mplc using the same gradient as chosen previously.

Fraction no. 148-155: 39.3 mg of **15**, **16** and **17** products.

Fraction no. 156-191: 100 mg of **15** (mostly), **16**, **17** and **18** products.

Several combined fractions were rechromatographed to achieve separation of these products in minimal amounts: **15**, **16**, **17** and **18**. The overall yield of exciplex products was 54% using the gc/fid method of calculation. The following spectra of **15**, **16**, **17**, and **18** are reported; also, computer simulations (^{1}H nmr) were performed on all four compounds as additional evidence to support the structures of these compounds.

7-*endo*-(3′-butenyl)-1,3-dicyanotricyclo[3.3.0.0^{2,8}]oct-3-ene (**15**)

The yield obtained was 29% ; ^{1}H nmr (361.08 MHz, CDCl$_3$) δ_{TMS}: 1.61-1.71 (m, 2H, $^2J_{1'a-1'b}$= 7.8 Hz, $^3J_{1'a-7}$= 7.7 Hz, $^3J_{1'b-7}$= 7.7 Hz, $^3J_{1'a-2'}$= 7.5 Hz, $^3J_{1'b-2'}$= 7.5 Hz, CH$_2$ adjacent to allylic methylene group (1′a-H, 1′b-H)), 1.80 (d, 1H, $^3J_{2-8}$= 13.2 Hz, H at bridgehead adjacent to cyano substituted alkene (2-H)), 2.15-2.22 (m, 2H, $^3J_{1'a-2'}$= 7.5 Hz, $^3J_{1'b-2'}$= 7.5 Hz, $^3J_{2'-3'}$= 7.0 Hz, $^4J_{2'-4'cis}$= 1.2 Hz, $^4J_{2'-4'trans}$= 1.6

Hz, allylic CH$_2$ group (2′-H)), 2.62 (dd, 1H, $^3J_{5\text{-}6exo}$=6.6 Hz, $^3J_{4\text{-}5}$=2.0 Hz, H at bridgehead adjacent to alkene H (5-H)), 2.69 (m, 1H, $^3J_{2\text{-}8}$= 13.2 Hz, $^3J_{7\text{-}8}$= 11.3 Hz, $^4J_{6endo\text{-}8}$= 5.5 Hz, H adjacent to 2-H (8-H)), 2.94 (m, 1H, $^3J_{7\text{-}8}$= 11.3 Hz, $^3J_{1'a\text{-}7}$= 7.7 Hz, $^3J_{1'b\text{-}7}$= 7.7 Hz, $^3J_{6exo\text{-}7}$= 0.9 Hz, $^3J_{6endo\text{-}7}$= 1.2 Hz, H on alkyl substituted carbon (7-H)), 3.45 (m, 1H, $^4J_{5\text{-}6exo}$= 6.6 Hz, $^2J_{6exo\text{-}6endo}$= 5.8 Hz, $^3J_{6exo\text{-}7}$= 0.9 Hz, *exo* H (not at a bridgehead) adjacent to 7-H (6*exo*-H)), 3.50 (m, 1H, $^2J_{6exo\text{-}6endo}$= 5.8 Hz, $^4J_{6endo\text{-}8}$= 5.5 Hz, $^3J_{6endo\text{-}7}$= 1.2 Hz, *endo* H (not at a bridgehead) adjacent to 7-H (6*endo*-H)), 5.03 (m, 1H, $^3J_{3'\text{-}4'cis}$= 10.2 Hz, $^2J_{4'cis\text{-}4'trans}$= 1.6 Hz, $^4J_{2'\text{-}4'cis}$= 1.2 Hz, terminal vinyl H (4′*cis*-H)), 5.08 (m, 1H, $^3J_{3'\text{-}4'trans}$= 17.1 Hz, $^2J_{4'trans\text{-}4'cis}$= 1.6 Hz, $^4J_{2'\text{-}4'trans}$= 1.6 Hz, terminal vinyl hydrogen (4′*trans*-H)), 5.77 (m, 1H, $^3J_{3'\text{-}4'trans}$= 17.1 Hz, $^3J_{3'\text{-}4'cis}$= 10.2 Hz, $^3J_{2'\text{-}3'}$= 7.0 Hz, vinyl H (not on ring) (3′-H)), 6.54 (d, 1H, $^3J_{4\text{-}5}$= 2.0 Hz, vinyl H on ring (4-H)); ^{13}C nmr (90.80 MHz, CDCl$_3$) δ: 33.03 (t, 126.5 Hz), 34.14 (t, 127.7 Hz), 41.04 (d, 173.2 Hz), 44.38 (t, 131.0 Hz), 44.53 (d, 130.8 Hz), 46.58 (d, 183.8 Hz), 52.80 (d, 145.1 Hz), 114.76 (s), 115.78 (t, 156.3 Hz, terminal vinyl CH$_2$), 120.83 (s, CN), 120.83 (s, CN), 122.83 (s), 137.08 (d, 150.7 Hz), 143.33 (d, 173.8 Hz); ms m/z: 55(100), 64(15), 77(34), 91(23), 104(42), 115(21), 120(20), 128(34), 141(26), 142(26), 155(21), 168(42), 195(26), 209(42), 210(10). Anal. calcd. C$_{14}$H$_{14}$N$_2$: C 79.96, H 6.71, N 13.32; found (using a mixture of 13% **17** and 87% **15**): C 79.70, H 6.77, N 13.28.

6-*exo*-(3′-butenyl)-4,8-dicyanotricyclo[3.3.0.0^{2,8}]oct-3-ene (**16**)

The yield obtained was 2% ; ^{1}H nmr (361.08 MHz, CDCl$_3$) δ_{TMS}: 1.59 (m, 2H, $^{3}J_{1'a-2'}$= 7.1 Hz, $^{3}J_{1'b-2'}$= 7.1 Hz, $^{3}J_{1'a-6}$= 6.8 Hz, $^{3}J_{1'b-6}$= 6.8 Hz, $^{2}J_{1'a-1'b}$= 5.5 Hz, CH_2 adjacent to allylic methylene (1'a-H, 1'b-H)), 1.92-2.02 (m, 2H, $^{2}J_{7exo-7endo}$= 5.7 Hz, $^{3}J_{6-7endo}$= 4.6 Hz, CH_2 on ring adjacent to cyano substituted (7*exo*-H, 7*endo*-H)), 2.07-2.18 (m, 2H, $^{3}J_{1'a-2'}$= 7.1 Hz, $^{3}J_{1'b-2'}$= 7.1 Hz, $^{3}J_{2'-3'}$= 6.6 Hz, $^{4}J_{2'-4'cis}$= 1.1 Hz, $^{4}J_{2'-4'trans}$= 1.5 Hz, allylic CH_2 (2'-H)), 2.20-2.30 (m, 1H, $^{3}J_{1'a-6}$= 6.8 Hz, $^{3}J_{1'b-6}$= 6.8 Hz, $^{3}J_{6-7endo}$= 4.6 Hz, H on alkyl substituted carbon (6-H)), 2.74 (m, 1H, $^{3}J_{1-2}$= 5.7 Hz, $^{3}J_{2-3}$= 2.5 Hz, H at bridgehead adjacent to alkene H (2-H)), 3.27 (d, 1H, $^{3}J_{1-5}$= 5.8 Hz, H at bridgehead adjacent to alkene cyano (5-H)), 3.29 (dd, 1H, $^{3}J_{1-5}$= 5.8 Hz, $^{3}J_{1-2}$= 5.7 Hz, H at apex of three bridgeheads (1-H)), 5.02 (m, 1H, $^{3}J_{3'-4'cis}$= 10.3 Hz, $^{2}J_{4'cis-4'trans}$= 1.6 Hz, $^{4}J_{2'-4'cis}$= 1.1 Hz, terminal vinyl H (4'*cis*-H)), 5.06 (m, 1H, $^{3}J_{3'-4'trans}$= 17.1 Hz, $^{2}J_{4'cis-4'trans}$= 1.6 Hz, $^{4}J_{2'-4'trans}$= 1.5 Hz, terminal vinyl H (4'*trans*-H)), 5.78 (m, 1H, $^{3}J_{3'-4'trans}$= 17.1 Hz, $^{3}J_{3'-4'cis}$= 10.3 Hz, $^{3}J_{2'-3'}$= 6.6 Hz, vinyl H not on ring (3'-H)), 6.46 (d, 1H, $^{3}J_{2-3}$= 2.5 Hz, vinyl H on ring (3-H)); ^{13}C nmr (90.80 MHz, $CDCl_3$) δ: 31.01 (t, 134.4 Hz), 31.58 (t, 135.02 Hz), 32.61 (t, 134.4 Hz), 42.37 (d, 133.8 Hz), 43.91 (d, 145.9 Hz), 52.97 (d, 133.6 Hz), 56.94 (d, 145.1 Hz), 114.64 (s), 115.76 (t, 154.4 Hz, terminal vinyl CH_2), 119.67 (s), 120.85 (s, CN), 120.85 (s, CN), 137.08 (d, 151.0 Hz), 141.25 (d, 174.1 Hz); Infrared (PE-180) ν: 3079(m), 2929(s), 2859(m), 2234(s), 2229(s), 1643(m), 1600(w), 1454(m), 1309(w), 1009(m), 997(m), 979(m), 899(m), 844(m), 829(w); ms m/z: 55(100), 77(18), 115(23), 128(32), 141(56), 142(25), 168(92), 182(33), 209(24), 210(7). Exact mass m/z calcd. $C_{14}H_{14}N_2$: 210.1138; found: 210.1133.

7-*exo*-(3′-butenyl)-1,3-dicyanotricyclo[3.3.0.0^{2,8}]oct-3-ene (17)

The yield obtained was 18% ; ^{1}H nmr (361.08 MHz, CDCl$_3$) δ_{TMS}: 1.61-1.71 (m, 2H, $^2J_{1'a\text{-}1'b}$= 7.8 Hz, $^3J_{1'a\text{-}7}$= 7.7 Hz, $^3J_{1'b\text{-}7}$= 7.7 Hz, $^3J_{1'a\text{-}2'}$= 7.5 Hz, $^3J_{1'b\text{-}2'}$= 7.5 Hz, CH$_2$ adjacent to allylic methylene group (1′a-H, 1′b-H)), 1.80 (d, 1H, $^3J_{2\text{-}8}$= 13.2 Hz, H at bridgehead adjacent to cyano substituted alkene (2-H)), 2.15-2.22 (m, 2H, $^3J_{1'a\text{-}2'}$= 7.5 Hz, $^3J_{1'b\text{-}2'}$= 7.5 Hz, $^3J_{2'\text{-}3'}$= 7.0 Hz, $^4J_{2'\text{-}4'cis}$= 1.2 Hz, $^4J_{2'\text{-}4'trans}$= 1.6 Hz, allylic CH$_2$ group (2′-H)), 2.62 (dd, 1H, $^3J_{5\text{-}6exo}$= 6.4 Hz, $^3J_{4\text{-}5}$= 2.6 Hz, H at bridgehead adjacent to alkene H (5-H)), 2.67 (m, 1H, $^3J_{2\text{-}8}$= 13.2 Hz, $^3J_{7\text{-}8}$= 3.2 Hz, $^4J_{6endo\text{-}8}$= 5.5 Hz, H adjacent to 2-H (8-H)), 2.94 (m, 1H, $^3J_{7\text{-}8}$= 3.2 Hz, $^3J_{1'a\text{-}7}$= 7.7 Hz, $^3J_{1'b\text{-}7}$= 7.7 Hz, $^3J_{6exo\text{-}7}$= 0.9 Hz, $^3J_{6endo\text{-}7}$= 0.9 Hz, H on alkyl substituted carbon (7-H)), 3.32 (m, 1H, $^4J_{5\text{-}6exo}$= 6.4 Hz, $^2J_{6exo\text{-}6endo}$= 5.5 Hz, $^3J_{6exo\text{-}7}$= 0.9 Hz, *exo* H (not at a bridgehead) adjacent to 7-H (6*exo*-H)), 3.50 (m, 1H, $^2J_{6exo\text{-}6endo}$= 5.5 Hz, $^4J_{6endo\text{-}8}$= 5.5 Hz, $^3J_{6endo\text{-}7}$= 0.9 Hz, *endo* H (not at a bridgehead) adjacent to 7-H (6*endo*-H)), 5.02 (m, 1H, $^3J_{3'\text{-}4'cis}$= 10.2 Hz, $^2J_{4'cis\text{-}4'trans}$= 1.6 Hz, $^4J_{2'\text{-}4'cis}$= 1.2 Hz, terminal vinyl H (4′*cis*-H)), 5.06 (m, 1H, $^3J_{3'\text{-}4'trans}$= 17.1 Hz, $^2J_{4'trans\text{-}4'cis}$= 1.6 Hz, $^4J_{2'\text{-}4'trans}$= 1.6 Hz, terminal vinyl hydrogen (4′*trans*-H)), 5.77 (m, 1H, $^3J_{3'\text{-}4'trans}$= 17.1 Hz, $^3J_{3'\text{-}4'cis}$= 10.2 Hz, $^3J_{2'\text{-}3'}$= 7.0 Hz, vinyl H (not on ring) (3′-H)), 6.48 (d, 1H, $^3J_{4\text{-}5}$= 2.6 Hz, vinyl H on ring (4-H)); ^{13}C nmr (75.47 MHz, DEPT, CDCl$_3$) δ: 31.76 (t), 32.22 (t), 36.22 (d), 42.06 (d), 45.61 (d), 46.78 (t), 51.45 (d), 114.58 (s), 115.68 (t, terminal vinyl CH$_2$), 119.34 (s, CN), 119.34 (s, CN), 120.00 (s), 137.25 (d), 141.49 (d); ms m/z: 55(59), 63(48), 64(29), 77(59), 91(28), 104(39), 115(100), 120(20), 128(48), 141(58), 142(90), 168(90), 182(45), 195(48), 209(76), 210(38). Anal. calcd.

