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Reactions Of Radical Ions Generated By Photosensitization (electron Transfer)

Apostolos J. Maroulis

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REACTIONS OF RADICAL IONS GENERATED BY PHOTOSENSITIZATION (ELECTRON TRANSFER)

by

Apostolos J. Maroulis

Department of Chemistry

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of the requirements for the degree of
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The University of Western Ontario
London, Canada
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ABSTRACT

The photosensitized (electron transfer) irradiation of some phenylated olefins with electron acceptor sensitizers such as 1-cyanonaphthalene, methyl p-cyanobenzoate, 1,4-dicyanobenzene or 1,4-dicyanonaphthalene in alcohol-acetonitrile, acetic acid-acetonitrile or aqueous acetonitrile solution yielded the products (ethers, acetates or alcohols) resulting from anti-Markovnikov addition of the nucleophilic solvent to the olefin.

When the phenylated olefins were irradiated with the same electron acceptor sensitizers, but in 2,2,2-trifluoroethanol-acetonitrile solution containing potassium cyanide, the anti-Markovnikov nitriles were obtained as the major products.

Irradiation of the phenylated olefins with electron acceptor sensitizers in the presence of 2-methylpropene or 2,3-dimethyl-2-butene in acetonitrile gave the [2+4] cross cycloadducts in addition to the dimers of the phenylated olefins.

Irradiation of β-phenethyl ethers, produced via the anti-Markovnikov addition of alcohols to 1,1-diphenylethylene, in the presence of electron acceptor sensitizers, led to cleavage of the α-carbon-carbon bond. For example, the photosensitized irradiation of 2,2-diphenylethyl isopropyl ether in acetonitrile-methanol solution gave diphenylmethane and the methyl isopropyl acetal of formaldehyde. The 1,1-diphenylethylene anion radical was prepared by photosensitization (electron transfer) using the electron-donor sensitizers 1-methoxynaphthalene, 1,4-dimethoxynaphthalene or 1-methylnaphthalene in acetonitrile solution. Subsequent reaction of the radical anion with methanol, water or hydrogen cyanide gave the Markovnikov addition products.

Electrochemical and photophysical evidence was obtained which supports the proposed mechanism. The primary process is an electron transfer which gives the sensitizer and the substrate (phenylated olefins or ether) radical ions. Fluorescence quenching studies indicated that the singlet states of the sensitizers were quenched by the substrates (phenylated olefins or ethers). Triplet-triplet transfer photosensitized experiments showed that in almost all cases, the triplet does not bring about reaction.

A thermodynamic relationship involving the reduction or oxidation potential of the sensitizer, the oxidation or reduction potential of the substrate (phenylated olefin or ether) and the available electronic-excitation energy has been used to correlate the thermodynamics of the electron transfer process with the experimental results.

στους γονεις μου

to my parents

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My thanks are also due to the faculty members of the organic chemistry department for being among the best teachers in my academic experience.

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CHAPTER I

GENERAL INTRODUCTION

A. INTRODUCTION TO THE NATURE AND BEHAVIOUR OF OLEFIN EXCITED STATES AND TO THE ELECTRON TRANSFER REACTIONS OF OLEFINS

Three types of electronic transitions have been associated with the C=C chromophore. With the exception of the heavily alkylated ethylenes, for which it is known that the lowest energy electronic transition is the π, R(3s),[1] the lowest energy electronic transition is the $\pi \rightarrow \pi^*$; this transition involves promotion of an electron from the highest occupied π molecular orbital to the lowest unoccupied π^* molecular orbital. Simple alkenes absorb ultraviolet light in the 180 - 200 nm region.[2] This absorption is due to the $\pi \rightarrow \pi^*$ transition and corresponds to an energy value of 160 - 140 kcal/mol. For a conjugated olefin, the energy required for the electronic excitation is less and the absorption maximum is shifted to much longer wavelengths. The highest energy electronic transition of general interest[3] is the $\sigma \rightarrow \pi^*$ excitation and involves promotion of an electron from a bonding σ molecular orbital to the lowest unoccupied π^* molecular orbital. The $\sigma \rightarrow \pi^*$ excitation being a high-energy process, requires the absorption of light of wavelength far lower than 200 nm.[2] It is generally the $\pi \rightarrow \pi^*$ type of excitation which leads to the plethora of photochemical phenomena involving olefin systems.

The $\pi \rightarrow \pi^*$ electronic excitation may lead to the first singlet excited state ($S_0 \rightarrow S_1$) or to the first triplet state ($S_0 \rightarrow T_1$).

The $S_0 \rightarrow S_1$ transition is highly allowed by selection rules and it is observed as the most intense absorption band of the olefin. The $S_0 \rightarrow T_1$ transition is highly forbidden and can be observed only in the presence of oxygen at high pressure.[4] It appears then as a series of weak absorption bands at long wavelengths. Organic photochemists have not, until recently,[5] concerned themselves with electronically excited states of olefins of higher energy than S_1 and T_1, mainly because of the short lifetimes of these higher excited states.

In the absorption spectra of ethylene and alkylated ethylenes, there is a series of sharp bands superimposed on the broad $\pi \rightarrow \pi^*$ absorption band. These bands are the first members of a Rydberg series which corresponds to promotion of an electron from the π orbital of the alkene to a large molecular orbital with size and shape similar to that of a 3s carbon atomic orbital.

Rydberg excited states seem to play a part in the photochemistry of certain olefins; however, the precise nature of their role has not been clarified yet.[6]

While the S_1 can be easily obtained upon direct irradiation, the T_1 is practically inaccessible in the case of the olefins, since intersystem crossing does not seem to occur to any appreciable extent and since, as has already been mentioned, direct population of the T_1 is highly forbidden. These facts imply that reactions involving the olefin triplet states have to be brought about by the use of a triplet sensitizer.

There are, therefore, two general ways of inducing an olefin photoreaction:

1. Direct irradiation, which generates the olefin singlet

state.

2. Sensitized excitation, involving energy transfer to the olefin from the excited sensitizer.

Sensitized excitations up to the present have been limited to the use of triplet sensitizers. Recently, the photosensitized electron transfer, a new mode of photosensitization, is beginning to appear in the area of olefin photochemistry and organic photochemistry in general. The effective activation of the substrate is achieved by the use of electron transfer sensitizers, which are organic compounds capable of donating or accepting an electron to or from the organic substrate, upon photoexcitation.

There are substantial differences in reactivity between the S_1 and T_1 states of olefins. These differences stem partly from the fact that the two states differ in energy and partly from the fact that the triplet-state behaviour bears some resemblance to that of a radical whereas the singlet state is capable of undergoing concerted reaction as well.

The S_1 state of the olefins commonly has a lifetime of the order of 10^{-8} to 10^{-7} sec while the T_1 state is usually much longer lived with lifetime of the order of 10^{-5} to 10^{-3} sec.[7,8] As a result of the different lifetimes, one would expect that the S_1 would commonly engage in unimolecular transformations whereas the T_1 could participate more efficiently in bimolecular-type transformations.

Contrary to what the large array of olefin photoreactions studied to date might indicate, there are severe limitations in the scope of the direct and triplet sensitized photoreactions of olefins. These limitations are the existence of a <u>cis-trans</u> isomerization in both singlet and triplet manifolds,[9] and b. the short lifetime of the singlet, due to fast rates of fluorescence (aryl olefins) and radiationless decay;[7,8] in particular, the free-rotor effect, which is a kind of radiationless decay proceeding via rotation around the double bond, is responsible for the rapid deactivation of the triplets of acyclic or large ring cyclic olefins.[10]

Examples of olefin reactions initiated by electron transfer photosensitization are very few as yet and this important photosensitization process has received no attention in recent reviews dealing with the photochemistry of olefinic compounds.[6]

A molecule in the excited state has both lower ionization potential (IP*) (Eq. 1) and higher electron affinity (EA*) (Eq. 2) than the corresponding quantities for the same molecule in the ground state.[11a]

$$IP^* = IP - \Delta E_{o,o} \qquad (1)$$

$$EA^* = EA + \Delta E_{o,o} \qquad (2)$$

($\Delta E_{o,o}$ = zero-zero transition energy)

Its reactions, therefore, can be oxidative or reductive electron transfer depending upon the electron donating or electron accepting properties of the reactant which is not excited.

Naturally, the oxidation potential (ED/D^+) and the reduction potential (EA/A^-) of an excited molecule will have smaller absolute values than the ground state molecule, since they are linearly related to ionization potentials and electron affinities, respectively.

The direction of electron transfer is determined according to the inequality 3:[11b]

$$E(D/D^{+}) + E(D/D^{-}) < E(A/A^{+}) + E(A/A^{-}) \qquad (3)$$

This inequality implies that for any compound the sum of $E(M/M^{+}) + E(M/M^{-})$, which can be taken as a measure of the "molecular electronegativity" of the compound, determines its electron donating or accepting properties irrespective of the state of the compound is in (ground or excited state). With any two compounds, the one with the greater sum always acts as the acceptor.

The above statements can be better perceived with the aid of the following simplified molecular orbital scheme (Fig. 1), which shows the process of electron transfer from the donor to the acceptor.

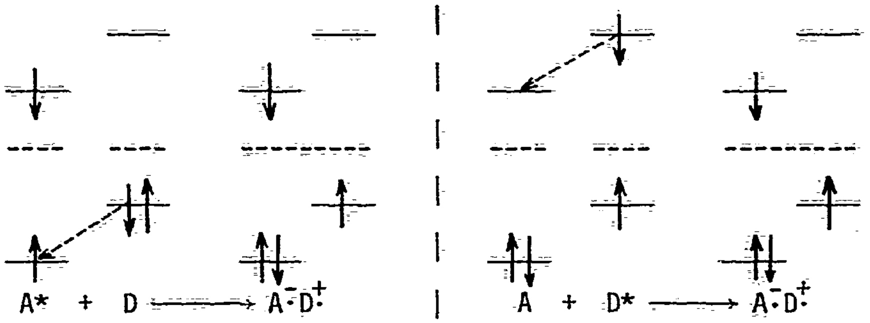


Figure 1. Simplified molecular orbital scheme for the electron transfer process.

On the left side of the figure, we have the case where the acceptor is excited while on the right hand side, the donor is the excited species.

We can identify in either molecule the energy of the highest bonding orbital with the respective ionization potential (or oxidation potential) and that of the lowest antibonding orbital with the electron affinity (or reduction potential).

Investigations by Weller and coworkers[11] have shown that depending upon the solvent polarity two different mechanisms of electron transfer, involving excited molecules, can be realized. Mechanism I predominates in highly polar solvents. It leads to the solvated radical ions and involves the intermediate formation of a solvated ion pair.

$$A^* + D \rightarrow A^{\overline{\cdot}}_{(S)} + D^{\overset{+}{\cdot}}_{(S)} \qquad \text{I}$$

Mechanism II predominates in less polar solvents and involves the formation of an excited charge-transfer complex (exiplex) which, generally, emits a broad structureless fluorescence band at longer wavelengths than the primary excited species.

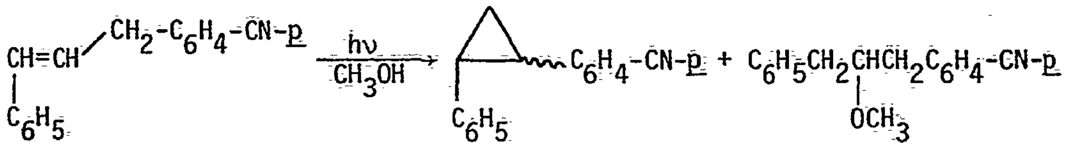
$$A^* + D \rightarrow (A^{\overline{\cdot}}D^{\overset{+}{\cdot}})^* \qquad \text{II}$$

Correlations exist between the singlet energy of the primary excited species (donor or acceptor), the oxidation potential of the donor and the reduction potential of the acceptor, and the fluorescence quenching of the primary excited state. These correlations will be discussed in the following chapters.

At the beginning of this work, only a few examples of olefin reactions proceeding via electron transfer (both intra- and intermolecular), were known.[12]

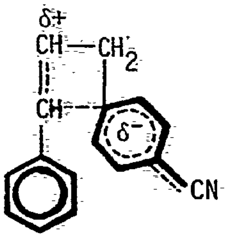
In 1971, Hixson[12a] showed that irradiation of methanolic solution of trans-3-(p-cyanophenyl)-1-phenyl-propene (I) provided in addition to 40% of a mixture of cis- and trans-I, 13% of a mixture of cis- and trans-1-(p-cyanophenyl)-2-phenylcyclopropane (II), and 18% of 1-(p-cyanophenyl)-2-methoxy-3-phenylpropane (III) (Reaction 1).

Reaction 1



(I) (II) (III)

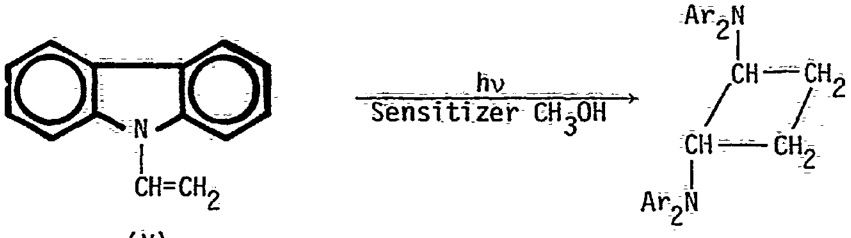
The anti-Markovnikov addition of methanol (product III) was rationalized in terms of an interaction involving electron transfer from the vinyl to p-cyanophenyl group (Structure IV).