$C_{14}H_{14}N_2$: C 79.96, H 6.71, N 13.32; found (using a mixture of 13% **17** and 87% **15**): C 79.70, H 6.77, N 13.28.

trans-4′-(3′-butenyl)-*cis*-3,8-dicyanobicyclo[4.2.0]octa-2,7-diene (**18**)

The yield obtained was 5% ; ^{1}H nmr (361.08 MHz, CDCl$_3$) δ_{TMS}: 1.35 (m, 1H, $^2J_{5a\text{-}5b}$= 13.5 Hz, $^3J_{4\text{-}5a}$= 10.3 Hz, $^3J_{5a\text{-}6}$= 5.9 Hz, H on methylene group adjacent to bridgehead (5a-H)), 1.58 (m, 1H, $^2J_{1'a\text{-}1'b}$= 13.7 Hz, $^3J_{1'a\text{-}2'}$= 8.8 Hz, $^3J_{1'a\text{-}4}$= 5.1 Hz, H on methylene group adjacent to allylic methylene group (1′a-H)), 1.64 (m, 1H, $^2J_{1'a\text{-}1'b}$= 13.7 Hz, $^3J_{1'b\text{-}2'}$= 8.8 Hz, $^3J_{1'b\text{-}4'}$= 5.1 Hz, H on methylene group adjacent to allylic methylene group (1′b-H)), 2.08 (m, 1H, $^2J_{5a\text{-}5b}$= 13.5 Hz, $^3J_{4\text{-}5b}$= 4.9 Hz, $^3J_{5b\text{-}6}$= 3.3 Hz, $^4J_{1\text{-}5b}$= 1.5 Hz, H on methylene group adjacent to bridgehead (5b-H)), 2.13 (m, 2H, $^3J_{1'a\text{-}2'}$= 8.8 Hz, $^3J_{1'b\,2'}$= 8.8 Hz, $^3J_{2'\text{-}3'}$= 6.8 Hz, $^4J_{2'\text{-}4'trans}$= 1.6 Hz, $^4J_{2'\text{-}4'cis}$= 1.3 Hz, allylic methylene group (2′-H)), 2.20 (m, 1H, $^3J_{4\text{-}5a}$= 10.3 Hz, $^3J_{1'a\text{-}4}$= 5.1 Hz, $^3J_{1'b\text{-}4}$= 5.1 Hz, $^3J_{4\text{-}5b}$= 4.9 Hz, $^4J_{2\text{-}4}$= 2.5 Hz, allylic H adjacent to cyano substituted alkene (4-H)), 3.34 (m, 1H, $^3J_{5a\text{-}6}$= 5.9 Hz, $^3J_{1\text{-}6}$= 4.1 Hz, $^3J_{5b\text{-}6}$= 3.3 Hz, $^3J_{6\text{-}7}$= 1.2 Hz, H on bridgehead (6-H)), 3.74 (m, 1H, $^3J_{1\text{-}2}$= 5.5 Hz, $^3J_{1\text{-}6}$= 4.1 Hz, $^4J_{1\text{-}5b}$= 1.5 Hz, H on bridgehead (1-H)), 5.02 (m, 1H, $^3J_{3'\text{-}4'cis}$= 10.2 Hz, $^2J_{4'cis\text{-}4'trans}$= 1.6 Hz, $^4J_{2'\text{-}4'cis}$= 1.3 Hz, terminal vinyl H (4′*cis*-H)), 5.07 (m, 1H, $^3J_{3'\text{-}4'trans}$= 16.9 Hz, $^2J_{4'trans\text{-}4'cis}$= 1.6 Hz, $^4J_{2'\text{-}4'trans}$= 1.6 Hz, terminal vinyl hydrogen (4′*trans*-H)), 5.80 (m, 1H, $^3J_{3'\text{-}4\,trans}$= 16.9 Hz, $^3J_{3'\text{-}4'cis}$= 10.2 Hz, $^3J_{2'\text{-}3'}$= 6.8 Hz, vinyl H (not on ring) (3′-H)), 6.79 (dd, 1H, $^3J_{1\text{-}2}$= 5.5 Hz, $^4J_{2\text{-}4}$= 2.5 Hz, vinyl H on six-membered ring (2-H)) 6.89 (d, 1H, $^3J_{6\text{-}7}$= 1.2 Hz, vinyl H on four-membered ring (7-H)); ^{13}C nmr (90.80 MHz, $CDCl_3$) δ: 29.72 (t, 130.2 Hz), 30.65 (t, 123.5 Hz), 32.06 (d, 140.8 Hz), 32.06 (t, 126.8 Hz), 41.16 (d, 145.6 Hz), 42.99 (d, 160.5 Hz), 112.34 (s), 115.70 (t, 154.2 Hz, terminal vinyl methylene), 116.35 (s), 117.55 (s), 121.42 (s), 137.18 (d, 150.6 Hz), 141.41 (d, 165.0 Hz), 154.48 (d, 179.5 Hz); Infrared (PE-180) ν: 3081(w), 2941(s), 2871(m), 2231(s), 1641(m), 1616(w), 1586(w), 1456(m), 1376(w), 1156(w), 981(m), 906(s), 871(m), 856(m), 786(w); ms m/z: 51(19), 55(6), 67(40), 77(10), 89(22), 116(100), 128(23), 129(16), 141(6), 156(33), 157(23), 168(8), 183(2), 209(5), 210(1). Exact mass calcd. $C_{14}H_{14}N_2$: 210.1112; found: 210.1115.

Using Biphenyl as a Co-Donor

A solution of 0.4 g (0.005 mol) **12**, 1.2 g (0.010 mol) **1** and 1.5 g (0.0097 mol) biphenyl (**9**) in 160 ml of acetonitrile-methanol (3:1) was degassed with nitrogen for 15 min and irradiated for 123 h. The solvent was removed by rotary evaporation and yielded 3.1 g (exciplex products: 9% yield). Identification of exciplex products was carried out, only by comparison of retention times from the gc/fid to retention times of products obtained from the direct irradiation.

Formation of the 2-Methyl-1,5-Hexadiene Adducts

A solution of 0.4 g (0.004 mol) 2-methyl-1,5-hexadiene (**13**), 0.2 g (0.001

mol) **1** in 40 ml of acetonitrile-methanol (3:1) was degassed with nitrogen for 15 min and irradiated for 119 h. The solvent was removed by rotary evaporation and yielded 0.4 g. This crude mixture was placed on the mplc using a gradient of hexanes versus 50% diethyl ether/ 50% hexanes. It was discovered that one of the compounds converted to **20** after it was placed upon the mplc (evidence: changed retention time).

Fraction no. 100-115: 9.1 mg **19**.

Fraction no. 125-140: 16.9 mg **20**.

Fraction no. 155-186: 35.9 mg **1**.

A solution of 1.7 g (0.017 mol) 2-methyl-1,5-hexadiene (**13**), 0.8 g (0.006 mol) **1** in 200 ml of acetonitrile-methanol (3:1) was degassed with nitrogen for 15 min and irradiated for 72 h. The crude mixture was placed on the mplc using a gradient of hexanes versus 50% diethyl ether/ 50% hexanes.

Fraction no. 66-79: **19**.

Fraction no. 80-110: 51.5 mg **20**.

Using a flash column (type "B") and dichloromethane as an eluent, fractions 125-140 and 80-110 were combined and **20** purified.

The total yield of products obtained was 11%.

5-(4-cyanophenyl)-6-methoxy-5-methyl-1-hexene (**19**)

The yield obtained was 4% ; the mass spectrum and retention time were identical to the compound obtained when co-donor was present.

1-(4-cyanophenyl)-2-methoxymethyl-2-methyl-5-hexen-1-one (**20**)

The yield obtained was 7% ; ^{1}H nmr (361.08 MHz, CDCl$_3$) δ_{TMS}: 1.29 (s, 3H, CH$_3$), 1.60 (m, 1H, H on methylene group), 1.95 (m, 3H, 3H of CH$_2$-CH$_2$), 3.29 (s, 3H, OCH$_3$), 3.37 (d, 1H, $^2J_{7a\text{-}7b}$= 9.0 Hz, H on methoxy substituted carbon (7a-H)), 3.55 (d, 1H, $^2J_{7a\text{-}7b}$= 9.0 Hz, H on methoxy substituted carbon (7b-H)), 4.96 (m, 1H, $^3J_{5\text{-}6cis}$= 10.4 Hz, $^2J_{6cis\text{-}6trans}$< 2.0 Hz, $^4J_{4\text{-}6cis}$< 2.0 Hz, terminal vinyl H (6*cis*-H)), 5.00 (m, 1H, $^3J_{5\text{-}6trans}$= 17.0 Hz, $^2J_{6cis\text{-}6trans}$< 2.0 Hz, $^4J_{4\text{-}6trans}$< 2.0 Hz, terminal vinyl H (6*trans*-H)), 5.73 (m, 1H, $^3J_{5\text{-}6trans}$= 17.0 Hz, $^3J_{5\text{-}6cis}$= 10.4 Hz, $^3J_{4\text{-}5}$= 6.3 Hz, vinyl H (5-H)), 7.61 (d, 2H, $^3J_{2'\text{-}3'}$= 8.2 Hz, $^3J_{5'\text{-}6'}$= 8.2 Hz, H's adjacent to carbonyl substituted aryl carbon (2'-H, 6'-H)), 7.69 (d, 2H, $^3J_{2'\text{-}3'}$= 8.2 Hz, $^3J_{5'\text{-}6'}$= 8.2 Hz, H's adjacent to cyano substituted aryl carbon (3'-H, 5'-H)); ^{13}C nmr (90.80 MHz, CDCl$_3$) δ: 20.19 (q, 128.0 Hz, CH$_3$), 28.43 (t, 124.1 Hz, CH$_2$ adjacent to allylic methylene), 35.00 (t, 126.0 Hz, allylic CH$_2$), 52.55 (s, quaternary carbon, methyl and aryl substituted), 59.14 (q, 141.2 Hz, OCH$_3$), 78.69 (t, 141.9 Hz, OCH$_2$), 113.79 (s, quaternary aryl carbon cyano substituted), 115.06 (t, 155.2 Hz, terminal vinyl CH$_2$), 118.15 (s, CN), 127.24 (dd, 166.4 Hz, 4.3 Hz, aromatic CH adjacent to carbonyl substituted aryl carbon), 131.87 (d, 165.8 Hz, aromatic CH adjacent to cyano substituted aryl carbon), 137.71 (d, 152.5 Hz, vinyl CH), 144.15 (s, quaternary aryl carbon carbonyl substituted), 208.10 (s, C=O); Infrared (PE-180) ν: 3084(m), 2987(s), 2932(s), 2245(s), 1687(s), 1642(m), 1606(w), 1557(w), 1477(m), 1452(m), 1417(w), 1397(m), 1386(m), 1367(w), 1277(w), 1227(m), 1202(m), 1107(w), 977(m), 937(m), 902(m), 832(m), 762(w), 722(w); ms m/z: 55(51), 67(34), 68(20), 81(100), 85(24), 95(48), 102(50), 130(52), 171(19), 203(17), 229(1), 257(1). Anal. calcd. $C_{16}H_{19}NO_2$: C 74.68, H 7.44, N 5.44; found: C 74.35, H 7.40, N 5.42.

Using Biphenyl as a Co-Donor

A solution of 0.4 g (0.004 mol) 2-methyl-1,5-hexadiene (**13**), 0.5 g (0.004 mol) **1** and 0.3 g (0.002 mol) **9** in 40 ml of acetonitrile-methanol (3:1) was degassed with nitrogen for 15 min and irradiated for 119 h. The solvent was removed by rotary evaporation and yielded 1.3 g. This crude mixture was placed on the mplc using a gradient of hexanes versus 50% diethyl ether/ 50% hexanes.

Fraction no. 92-108: 89.6 mg **19**.

Fraction no. 139-234: 376.1 mg **1**.

The overall yield of photo-NOCAS product was 31%.

5-(4-cyanophenyl)-6-methoxy-5-methyl-1-hexene (**19**)

The yield obtained was 31% ; ^{1}H nmr (361.08 MHz, CDCl$_3$) δ_{TMS}: 1.36 (s, 3H, CH_3), 1.65-1.95 (m, 4H, CH_2-CH_2 (allylic CH_2 (3-H))), 3.29 (s, 3H, OCH_3), 3.37 (d, 1H, $^2J_{6a\text{-}6b}$= 9.1 Hz, H on methoxy substituted carbon (6a-H)), 3.49 (d, 1H, $^2J_{6a\text{-}6b}$= 9.1 Hz, H on methoxy substituted carbon (6b-H)), 4.90 (dd, 1H, $^3J_{1cis\text{-}2}$= 10.6 Hz, $^2J_{1cis\text{-}1trans}$< 2.0 Hz, $^4J_{1cis\text{-}3}$< 2.0 Hz, terminal vinyl H (1*cis*-H)), 4.94 (dd, 1H, $^3J_{1trans\text{-}2}$= 16.8 Hz, $^2J_{1cis\text{-}1trans}$ < 2.0 Hz, $^4J_{1trans\text{-}3}$< 2.0 Hz, terminal vinyl H (1*trans*-H)), 5.72 (m, 1H, $^3J_{1trans\text{-}2}$= 16.8 Hz, $^3J_{1cis\text{-}2}$= 10.6 Hz, $^3J_{2\text{-}3}$= 6.2 Hz, vinyl H (2-H)), 7.44 (d, 2H, $^3J_{2'\text{-}3'}$= 8.5 Hz, $^3J_{5'\text{-}6'}$= 8.5 Hz, H's adjacent to alkyl substituted aryl carbon (2'-H, 6'-H)), 7.61 (d, 2H, $^3J_{2'\text{-}3'}$= 8.5 Hz, $^3J_{5'\text{-}6'}$= 8.5 Hz, H's adjacent to cyano substituted aryl carbon (3'-H, 5'-H)); ^{13}C nmr (90.80 MHz, $CDCl_3$) δ: 22.51 (q, 127.7 Hz, CH_3), 28.22 (t, 127.2 Hz, CH_2), 38.19 (t, 129.2 Hz, CH_2), 42.76 (s, quaternary carbon, methyl and aryl substituted), 59.34 (q, 140.7 Hz, OCH_3), 81.10 (t, 140.6 Hz, OCH_2), 109.72 (s, quaternary aryl carbon cyano substituted), 114.41 (t, 155.4 Hz, terminal vinyl CH_2), 119.04 (s, CN), 127.35 (dd, 160.7 Hz, 6.0 Hz, aromatic CH adjacent to alkyl substituted aryl carbon), 131.88 (dd, 165.4 Hz, 5.8 Hz, aromatic CH adjacent to cyano substituted aryl carbon), 138.35 (d, 151.0 Hz, vinyl CH), 151.61 (s, quaternary aryl carbon alkyl substituted); Infrared (PE-180) ν: 3080(w), 2980(s), 2932(s), 2880(s), 2836(m), 2825(m), 2246(s), 1641(m), 1610(m), 1509(m), 1458(m), 1409(w), 1390(w), 1370(w), 1194(w), 1101(s), 1018(w), 985(w), 905(m), 830(m), 730(w); ms m/z: 55(31), 103(16), 116(56), 127(6), 130(100), 142(31), 158(27), 184(5), 188(16), 229(2). Anal. calcd. $C_{15}H_{19}NO$: C 78.56, H 8.35, N 6.11; found: C 78.71, H 8.39, N 6.22.

Using Magnesium Perchlorate and Co-Donor Biphenyl

A solution of 0.020 g (0.00021 mol) **13**, 0.027 g (0.00021 mol) **1** and 0.016 g (0.0001 mol) **9** in 2 mls of acetonitrile-methanol (3:1) was degassed with nitrogen for 7 min and irradiated for 43 h. The only product formed was **19**.

Formation of the 2,5-Dimethyl-1,5-Hexadiene Adducts

A solution of 0.8 g (0.009 mol) 2,5-dimethyl-1,5-hexadiene (**14**) and 0.5 g (0.004 mol) **1** in 80 ml of acetonitrile-methanol (3:1) was degassed with nitrogen for 15 min and irradiated for 115 h. The solvent was removed by rotary evaporation and yielded 1.3 g. This crude mixture was placed on the mplc using a gradient of hexanes versus 50% diethyl ether/ 50% hexanes. It was discovered that one of the compounds converted to **22** after it was placed upon the mplc (evidence: changed retention time).

Fraction no 75-83: 24.1 mg **21**.

Fraction no. 94-100: 12.6 mg **22**.

Fraction no. 121-234: 373.5 mg **1**.

The total yield of products was 11%.

5-(4-cyanophenyl)-6-methoxy-2,5-dimethyl-1-hexene (**21**)

The yield obtained was 8% ; ^{1}H nmr (361.08 MHz, $CDCl_3$) δ_{TMS}: 1.37 (s, 3H, CH_3), 1.66 (s, 3H, CH_3), 1.62-1.89 (m, 4H, CH_2-CH_2), 3.29 (s, 3H, OCH_3), 3.38 (d, 1H, $^2J_{6a\text{-}6b}$= 9.1 Hz, H on methoxy substituted carbon (6a-H)), 3.49 (d, 1H, $^2J_{6a\text{-}6b}$= 9.1 Hz, H on methoxy substituted carbon (6b-H)), 4.60 (s, 1H, terminal vinyl H), 4.66 (s, 1H, terminal vinyl H), 7.44 (d, 2H, $^3J_{2'\text{-}3'}$= 8.4 Hz, $^3J_{5'\text{-}6'}$= 8.4 Hz, H's adjacent to alkyl substituted aryl carbon (2'-H, 6'-H)), 7.61 (d, 2H, $^3J_{2'\text{-}3'}$= 8.4 Hz, $^3J_{5'\text{-}6'}$= 8.4 Hz, H's adjacent to cyano substituted aryl carbon (3'-H, 5'-H)); ^{13}C nmr (90.80 MHz, $CDCl_3$) δ: 22.49 (q, 126.2 Hz, CH_3), 22.60 (q, 126.2 Hz, CH_3), 31.97 (t, 123.3 Hz, CH_2), 37.14 (t, 127.1 Hz, CH_2), 42.76 (s, quarternary carbon, methyl and aryl substituted), 59.34 (q, 140.6 Hz, OCH_3), 81.23 (t, 141.2 Hz, OCH_2), 109.62 (t, 153.2 Hz, terminal vinyl CH_2), 109.72 (s, quaternary aryl carbon cyano substituted), 119.03 (s, CN), 127.37 (dd, 160.9 Hz, 5.4 Hz, aromatic CH adjacent to alkyl substituted aryl carbon), 131.89 (dd, 165.3 Hz, 5.4 Hz, aromatic CH adjacent to cyano substituted aryl carbon), 145.70 (s, vinyl quaternary carbon), 151.67 (s, quarternary aryl carbon alkyl substituted); Infrared (PE-180) ν: 3073(w), 2973(s),2933(s), 2883(s), 2841(m), 2241(s), 1648(m), 1608(m), 1507(m), 1451(m), 1405(w), 1386(w), 1373(m), 1195(m), 1173(w), 1305(s), 1018(w), 953(w), 948(w), 878(m), 828(m), 728(w); ms m/z: 55(66), 69(100), 102(7), 116(49), 129(12), 130(88), 142(42), 143(40), 174(12), 175(65), 188(16), 198(12), 243(2). Anal. calcd. $C_{16}H_{21}NO$: C 78.97, H 8.70, N 5.76; found: C 78.99, H 8.55, N 5.84.

1-(4-cyanophenyl)-2-methoxymethyl-2,5-dimethyl-5-hexen-1-one (22)

The yield obtained was 3% ; ^{1}H nmr (361.08 MHz, $CDCl_3$) δ_{TMS}: 1.30 (s, 3H, CH_3), 1.68 (s, 3H, CH_3), 1.80-2.10 (m, 4H, CH_2-CH_2), 3.29 (s, 3H, OCH_3), 3.37 (d, 1H, $^2J_{7a\text{-}7b}$= 9.0 Hz, H on methoxy substituted carbon (7a-H)), 3.56 (d, 1H, $^2J_{7a\text{-}7b}$= 9.0 Hz, H on methoxy substituted carbon (7b-H)), 4.63 (s, 1H, terminal vinyl H), 4.70 (s, 1H, terminal vinyl H), 7.62 (d, 2H, $^3J_{2'\text{-}3'}$= 8.2 Hz, $^3J_{5'\text{-}6'}$= 8.2 Hz, H's adjacent to carbonyl substituted aryl carbon (2'-H, 6'-H)), 7.69 (d, 2H, $^3J_{2'\text{-}3'}$= 8.2 Hz, $^3J_{5'\text{-}6'}$= 8.2 Hz, H's adjacent to cyano substituted aryl carbon (3'-H, 5'-H)); ^{13}C nmr (90.80 MHz, $CDCl_3$) δ: 20.21 (q, 127.7 Hz, CH_3), 22.48 (q, 127.3 Hz, CH_3), 32.16 (t, 123.5 Hz, CH_2), 34.02 (t, 127.5 Hz, CH_2), 52.59 (s, quaternary carbon, methyl and aryl substituted), 59.15 (q, 141.2 Hz, OCH_3), 78.74 (t, 138.5 Hz, OCH_2), 110.28 (t, 152.7 Hz, terminal vinyl CH_2), 113.82 (s, quaternary aryl carbon cyano substituted), 118.16 (s, CN), 127.27 (dd, 165.6 Hz, 5.2 Hz, aromatic CH adjacent to carbonyl substituted aryl carbon), 131.90 (dd, 166.4 Hz, 4.4 Hz, aromatic CH adjacent to cyano substituted aryl carbon), 144.16 (s, quaternary carbon), 145.02 (s, quaternary carbon), 208.54 (s, C=O); Infrared (PE-180) ν: 3075(w), 2926(s), 2235(s), 1726(m), 1688(s), 1651(m), 1606(w), 1454(m), 1398(m), 1386(m), 1376(m), 1278(m), 1236(m), 1196(m), 1176(m), 1106(s), 1018(w), 976(w), 941(m), 876(w), 836(m), 761(w); ms m/z: 55(93), 67(84), 68(75), 69(24), 81(35), 85(47), 95(75), 102(87), 109(57), 130(99), 171(100), 203(97), 271(1). Anal. calcd. $C_{17}H_{21}NO_2$: C 75.24, H 7.80, N 5.16; found: C 74.80, H 7.92, N 4.98. Exact mass calcd. $C_{17}H_{21}NO_2$: 271.1573; found: 271.1572.

Using Biphenyl as a Co-Donor

A solution of 1.8 g (0.016 mol) **14**, 1.8 g (0.014 mol) **1** and 1.1 g (0.0071 mol) **9** in 160 ml of acetonitrile-methanol (3:1) was degassed with nitrogen for 15 min and irradiated for 88 h. The solvent was removed by rotary evaporation and yielded 4.5 g of crude mixture. This crude mixture was placed on the mplc using a gradient of hexanes versus 50% diethyl ether/ 50% hexanes. The yields of photo-NOCAS products are: 2% **28**, 3% **29**, 3% **24**, 6% **23** and 13% **21**.

Fraction no. 83-90: 39.9 mg **26**.

Fraction no. 91-95: 29.7 mg **25**, **26** and **29**.

Fraction no. 96-99: 20.0 mg **25**, **29** and **21**.

Fraction no. 100-102: 14.3 mg **29** and **21**.

Fraction no. 103-115: 309.7 mg **21**.

Fraction no. 116-120: 24.5 mg **28** and **21**.

Fraction no. 121-124: 12.5 mg **28** and **24**.

Fraction no. 138-145: 109.2 mg **23**.

Fraction no. 146-150: 89 mg **23** and **24**.

Fraction no. 210-220: 203.7 mg **27** and **1**.

Fractions 138-145 were placed on the mplc using the same gradient as stated above.

Fraction no. 130-132: 39 mg **23**.

Fractions 146-150 were placed on a flash column "B" using methylene chloride as an eluent.

Fraction no. 70-79: 3 mg **24** and other product not yet analysed.

Fraction no. 80-89: 7 mg (mostly) **24**.

Fraction no. 90-100: 10 mg **24**.

Fractions 210-220 were placed on flash column "A" using 40% diethyl ether/ 60% hexanes as the eluent. **1** was removed and fractions 10-23 were combined and placed on a gravity column (50 mm x 170 mm) using the same eluent as previously used.

Fraction no. 56-70: 28.6 mg, **27**.

Fraction no. 50-55: **27** and impurities.

Several combined fractions were rechromatographed by flash and mplc columns to achieve separation and identification of **21**, **23**, **24**, **25**, **26**, **27**, **28** and **29**.

5-(4-cyanophenyl)-6-methoxy-2,5-dimethyl-1-hexene (**21**)

The yield obtained was 13% ; the mass spectrum and ^{1}H nmr were identical to the spectrum of the compound obtained when no co-donor was present.

cis-1-(4-cyanophenyl)-4-methoxy-1,4-dimethylcyclohexane (**23**)

The yield obtained was 6% ; ^{1}H nmr (361.08 MHz, $CDCl_3$) δ_{TMS}: 1.00 (s, 3H, equatorial CH_3 attached to a methoxy substituted quaternary carbon), 1.14 (s, 3H, axial CH_3 attached to an aryl substituted quaternary carbon), 1.70 (bd, 2H, $^2J_{3eq\text{-}3ax}$= $^2J_{5eq\text{-}5ax}$= 13.7 Hz, equatorial H's adjacent to CH_3, OCH_3 substituted carbon (3eq-H, 5eq-H)), 1.70-1.84 (m, 4H, axial H's adjacent to CH_3, OCH_3 substituted carbon and axial H's adjacent to CH_3, aryl substituted carbon (2ax-H, 3ax-H, 5ax-H, 6ax-H)), 2.01 (bd, 2H, $^2J_{2eq\text{-}2ax}$= $^2J_{6eq\text{-}6ax}$= 14.2 Hz, equatorial H's adjacent to CH_3, aryl substituted carbon (2eq-H, 6eq-H)), 3.20 (s, 3H, axial OCH_3 attached to methyl substituted carbon), 7.48 (d, 2H, $^3J_{2'\text{-}3'}$= 8.5 Hz, $^3J_{5'\text{-}6'}$= 8.5 Hz, H's adjacent to alkyl substituted aryl carbon (2'-H, 6'-H)), 7.62 (d, 2H, $^3J_{2'\text{-}3'}$= 8.5 Hz, $^3J_{5'\text{-}6'}$= 8.5 Hz, H's adjacent to cyano substituted aryl carbon (3'-H, 5'-H)).

NOE Experiment

The high frequency methyl signal was irradiated and an increase in peak intensity of ca. 6% occurred in the cyclohexane hydrogen region indicating an axial methyl group. The low frequency methyl signal was irradiated and no change was observed of peak intensities within the cyclohexane hydrogen region, thus indicating an equatorial methyl group.

Shift Reagent Used to Assign Chemical Shifts to Methyl Groups

Europium (III) tris 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,5-octanedione (Eu(fod)$_3$) was used as the shift reagent. To 5 mg of *cis*-4-(4-cyanophenyl)-1-methoxy-1,4-dimethylcyclohexane was added 4.5x10^{-5} mol of Eu(fod)$_3$ in five increments. With each addition a ^{1}H nmr spectrum was taken and the shift of each methyl group signal measured. A graph of chemical shift of each methyl group versus moles of Eu(fod)$_3$ yielded slopes for the low and high frequency methyl group signals to be 4.4x10^5 mm/mol and 2.7x10^5 mm/mol, respectively. The low frequency methyl group is thus attached to the methoxy substituted carbon and the high frequency methyl group to the aryl substituted carbon.

^{13}C nmr (90.80 MHz, CDCl$_3$) δ: 24.05 (q, 125.6 Hz, CH$_3$), 24.05 (q, 125.6 Hz, CH$_3$), 32.24 (t, 125.8 Hz, two CH$_2$ groups), 32.32 (t, 125.8 Hz, two CH$_2$ groups), 38.60 (s, quaternary carbon, aryl methyl substituted), 48.54 (q, 141.3 Hz, OCH$_3$), 72.53 (s, methoxy, methyl substituted quaternary carbon), 109.25 (s, quaternary carbon cyano substituted), 119.08 (s, CN), 127.00 (d, 165.0 Hz, aromatic CH adjacent to alkyl substituted aryl carbon), 132.20 (d, 171.0 Hz, aromatic CH adjacent to cyano substituted aryl carbon), 153.54 (s, quaternary aryl carbon alkyl substituted); Infrared (PE-180) ν: 3054(w), 2939(s), 2874(m), 2826(m), 2234(s), 1604(m), 1504(m), 1462(m), 1451(m), 1394(w), 1374(m), 1304(w), 1274(m), 1197(w), 1139(m), 1114(m), 1076(s), 1039(w), 1014(w), 934(m), 859(m), 824(m), 726(w); ms m/z: 55(75), 72(75), 77(12), 85(100), 86(24), 115(16), 116(40), 128(12), 130(12), 142(12), 143(19), 196(13), 212(2), 228(21), 243(1). Anal. calcd. $C_{16}H_{21}NO$: C 78.97, H 8.70, N 5.76; found: C 79.37, H 8.82, N 5.85.

trans-1-(4-cyanophenyl)-4-methoxy-1,4-dimethylcyclohexane (**24**)

The yield obtained was 3% ; ^{1}H nmr (361.08 MHz, $CDCl_3$) δ_{TMS}: 1.18 (s, 3H, equatorial CH_3 attached to a methoxy substituted quaternary carbon), 1.24 (s, 3H, equatorial CH_3 attached to an aryl substituted quaternary carbon), 1.50-1.60 (m, 4H, axial and equatorial H's adjacent to CH_3, OCH_3 substituted carbon (3eq-H, 3ax-H, 5eq-H, 5ax-H)), 1.72 (bd, 2H, equatorial H's adjacent to CH_3, aryl substituted carbon (2eq-H, 6eq-H)), 1.99 (m, 2H, axial H's adjacent to CH_3, aryl substituted carbon (2ax-H, 6ax-H)), 3.15 (s, 3H, axial OCH_3 attached to methyl substituted carbon), 7.49 (d, 2H, $^3J_{2'-3'}$= 8.3 Hz, $^3J_{5'-6'}$= 8.3 Hz, H's adjacent to alkyl substituted aryl carbon (2'-H, 6'-H)), 7.60 (d, 2H, $^3J_{2'-3'}$= 8.3 Hz, $^3J_{5'-6'}$= 8.3 Hz, H's adjacent to cyano substituted aryl carbon (3'-H, 5'-H)).