(IV)

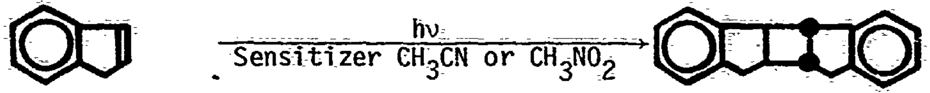
In 1971, Ledwith reported the photoinduced cyclodimerization of N-vinylcarbazole (V)[12b] and Farid and Shealer[12c] the photochemical dimerization of indene (VI) or 1,1-dimethylindene (VII) in the presence of electron acceptor sensitizers (Reactions 2 and 3, respectively).

Reaction 2



(V)

Reaction 3

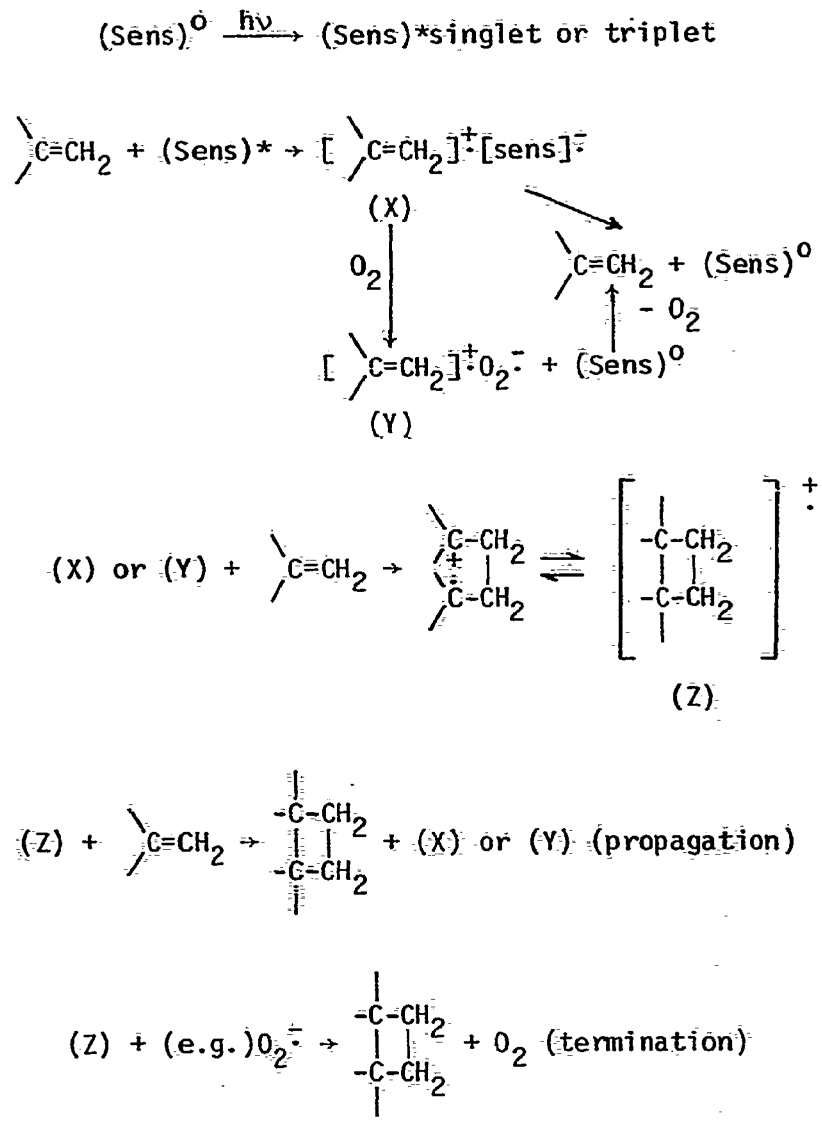


(VI)

Both results were explained in terms of an electron transfer mechanism. The mechanism proposed by Ledwith[12b] for the N-vinylcarbazole (V) dimerization is shown in Scheme 1.

The oxygen played a cocatalytic role, especially when long wavelength dye sensitizers were used. Sensitizers capable of forming stable anion radicals functioned well in the absence of oxygen. The propagation step, which involves electron transfer from the ground state olefin to the cyclized radical cation (Z), accounts for the observed chain reaction.

Farid and Shealer[12c] have proposed an analogous mechanism for reaction 3.



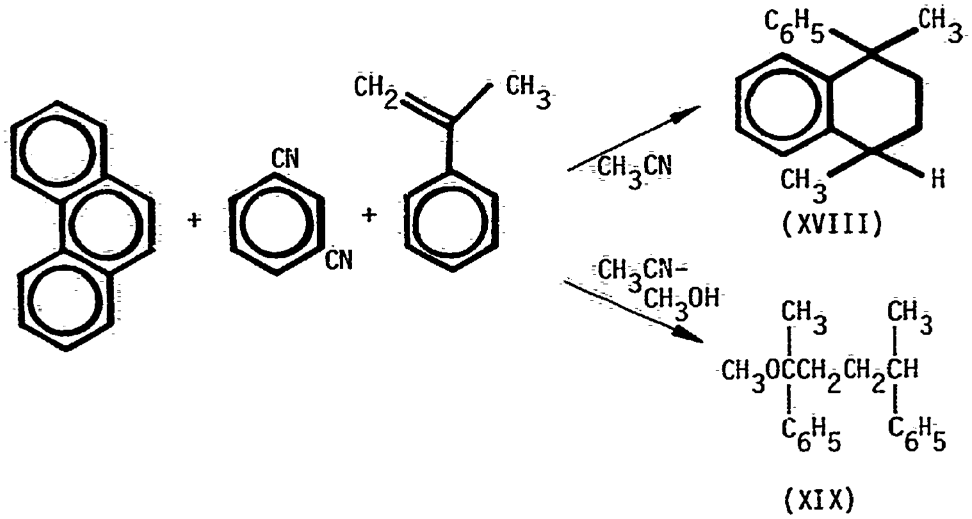
Scheme 1 The porposed mechanism for the N-vinylcarbazole (V) dimerization.[12b]

While our work was in progress, several other olefin photoreactions proceeding via cation radicals appeared in the literature.[13] Evans and coworkers[13a] studied the dimerization of phenyl vinyl ether (VIII), in the presence of electron acceptor sensitizers such as dimethyl terephthalate (IX), methyl benzoate (X) or 9,10-dicyanoanthracene (XI). Farid and coworkers[13b] studied the mixed addition of 1,1-dimethylindene (VII) with phenyl vinyl ether (VIII). The mechanism which has been proposed for these reactions is similar to that depicted in Scheme 1.

Asanuma and coworkers[13c] have studied the photodimerization of styrene (XII), p-methylstyrene (XIII) and α-methylstyrene (XIV) in the presence of 1,2,3,4-tetracyanobenzene (XV). The reaction yields 1,2,3,4-tetrahydronaphthalene derivatives as the main products in addition to 1,2-cis- and 1,2-trans-disbustituted cyclobutanes. An ionic mechanism was proposed[13c] involving photoionization of the exciplex of styrene derivatives with 1,2,3,4-tetracyanobenzene (XV).

Asanuma and coworkers[13d] have also shown that upon irradiation of a solution of phenanthrene (XVI), α-methylstyrene (XIV), and 1,3-dicyanobenzene (XVII) in acetonitrile or acetonitrile-methanol, 1,4-dimethyl-1-phenyl-1,2,4,5-tetrahydronaphthalene (XVIII) and 1,4-dimethyl-1-methoxy-1,4-diphenylbutane (XIX) were respectively obtained (Reaction 4).

Reaction 4



They proposed that the products were formed from the α-methylstyrene radical cation, which was in turn formed by "radical cation transfer" from the phenanthrene radical cation to α-methystyrene (XIV).

The *anti*-Markovnikov addition of methanol to 1,1-diphenylethylene (XX), which occurs upon irradiation of a solution of phenanthrene (XVI), 1,1-diphenylethylene (XX) and 1,4-dicyanobenzene (XXI) in methanol was explained[13e] in terms of a mechanism similar with that proposed for the α-methylstyrene (XIV) dimerization.[13d]

Finally, the photochemical *anti*-Markovnikov addition of acetic acid to some phenylalkenes has been interpreted[13f] in terms of a polarized excited state analogous to that postulated by Hixson[12a] for the *anti*-Markovnikov addition of methanol to *trans*-3-(*p*-cyanophenyl)-1-phenylpropene (I).

The characteristic feature of all the photosensitized reactions of phenylated olefins, described in this work, is that due to back electron transfer from or toward the radical ion of the sensitizer, the latter is regenerated and therefore behaves as a photocatalyst (see mechanism on Scheme II).

Additionally, it can be said that none of the electron transfer reactions described here can be brought about via direct or triplet-triplet sensitized irradiation. Depending upon the nature of the photosensitizer, the phenylated olefins which are included in this work can behave as potential electron donors or potential electron acceptors.

B. INTRODUCTION TO THE PHOTOCHEMISTRY OF ETHERS

The photochemistry of ethers includes two main types of reactions:

1. Direct light-induced or nonsensitized reactions.
2. Reactions where the ether serves as the coreactant with another molecule in the excited state.

Saturated ethers and acetals absorb light at wavelengths below 200 nm.[14] Accordingly, their photoreactions must be induced, directly by light of relatively short wavelengths. Few organic photochemical experiments have been conducted using this region of the ultraviolet spectrum. The sensitizer induced reactions generally involve the use of a triplet sensitizer.

Since ethers possess a potentially reactive C-H bond in the α position to the ether linkage[15] cleavage of this bond (i.e. by hydrogen abstraction by an excited state such as the n → π* state of acetophenone or benzophenone) leads to the formation of free radicals of the type $R^1\dot{C}HOR^2$. In the electron transfer photosensitized experiments reported in this study, the ether molecules are effectively activated by the use of an electron acceptor sensitizer. This represents an entirely new class of ether photoreactions.

The generalities presented in the previous section, with regard to the electron transfer process, can be applied equally well to olefin or ether molecules. Due to their relatively low oxidation potential, the β-phenethyl ethers of this study behaved as electron donors.

CHAPTER II

THE PHOTOSENSITIZED (ELECTRON TRANSFER) ANTI-MARKOVNIKOV ADDITION OF NUCLEOPHILES TO PHENYLATED OLEFINS

A. THE PHOTOSENSITIZED (ELECTRON TRANSFER) ANTI-MARKOVNIKOV ADDITION OF OXYGEN CENTERED NUCLEOPHILES TO PHENYLATED OLEFINS

a. Introduction

Olefinic compounds undergo numerous transformations upon direct or triplet sensitized irradiation. These transformations include cis-trans isomerization, cycloaddition, reduction and addition of protic solvents. The latter, pertinent to our studies, depends on the nature of the double bond, the solvent and the sensitizer.[2] The behaviour of six- and seven-membered cycloalkenes is the best documented.[16-18] The addition of polar nucleophilic solvents to styrene derivatives and phenylallenes has also been studied and the reactivity has been interpreted in terms of a reactive excited state (triplet or singlet) displaying a charge transfer character.[12a,13f]

Neunteufel and Arnold[19] in their effort to define the scope and limitations of the photocycloaddition of carbonyl compounds to olefins, found that when a solution of methyl p-cyanobenzoate (XXII) and 1,1-diphenylethylene (XX) was irradiated in benzene-d_6 and in acetonitrile-d_3 under comparable conditions, the yield of formation of 2-methoxy-2-(p-cyanophenyl)-3,3-diphenyloxetane (XXIII) decreased slightly with increasing solvent polarity, whereas XX was consumed much faster in the nitrile solution. The formation of the new product of the reaction 1,1,4-triphenyl-1,2,3,4-tetrahydronaphthalene (XXIV) was rationalized as resulting from electrophilic attack by the radical cation of 1,1-diphenylethylene (XX) on the ground state olefin, ring closure, back electron transfer from the radical anion of methyl p-cyanobenzoate (XXII) and finally aromatization. When 1,1-diphenylethylene (XX) and methyl p-cyanobenzoate (XXII) were irradiated in methanol and 2-propanol they found formation of 2,2-diphenylethyl methyl ether (XXV) and 2,2-diphenylethyl isopropyl ether (XXVI) respectively occurred, arising from nucleophilic attack of the alcohol on the 1,1-diphenylethylene radical cation. Since it was concluded that oxetane formation was suppressed in polar solvent, presumably, because of the dissociation of the exciplex, we decided to study the synthetically useful anti-Markovnikov addition of nucleophiles to 1,1-diphenylethylene (XX) and other phenylated olefins, such as 1-phenylcyclohexene (XXVII) and 2-phenylnorbornene (XXVIII), in acetonitrile.