NOE Experiment

Both methyl group signals were irradiated, each individually, and no increase of peak intensity was observed in the cyclohexane hydrogen region. This indicates both methyl groups are equatorial.

^{13}C nmr (90.80 MHz, $CDCl_3$) δ: 23.87 (q, 123.7 Hz, CH_3), 25.89 (q, 128.3

Hz, CH_3), 31.92 (t, 125.9 Hz, two CH_2 groups), 32.83 (t, 126.6 Hz, two CH_2 groups), 37.22 (s, quaternary carbon, aryl methyl substituted), 48.45 (q, 140.5 Hz, OCH_3), 72.41 (s, quaternary carbon, methoxy methyl substituted), 109.26 (s, quaternary carbon cyano substituted), 119.12 (s, CN), 126.30 (d, 159.6 Hz, aromatic CH adjacent to alkyl substituted aryl carbon). 131.99 (d, 159.5 Hz, aromatic CH adjacent to cyano substituted aryl carbon), 156.62 (s, quaternary aryl carbon alkyl substitutedstituted); Infrared (PE-180) ν: 2973(s), 2943(s), 2833(m), 2241(s), 1605(m), 1504(m), 1465(m), 1433(w), 1403(w), 1373(m), 1271(m), 1218(w), 1188(w), 1128(m), 1078(s), 1013(m), 953(w), 843(m), 828(s); ms m/z: 55(16), 72(17), 77(3), 85(100), 86(5), 115(4), 116(10), 128(3), 130(4), 142(4), 143(5), 196(5), 212(1), 228(6), 243(1). Anal. calcd. $C_{16}H_{21}NO$: C 78.97, H 8.70, N 5.76; found: C 78.98, H 8.70, N 5.76.

2-Cyanobiphenyl (**25**) and 4-Cyanobiphenyl (**26**)

25 has a similar mass spectrum and retention time as the actual sample synthesized from a photo-NOCAS reaction involving cyclohexene (9).

26 shows a similar mass spectrum, retention time and 1H nmr as the actual sample synthesized from a photo-NOCAS reaction involving cyclohexene (9).

4-(4-cyanophenyl)-5-methoxy-2,5-dimethyl-1-hexene (**28**)

The yield obtained was 2% ; the mass spectrum and retention time are similar to those of the product prepared from the tautomer of **14** (**32**).

5-(4-cyanophenyl)-4-methoxy-2,5-dimethyl-1-hexene (**29**)

The yield obtained was 3% ; the mass spectrum and retention time are similar to those of the product prepared from the tautomer of **14** (**32**).

3,5-Dimethoxy-4-phenylcyclohexanecarbonitrile (**27**)

The melting point was 125.6-125.9°C; ^{1}H nmr (361.08 MHz, $CDCl_3$) δ_{TMS}: 1.75 (ddd, 2H, $^2J_{2ax\text{-}2eq}$= 13.9 Hz, $^3J_{1\text{-}2ax}$= 12.7 Hz, $^3J_{2ax\text{-}3}$= 2.5 Hz, axial H's on methylene groups (2ax-H)), 2.49 (ddd, 2H, $^2J_{2ax\text{-}2eq}$= 13.9 Hz, $^3J_{1\text{-}2eq}$= 3.1 Hz, $^3J_{2eq\text{-}3}$= 2.0 Hz, equatorial H's on methylene groups (2eq-H)), 2.68 (t, 1H, $^3J_{3\text{-}4}$= 3.2 Hz, benzyl H (4-H)), 3.25 (m, 1H, $^3J_{1\text{-}2ax}$= 12.7 Hz, $^3J_{1\text{-}2eq}$= 3.1 Hz, H on cyano substituted methylene (1-H)), 3.26 (s, 6H, OCH_3), 3.67 (ddd, 2H, $^3J_{3\text{-}4}$= 3.2 Hz, $^3J_{2ax\text{-}3}$= 2.5 Hz, $^3J_{2eq\text{-}3}$= 2.0 Hz, H's on methoxy substituted methylene (3-H)), 7.23-7.51 (m, 5H, aryl H's); ^{13}C nmr (90.80 MHz, $CDCl_3$) δ: 18.52 (d, 140.8 Hz, CH), 32.37 (t, 129.7 Hz, two CH_2 groups), 49.28 (d, 118.2 Hz, CH), 58.18 (q, 140.9 Hz, OCH_3), 77.99 (d, OCH), 122.96 (s, CN), 126.72 (d, 159.8 Hz, aryl CH), 128.03 (d, 159.7 Hz, aryl CH), 129.27 (d, 158.9 Hz, aryl CH), 140.42 (s, quaternary aryl carbon); Infrared (PE-180) ν: 2987(m), 2957(s), 2930(s), 2884(s), 2832(m), 2242(s), 1606(w), 1497(m), 1454(m), 1442(m), 1384(w), 1372(m), 1310(w), 1192(m), 1107(s), 1077(s), 1037(m), 958(w), 852(w), 767(m), 727(w), 697(s); ms m/z: 51(3), 55(3), 58(6), 65(5), 75(3), 77(4), 88(3), 91(19), 96(21), 101(3), 115(22), 116(3), 117(21), 127(3), 128(5), 155(100), 156(11), 177(7), 213(7), 245(3), 246(1). X-Ray Data: Appendix; $C_{15}H_{19}NO_2$.

Identification of 28 and 29

After identification of **28** and **29**, it was discovered that they were formed from a tautomer of **14**. The tautomer was found as an impurity in Aldrich (90% pure) **14**. Using Aldrich (99% pure) **14**, **28** and **29** were produced in smaller amounts as compared to an irradiation with 90% **14**.

Evidence: two tubes were prepared, each with 23 mg (0.0002 mol) **1**, 56 mg (0.0004 mol) **9** and 2 mls of acetonitrile-methanol (3:1). Each tube was degassed and then 90% pure **14** was added to one tube while 99% pure **14** was added to another. After irradiation for 90 h, the tube with 90% pure **14** yielded a ratio of **28/21**= 0.12 and **29/21**= 0.35 and the tube with 99% pure **14** yielded a ratio of **28/21**= 0.04 and **29/21**= 0.05. (Ratios were achieved using areas from the gc(fid)).

Biphenyl was Increased to Increase Cyclization Adducts

A solution of 0.9 g (0.008 mol) **14**, 0.9 g (0.007 mol) **1** and 4.3 g (0.028 mol) **9** in 80 ml of acetonitrile-methanol (3:1) was degassed with nitrogen for 15 min and irradiated for 51 h. The solvent was removed by rotary evaporation and yielded 4.0 g of crude mixture. This crude mixture was placed on the mplc using a gradient of hexanes versus 50% diethyl ether/ 50% hexanes. The yield of photo-NOCAS products were: 16% **21**, 10% **23**, 4% **24**.

Evidence of Cyclization Increasing with Decreased Methanol

Five tubes were prepared each with 23 mg (0.00018 mol) **1**, 28 mg (0.00018 mol) **9**, 22 mg (0.00018 mol) **14** and varying amounts of acetonitrile-methanol (Table 1.1). (Ratios were achieved using areas from the gc(fid)). This procedure was then repeated, using nine tubes, and prepared as above with varying amounts of acetonitrile-methanol (Table 1.2).

Using Phenanthrene as a Sensitizer

A solution of 0.4 g (0.005 mol) **14**, 0.5 g (0.004 mol) **1** and 0.3 g (0.002 mol) phenanthrene **5** in 40 ml of acetonitrile-methanol (3:1) was degassed with nitrogen for 15 min and irradiated for 121 h. The solvent was removed by rotary evaporation and yielded 1.1 g. This crude mixture was placed on the mplc using a gradient of hexanes versus methylene chloride. The overall yield of photo-NOCAS products was 2% .

Fraction no. 156-179: 25.1 mg **51** and **52**.

Fraction no. 182-202: 16.8 mg **21** and other product.

Fraction 156-179 was placed on flash column "B", eluent was methylene chloride.

Fraction no. 11-13: 11 mg **52**.

5-(4-cyanophenyl)-6-methoxy-2,5-dimethyl-1-hexene (**21**)

The yield was 2%. The mass spectrum and ^{1}H nmr obtained were identical to the spectrum of the compound obtained when no sensitizer was present.

9-cyano-9,10-dihydrophenanthrene (**51**)

^{1}H nmr (361.08 MHz, $CDCl_3$) δ_{TMS}: 3.19 (d, 2H), 4.05 (dd, 1H), 7.2-7.4 (m, 4H), 7.5-7.6 (m, 4H). This spectrum appeared to be similar to the ^{1}H nmr spectrum reported in the literature (30).

9-methoxy-9,10-dihydrophenanthrene (**52**)

^{1}H nmr (361.08 MHz, $CDCl_3$) δ_{TMS}: 3.14 (dd, 2H), 3.33 (s, 3H, OCH_3), 4.37(dd, 1H), 7.25-7.45 (m, 6H), 7.8-7.83 (m, 2H); ^{13}C nmr (90.80 MHz, $CDCl_3$) δ: 34.81 (t, 129.6 Hz, CH_2), 56.26 (q, 139.2 Hz, OCH_3), 77.06 (d, 141.4 Hz, CH), 123.50 (d, CH), 124.14 (d, CH), 127.17 (d, CH), 127.17 (d, CH), 127.83 (d, CH), 128.31 (d, CH), 129.08 (d, CH), 133.34 (d, CH), 133.72 (d, CH), 133.84 (d, CH), 134.95 (d, CH); ms m/z: 76(28), 152(32), 176(44), 177(33), 178(100), 179(100), 210(44).

Preparation of 5-Methyl-4-Hexen-2-one (34)

34 was made using a method described by Yang and Jorgenson (63). 5-

Methyl-3-hexen-2-one was irradiated in a solution of diethyl ether which yielded the β,γ-isomer; **34**.

Preparation of 2,5-Dimethyl-1,4-Hexadiene (32)

Using a procedure published by Bestmann (64), 0.8 g (0.04 mol) sodium was placed in a three-necked round bottom flask with a dry-ice condenser attached (a calcium chloride tube was added to the condenser). A gas inlet tube was connected to an ammonia tank which then led to the round bottom flask. Ammonia was allowed to condense until approximately 100 mls was present. A small amount of ferric nitrate was added to catalyse the reaction (observation: the color of the solution changed from blue to dark gray in approximately 15 minutes). Triphenylphosphonium bromide (10 g, 0.028 mol) was then added via a solid addition funnel and the reaction was stirred for approximately 1/2 h. The ketone (**34**) (3.1 g, 0.028 mol) was then added with 100 mls of decalin (distilled under reduced pressure and stored over molecular sieves (4Å)). The ammonia was allowed to evaporate and the dry-ice condenser was replaced by a water condenser with a drying tube. The mixture was left to stir overnight. The mixture was washed with water several times until the water layer was no longer basic. The organic layer was distilled under atmospheric pressure to remove the decalin. There were several fractions collected:

Fraction 1: 142-185°C

Fraction 2: 188-189°C

Fraction 3: 190-191°C

Fraction 4: 191-192°C

Fraction 5: 192°C

Fraction 6: 193-194°C

Fraction 7: 194°C

Fractions 1 and 2 were placed on the prep/gc (40% SE-30). The tautomer (**32**) was collected and identified. The amount collected was 0.2 g (0.3 mls, 0.002 mol) of **32**.

2,5-dimethyl-1,4-hexadiene (**32**)

This compound (**32**) was identified by comparison of its ^1H nmr to the described ^1H nmr of the sample in a publication by Bly *et al.* (138).

^1H nmr (361.08 MHz, $CDCl_3$) δ_{TMS}: 1.62 (s, 3H, CH_3), 1.71 (s, 3H, CH_3), 1.73 (s, 3H, CH_3), 2.68 (d, 2H, $^3J_{3\text{-}4}$= 7.6 Hz, CH_2 (3-H)), 4.68 (broad s, 2H, $^2J_{1\text{-}1'}$= 1.1 Hz, terminal vinyl methylene (1-H, 1'-H)), 5.18 (m, 1H, $^3J_{3\text{-}4}$= 7.6 Hz, vinyl CH (4-H)); ^{13}C nmr (90.80 MHz, $CDCl_3$) δ: 17.62 (q, 133.9 Hz, CH_3), 22.55 (q, 125.0 Hz, CH_3), 25.77 (q, 126.2 Hz, CH_3), 36.53 (t, 126.8 Hz, CH_2), 109.62 (t, 154.8 Hz, terminal vinyl CH_2), 121.84 (d, 153.0 Hz, vinyl CH), 132.88 (s, quaternary carbon with two CH_3 groups), 145.44 (s, quarternary carbon mono-methylated); ms m/z: 53(24), 55(43), 67(92), 95(100), 110(30), 111(3).

Formation of the 2,5-Dimethyl-1,4-Hexadiene Adducts

A solution of 0.5 g (0.004 mol) 2,5-dimethyl-1,4-hexadiene (**32**), 0.6 g (0.005 mol) **1** and 1.5 g (0.010 mol) **9** in 80 ml of acetonitrile-methanol (3:1) was degassed with nitrogen for 15 min and irradiated for 26 h. The crude mixture was placed on the mplc using a gradient of hexanes versus 50% diethyl ether/ 50% hexanes. The yield of photo-NOCAS products was: 9% **28**, 16% **29**, 20% **35**.

Fraction no. 72-83: 181.6 mg **29** and **9**.
Fraction no. 84-86: 30.0 mg **28**, **29** and **9**.
Fraction no. 87-98: 84.2 mg **28**, **29** and **9**.
Fraction no. 99-104: 27.8 mg **28**, **35**, and **9**.
Fraction no. 105-117: 106.5 mg **35** and **9**.
Fraction no. 118-120: 12 mg **35**, **1** and **9**.

Fractions 87-98 were placed on a dc/fc. The dimensions of the column were 40 mm x 40 mm and the eluent used was dichloromethane.

Fraction no. 6-9: 48.0 mg **28** and **29**.
Fraction no. 10-11: 19.2 mg **28**.

Using fractions 6-9, another dry column was prepared using 70% hexanes/ 30%

diethyl ether. A few more dry columns were carried out to achieve separation of **29**. Once separated, a prep/gc (10% FFAP) was carried out to further purify the sample for analysis.

For **28** and **35**, several dry columns were done to achieve separation of the fractions from the initial mplc. Further purification was achieved using a micro-distillation apparatus. For **28**, the oil bath temperature was 180°C and the vacuum was 30 μTorr. The distillate was placed in a freezer and crystals appeared. Recrystallization was achieved with methanol. For **35**, the oil bath temperature was 100°C and the vacuum was 30 μTorr. The distillate was dissolved in methanol and placed in the freezer. Crystals formed and were then washed with methanol several times.

It was found that after identification of **35**, the compound was produced from a tautomer of **32** which was formed during the irradiation. The gc/ms of **32** shows purity; there is no tautomer **36** present before irradiation.

4-(4-cyanophenyl)-5-methoxy-2,5-dimethyl-1-hexene (**28**)

The yield obtained was 9% ; the melting point was 62.9-63.9°C ; ^{1}H nmr (361.08 MHz, $CDCl_3$) δ_{TMS}: 1.05 (s, 3H, CH_3), 1.12 (s, 3H, CH_3), 1.56 (s, 3H, CH_3), 2.50 (dd, 1H, $^3J_{3a\text{-}3b}$= 14.5 Hz, $^3J_{3a\text{-}4}$= 12.0 Hz, H on methylene group (3a-H)), 2.64 (bd, 1H, $^3J_{3a\text{-}3b}$= 14.5 Hz, $^3J_{3b\text{-}4}$= 3.2 Hz, H on methylene group (3b-H)), 2.95 (dd, 1H, $^3J_{3a\text{-}4}$= 12.0 Hz, $^3J_{3b\text{-}4}$= 3.2 Hz, H on aryl substituted carbon (4-H)), 3.22 (s, 3H, OCH_3), 4.44 (bs, 1H, terminal vinyl H), 4.55 (bs, 1H, terminal vinyl H), 7.33 (d, 2H, $^3J_{2'-3'}$ = 8.3 Hz, $^3J_{5'-6'}$ = 8.3 Hz, H's adjacent to alkyl substituted aryl carbon (2′-H, 6′-H)), 7.54 (d, 2H, $^3J_{2'-3'}$ = 8.3 Hz, $^3J_{5'-6'}$ = 8.3 Hz, H's adjacent to cyano substituted aryl carbon (3′-H, 5′-H)); ^{13}C nmr (90.80 MHz, $CDCl_3$) δ: 22.37 (q, 123.9 Hz, CH_3), 22.83 (q, 126.5 Hz, CH_3), 23.52 (q, 125.5 Hz, CH_3), 37.30 (t, 126.6 Hz, CH_2), 49.22 (q, 140.5 Hz, OCH_3), 53.38 (d, 125.5 Hz, CH, aryl substituted), 76.44 (s, quaternary carbon, methoxy substituted), 109.99 (s, quaternary aryl carbon, cyano substituted), 112.43 (t, 153.7 Hz, terminal vinyl CH_2), 119.13 (s, CN), 130.56 (d, 162.8 Hz, aromatic CH adjacent to alkyl substituted aryl carbon), 131.35 (d, 160.8 Hz, aromatic CH adjacent to cyano substituted aryl carbon), 143.29 (s, quaternary aryl carbon, alkyl substituted), 147.51 (s, vinyl quarternary carbon); ^{13}C nmr (90.80 MHz, $(CD_3)_2CO$) δ: 22.24 (q), 22.94 (q), 23.51 (q), 37.75 (t), 49.11 (q, OCH_3), 53.65 (d), 76.96 (s, quaternary carbon, methoxy substituted), 110.58 (s, quaternary aryl carbon, cyano substituted), 112.47 (t, terminal vinyl CH_2), 119.50 (s, CN), 131.72 (d, aromatic CH adjacent to alkyl substituted aryl carbon), 131.76 (d, aromatic CH adjacent to cyano substituted aryl carbon), 144.49 (s, quaternary aryl carbon, alkyl substituted), 148.74 (s, vinyl quarternary carbon); Infrared (PE-180) ν: 3181(w), 3081(m), 3036(m), 2829(m), 2229(s), 1831(w), 1801(w), 1646(m), 1606(s), 1506(s), 1461(s), 1418(s), 1382(s), 1374(s), 1365(s), 1306(w), 1276(m), 1236(s), 1181(s), 1140(s), 1066(s), 1019(m), 939(w), 884(s), 854(s), 826(s), 787(m), 753(m), 716(w); ms m/z: 53(5), 55(12), 73(100), 74(16), 89(6), 103(10), 115(12), 116(23), 127(10), 128(12), 129(12), 130(16), 140(12), 154(12), 156(19), 196(12), 211(1), 243(1). Anal. calcd. $C_{16}H_{21}NO$: C 78.97, H 8.70, N 5.76; found: C 78.68, H 8.32, N 5.72.

5-(4-cyanophenyl)-4-methoxy-2,5-dimethyl-1-hexene (**29**)

The yield obtained was 16% ; the melting point was 42.1-42.8°C ; ^1H nmr (361.08 MHz, $CDCl_3$) δ_{TMS}: 1.34 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.71 (s, 3H, CH_3), 1.91 (d, 2H, $^3J_{3\text{-}4}$= 5.9 Hz, CH_2 (3-H)), 3.27 (s, 3H, OCH_3), 3.32 (t, 1H, $^3J_{3\text{-}4}$= 5.9 Hz, CH (4-H)), 4.71 (bs, 1H, terminal vinyl H), 4.74 (bs, 1H, terminal vinyl H), 7.52 (d, 2H, $^3J_{2'\text{-}3'}$= 8.6 Hz, $^3J_{5'\text{-}6'}$= 8.6 Hz, H's adjacent to alkyl substituted aryl carbon (2′-H, 6′-H)), 7.60 (d, 2H, $^3J_{2'\text{-}3'}$= 8.6 Hz, $^3J_{5'\text{-}6'}$= 8.6 Hz, H's adjacent to cyano substituted aryl carbon (3′-H, 5′-H)); ^{13}C nmr (90.80 MHz, $CDCl_3$) δ: 22.67 (q, 122.1 Hz, CH_3), 23.89 (q, 120.0 Hz, CH_3), 25.16 (q, 122.3 Hz, CH_3), 40.11 (t, 125.7 Hz, CH_2), 43.74 (s, quaternary carbon aryl substituted), 61.14 (q, 141.1 Hz, OCH_3), 87.98 (d, 139.9 Hz, OCH), 109.60 (s, quaternary aryl carbon, cyano substituted), 112.78 (t, 154.1 Hz, terminal vinyl CH_2), 119.05 (s, CN), 127.47 (d, 160.2 Hz, aromatic CH adjacent to alkyl substituted aryl carbon), 131.66 (d, 165.3 Hz, aromatic CH adjacent to cyano substituted aryl carbon), 143.19 (s, quaternary aryl carbon, alkyl substituted), 153.26 (s, vinyl quarternary carbon); Infrared (PE-180) ν: 3072(w), 2970(s), 2930(s), 2825(m), 2128(s), 1644(w), 1602(m), 1500(m), 1440(m), 1400(m), 1380(m), 1360(m), 1171(m), 1090(s), 1050(m), 1010(m), 971(m), 820(m); ms m/z: 55(6), 57(4), 67(25), 69(16), 71(6), 99(100), 100(6), 116(16), 129(8), 130(7), 156(13), 188(24), 243(1). Anal. calcd. $C_{16}H_{21}NO$: C 78.97, H 8.70, N 5.76; found: C 78.90, H 8.84, N 5.72.

trans-2-(4-cyanophenyl)-5-methoxy-2,5-dimethyl-3-hexene (**35**)

The yield obtained was 20% ; the melting point was 44.6-45.6°C ; ^{1}H nmr (361.08 MHz, $CDCl_3$) δ_{TMS}: 1.28 (s, 6H, two CH_3 groups), 1.42 (s, 6H, two CH_3 groups), 3.16 (s, 3H, OCH_3), 5.48 (d, 1H, $^3J_{3\text{-}4}$= 16.2 Hz, vinyl H), 5.72 (d, 1H, $^3J_{3\text{-}4}$= 16.2 Hz, vinyl H), 7.43 (d, 2H, $^3J_{2'\text{-}3'}$= 8.4 Hz, $^3J_{5'\text{-}6'}$= 8.4 Hz, H's adjacent to alkyl substituted aryl carbon (2'-H, 6'-H)), 7.59 (d, 2H, $^3J_{2'\text{-}3'}$= 8.4 Hz, $^3J_{5'\text{-}6'}$= 8.4 Hz, H's adjacent to cyano substituted aryl carbon (3'-H, 5'-H)); ^{13}C nmr (90.80 MHz, $CDCl_3$) δ: 25.90 (q, 126.2 Hz, CH_3), 28.57 (q, 126.7 Hz, CH_3), 40.73 (s, quaternary carbon, aryl substituted), 50.29 (q, 140.2 Hz, OCH_3), 74.73 (s, quaternary carbon, methoxy substituted), 109.64 (s, quaternary aryl carbon, cyano substituted), 119.01 (s, CN), 126.94 (dd, 158.6 Hz, 5.2 Hz, aromatic CH adjacent to alkyl substituted aryl carbon), 131.99 (dd, 165.5 Hz, 4.8 Hz, aromatic CH adjacent to cyano substituted aryl carbon), 132.87 (d, 146.9 Hz, vinyl CH), 138.03 (d, 148.9 Hz, vinyl CH), 154.39 (s, quaternary aryl carbon, alkyl substituted); Infrared (PE-180) ν: 2970(s), 2930(m), 2821(w), 2230(s), 1608(m), 1501(m), 1465(m), 1401(w), 1379(m), 1362(m), 1292(w), 1255(w), 1170(m), 1160(w), 1072(s), 1020(w), 1000(w), 970(m), 825(s), 750(w), 725(w); ms m/z: 55(23), 73(53), 77(26), 99(96), 116(53), 154(31), 168(58), 170(27), 181(31), 196(71), 228(100). Anal. calcd. $C_{16}H_{21}NO$: C 78.97, H 8.70, N 5.76; found: C 78.88, H 8.76, N 5.79.

Formation of the 2,5-Dimethyl-2,4-Hexadiene Adducts

A solution of 4.9 g (0.04 mol) 2,5-dimethyl-2,4-hexadiene (**36**), 2.8 g (0.02 mol) **1** and 6.7 g (0.04 mol) **9** in 180 ml of acetonitrile-methanol (3:1) was degassed with nitrogen for 15 min and irradiated for 123 h using a 450 W lamp. The yield of the crude mixture was 12.8g. This crude mixture was placed on a mplc using a gradient of hexanes/dichloromethane. The yield of photo-NOCAS products were: 82% **35** and 4% **40**.

Fraction no. 235-250: 375.5 mg **35**.

Fraction no. 180-234, 251-300: 4.1362 g **35**, **40** and **1**.

Fractions 235-250 were placed on a dc/fc. The dimensions of the column were 45 mm x 40 mm and the eluent used was 10% diethyl ether/ 90% hexanes.

Fraction no. 20-24: **35**.

Fraction no. 14-19, 25-32: **35** and some impurities.

Using fractions 180-234, 251-300 from the above mplc, another dc/fc was prepared. The dimensions of the column were 50 mm x 65 mm and the eluent was 10% diethyl ether/ 90% hexanes. Before the above mixture was placed on the dc/fc, hexanes were used to decant off 430 mg of **1**.

Fraction no. 12-28: 2.75 g of **35**.

Fraction no. 29-63: 739.8 mg of **35** and **40**.

Fraction no. 64-78: 33.3 mg of **40**.

Fractions 29-63 were placed on another dc/fc with the same conditions as the previous dry column.

Fraction no. 18-26: 322.2 mg of **35**.

Fraction no. 27-44: 338.3 mg of **35** and **40**.

Fraction no. 45-60: 59.5 mg of **40**.

Fraction 45-60 was dissolved in methanol and placed in a freezer to allow crystals to form. The crystals were repeatedly washed with methanol and then dried in a vacuum oven.

trans-2-(4-cyanophenyl)-5-methoxy-2,5-dimethyl-3-hexene (**35**)

The yield was 82%. The mass spectrum and retention time were identical to the spectrum of the compound obtained from **32**.

trans-5-(4-cyanophenyl)-2,2,5-trimethyl-3-hexenenitrile (**40**)

The yield obtained was 4% ; the melting point was 84.2-85.0°C ; ^{1}H nmr (361.08 MHz, CDCl$_3$) δ_{TMS}: 1.43 (s, 6H, two CH$_3$ groups), 1.46 (s, 6H, two CH$_3$ groups), 5.34 (d, 1H, $^3J_{3\text{-}4}$= 15.8 Hz, vinyl H), 6.01 (d, 1H, $^3J_{3\text{-}4}$= 15.8 Hz, vinyl

H), 7.41 (d, 2H, $^3J_{2'-3'}$ = 8.7 Hz, $^3J_{5'-6'}$ = 8.7 Hz, H's adjacent to alkyl substituted aryl carbon (2'-H, 6'-H)), 7.60 (d, 2H, $^3J_{2'-3'}$ = 8.7 Hz, $^3J_{5'-6'}$ = 8.7 Hz, H's adjacent to cyano substituted aryl carbon (3'-H, 5'-H)); ^{13}C nmr (90.80 MHz, $CDCl_3$) δ: 27.70 (q, 131.2 Hz, CH_3), 28.01 (q, 127.9 Hz, CH_3), 34.56 (s, quaternary carbon, cyano substituted), 40.64 (s, quaternary carbon, aryl substituted), 109.99 (s, quaternary aryl carbon, cyano substituted), 118.90 (s, CN), 123.52 (s, CN), 126.88 (d, 161.3 Hz, aromatic CH adjacent to alkyl substituted aryl carbon), 129.08 (d, 149.5 Hz, vinyl CH), 132.12 (d, 169.8 Hz, aromatic CH adjacent to cyano substituted aryl carbon), 138.90 (d, 152.1 Hz, vinyl CH), 153.38 (s, quaternary aryl carbon, alkyl substituted); Infrared (PE-180) ν: 2970(w), 2917(w), 2892(s), 2846(s), 2982(m), 2226(s), 1604(s), 1522(w), 1500(s), 1467(s), 1446(m), 1388(m), 1371(m), 1360(m), 1300(m), 1247(m), 1228(m), 1216(m), 1203(w), 1180(w), 1136(m), 1110(w), 1090(s), 1014(m), 1010(w), 987(w), 964(s), 934(m), 911(w), 852(m), 828(s), 813(s), 722(w); ms m/z: 51(7), 77(8), 89(6), 115(7), 116(16), 127(8), 128(8), 140(8), 142(20), 143(8), 153(8), 154(15), 155(12), 168(8), 170(100), 171(12), 181(9), 196(29), 238(1). Anal. calcd. $C_{16}H_{18}N_2$: C 80.63, H 7.61, N 11.76; found: C 80.41, H 7.78, N 11.57.