We found that when 1,1-diphenylethylene (XX), 1-phenylcyclohexene (XXVII), or 2-phenylnorbornene (XXVIII) was irradiated in acetonitrile-alcohol solution in the presence of an electron acceptor sensitizer, such as 1-cyanonaphthalene (XXIX) or methyl p-cyanobenzoate (XXII), reasonable yields (between 20 and 50%) of the ethers having the anti-Markovnikov orientation (XXV, XXVI, XXX, XXXI, XXXII, XXXIII) were obtained (Reactions 5, 6 and 7). When 1,1-diphenylethylene (XX) and an electron acceptor sensitizer were irradiated in acetonitrile-water or in acetonitrile-acetic acid solution fair yields of the 2,2-diphenylethyl alcohol (XXXIV) and 2,2-diphenylethyl acetate (XXXV) respectively were obtained (Reaction 5).

Reaction 5

$$\underset{\text{(XX)}}{(C_6H_5)_2C{=}CH_2} + ROH \xrightarrow[CH_3CN]{h\nu,\ \text{Sens.}} \underset{\text{(XXV, XXVI, XXX, XXXIV, XXXV)}}{(C_6H_5)_2CHCH_2OR}$$

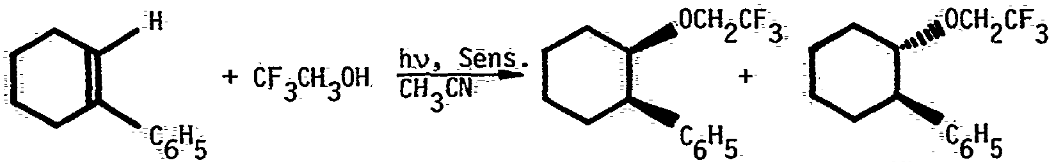
	R	Yield II (%)
XXV	$-CH_3$	36
XXVI	$-CH(CH_3)_2$	49
XXX	$-C(CH_3)_3$	17
XXXIV	$-H$	25
XXXV	$-COCH_3$	5

Sens: methyl p-cyanobenzoate (XXII)

1,4-dicyanobenzene (XXI)

1-cyanonaphthalene (XXIX)

Reaction 6

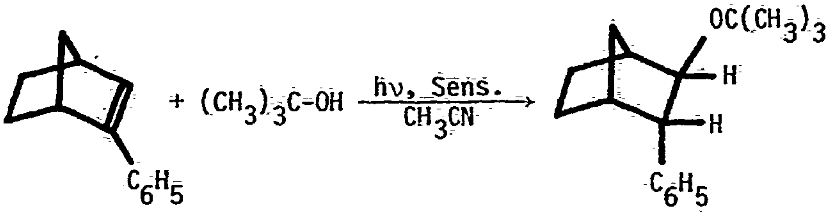


(XXVII) (XXXI) (XXXII)

Yield (%)	
XXXI	8
XXXII	12

Sens: 1-cyanonaphthalene (XXIX)

Reaction 7



(XXVIII) (XXXIII)

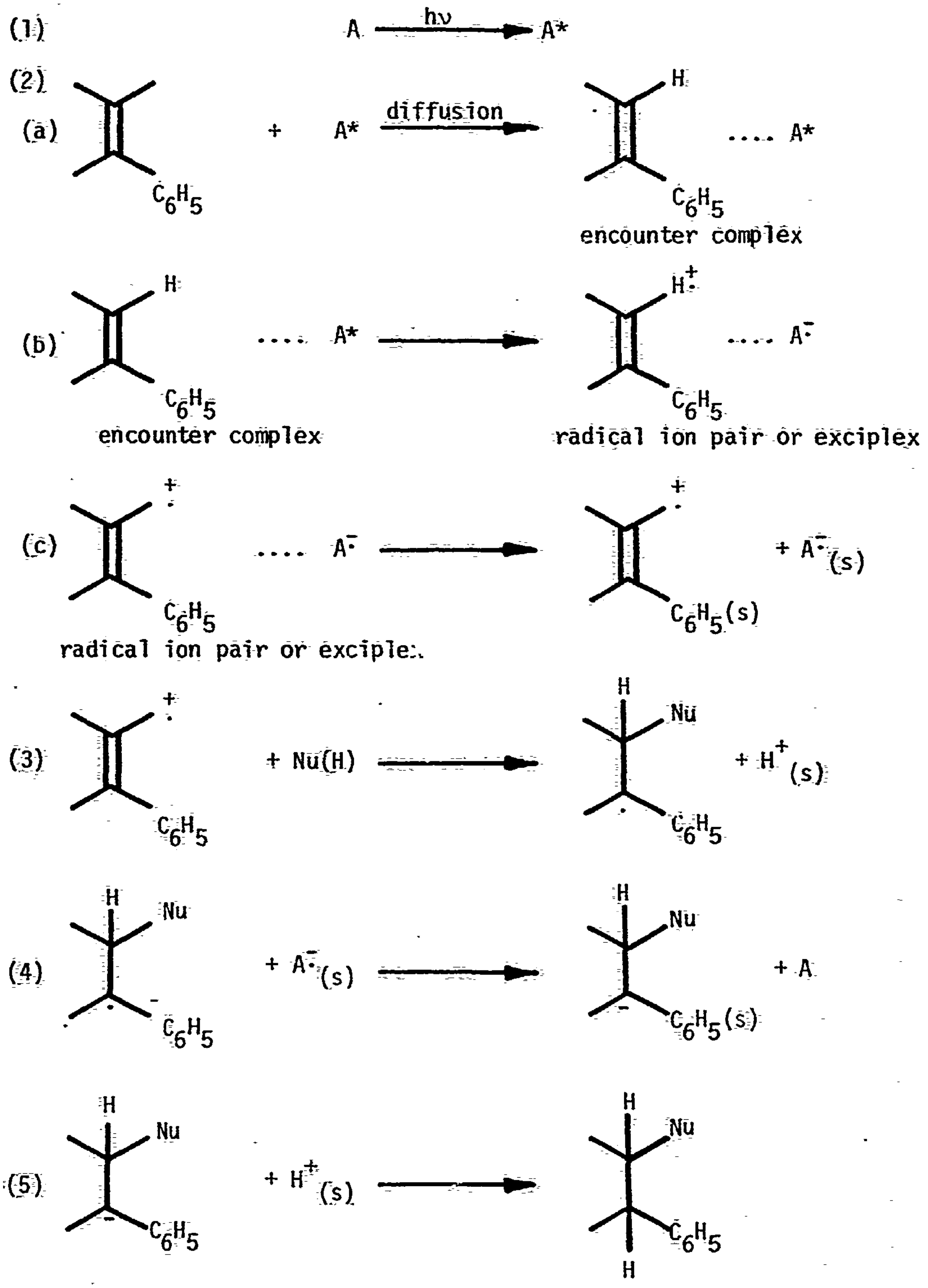
Sens: methyl p-cyanobenzoate (XXII)

The mechanism we propose for the photosensitized (electron transfer) addition of oxygen centered nucleophiles to phenylated olefins is summarized in Scheme II.

In this section of the present work, we report the characterization of the products from the photosensitized (electron transfer) addition of oxygen centered nucleophiles to olefins (XX, XXVII and XXVIII) in acetonitrile-alcohol (or water or acetic acid) solutions and the results of photophysical studies which support the proposed mechanism (Scheme II). We also report the oxidation potentials of the olefins XX, XXVII and XXVIII in acetonitrile, and discuss the thermodynamics of the electron transfer step (step 2 in Scheme II).

b. Results

Typical conditions for the photosensitized (electron transfer) addition of oxygen centered nucleophiles to phenylated olefins (reactions 5, 6 and 7) involve irradiation of a solution of olefin (0.15 M) and sensitizer (0.08 M), in nucleophilic reagent-acetonitrile through



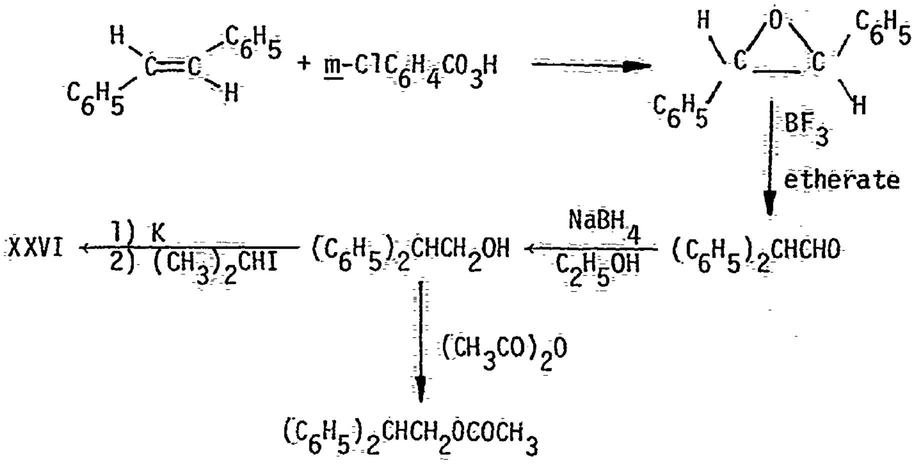
Scheme II. The proposed mechanism for the photosensitized (electron transfer) *anti*-Markovnikov addition of nucleophiles [Nu(H)] to phenylated olefins.

a Pyrex filter (λ > 280 nm). Under these conditions, the light is absorbed only by the sensitizer.

Under identical conditions, but in the absence of the sensitizer, no reaction occurred upon prolonged irradiation. The sensitizer was largely recovered. The progress of the reaction was followed by nuclear magnetic resonance spectroscopy (^{1}Hnmr), and/or by vapour phase chromatography (vpc). The products were isolated from the reaction mixture by column chromatography and were further purified by preparative vpc. Details can be found in the Experimental Section (Chapter VI).

The structure of the products of reaction 5 (except for the 2,2-diphenyl-tert-butyl ether (XXX)) rests on direct comparison of their infrared (ir) spectra with those of authentic samples. 2,2-Diphenyl methyl ether (XXV) was prepared as described by Bonner and Mango[20] and 2,2-diphenyl isopropyl ether (XXVI) was prepared by a multi step synthesis, and in low overall yield, as outlined in reaction 8. 2,2-Diphenyl ethyl acetate (XXXV) was prepared by acetylation of 2,2-diphenylethyl alcohol (XXXIV) (reaction 8).

Reaction 8



(XXXV)

The structures and the stereochemistry assigned to the products from reaction 6 and reaction 7 were based on an analysis of their ^{1}Hnmr spectra. An attempt to confirm the structures of the products from reaction 6 via a Williamson synthesis using the potassium alcoholates of the corresponding alcohols and 2,2,2-trifluoroethyl iodide failed to produce any 2,2,2-trifluoroethyl ether.

Reaction 6 gave the epimeric ethers XXXI and XXXII.[21] The H α- to the 2,2,2-trifluoroethoxy group in _cis_-(XXXI), being equatorial, is not coupled significantly[22] to the axial hydrogens in the 2 and 6 positions; therefore, it appeared as broad singlet at 3.68 ppm. Furthermore, the signal due to the H α- to the 2,2,2-trifluoroethoxy group was at lower field than the corresponding signal in the _trans_- isomer, a trend found also in the case of the 2-phenyl-1-methoxy-cyclohexanes.[23] Surprisingly, the chromatographic behaviour of this isomeric pair was not as one would predict on the basis of the observed empirical trend.[24] The _cis_ ether (XXXI), having the dipolar 2,2,2-trifluoroethoxy group in the axial position run slower than the _trans_ ether (XXXII) upon elution on a silica gel column. In the ^{1}Hnmr spectrum of 2-_exo_-_tert_-butoxy-3-_endo_-phenylnorbornane (XXXIII) the signal due to the H α- to the _tert_-butoxy group (H_2) appeared as a doublet of doublets at 3.66 ppm. This band remained unchanged while irradiating H_1 (δ 2.22), and collapsed to sharp doublet while irradiating H_{7a} (δ around 1.35). The spacing of the doublet was equal to 4.0 Hz. This value is consistent with a coupling constant between _endo_-_exo_ protons.[25] These facts indicated that H_2 was not significantly coupled to H_1 but coupled to H_{7a} through long range interaction. We conclude, therefore, that H_2 must be in the _endo_ position. The signal for H_3 appeared as a broad triplet at δ 2.98. This band collapsed to a doublet while irradiating H_2 or H_4 (δ 2.22) respectively. An approximate value for $J_{3,4}$ was estimated to be ca. 4.0 Hz. This is a reasonable value for $J_{3,4}$ (H_3 exo).[25] The latter reveals that H_3 is in the exo position and it is coupled to H_4 as well as to H_2.

In order to identify the excited state responsible for the reaction, we have studied the fluorescence of 1-cyanonaphthalene (XXIX) as a function of the olefin (XX, XXVII and XXVIII) concentration in acetonitrile solution. The quenching rate constants obtained from these Stern-Volmer plots and the measured fluorescence lifetimes in the absence of quencher (τ) are summarized in Table I. The calculated diffusion limited rate constant for acetonitrile solution at 20° C is k_q (diffusion) = $1.8 \times 10^{10}\ M^{-1}s^{-1}$.[26] Therefore, the fluorescence quenching of XXIX by all olefins studied is essentially diffusion-controlled.

To obtain some indication about the energetics of the electron transfer step (step 2), we have studied the electrooxidation and/or reduction processes of our compounds using cyclic voltametry. Half-wave oxidation and reduction potentials have been calculated from these data and are summarized in Table II.

c. Discussion

The first step in the proposed mechanism (Scheme II) involves excitation of the sensitizer (A). This can be achieved by irradiating through a Pyrex filter. There was no evidence in the UV/VIS absorption spectra, of charge transfer complex formation between the ground-state

Table I. Fluorescence quenching of 1-cyanonaphthalene (XXIX) by 1,1-diphenylethylene (XX), 2-phenylnorbornene (XXVIII) and 1-phenylcyclohexene (XXVII) in acetonitrile solution at 20° C.

		k_q, $M^{-1}s^{-1}$ [a]		
		Experimental (Calculated)[b]		
Fluorophor	τ(ns)	XX	XXVIII	XXVII
1-cyanonaphthalene	8.9	1.3×10^{10}	4.8×10^{10} [c]	1.4×10^{10}
		$(7.5 \cdot 10^{9})$	$(1.2 \cdot 10^{10})$	$(0.8 \cdot 10^{10})$

a. Exciting the fluorophor at 313 nm.

b. Using the nomograph on page 267 of reference 11b.

c. We consider this value an indication of the order of magnitude of k_q rather than an accurate value, since rapid polymerization and colloid formation occurred after distillation of the purified sample (XXVIII).

Table II. Half-wave oxidation and reduction potentials obtained by cyclic voltametry.[a]

Compound	$E_{1/2}^{red}$, V[b]	$E_{1/2}^{ox}$, V[b]
1-cyanonaphthalene (XXIX)	2.33	c
methyl p-cyanobenzoate (XXII)	2.10	c
1,1-diphenylethylene (XX)	d	1.48[e]
2-phenylnorbornene (XXVIII)	d	1.07[f]
1-phenylcyclohexene (XXVII)	d	1.26[e]

a. Pt electrode, tetraethylammonium perchlorate (TEAP, 0.1 M) in acetonitrile solution, vs Ag/0.1 M $AgNO_3$.

b. Taken as 0.028 V before the anodic peak potential and 0.029 V before the cathodic peak potential (R.S. Nicholson and I. Shain, Anal. Chem., 36, 706 (1964)).

c. In these cases the oxidation wave was not observed, i.e., > 2.0 V.

d. In these cases the reduction wave was not observed, i.e., < 2.2 V.

e. The oxidative process was not reversible, the half-wave potential was estimated using the 100 mV/s sweep rate.

f. As above (e), only the 200 mV/s sweep rate was used.

molecules.

Step 2 is the electron transfer step which may involve the sequential formation of an encounter complex, an exciplex, a radical ion pair and finally the solvent-separated radical ions. We have little evidence pertaining to the various stages involved. However, a reasonable correlation concerning the free-energy change (ΔG) associated with the electron transfer process can be made using fluorescence emission quenching, oxidation and reduction potentials, and singlet energy.[11,27,28] We have used Eq. (4), first proposed by Weller[11b] to correlate (experimental and calculated) electron transfer quenching, in order to obtain some indication about the energetics of step 2.

$$\Delta G(\mathrm{kcal\ mol^{-1}}) = 23.06\ [E(D/D^+)v - E(A/A^-)v - \frac{e_0^2}{\varepsilon\alpha}] - \Delta E_{0,0}(\mathrm{kcal\ mol^{-1}}) \qquad (4)$$

The term in brackets represents the energy required for the electron transfer and it is a function of the oxidation potential of the donor ($E(D/D^+)$), (in this case the olefin), the reduction potential of the acceptor ($E(A/A^-)$), (in this case the sensitizer), and the Coulombic attraction term. Fig. 2 is a schematic representation of the energy profile for the electron transfer process.[11b]

Usually half-wave potentials determined by polarography are used here; we have chosen cyclic voltametry to obtain these data. There are advantages and disadvantages to both methods. The main advantages for cyclic voltametry are that it is convenient experimentally, both the oxidation and reduction potentials can be determined under identical conditions, it is easily seen if the electron transfer process

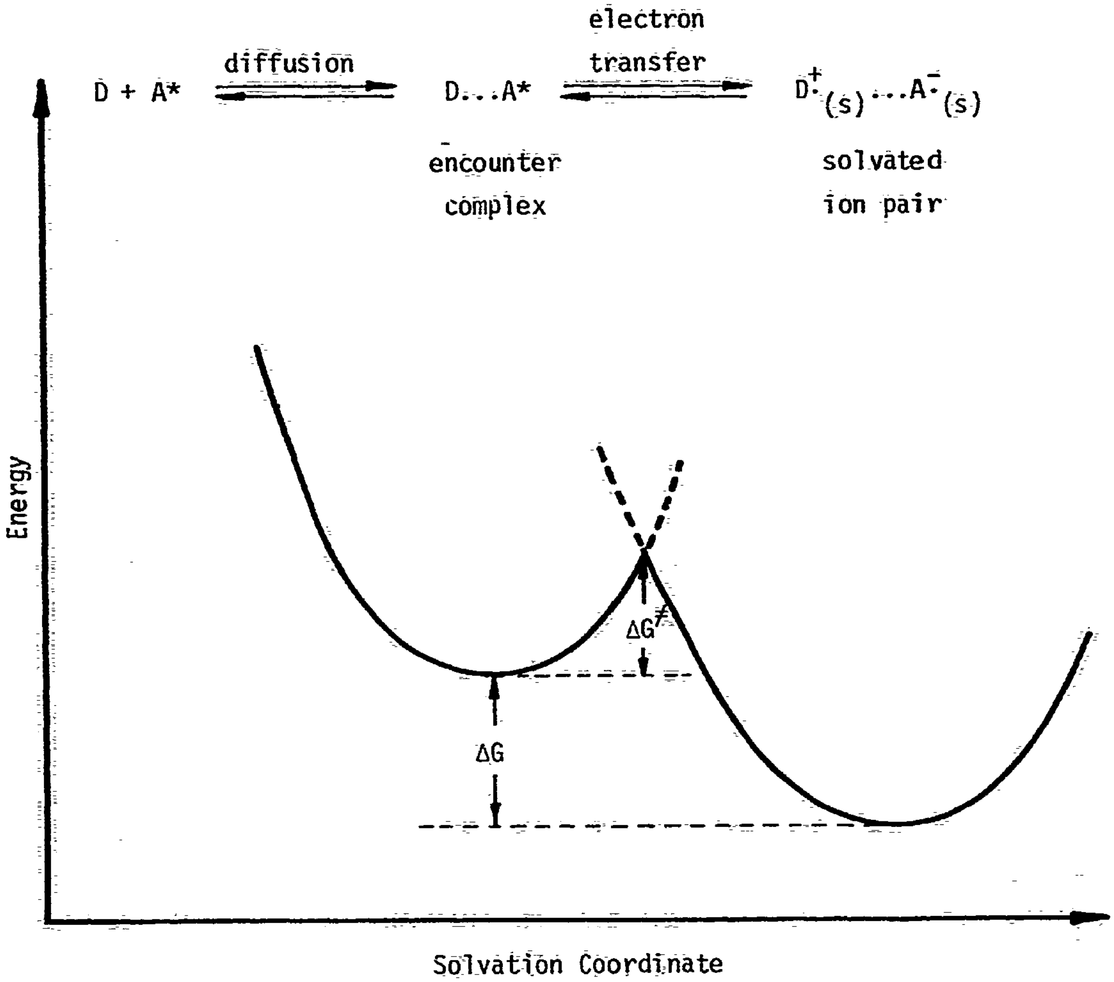


Figure 2. Schematic representation of the energy profile for the electron transfer process.[11b] D = Donor, A = Acceptor.

is reversible, and, if there are reactions following the electron transfer process, they can, in principle, be studied by this technique. A major problem with either polarography or cyclic voltametry is the inability to obtain thermodynamically significant oxidation or reduction potentials when the electron transfer process is not reversible. The values in Table II were taken as 0.028 V before the anodic peak potential and 0.029 V before the cathodic peak potential.[29] If the electron transfer process were not reversible, the peak potential was a function of sweep rate. The half-wave was then estimated using the 100 mV/sec sweep, and these values are therefore less reliable. Rigorously, they have no thermodynamic significance; nevertheless, meaningful correlations can be obtained from them.[30]

The Coulombic attraction term allows for the energy gained from the radical ion interaction at the separation distance (α) and is a function of the solvent dielectric (ε); it has the value $14.39/\varepsilon\alpha$ (Å) (eV). In this polar medium (acetonitrile, $\varepsilon_{25^\circ} = 36.7$), when the separation is within the encounter distance (ca. 7 Å) this coulombic attraction term is small (1.3 kcal mole^{-1}) and we believe the radical ions can dissociate before reaction.

The energy available for the electron transfer process is the lowest singlet or triplet energy of the donor or acceptor. The singlet energies of the sensitizers were obtained from the fluorescence emission and/or absorption spectra (Figs. 3 and 4). A distinct 0-0 band was observed with 1-cyanonaphthalene (XXIX). In the case of methyl p-cyanobenzoate (XXII) no fluorescence emission was observed,[61] so the singlet energy was estimated from the onset of the long wavelength absorption band. In the case of the singlet, the sensitizers (acceptors) have the

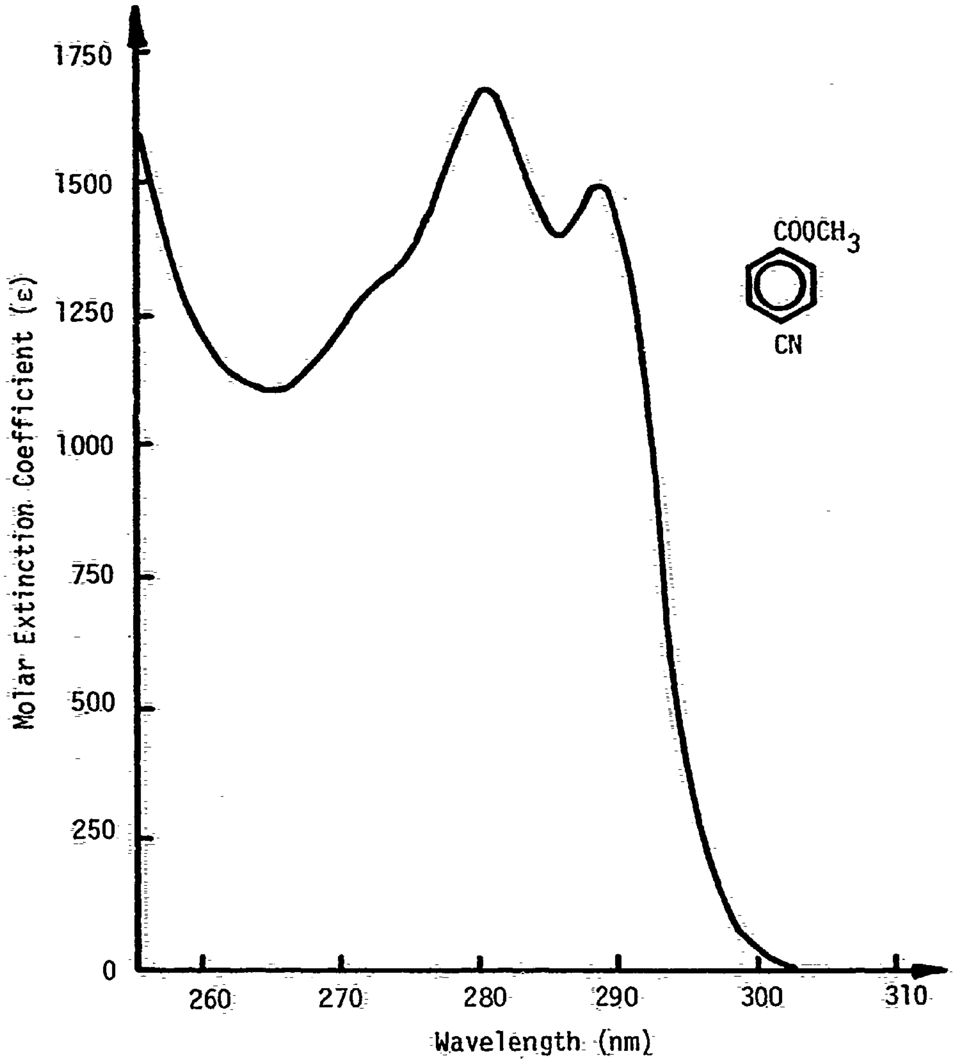
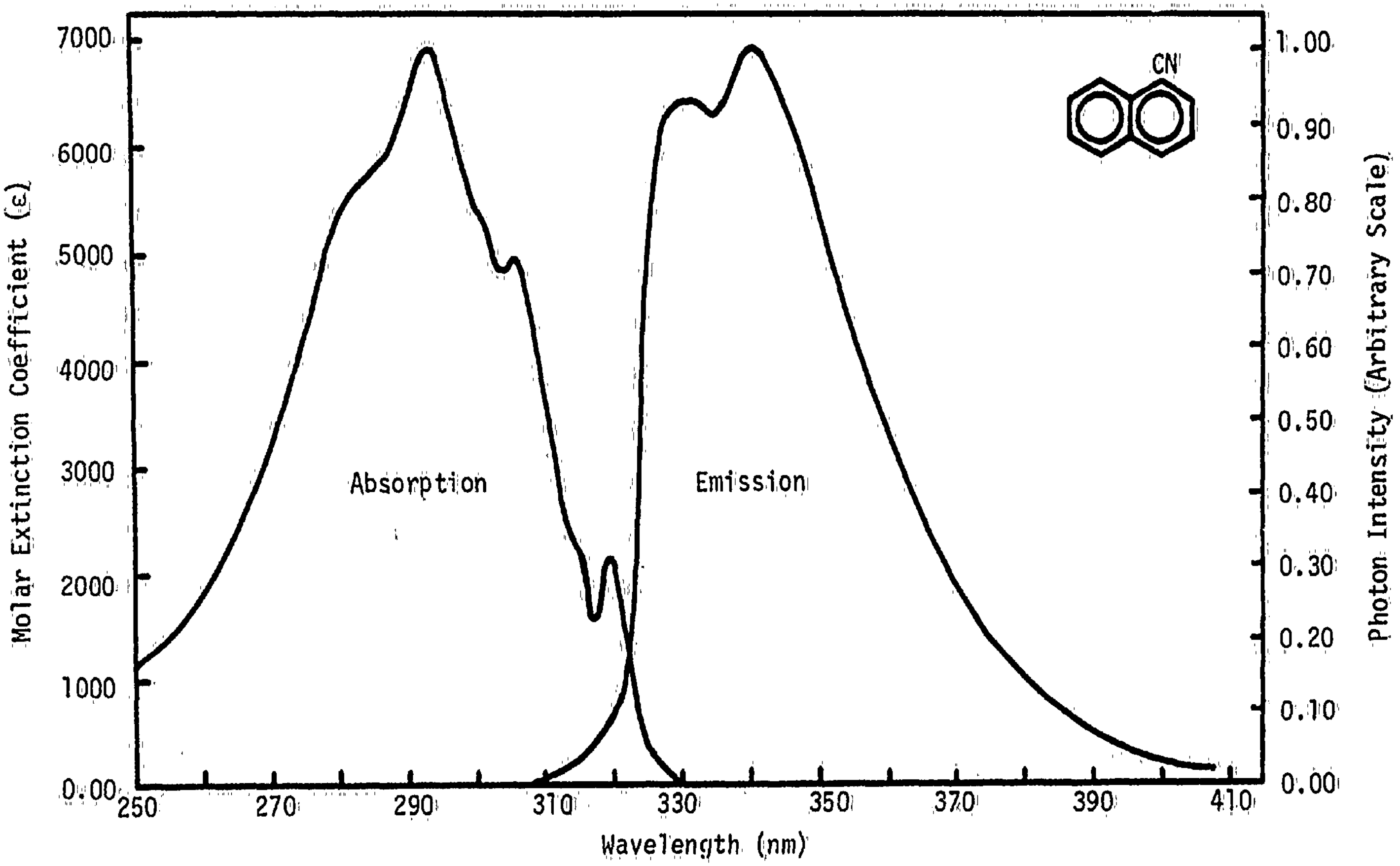