Formation of the 2,5-Dimethyl-2,4-Hexadiene Adducts Using Only Acetonitrile

A solution of 1.1 g (0.01 mol) **36** and 0.6 g (0.005 mol) **1** in 40 ml of acetonitrile was degassed with nitrogen for 5 min and irradiated for 74 h using a 450 W lamp. The yield of the crude mixture was 1.1 g. This crude mixture was placed on a dc/fc. The dimensions of the dc/fc were 45 mm x 40 mm and the eluent used was 30% diethyl ether/ 70% hexanes.

Fraction no. 7-9, 13-18: 432.4 mg of **1** and **40**.

Fraction no. 10-12: 377.2 mg of **40**.

Fraction no. 19-44: 261.6 mg of **1**.

Fractions 7-9 and 13-18 were placed on a dc/fc. Using the same conditions for dc/fc as outlined above, the following fractions were collected:

Fraction no. 20-26: 271.0 mg of **1** and **40**.

Fraction no. 27-38: **1**, **40** and impurities.

Fractions 20-26 were placed on a dc/fc (same conditions as outlined above).

Fraction no. 11-14: 150.4 mg of **40**.

Fraction no. 15-18: 85.4 mg of **1** and **40**.

Fraction 27-38 and 15-18 were combined and placed on a dc/fc (same conditions as outlined above).

Fraction no. 8-13: 94.6 mg of **40**.

Fraction no. 14-25: 28.4 mg of **40** and impurities.

The yield of **40** was based on isolated 1,4-dicyanobenzene and was 94% .

trans-5-(4-cyanophenyl)-2,2,5-trimethyl-3-hexenenitrile (**40**)

The yield obtained was 94% . The mass spectrum and retention time were identical to the spectrum of the compound obtained from **36** with methanol present.

Does 40 Form Via A Radical Mechanism?

Two reactions were carried out using di-t-butyl peroxide. One reaction was carried out with 0.31 g of **1**, 0.7 ml of **36**, and 0.03 ml of di-t-butyl peroxide in 20 mls of acetonitrile-methanol (3:1). The second reaction was the same except the solvent was acetonitrile-t-butanol. Both reactions were placed in separate thick-walled tubes and covered in foil. The tubes were sealed and placed in an oil bath at 110°C for 5 days. Both reactions showed no presence of **40**.

Does 40 Occur From A Charge-Transfer Complex?

<u>A Charge-Transfer Complex Exists</u>: UV analysis of a standard concentration of **1** with varying amounts of **36** was examined. Five different concentrations were examined: 0.06 M of **1**, 0.06 M of **1** and 0.05 M of **36**, 0.06 M of **1** and 0.075 M of **36**, 0.06 M of **1** and 0.10 M of **36**, and 0.06 M of **1** and 0.125 M of **36**.

Selectively Irradiate 1

A filter absorbing up to 360 nm was chosen as well as the sensitizer anthracene. Two reactions were performed: one with the glass filter, 21.6 mg of anthracene (**41**), 31.0 mg of **1** and 0.07 ml **36** in 10 ml acetonitrile-methanol (3:1); the second with the same components except 2 mg of KCN (99 atom % ^{13}C) was added.

Selectively Irradiate the Charge-Transfer Complex

A filter of **1** was used to selectively irradiate the charge-transfer complex. A special tube with a pyrex jacket was used. The width from the outside wall to the inner tube is 2.0 cm. The solution for the inner tube remained constant while the filter varied. The solution for the inner tube consisted of 0.09 M **1** and 0.28 ml **36** in 8 ml of acetonitrile-methanol (3:1). There were four runs prepared with varying concentrations of filter: 0.00 M **1**, 0.03 M **1**, 0.06 M **1**, and 0.09 M **1**.

Formation of the 1,3-Butadiene Adducts

A solution of 1.2 g (0.022 mol) 1,3-butadiene (**37**), 1.0 g (0.0078 mol) **1** and 1.2 g (0.0078 mol) **9** in 60 ml of acetonitrile-methanol (3:1) was degassed with nitrogen for 5 min and irradiated for 98 h using a 450 W lamp. The crude mixture was placed on a dc/fc (diameter: 50 mm) and the eluent used was 10% ethyl acetate/ 90% hexanes. The yield of photo-NOCAS products were: 30% **43** and 35% **42**.

Fraction no. 17-18: 82.3 mg of **42** and impurities.

Fraction no. 19-22: 133.6 mg of **42**.

Fraction no. 23-25: 50.4 mg of **42** and **1**.

Fraction no. 26-42: 234 mg of **43** and small amount of **1**.

Fraction no. 43-55: 413.6 mg of **1**.

Fractions 23-25 and 26-42 had **1** removed quite easily by addition of a mixture of ethyl acetate and hexanes. The solvent was decanted and **1** was left behind.

Fractions 26-42 were placed on a dc/fc (diameter: 30 mm) and the eluent used was 10% ethyl acetate/ 90% hexanes.

Fraction no. 8-10: **43** and some impurities.

Fraction no. 11: **43**.

Fraction no. 12-13: **43** and some impurities.

3-(4-cyanophenyl)-4-methoxybutene (**42**)

The yield obtained was 35% ; ^{1}H nmr (361.08 MHz, $CDCl_3$) δ_{TMS}: 3.33 (s, 3H, OCH_3), 3.70 (m, 3H, H of methylene and methine groups), 5.10 (d, 1H, $^3J_{1\textit{trans}-2}$= 17.2 Hz, vinyl H (1*trans*-H)), 5.19 (d, 1H, $^3J_{1\textit{cis}-2}$= 10.4 Hz, vinyl H (1*cis*-H)), 5.96 (m, 1H, $^3J_{1\textit{trans}-2}$= 17.2 Hz, $^3J_{1\textit{cis}-2}$= 10.4 Hz, $^3J_{2-3}$= 6.6 Hz, vinyl H (2-

H)), 7.35 (d, 2H, $^3J_{2'-3'}$= 8.3 Hz, $^3J_{5'-6'}$= 8.3 Hz, H's adjacent to alkyl substituted aryl carbon (2'-H, 6'-H)), 7.60 (d, 2H, $^3J_{2'-3'}$= 8.3 Hz, $^3J_{5'-6'}$= 8.3 Hz, H's adjacent to cyano substituted aryl carbon (3'-H, 5'-H)); ^{13}C nmr (90.80 MHz, $CDCl_3$) δ: 49.63 (d, 129.8 Hz, CH, aryl substituted), 58.95 (q, 141.4 Hz, OCH_3), 75.40 (t, 141.9 Hz, OCH_2), 110.39 (s, quaternary aryl carbon, cyano substituted), 117.08 (t, 157.6 Hz, terminal vinyl CH_2), 118.87 (s, CN), 128.79 (d, 160.1 Hz, aromatic CH adjacent to alkyl substituted aryl carbon), 132.18 (d, 165.4 Hz, aromatic CH adjacent to cyano substituted aryl carbon), 137.26 (d, 155.2 Hz, vinyl CH), 146.98 (s, quaternary aryl carbon, alkyl substituted); Infrared (PE-180) ν: 3081(w), 2981(m), 2931(m), 2881(m), 2829(m), 2239(s), 1636(w), 1606(m), 1503(m), 1476(w), 1456(w), 1411(w), 1377(w), 1181(m), 1111(s), 991(w), 971(w), 946(w), 903(m), 821(m); ms m/z: 51(51), 62(25), 63(52), 75(42), 89(66), 114(30), 115(96), 116(82), 127(25), 140(77), 141(25), 142(47), 156(45), 157(100), 187(19). Exact mass m/z calcd. $C_{12}H_{13}NO$: 187.0997; found: 187.0992.

trans-1-(4-cyanophenyl)-4-methoxy-2-butene (**43**)

The yield obtained was 30% ; ^{1}H nmr (361.08 MHz, $CDCl_3$) δ_{TMS}: 3.33 (s, 3H, OCH_3), 3.45 (d, 2H, $^3J_{3-4}$= 6.7 Hz, CH_2, aryl substituted (4-H)), 3.90 (d, 2H, $^3J_{1-2}$= 5.5 Hz, CH_2, methoxy substituted (1-H)), 5.64 (m, 1H, $^3J_{2-3}$= 15.4 Hz, $^3J_{1-2}$= 5.5 Hz, vinyl H (2-H)), 5.83 (m, 1H, $^3J_{2-3}$= 15.4 Hz, $^3J_{3-4}$= 6.7 Hz, vinyl H (3-H)), 7.30 (d, 2H, $^3J_{2'-3'}$= 8.1 Hz, $^3J_{5'-6'}$= 8.1 Hz, H's adjacent to alkyl substituted aryl carbon (2'-H, 6'-H)), 7.57 (d, 2H, $^3J_{2'-3'}$= 8.1 Hz, $^3J_{5'-6'}$= 8.1 Hz, H's adjacent to cyano substituted aryl carbon (3′-H, 5′-H)); ^{13}C nmr (90.80 MHz, $CDCl_3$) δ: 38.68 (t, 128.7 Hz, CH_2, aryl substituted), 58.00 (q, 140.2 Hz, OCH_3), 76.62 (t, 139.2 Hz, OCH_2), 110.00 (s, quaternary aryl carbon, cyano substituted), 118.93 (s, CN), 129.05 (d, 157.1 Hz, vinyl CH), 129.31 (d, 160.9 Hz, aromatic CH adjacent to alkyl substituted aryl carbon), 130.69 (d, 163.8 Hz, aromatic CH adjacent to cyano substituted aryl carbon), 132.20 (d, 150.6 Hz, vinyl CH), 145.55 (s, quaternary aryl carbon, alkyl substituted); Infrared (PE-180) ν: 2978(w), 2928(m), 2898(m), 2803(m), 2223(s), 1603(m), 1503(m), 1448(w), 1413(w), 1381(w), 1193(w), 1173(w), 1113(s), 953(m), 893(w), 828(w), 803(m); ms m/z: 51(38), 58(24), 63(33), 71(100), 72(22), 75(22), 76(20), 89(48), 115(40), 116(49), 127(25), 128(24), 129(24), 140(25), 154(25), 155(20), 187(1). Anal. calcd. $C_{12}H_{13}NO$: C 76.97, H 7.00, N 7.48; found: C 76.70, H 7.09, N 7.45.

Formation of the 2-Methyl-1,3-Butadiene Adducts

A solution of 2.6 g (0.04 mol) 2-methyl-1,3-butadiene (**38**) (the stabilizer, hydroquinone, was removed by distillation at atmospheric pressure), 2.5 g (0.02 mol) **1** and 6.0 g (0.04 mol) **9** in 160 ml of acetonitrile-methanol (3:1) was degassed with nitrogen for 5 min and irradiated for 136 h. The crude mixture was placed on a mplc and the eluent used was a gradient of hexanes/dichloromethane. The yields of photo-NOCAS products were: 24% **44**, 7% **45**, 3% **46** and 22% **47**.

Fraction no. 105-116: 1.1562 g of **44** and small amount of **45**.

Fraction no. 117: 108.7 mg of **45**.

Fraction no. 118: **45** and some small impurities.

Fraction no. 119-124: 447.0 mg of **45**, **46** and **47**.

Fraction no. 125-159: 778.5 mg of **46** (little) and **47**.

After the above separation, several combined fractions were rechromatographed by dc/fc and mplc to achieve purity of the four photo-NOCAS products.

3-(4-cyanophenyl)-4-methoxy-3-methylbutene (**44**)

The yield obtained was 24% ; ^{1}H nmr (361.08 MHz, $CDCl_3$) δ_{TMS}: 1. 0 (s, 3H, CH_3), 3.31 (s, 3H, OCH_3), 3.53 (d, 1H, $^2J_{4\text{-}4'}$= 9.1 Hz, H of methylene group (4-H)), 3.57 (d, 1H, $^2J_{4\text{-}4'}$= 9.1 Hz, H of methylene group (4′-H)), 5.08 (d, 1H, $^3J_{1\mathit{trans}\text{-}2}$= 17.6 Hz, terminal vinyl H (1*trans*-H), 5.20 (d, 1H, $^3J_{1\mathit{cis}\text{-}2}$= 10.8 Hz, terminal vinyl H (1*cis*-H)), 6.02 (dd, 1H, $^3J_{1\mathit{trans}\text{-}2}$= 17.6 Hz, $^3J_{1\mathit{cis}\text{-}2}$= 10.8 Hz, vinyl H (2-H)), 7.45 (d, 2H, $^3J_{2'\text{-}3'}$= 8.2 Hz, $^3J_{5'\text{-}6'}$= 8.2 Hz, H's adjacent to alkyl substituted aryl carbon (2′-H, 6′-H)), 7.57 (d, 2H, $^3J_{2'\text{-}3'}$= 8.2 Hz, $^3J_{5'\text{-}6'}$= 8.2 Hz, H's adjacent to cyano substituted aryl carbon (3′-H, 5′-H)); ^{13}C nmr (90.80 MHz, $CDCl_3$) δ: 23.06 (q, 128.0 Hz, CH_3) 46.11 (s, quaternary carbon, aryl substituted), 59.29 (q, 141.1 Hz, OCH_3), 79.68 (t, 142.3 Hz, OCH_2), 109.89 (s, quaternary aryl carbon, cyano substituted), 114.27 (t, 156.7 Hz, terminal vinyl CH_2), 118.99 (s, CN), 127.79 (dd, 161.6 Hz, 5.0 Hz, aromatic CH adjacent to alkyl substituted aryl carbon), 131.83

(dd, 165.4 Hz, 4.2 Hz, aromatic CH adjacent to cyano substituted aryl carbon), 142.83 (d, 154.6 Hz, vinyl CH), 150.88 (s, quaternary aryl carbon, alkyl substituted); Infrared (PE-180) ν: 3087(w), 2977(m), 2927(m), 2877(m), 2827(m), 2232(s), 1602(w), 1603(m), 1502(m), 1477(w), 1452(w), 1412(w), 1382(w), 1362(w), 1272(w), 1192(w), 1180(w), 1107(s), 1012(w), 982(w), 962(w), 902(m), 820(m); ms m/z: 51(55), 53(27), 63(42), 75(33), 76(28), 77(42), 89(44), 115(45), 116(100), 127(49), 128(54), 129(89), 140(55), 141(27), 154(36), 156(89), 170(42), 171(55), 201(13). Anal. calcd. $C_{13}H_{15}NO$: C 77.58, H 7.51, N 6.96; found: C 77.82, H 7.65, N 7.04.