Figure 3. The absorption spectrum of methyl p-cyanobenzoate (XXII) in acetonitrile.



<u>Figure 4</u>. The absorption and fluorescence emission spectra of 1-cyanonaphthalene (XXIX) in acetonitrile.

lowest energy and in fact, the fluorescence quenching studies summarized in Table I and Fig. 5 indicate that the singlet state of sensitizer XXIX was involved in the reaction. In Table III are listed the singlet energies of the sensitizers, and the calculated ΔG values for the electron transfer process, derived from Eq. (4). It can be seen that in all cases the electron transfer process is spontaneous.

We have used the nomograph on page 267 of reference 11b to obtain calculated values for the fluorescence quenching process (Table I). With XX and XXVII the agreement is fairly good (within a factor of two) while XXVIII shows a slightly higher than the calculated experimental value. (Agreement within a factor of four.) We believe the observed quenching rate constant with XXVIII is anomalously high due to partial polymerization and subsequent formation of polymer suspension in acetonitrile. We consider this agreement between the calculated and experimental quenching rate constants as evidence in favour of the electron transfer quenching mechanism. This is a reasonable conclusion in view of the large difference in the oxidation and reduction potentials of the fluorescer and quencher and the high polarity of the solvent.

During step 2 of the proposed mechanism (Scheme II) the reaction progresses from an excited-state reaction to a ground state one. Whether or not this transition occurs via an excited-state complex (exciplex) is an interesting and difficult question. The best way to prove the involvement of an exciplex is to observe emission from it. Exciplex emission, common in nonpolar solvents, is usually quenched by the addition of polar solvents due to the rapid dissociation of the exciplex to give the radical ions. Although weak exciplex emission has

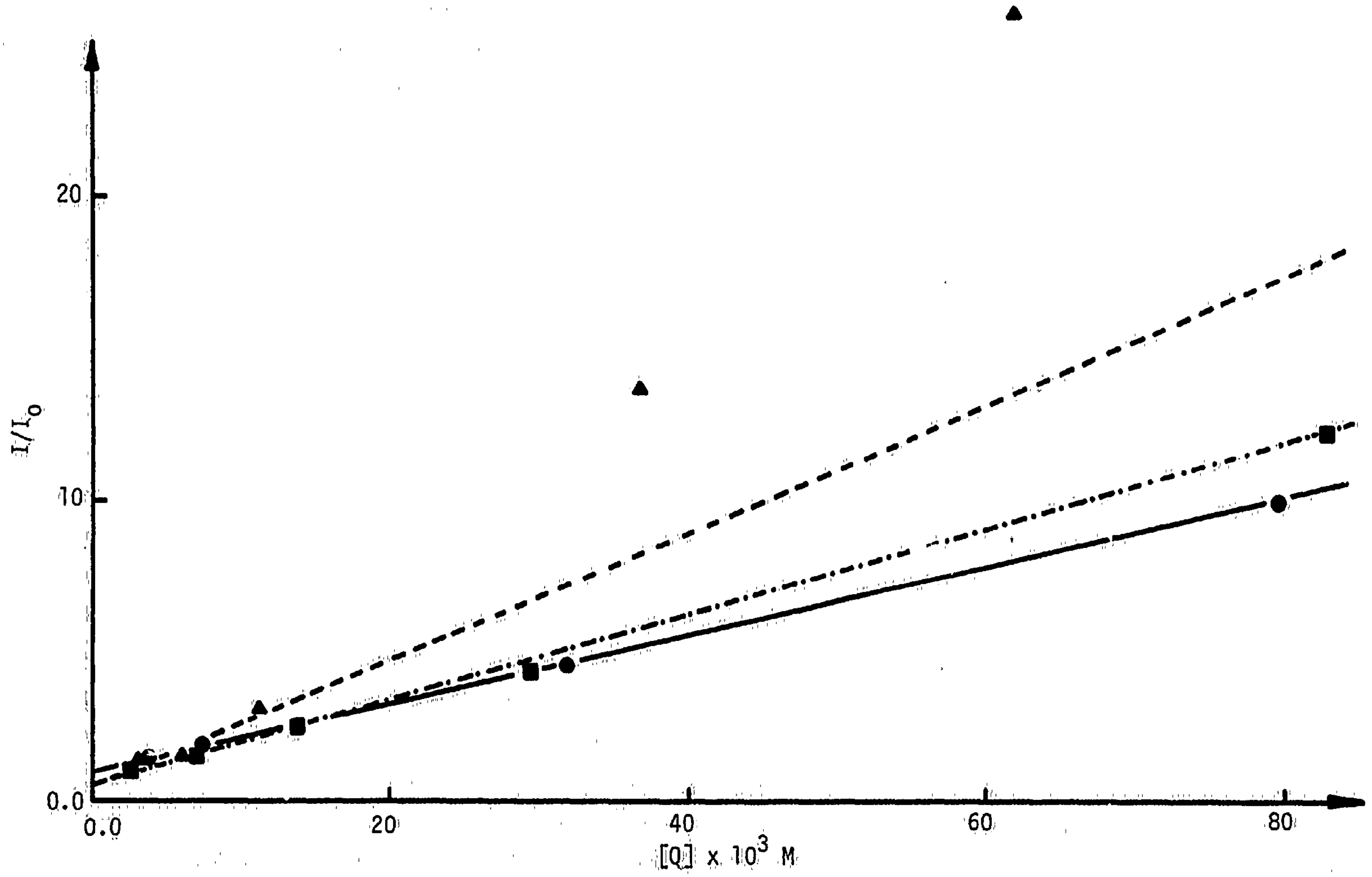


Figure 5. Stern-Volmer plots for the fluorescence quenching of 1-cyanonaphthalene (XXIX) by a) 1,1-diphenylethylene (XX, ●), b) 1-phenylcyclohexene (XXVII, ■), c) 2-phenylnorbornene (XXVIII, ▲).

Table III. Calculated ΔG for the electron transfer process (step 2) using Eq. (4).

Sensitizer	Singlet and Triplet Energy kcal mol^{-1}	Calculated ΔG^{a,b} kcal mol^{-1} Singlet (Triplet)		
		XX	XXVIII	XXVII
XXIX	89.4 57.4	-2.8(+29.2)	-12.3(+19.7)	-7.9(+24.1)
XXII	95.3 72.0^{c}	-14.0(+8.3)	-23.5(-0.17)	-19.2(+4.1)

a. The energy required for the electron transfer process (step 2b), assuming the encounter distance to be 7 Å and the dielectric constant of acetonitrile (ε_{25° = 36.7).

b. The singlet and the triplet energy of the sensitizer was used. From the absorption spectra of the olefins we estimated their singlet energies to be: E_S(XX) ⩾ 97.9 kcal mol^{-1}, (XXVIII) ⩾ 96.9 kcal mol^{-1}, (XXVII) ⩾ 98.6 kcal mol^{-1}. The triplet energies of the olefins (XX, XXVIII, XXVII) while not known are certainly less than the triplet energies of XXIX and XXII and therefore the electron transfer process cannot be more favourable than calculated here.

c. D.R. Arnold, J.R. Bolton, G.E. Palmer and K.V. Prabhu, Can. J. Chem. 55, 2728 (1977).

been observed in some cases even in acetonitrile solution,[11d,28b] we were unable to detect it from solutions of XXIX quenched by high concentrations of the olefins (XX, XXVIII, XXVII).

As can be seen from the data in Table III, electron transfer to the triplet of the sensitizers is in all cases but one, a non-spontaneous process. Furthermore, it is well established[16] that triplet-triplet energy transfer would not lead to <u>anti</u>-Markovnikov products. The triplet of XX will rapidly deactivate due to the free-rotor effect, while the triplet of XXVIII and XXVII would be expected to yield the Markovnikov addition products.[16a,17] Indeed, 1-phenylcyclohexene (XXVII) irradiated in the presence of 1-acetonaphthone (XXXVI, E_T = 56.4 kcal mol^{-1})[31] and 2,2,2-trifluoroethanol in acetonitrile gave a good yield of 1-phenyl-1-(2,2,2-trifluoroethoxy)cyclohexane (XXXVII).

Step 3 in the proposed mechanism involves reaction of the radical cation of the olefin (XX, XXVIII, XXVII) with the oxygen centered nucleophile (ROH). Radical cations are highly reactive species and a fast reaction normally occurs with a nucleophilic species present in solution.[32] The low yield realized in the photosensitized (electron transfer) addition of acetic acid (Reaction 5) to 1,1-diphenylethylene (XX) and the lack of photosensitized (electron transfer) addition of 2,2,2-trifluoroethanol to the same molecule reflect the low intrinsic nucleophilicity[33] of these compounds. Attempts to improve the chemical yields of the above two reactions using potassium acetate and potassium 2,2,2-trifluoroethoxide respectively did not succeed.

In Step 4 of the proposed reaction sequence, the radical resulting from the addition of the nucleophile is reduced by the radical anion of the sensitizer to give the corresponding anion.

This type of electron transfer process has received some attention.[34] Particularly relevant is the reduction of alkyl halides upon treatment with alkali naphthalenes. The mechanism of this reaction has been reviewed by J.F. Garst and is shown, in abbreviated form, in Scheme III.[34] Step b is analogous to Step 4, Scheme III.

Scheme III

a)	$\mathrm{Naph}^{\overline{\cdot}} + \mathrm{R{-}X} \longrightarrow \mathrm{Naph} + \mathrm{X}^{-} + \mathrm{R}^{\cdot}$	(electron detachment - dissociative electron attachment)
b)	$\mathrm{R}\cdot + \mathrm{Naph}^{\overline{\cdot}} \longrightarrow \mathrm{R}^{-} + \mathrm{Naph}$	(electron detachment - electron attachment)
c)	$\mathrm{R}^{-} + [\mathrm{H}^{+}] \longrightarrow \mathrm{RH}$	(proton transfer)
d)	$\mathrm{R}\cdot + \mathrm{Naph}^{\overline{\cdot}} \longrightarrow \mathrm{R\ Naph}^{-}$	(radical, radical anion complex)
e)	$\mathrm{R\ Naph}^{-} + [\mathrm{H}^{+}] \longrightarrow \mathrm{R\ Naph\ H}$	(proton transfer to give dihydroalkylnaphthalene)

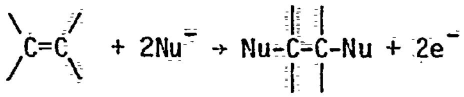
While it seems reasonable that the electron transfer involved in Step 4 (Scheme II) will occur in the cases reported here, the energy associated with this type of process is difficult to predict in view of the dearth of quantitative data for the reduction of radicals[35] (or for the one-electron oxidation of anions). In fact, a useful empirical correlation of radical reduction potentials may result from a study of the proficiency of this step. We expect Step 4 will present a limitation to the generality of reactions 5, 6 and 7, particularly when the reaction is applied to alkylated olefins and the resulting carbanion, after step 4 is tertiary.

During the reduction of alkyl halides upon treatment with alkali naphthalenes, a major competing reaction is coupling of the radical with the radical anion to give, ultimately, dihydroalkylnaphthalenes (Step d and e in Scheme III). This type of reaction may account for the partial consumption of the sensitizer during reactions 5, 6 and 7. However, since the sensitizers are largely recovered, step b must be favoured over step d with the diphenylethyl radical and the sensitizer radical anions we have used in reactions 5, 6 and 7.

We want to emphasize the fact that because of the occurrence of this particular step (step 4), the photosensitized (electron transfer) addition of nucleophiles to phenylated olefins is different from the reported electrolytic oxidations of aryl olefins in nucleophilic solvents.[36,37]

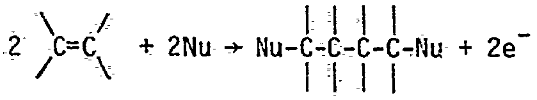
Two pathways are open to aryl olefins upon electrolytic oxidation in nucleophilic solvents:

a) Oxidative addition:



$$>C=C< + 2Nu^- \rightarrow Nu-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-Nu + 2e^-$$

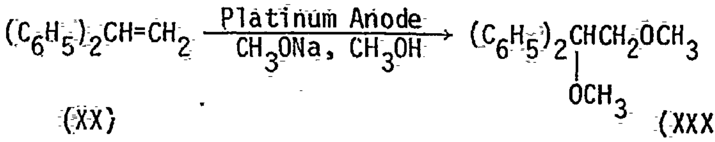
b) Oxidative coupling with addition:



$$2\ >C=C< + 2Nu \rightarrow Nu-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-Nu + 2e^-$$

Reaction 9[36a] and reaction 10[37c] are representative examples.

Reaction 9

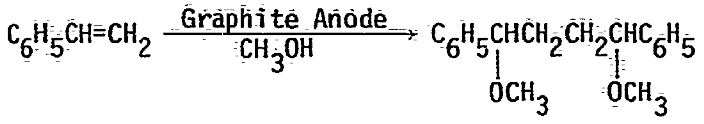


$$(C_6H_5)_2CH=CH_2 \xrightarrow[CH_3ONa,\ CH_3OH]{\text{Platinum Anode}} (C_6H_5)_2\underset{\underset{OCH_3}{|}}{CH}CH_2OCH_3$$

(XX) (XXXVIII, 31%)

When 1,1-diphenylethylene (XX) was oxidized, under controlled current conditions, on a platinum anode, in the presence of sodium methoxide in methanol, 1,1-diphenylethylene glycol dimethyl ether (XXXVIII) was obtained as the main product (Reaction 9).[36a]

Reaction 10



$$C_6H_5CH{=}CH_2 \xrightarrow[CH_3OH]{\text{Graphite Anode}} C_6H_5\underset{\displaystyle OCH_3}{\underset{|}{CH}}CH_2CH_2\underset{\displaystyle OCH_3}{\underset{|}{CH}}C_6H_5$$

(XII) (XL, 60%)

When styrene (XII) was oxidized in methanol using sodium methoxide, sodium perchlorate, or sodium iodide as supporting electrolyte, on a graphite electrode, 1,4-dimethoxy-1,4-diphenylbutane (XL) was produced in 60% yield[37c] (Reaction 10).

The exact mechanism of the electrolytic oxidation of alkenes is still under investigation. However, it is apparently obvious that in the case of oxidative addition the number of electrons transferred per molecule of substrate is two. Presumably, the radical resulting from the addition of the nucleophile to the radical cation is further oxidized to a carbonium ion (ECE mechanism). The latter is not possible in the photosensitized (electron transfer) reaction, and as a result of the back electron transfer, monoaddition is the only mode of addition observed. Oxidative coupling with addition is also unlikely in the photosensitized (electron transfer reaction since the concentration of the radical cations and/or the radicals resulting from the addition of the nucleophile is comparatively low.

Step 5, the protonation of carbanion, is a well known reaction which completes the mechanistic sequence.

B. THE PHOTOSENSITIZED (ELECTRON TRANSFER) ANTI-MARKOVNIKOV CYANATION OF PHENYLATED OLEFINS

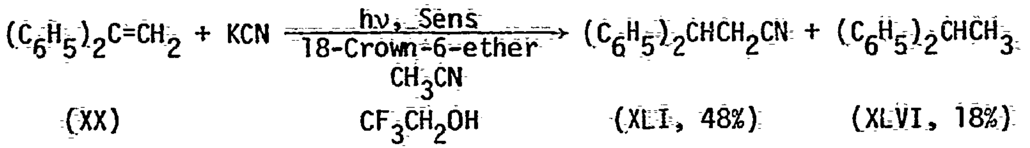
a. Introduction

We have shown in the previous part of this chapter, that the photosensitized (electron transfer) addition of oxygen centered nucleophiles to olefins can be a synthetically useful reaction for the preparation of alcohols, ethers and esters having the anti-Markovnikov orientation. The utility of this type of reaction has been extended to include carbon-carbon bond formation; we have found conditions where cyanide ion can serve as the nucleophile.

There are many photochemically induced nucleophilic aromatic substitution reactions.[38] Several of these examples involve substitution with cyanide ion. However, the examples of photoaddition of nucleophiles to aromatic hydrocarbons[39] are rare and this part of Chapter II describes the first examples of the addition of cyanide ion to olefins.

We found[40] that when 1,1-diphenylethylene (XX), 2-phenylnorbornene (XXVIII) or 1-phenylcyclohexene (XXVII), in acetonitrile-2,2,2-trifluoroethanol solution, was irradiated in the presence of 1-cyanonaphthalene (XXIX) or methyl p-cyanobenzoate (XXII), (electron acceptor sensitizer), and potassium cyanide, (reactions 11, 12 and 14), good yields, (between 40 and 50%) of the nitriles having the anti-Markovnikov orientation (XLI, XLII, XLIII, XLIV, XLV) were obtained. Products having the Markovnikov orientation were not detected.

Reaction 11

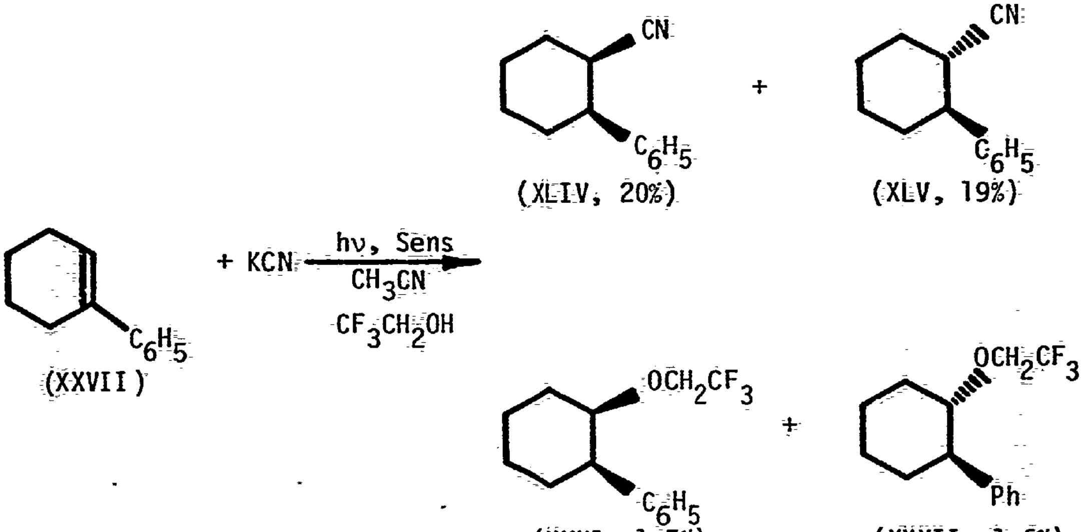


$$(C_6H_5)_2C{=}CH_2 + KCN \xrightarrow[\text{CH}_3\text{CN},\ \text{CF}_3\text{CH}_2\text{OH}]{h\nu,\ \text{Sens},\ \text{18-Crown-6-ether}} (C_6H_5)_2CHCH_2CN + (C_6H_5)_2CHCH_3$$

(XX) (XLI, 48%) (XLVI, 18%)

Sens: 1-cyanonaphthalene (XXIX), methyl p-cyanobenzoate (XXII)

Reaction 14



(XLIV, 20%) (XLV, 19%)

(XXVII)

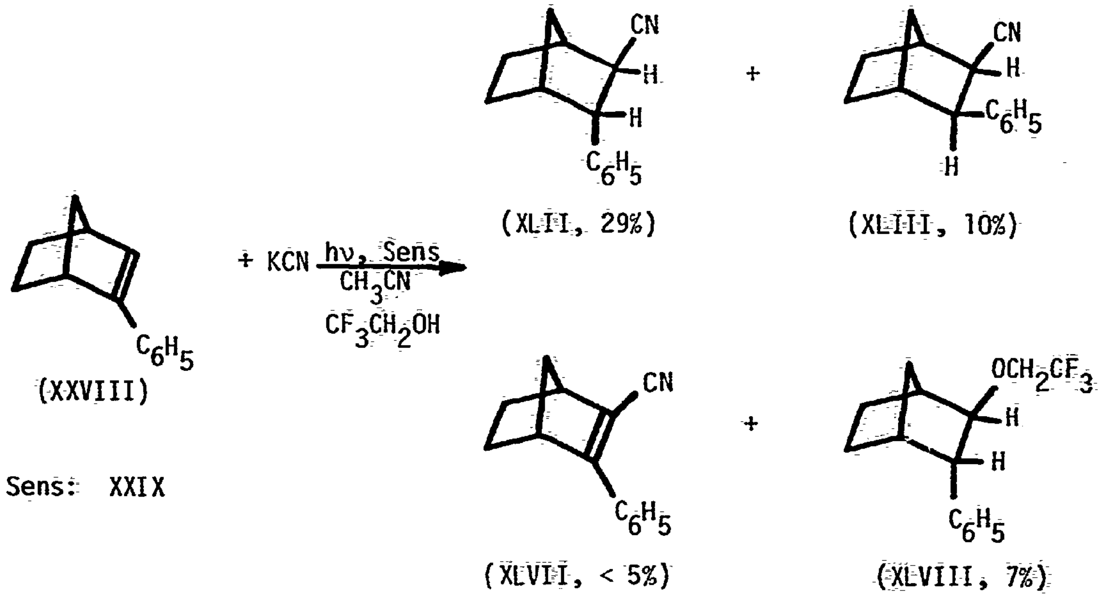
(XXXI, 1.5%) (XXXII, 1.6%)

Sens: XXIX

Ethers resulting from the anti-Markovnikov addition of the 2,2,2-trifluoroethanol, present as a non nucleophilic proton source in the reaction mixture, were sometimes formed in small yield (< 7%).

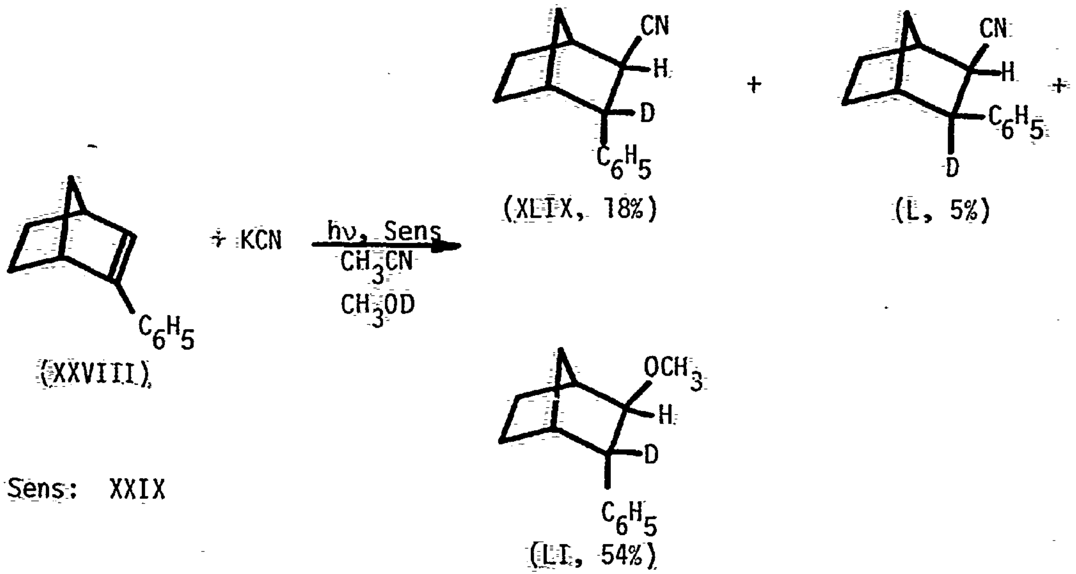
The mechanism we propose for the photosensitized (electron transfer) cyanation of olefins is similar to that invoked for the addition of oxygen centered nucleophiles, and has been presented in

Reaction 12



Sens: XXIX

Reaction 13



Sens: XXIX

Scheme II.