3-(4-cyanophenyl)-4-methoxy-2-methylbutene (**45**)

The yield obtained was 7% ; ^{1}H nmr (361.08 MHz, $CDCl_3$) δ_{TMS}: 1.62 (s, 3H, CH_3), 3.34 (s, 3H, OCH_3), 3.59 (dd, 1H, $^3J_{3\text{-}4}$= 7.6 Hz, $^3J_{3\text{-}4'}$= 6.4 Hz, H of methine group (3-H)), 3.67 (dd, 1H, $^2J_{4\text{-}4'}$= 9.1 Hz, $^3J_{3\text{-}4}$= 7.6 Hz, H of methylene group (4-H)), 3.76 (dd, 1H, $^2J_{4\text{-}4'}$= 9.1 Hz, $^3J_{3\text{-}4'}$= 6.4 Hz, H of methylene group (4'-H)), 4.88 (s, terminal vinyl H), 4.98 (s, terminal vinyl H), 7.35 (d, 2H, $^3J_{2'\text{-}3'}$= 8.2 Hz, $^3J_{5'\text{-}6'}$= 8.2 Hz, H's adjacent to alkyl substituted aryl carbon (2'-H, 6'-H)), 7.60 (d, 2H, $^3J_{2'\text{-}3'}$= 8.2 Hz, $^3J_{5'\text{-}6'}$= 8.2 Hz, H's adjacent to cyano substituted aryl carbon (3'-H, 5'-H)); ^{13}C nmr (90.80 MHz, $CDCl_3$) δ: 21.80 (q, 125.9 Hz, CH_3), 52.39 (d, 129.1 Hz, CH, aryl substituted), 59.00 (q, 140.9 Hz, OCH_3), 74.14 (t, 142.6 Hz, OCH_2), 110.49 (s, quaternary aryl carbon, cyano substituted), 112.59 (t, 155.8 Hz, terminal vinyl CH_2), 118.94 (s, CN), 128.91 (d, 160.3 Hz, aromatic CH adjacent to alkyl substituted aryl carbon), 132.12 (d, 164.4 Hz, aromatic CH adjacent to cyano substituted aryl carbon), 144.02 (s, vinyl quaternary carbon), 146.72 (s, quaternary aryl carbon, alkyl substituted); Infrared (PE-180) ν: 3090(w), 2980(m), 2920(m), 2890(m), 2830(m), 2210(s), 1648(m), 1610(s), 1505(m), 1450(m), 1411(w), 1374(m), 1230(w), 1190(m), 1175(w), 1115(s), 1020(w), 955(w), 940(w), 884(m), 820(m); ms m/z: 51(53), 63(49), 77(32), 89(59), 116(100), 127(49), 128(53), 129(64), 140(64), 154(43), 156(33), 170(57), 171(58), 201(49). Anal. calcd. $C_{13}H_{15}NO$: C 77.58, H 7.51, N 6.96; found: C 77.50, H 7.59, N 6.91.

(Z)-4-(4-cyanophenyl)-1-methoxy-2-methyl-2-butene (**46**)

The yield obtained was 3% ; ^{1}H nmr (361.08 MHz, $CDCl_3$) δ_{TMS}: 1.82 (s, 3H, CH_3), 3.33 (s, 3H, OCH_3), 3.48 (d, 2H, $^3J_{3\text{-}4}$= 7.4 Hz, CH_2 group, aryl substituted (4-H)), 3.99 (s, 2H, CH_2 group, methoxy substituted), 5.50 (t, 1H, $^3J_{3\text{-}4}$= 7.4 Hz, vinyl H (3-H)), 7.28 (d, 2H, $^3J_{2'\text{-}3'}$= 8.1 Hz, $^3J_{5'\text{-}6'}$= 8.1 Hz, H's adjacent to alkyl substituted aryl carbon (2'-H, 6'-H)), 7.57 (d, 2H, $^3J_{2'\text{-}3'}$= 8.1 Hz, $^3J_{5'\text{-}6'}$= 8.1 Hz, H's adjacent to cyano substituted aryl carbon (3'-H, 5'-H)); **NOE experiment**: The methylene group (methoxy substituted) was irradiated. A 2% NOE on the methyl group, 2% on the methoxy group, and 3% on the methylene group (aryl substituted) signals was observed; no NOE was observed for the vinyl hydrogen. The methylene group (aryl substituted) was irradiated. A 4% NOE on the methylene group (methoxy substituted), 3% on aryl hydrogens and 4% on the vinyl hydrogen was observed. ^{13}C nmr (90.80 MHz, $CDCl_3$) δ: 21.80 (q, 125.8 Hz, CH_3), 34.04 (t, 126.8 Hz, CH_2, aryl substituted), 58.06 (q, 140.7 Hz, OCH_3), 70.96 (t, 139.2 Hz, OCH_2), 109.82 (s, quaternary aryl carbon, cyano substituted), 119.03 (s, CN), 125.72 (d, 149.9 Hz, vinyl CH), 129.11 (d, 160.5 Hz, aromatic CH adjacent to alkyl substituted aryl carbon), 132.23 (d, 164.0 Hz, aromatic CH adjacent to cyano substituted aryl carbon), 134.74 (s, vinyl quaternary carbon), 146.59 (s, quaternary aryl carbon, alkyl substituted); Infrared (PE-180) ν: 2978(m), 2926(s), 2830(m), 2231(s), 1606(m), 1506(m), 1451(m), 1413(w), 1378(w), 1191(m), 1176(w), 1100(s), 1021(w), 946(m), 896(w), 851(w), 812(m); ms m/z: 51(20), 75(23), 76(12), 77(14), 101(27), 102(14), 128(77), 129(10), 156(100), 157(14), 170(24), 171(38). Exact mass m/z calcd. $C_{13}H_{15}NO$: 201.1153; found: 201.1148.

(E)-4-(4-cyanophenyl)-1-methoxy-2-methyl-2-butene (**47**)

The yield obtained was 22% ; ^{1}H nmr (361.08 MHz, $CDCl_3$) δ_{TMS}: 1.74 (s, 3H, CH_3), 3.31 (s, 3H, OCH_3), 3.46 (d, 2H, $^3J_{3\text{-}4}$= 7.3 Hz, CH_2 group, aryl substituted (4-H)), 3.84 (s, 2H, CH_2 group, methoxy substituted), 5.56 (t, 1H, $^3J_{3\text{-}4}$= 7.3 Hz, vinyl H (3-H)), 7.28 (d, 2H, $^3J_{2'\text{-}3'}$= 8.1 Hz, $^3J_{5'\text{-}6'}$= 8.1 Hz, H's adjacent to alkyl substituted aryl carbon (2'-H, 6'-H)), 7.57 (d, 2H, $^3J_{2'\text{-}3'}$= 8.1 Hz, $^3J_{5'\text{-}6'}$= 8.1 Hz, H's adjacent to cyano substituted aryl carbon (3'-H, 5'-H)); **NOE experiment**: The methylene group (methoxy substituted) was irradiated. A 4% NOE on the methyl group and 2% on the methoxy group signals was observed; no NOE was observed for the vinyl hydrogen or the methylene group (aryl substituted). The methylene group (aryl substituted) was irradiated. An 11% NOE on the methyl group and 10% on aryl hydrogens signals was observed. ^{13}C nmr (90.80 MHz, $CDCl_3$) δ: 14.05 (q, 126.0 Hz, CH_3), 34.05 (t, 126.9 Hz, CH_2, aryl substituted), 57.75 (q, 140.4 Hz, OCH_3), 78.04 (t, 143.0 Hz, OCH_2), 109.87 (s, quaternary aryl carbon, cyano substituted), 118.98 (s, CN), 124.08 (d, 158.2 Hz, vinyl CH), 129.09 (d, 158.3 Hz, aromatic CH adjacent to alkyl substituted aryl carbon), 132.22 (d, 163.8 Hz, aromatic CH adjacent to cyano substituted aryl carbon), 134.79 (s, vinyl quaternary carbon), 146.59 (s, quaternary aryl carbon, alkyl substituted); Infrared (PE-180) ν: 2990(m), 2930(s), 2825(m), 2231(s), 1606(m), 1505(m), 1449(m), 1415(w), 1377(w), 1192(m), 1110(s), 1090(s), 1020(w), 939(w), 900(w), 855(w), 809(m); ms m/z: 51(11), 55(48), 63(11), 72(12), 85(100), 89(19), 116(24), 127(19), 129(12), 153(10), 154(42), 169(11), 201(2). Exact mass m/z calcd. $C_{13}H_{15}NO$: 201.1153; found: 201.1158.

Formation of the 2,3-Dimethyl-1,3-Butadiene Adducts

A solution of 1.2 g (0.02 mol) 2,3-dimethyl-1,3-butadiene (**39**) (the stabilizer, hydroquinone, was removed by distillation at atmospheric pressure), 1.9 g (0.02 mol) **1** and 1.1 g (0.01 mol) **9** in 120 ml of acetonitrile-methanol (3:1) was degassed with nitrogen for 5 min and irradiated for 144 h. The crude mixture was placed on a mplc and the eluent used was a gradient of hexanes/ (50% dichloromethane/ 50% hexanes). The yield of photo-NOCAS products were: 8% **49**, 12% **50** and 34% **48**.

Fraction no. 60-110: mostly **48**.

Fraction no. 158-200: **49** and some small impurities.

Fraction no. 201-215: **49**, little **50** and some small impurities.

Fraction no. 216-225: **49** and **50**.

Fraction no. 226-239: **50** and some small impurities.

Fraction no. 240-300: **50**.

Fractions 158-200 were placed on a dc/fc (diameter: 50 mm) and the eluent used was 10% ethyl acetate/ 90% hexanes.

Fraction no. 11-16: **49**, **50** and some small impurities.

Fraction no. 17-22: **49** and **50**.

Fraction no. 23-34: **50** and some small impurities.

Fractions 17-22 were placed on a dc/fc with the same conditions as used in the previous dc/fc.

Fraction no. 14-15: **49**.

Fraction no. 16: **49** and **50** (little).

Fraction no. 17-22: **49** and **50**.

3-(4-cyanophenyl)-4-methoxy-2,3-dimethylbutene (**48**)

The yield obtained was 34% ; ^{1}H nmr (361.08 MHz, CDCl$_3$) δ_{TMS}: 1.46 (s, 3H, CH$_3$), 1.51 (s, 3H, CH$_3$), 3.31 (s, 3H, OCH$_3$), 3.59 (d, 1H, $^2J_{4\text{-}4'}$= 8.9 Hz, H of methylene group (4-H)), 3.63 (d, 1H, $^2J_{4\text{-}4'}$= 8.9 Hz, H of methylene group (4'-H)), 4.93 (s, 1H, terminal vinyl H), 5.01 (s, 1H, terminal vinyl H), 7.40 (d, 2H, $^3J_{2'\text{-}3'}$= 8.3 Hz, $^3J_{5'\text{-}6'}$= 8.3 Hz, H's adjacent to alkyl substituted aryl carbon (2'-H, 6'-H)), 7.56 (d, 2H, $^3J_{2'\text{-}3'}$= 8.3 Hz, $^3J_{5'\text{-}6'}$= 8.3 Hz, H's adjacent to cyano substituted aryl carbon (3'-H, 5'-H)); ^{13}C nmr (90.80 MHz, CDCl$_3$) δ: 21.63 (q, 127.9 Hz, CH$_3$), 23.05 (q, 128.4 Hz, CH$_3$), 48.70 (s, quaternary carbon, aryl substituted), 59.33 (q, 141.0 Hz, OCH$_3$), 79.13 (t, 141.9 Hz, OCH$_2$), 109.87 (s, quaternary aryl carbon, cyano substituted), 112.19 (t, 154.6 Hz, terminal vinyl CH$_2$), 119.02 (s, CN), 127.70 (dd, 159.3 Hz, 4.9 Hz, aromatic CH adjacent to alkyl substituted aryl carbon), 131.85 (dd, 165.5 Hz, 4.2 Hz, aromatic CH adjacent to cyano substituted aryl carbon), 148.13 (s, quaternary vinyl carbon), 150.90 (s, quaternary aryl carbon, alkyl substituted); Infrared (PE-180) ν: 2979(m), 2929(m), 2889(m), 2919(m), 2237(s), 1643(w), 1609(m), 1507(m), 1454(m), 1405(w), 1379(m), 1197(m), 1163(w), 1108(s), 1071(w), 1029(w), 967(w), 944(w), 886(m), 828(m); ms m/z: 51(23), 77(23), 89(23), 115(38), 116(46), 127(28), 128(33), 130(22), 140(28), 142(92), 143(38), 153(28), 154(46), 155(27), 168(46), 169(21), 170(100), 184(43), 215(27). Anal. calcd. C$_{14}$H$_{17}$NO: C 78.10, H 7.96, N 6.51; found: C 77.83, H 7.85, N 6.54.

(Z)-1-(4-cyanophenyl)-4-methoxy-2,3-dimethyl-2-butene (**49**)

The yield obtained was 8% ; ^{1}H nmr (361.08 MHz, CDCl$_3$) δ_{TMS}: 1.60 (s, 3H,

CH_3), 1.81 (s, 3H, CH_3), 3.33 (s, 3H, OCH_3), 3.52 (s, 2H, CH_2 group, aryl substituted), 3.98 (s, 2H, CH_2 group, methoxy substituted), 7.25 (d, 2H, $^3J_{2'-3'}$ = 7.6 Hz, $^3J_{5'-6'}$ = 7.6 Hz, H's adjacent to alkyl substituted aryl carbon (2'-H, 6'-H)), 7.56 (d, 2H, $^3J_{2'-3'}$ = 7.6 Hz, $^3J_{5'-6'}$ = 7.6 Hz, H's adjacent to cyano substituted aryl carbon (3'-H, 5'-H)); **NOE experiment**: The methylene group (methoxy substituted) was irradiated. A 2% NOE on one methyl group and 4% on the methylene group (aryl substituted) signal was observed. The methylene group (aryl substituted) was irradiated. A 2% NOE on one methyl group and 3% on the methylene group (methoxy substituted) signal was observed. ^{13}C nmr (90.80 MHz, $CDCl_3$) δ: 17.19 (q, 129.1 Hz, CH_3), 18.74 (q, 128.4 Hz, CH_3), 40.01 (t, 128.2 Hz, CH_2, aryl substituted), 58.11 (q, 140.0 Hz, OCH_3), 73.35 (t, 144.1 Hz, OCH_2), 110.00 (s, quaternary aryl carbon, cyano substituted), 118.98 (s, CN), 128.95 (s, quaternary vinyl carbon), 129.32 (d, 161.9 Hz, aromatic CH adjacent to alkyl substituted aryl carbon), 130.80 (s, quaternary vinyl carbon), 132.16 (d, 163.3 Hz, aromatic CH adjacent to cyano substituted aryl carbon), 146.11 (s, quaternary aryl carbon, alkyl substituted); Infrared (PE-180) ν: 2980(m), 2820(m), 2230(s), 1608(m), 1505(m), 1450(m), 1413(w), 1385(m), 1190(m), 1145(w), 1090(s), 1020(w), 925(w), 830(w), 801(m); ms m/z: 51(5), 53(6), 63(6), 67(9), 69(9), 89(12), 99(37), 115(7), 116(14), 127(5), 140(8), 141(9), 142(8), 143(5), 153(11), 154(8), 166(5), 168(100), 169(12), 183(30), 184(5). Exact mass m/z calcd. $C_{14}H_{17}NO$: 215.1310; found: 215.1285.