In this part of Chapter II, we report the characterization of the products from the photosensitized (electron transfer) addition of cyanide ion to olefins (XX, XXVIII, XXVII) in acetonitrile and 2,2,2-trifluoroethanol (or methanol-O-d) mixtures and discuss the results of photophysical studies which support the proposed mechanism (Scheme II).

This reaction is related to, and in fact should complement, controlled potential anodic cyanation. In the electrolytic process the radical resulting from step 3 would be near the anode and would thus be oxidized to the corresponding carbonium ion, which subsequently should yield a dinitrile (ECE process).[41]

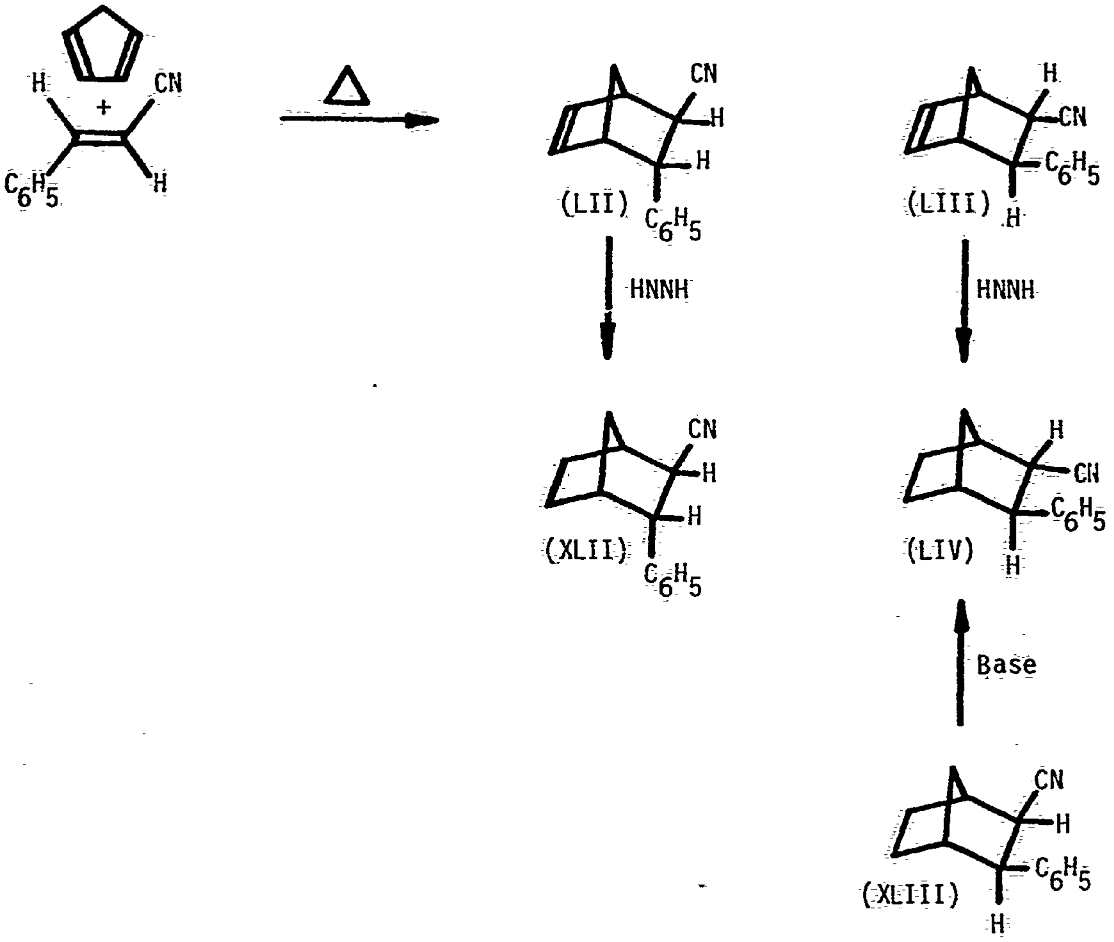
b. Results

The conditions for the photocyanations were similar to those employed in the addition of oxygen centered nucleophiles. In the case of 1,1-diphenylethylene (XX) the reaction was more efficient and the yield of nitrile (XLI) higher, when the 18-crown-6-ether-potassium cyanide complex was used.

The structure of the products of reaction 11 rests on direct comparison of their infrared (ir) spectra with those of authentic samples. The structures and the stereochemistry assigned to the products from reaction 12 were based on an analysis of the ^{1}Hnmr spectrum, in conjunction with the corresponding deuterated products from reaction 13, and were confirmed by independent synthesis as outlined in Scheme IV.

The triplet signal at δ 3.52 of XLII indicated the presence of one exo-proton. Irradiation of a solution of 2-phenyl norbornene (XXVIII) in methanol-O-d and acetonitrile, in the presence of XXIX and

Scheme IV


H
CN
+
C6H5
H
Δ
CN
H
H
(LII)
C6H5
H
CN
C6H5
(LIII)
H
HNNH
HNNH
CN
H
H
(XLII)
C6H5
H
CN
C6H5
(LIV)
H
Base
CN
H
C6H5
(XLIII)
H

potassium cyanide (reaction 13) afforded XLIX which is the corresponding monodeuterated nitrile of XLII and L which is the monodeuterated nitrile of XLIII. (In addition to these products, LI was obtained and identified by comparison with an authentic sample.)[42] The ^{1}Hnmr spectrum of XLIX showed complete loss of the triplet at δ 3.52, which indicates that this triplet is due to H_3. Therefore, the structure of XLII was 2-_exo_-cyano-3-_endo_-phenylnorbornane.

The ^{1}Hnmr spectrum of XLIII displayed a typical ABX multiplet at δ 3.01. This multiplet collapsed to a doublet pair ($J_{2,3}$ = 9 Hz)[25] while H_{7a} was irradiated (δ around 1.53). This indicates that both H_2 and H_3 are coupled to H_{7a} through long-range interaction and is consistent with these two protons being in the _endo_ position. The signal assignment for H_2 and H_3 was consistent with an analysis of the ^{1}Hnmr spectrum of the deuterated nitrile L, which showed a broad singlet at δ 3.0 attributable to H_2 coupled to H_{7a}. This indicates that H_2 is not significantly coupled to H_1 and therefore must be in the _endo_ position. The structure assigned then to XLIII was 2-_exo_-cyano-3-_exo_-phenylnorbornane.

The presence of a double bond in the minor product XLVII was verified by the presence of a weak absorption band in the ir spectrum at 1570 cm^{-1}.[43] The mass spectrum of XLVII showed a peak (m/e 195) assigned to the parent ion. The ^{1}Hnmr spectrum showed no olefinic hydrogens. Therefore, the structure tentatively assigned to XLVII was 2-cyano-3-phenylnorbornene-2. The structures assigned to XLII and XLIII were confirmed by the alternative synthesis outlined in Scheme IV. The spectra (ms, ir, ^{1}Hnmr) of the intermediates LII, LIII and LIV are consistent with the structural assignments and are summarized in detail in the Experimental Section.

An expected minor product which resulted from the competing addition of 2,2,2-trifluoroethoxide anion was XLVIII. Its structure and stereochemistry were established by analysis of its ^{1}Hnmr spectrum in a manner similar to that described for XLII above.

Reaction 14 gave the epimeric nitriles XLIV and XLV and also the epimeric ethers XXXI and XXXII. Both nitriles gave the equilibrium mixture, upon treatment with base. In accord with conformational energy considerations, the trans- (XLV) was slightly favoured (58:42) over the cis- (XLIV).[44] Additional support for the assigned stereochemistry of the nitriles comes from their ^{1}Hnmr spectra. The H α- to the cyano group in cis- (XLIV), being equatorial, is coupled to the axial hydrogens in the 2 and 6 positions, to a lesser extent than is the corresponding axial hydrogen in XLV. Furthermore, the chromatographic behaviour of this isomeric pair is as one would predict on the basis of the observed trend.[24] The nitrile XLIV, having the dipolar cyano group axial, runs faster than nitrile XLV upon elution on a silica gel column.

The identification and the assignment of the stereochemistry of the ethers XXXI and XXXII was based on analogous reasoning and has been discussed already in the first part of this chapter.

The data (fluorescence quenching studies and electrochemical results) pertinent to the identification of the excited state have been summarized in the first part of this chapter (Tables I and II).

c. Discussion

The proposed mechanism for the photosensitized (electron transfer) cyanation is similar to that proposed for the photosensitized (electron transfer) addition of oxygen centered nucleophiles to phenylated olefins (see part A of this chapter, Scheme II). The first two steps are identical.

Step 3 in the proposed mechanism involves reaction of the radical cation of the olefin (XX, XXVIII, XXVII) with the nucleophile (CN^-). The advantage of 2,2,2-trifluoroethanol as a solvent of low intrinsic nucleophilicity,[33a,b] good ionizing ability[45] and acceptably low acidity[46] ($pK_{a_{H_2O}}$ = 12.37), which can also serve as a proton source later on in the reaction, is evident upon comparing the yields of nitriles, XLII (LI) and XLIII (L) versus that of the ethers XLVIII and LI. The low acidity permits the dissociation of hydrogen cyanide ($pK_{a_{H_2O}}$ = 9.1) and also prevents possible protonation of the olefins to give the Markovnikov products via a ground state reaction. We have tried to increase the concentration of cyanide ion in solution by the use of 18-crown-6-ether;[38b] this resulted in higher yields of nitriles for reaction 11 but lower yields and longer irradiation times for reactions 12 and 14. The inability to improve the reaction generally with 18-crown-6-ether probably results from the rapid development of coloured side products which prevent the further efficient irradiation of the solution. It has been shown that the 18-crown-6-ether (and other polycyclic ethers) undergo transformations when irradiated without potassium cyanide in the presence of aromatic hydrocarbons.[38b] The approach of the nucleophile during this step is to the less hindered side and formation of the more stable radical requires the addition in the <u>anti</u>-Markovnikov orientation.

An alternative mechanism can be considered for this step.

This would involve an electron transfer from the cyanide ion to the singlet of the sensitizer with the concomitant formation of cyano radical. Subsequent addition of the cyano radical to the olefin would similarly lead to the formation of the more stable radical. However, fluorescence quenching studies indicated that the fluorescence of XXIX is not quenched by cyanide ion ([KCN] = 10^{-2} M), under conditions similar to those employed for the synthetic work.

In step 4 of the proposed reaction sequence, the radical resulting from the addition of cyanide ion is reduced by the radical anion of the sensitizer to give the corresponding anion. While this type of electron transfer has received some attention, particularly in the reduction of alkyl halides upon treatment with alkali naphthalenes,[34] it is difficult to predict the energy associated with it (see also part A of this chapter, discussion). Nevertheless, considering the lack of any products resulting from coupling of the radicals, and the fact that the sensitizer is largely recovered, the electron transfer involved in step 4 (Scheme II) seems reasonable. As a consequence of this step, the photochemical (electron transfer) addition of cyanide ion (and other potential nucleophiles) takes a completely different course than that of the anodic addition processes commonly occurring[41] by an ECE mechanism and resulting in the oxidative addition of two nucleophilic groups. A further oxidation of the intermediate radical to give a carbonium ion is inconceivable here since the radical is not subjected to the oxidative environment of the anode, and protonation following back electron transfer results in the formation of monoaddition products.

The final step in the reaction sequence (step 5) deserves some attention. It has been observed with the oxygen nucleophiles (this chapter, part A, Ref. 42), that the proton source approaches the norbornyl anion from the less hindered side yielding exclusively the *endo*-phenyl-*exo*-substituted norbornanes, while the ratio of isomers from 1-phenylcyclohexene (XXVII) indicates comparable rates of protonation from either side of the carbanion intermediate. We were intrigued by the fact that among the products of reaction 12, a considerable amount (10%) of 2-*exo*-cyano-3-*exo*-phenylnorbornane (XLIII) was present implying that some *endo*-protonation (i.e., *trans* addition) took place. Control experiments indicated that XLII did not isomerize to XLIII under the basic conditions of the irradiation and XLIII was therefore a primary product. In order to determine the factors responsible for the unexpected formation of this product XLIII, we studied reaction 14. The observed product ratio (*cis*:*trans*, 20:19) indicates no preference for *trans* addition.

Finally, we wish to emphasize the fact that these results greatly enhance the synthetic utility of this type of reaction which previously (Part A of this chapter) was demonstrated only with oxygen centered nucleophiles (water, alcohols and carboxylic acids). With the exception of XLVI products, XLII - LIV are new compounds. Successful attempts to extend further the reaction in other directions (use of olefins in the place of the nucleophiles) are presented in the following chapter (Chapter III).