(E)-1-(4-cyanophenyl)-4-methoxy-2,3-dimethyl-2-butene (**50**)

The yield obtained was 12% ; ^{1}H nmr (361.08 MHz, $CDCl_3$) δ_{TMS}: 1.65 (s, 3H, CH_3), 1.82 (s, 3H, CH_3), 3.32 (s, 3H, OCH_3), 3.48 (s, 2H, CH_2 group, aryl substituted), 3.97 (s, 2H, CH_2 group, methoxy substituted), 7.25 (d, 2H, $^3J_{2'-3'}$= 7.9 Hz, $^3J_{5'-6'}$= 7.9 Hz, H's adjacent to alkyl substituted aryl carbon (2'-H, 6'-H)), 7.55 (d, 2H, $^3J_{2'-3'}$= 7.9 Hz, $^3J_{5'-6'}$= 7.9 Hz, H's adjacent to cyano substituted aryl carbon (3'-H, 5'-H)); **NOE experiment**: The methylene group (methoxy substituted) was irradiated. A 4% NOE on one methyl group, 2% on the other methyl group and 1% on the methoxy group were observed. The methylene group (aryl substituted) was irradiated. A 3% NOE on one methyl group and 5% on the other methyl group were observed. ^{13}C nmr (90.80 MHz, $CDCl_3$) δ: 16.83 (q, 125.6 Hz, CH_3), 18.12 (q, 122.0 Hz, CH_3), 40.65 (t, 126.7 Hz, CH_2, aryl substituted), 57.80 (q, 140.4 Hz, OCH_3), 73.15 (t, 140.2 Hz, OCH_2), 110.07 (s, quaternary aryl carbon, cyano substituted), 118.89 (s, CN), 128.94 (s, quaternary vinyl carbon), 129.18 (d, 162.2 Hz, aromatic CH adjacent to alkyl substituted aryl carbon), 130.55 (s, quaternary vinyl carbon), 132.18 (d, 164.8 Hz, aromatic CH adjacent to cyano substituted aryl carbon), 145.86 (s, quaternary aryl carbon, alkyl substituted); Infrared (PE-180) ν: 2983(m), 2928(s), 2819(m), 2236(s), 1606(m), 1503(m), 1445(m), 1421(w), 1373(m), 1183(w), 1093(s), 1018(w), 923(w), 883(w), 828(w), 801(m); ms m/z: 51(4), 53(4), 65(5), 67(12), 69(8), 89(12), 99(100), 100(7), 115(7), 116(15), 128(4), 140(8), 141(8), 142(11), 143(4), 153(9), 154(14), 166(4), 168(53), 169(7), 182(7), 183(25), 184(4), 215(1). Exact mass m/z calcd. $C_{14}H_{17}NO$: 215.1310; found: 215.1291.

Appendix

Data Collection

A crystal of suitable size was mounted on a glass fibre. An Enraf-Nonius CAD4 diffractometer was used to measure the unit cell dimensions and to collect the data. The crystal and data collection parameters are listed in Table 1. The unit cell constants were obtained by least squares analysis of the diffractometer setting angles of 25 well centered reflections in the range $2\theta = 20\text{-}30°$. The intensities were reduced to a standard scale using routine procedures (143). Lorentz and polarization corrections were applied and absorption corrections (144) were performed. Scattering factors for neutral atoms were taken from reference 145 and were corrected for the real part of anomalous dispersion. All calculations and refinements were performed by using SHELX-76 (146).

Structural analysis and refinement

The systematically absent reflections confirmed the space group as $P2_1/a$. The positions of the non-hydrogen atoms were determined from the E-map (SHELXS).(The structure was solved by Direct Methods (SHELXS)).

The structure was refined initially by a full-matrix least-squares procedure with independent isotropic temperature factors on the atoms. Absorption corrections were then applied. Hydrogen atoms were placed in their geometrically calculated positions [d(C-H) = 1.08 A]. The final refinements were with anisotropic temperature factors on the non-hydrogen atoms and individual isotropic temperature factors on the hydrogen atoms. A 2-block matrix least-squares method was employed. The function minimised was $\Sigma w(|F_o|-|F_c|)^2$ where w is the weight. Final R = 0.0624, R_w = 0.0688. No correction for extintion was applied. The final difference map had no recognizable residual features. The figures were produced with CHEMGRAF (147).

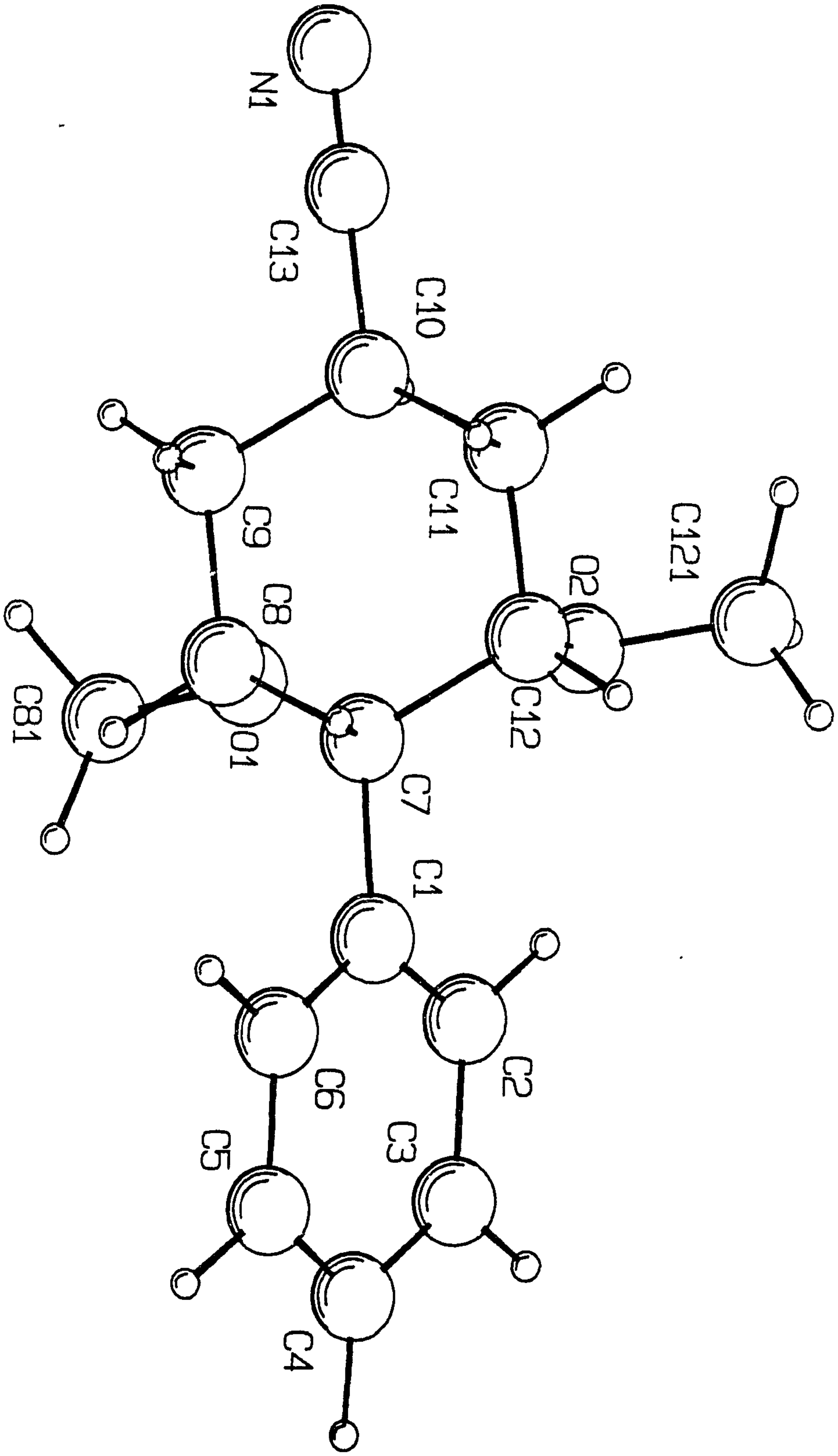


Figure 9. X-ray crystal structure of 3,5-dimethoxy-4-phenylcyclohexanecarbonitrile (**27**).

Table 1. Interatomic distances (Å) for $C_{15}H_{19}NO_2$

Interatomic Distances (Å)		
C(1)	-C(2)	1.37 (2)
C(1)	-C(6)	1.36 (2)
C(1)	-C(7)	1.56 (2)
C(2)	-C(3)	1.41 (2)
C(3)	-C(4)	1.38 (2)
C(4)	-C(5)	1.32 (2)
C(5)	-C(6)	1.39 (2)
C(7)	-C(8)	1.52 (2)
C(7)	-C(12)	1.57 (2)
C(8)	-O(1)	1.45 (2)
C(8)	-C(9)	1.53 (2)
O(1)	-C(81)	1.36 (2)
C(9)	-C(10)	1.55 (2)
C(10)	-C(11)	1.52 (2)
C(10)	-C(13)	1.48 (2)
C(11)	-C(12)	1.52 (2)
C(12)	-O(2)	1.462(14)
O(2)	-C(121)	1.42 (2)
C(13)	-N(1)	1.14 (2)

Table 2. Interbond angles (degrees) for $C_{15}H_{19}NO_2$

Interbond Angles (degrees)			
C(2)	-C(1)	-C(6)	120.6 (12)
C(2)	-C(1)	-C(7)	127.3 (11)
C(6)	-C(1)	-C(7)	112.1 (11)
C(1)	-C(2)	-C(3)	119.7 (12)
C(2)	-C(3)	-C(4)	119.8 (13)
C(3)	-C(4)	-C(5)	117.5 (14)
C(4)	-C(5)	-C(6)	125.1 (14)
C(1)	-C(6)	-C(5)	117.2 (12)
C(1)	-C(7)	-C(8)	109.1 (10)
C(1)	-C(7)	-C(12)	114.5 (10)
C(8)	-C(7)	-C(12)	112.8 (10)
C(7)	-C(8)	-O(1)	112.1 (10)
C(7)	-C(8)	-C(9)	109.9 (10)
O(1)	-C(8)	-C(9)	109.6 (10)
C(8)	-O(1)	-C(81)	112.5 (11)
C(8)	-C(9)	-C(10)	110.1 (10)
C(9)	-C(10)	-C(11)	112.9 (10)
C(9)	-C(10)	-C(13)	109.7 (10)
C(11)	-C(10)	-C(13)	110.2 (11)
C(10)	-C(11)	-C(12)	109.6 (10)
C(7)	-C(12)	-C(11)	109.9 (10)
C(7)	-C(12)	-O(2)	111.2 (9)
C(11)	-C(12)	-O(2)	108.5 (9)
C(12)	-O(2)	-C(121)	112.4 (9)
C(10)	-C(13)	-N(1)	175.5 (14)

Table 3. Torsional angles (degrees) for $C_{15}H_{19}NO_2$

Torsional Angles (degrees)				
C(2)	-C(1)	-C(6)	-C(5)	-4.1 (16)
C(6)	-C(1)	-C(2)	-C(3)	2.5 (17)
C(2)	-C(1)	-C(7)	-C(8)	92.2 (12)
C(2)	-C(1)	-C(7)	-C(12)	-35.2 (14)
C(7)	-C(1)	-C(2)	-C(3)	-177.6 (10)
C(6)	-C(1)	-C(7)	-C(8)	-87.8 (11)
C(6)	-C(1)	-C(7)	-C(12)	144.8 (10)
C(7)	-C(1)	-C(6)	-C(5)	176.0 (11)
C(1)	-C(2)	-C(3)	-C(4)	-0.6 (18)
C(2)	-C(3)	-C(4)	-C(5)	0.5 (19)
C(3)	-C(4)	-C(5)	-C(6)	-2.3 (20)
C(4)	-C(5)	-C(6)	-C(1)	4.2 (18)
C(1)	-C(7)	-C(8)	-O(1)	-61.8 (11)
C(1)	-C(7)	-C(8)	-C(9)	175.9 (9)
C(1)	-C(7)	-C(12)	-C(11)	-178.0 (8)
C(1)	-C(7)	-C(12)	-O(2)	61.9 (11)
C(8)	-C(7)	-C(12)	-C(11)	56.5 (11)
C(8)	-C(7)	-C(12)	-O(2)	-63.6 (11)
C(12)	-C(7)	-C(8)	-O(1)	66.5 (11)
C(12)	-C(7)	-C(8)	-C(9)	-55.7 (11)
C(7)	-C(8)	-O(1)	-C(81)	141.9 (11)
C(7)	-C(8)	-C(9)	-C(10)	54.8 (11)
O(1)	-C(8)	-C(9)	-C(10)	-68.9 (11)
C(9)	-C(8)	-O(1)	-C(81)	-95.7 (11)
C(8)	-C(9)	-C(10)	-C(11)	-57.7 (12)
C(8)	-C(9)	-C(10)	-C(13)	179.0 (9)
C(9)	-C(10)	-C(11)	-C(12)	58.3 (11)
C(13)	-C(10)	-C(11)	-C(12)	-178.7 (9)
C(10)	-C(11)	-C(12)	-C(7)	-55.8 (11)
C(10)	-C(11)	-C(12)	-O(2)	66.0 (10)
C(7)	-C(12)	-O(2)	-C(121)	-157.2 (8)
C(11)	-C(12)	-O(2)	-C(121)	81.8 (10)
N(1)	-C(13)	-C(10)	-C(9)	66.1 (**)
N(1)	-C(13)	-C(10)	-C(11)	-58.8 (**)

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