CHAPTER III

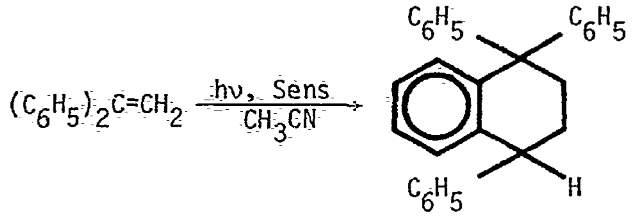
THE PHOTOSENSITIZED (ELECTRON TRANSFER) CROSS CYCLOADDITION OF ALKYLATED OLEFINS TO SOME PHENYLATED OLEFINS

a. Introduction

The traditional photocyloaddition of olefins via direct irradiation or triplet-triplet transfer sensitization has innumerable examples.[47,48] Recently, a new mode of olefin photocyclodimerization via cation radicals has been extensively studied.[12,13,19]

Contrary to the traditional photocycloadditions, which almost exclusively proceed to give the [2+2] cycloaddition products,[49,50] this novel mode of cycloaddition (electron transfer) results, in the case of styrene (XII), substituted styrenes, or 1,1-diphenylethylene (XX) in products derived from what might be considered as a formal [2+4] cycloaddition mode.[13c,d,19]

When Neunteufel and Arnold[19] irradiated a solution of 1,1-diphenylethylene (XX) and methyl p-cyanobenzoate (XXII) in acetonitrile, a good yield (70%) of 1,1,4-triphenyl-1,2,3,4-tetrahydronaphthalene (XXIV) was isolated.



(XX) (XXIV, 70%)

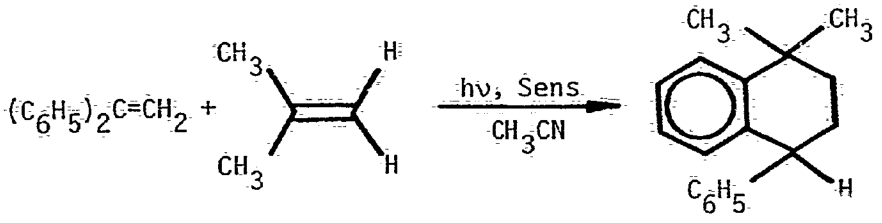
The reaction of styrene derivatives in the presence of 1,2,4,5-tetracyanobenzene[13c] or in the presence of phenanthrene (XVI) and 1,3-dicyanobenzene (XVII)[13d] in acetonitrile proceded similarly to give the corresponding tetrahydronaphthalene derivatives.

There are only a few examples of cross photocycloadditions (cycloaddition of unlike species) involving two unactivated olefins and all of them proceed via a [2+2] cycloaddition mode.[50b,c] This chapter describes the first examples of a formal [2+4] cross cycloaddition involving two unactivated olefins via electron transfer photosensitization. It also describes the results of those preliminary experiments where it was found that, in the case of the 2-phenylnorbornene (XXVIII) - 2-methylpropene (XXXIX) cycloaddition, the same [2+4] cycloaddition product was obtained upon triplet sensitization in significantly lower yields. The latter might be the first triplet sensitized cross cyclodimerization which leads to the formation of a six membered ring ([2+4] cycloaddition).

When 1,1-diphenylethylene (XX) or 2-phenylnorbornene (XXVIII) and 2-methylpropene (XXXIX) were irradiated in acetonitrile solution in the presence of methyl p-cyanobenzoate (XXII) or 1,4-dicyanobenzene (XXI), (electron acceptor sensitizers), (reactions 15 and 16), yields between 12 and 45% of the cross cycloadducts LV and LVI having the tetrahydronaphthalene skeleton were obtained.

When 1,1-diphenylethylene (XX) and 2,3-dimethyl-2-butene (LVII) were irradiated in acetonitrile solution in the presence of 1,4-dicyanobenzene (XXI) (electron acceptor sensitizer), (reaction 17), a yield of 15% of 1,1,2,2-tetramethyl-4-phenyl-1,2,3,4-tetrahydronaphthalene (LVIII) was obtained.

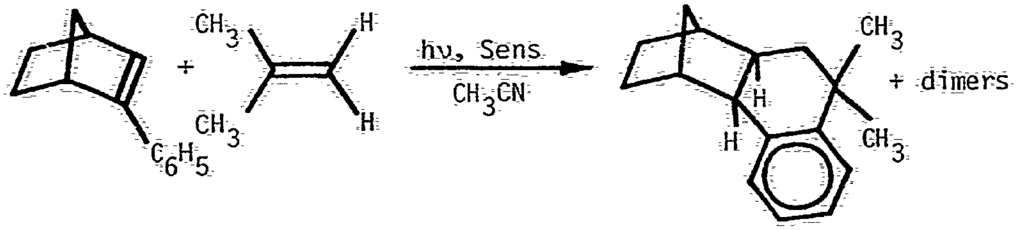
Reaction 15



(XX) (XXXIX) (LV)

Sens	Yield (%)
XXII	12
XXI	24

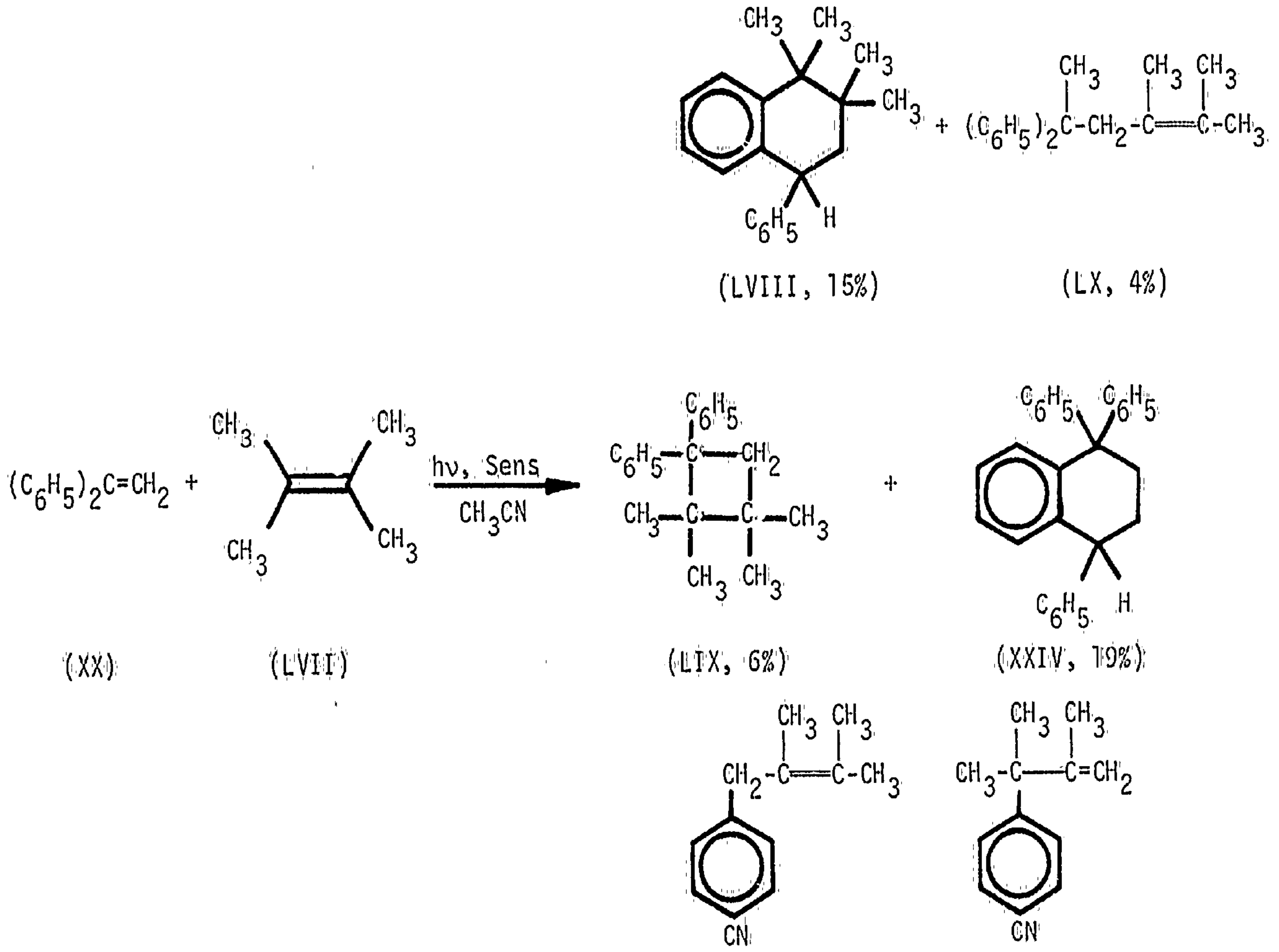
Reaction 16



(XXVIII) (XXXIX) (LVI, 45%) (15%)

Sens. XXII

Reaction 17



(LVIII, 15%) (LX, 4%)

(XX) (LVII) (LIX, 6%) (XXIV, 19%)

(LI, 34%) (LII, 22%)

Sens: XXI

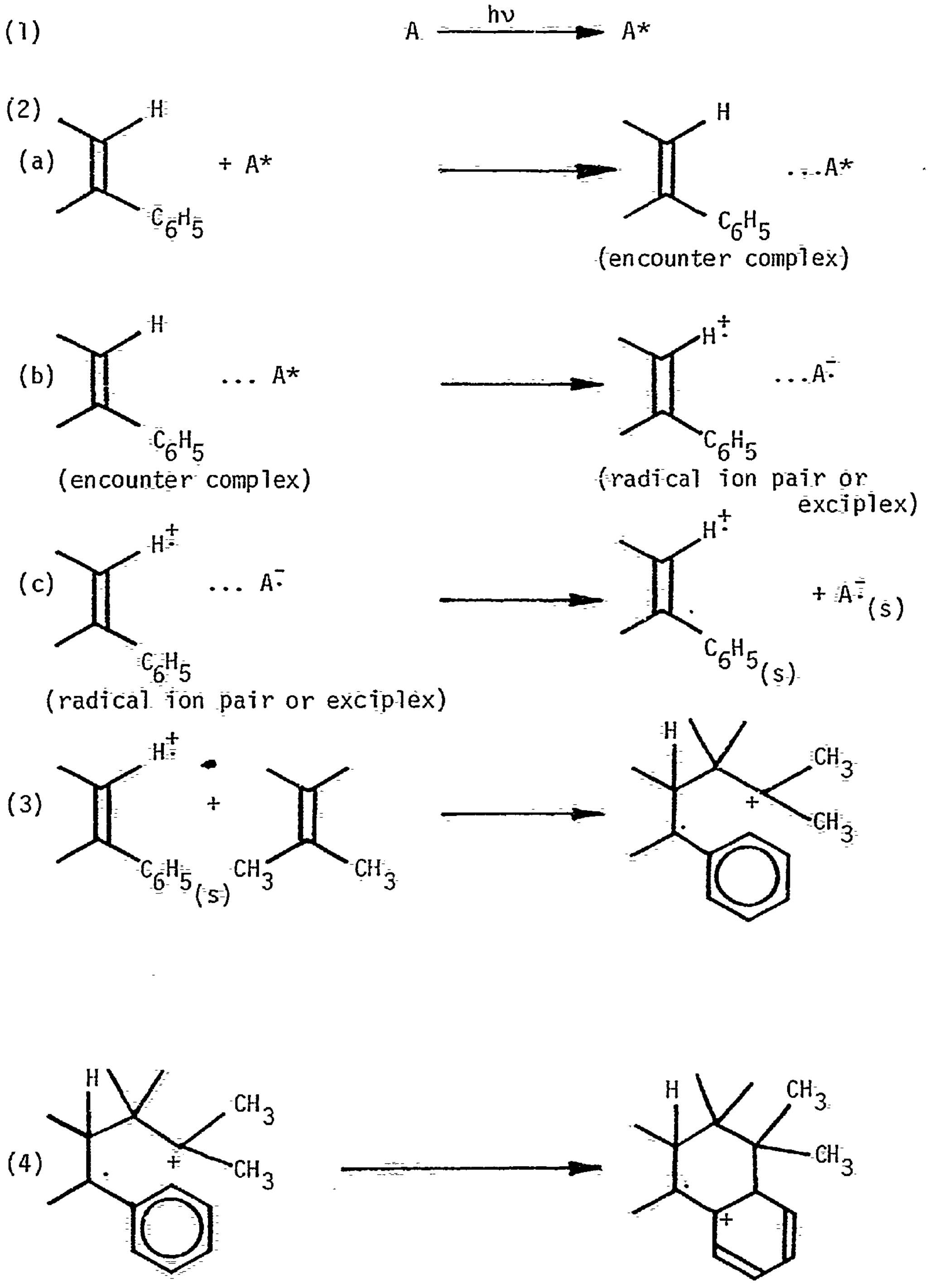
The reaction gave also 1,1,4-triphenyl-1,2,3,4-tetrahydronaphthalene (XXIV), small amounts of the [2+2] product 1,1,2,2-tetramethyl-3,3-diphenylcyclobutane (LIX), 2,3-dimethyl-5,5-diphenyl-2-hexene (LX) and 2.3% of a 4:1 mixture of 2,3,6,7-tetramethylocta-2,6-diene (LXI) and 2,3,3,4,4,5-hexamethyl-1,5-diene (LXII). The sensitizer was largely consumed to give 2,3-dimethyl-1-(4-cyanophenyl)-2-butene (LXIII) and 2,3-dimethyl-3-(4-cyanophenyl)-1-butene (LXIV). The mechanism we propose for the photosensitized (electron transfer) cross cycloaddition of phenylated olefins with alkylated olefins is summarized in Scheme V.

The first step involves the excitation of the sensitizer (A) which is a potential electron acceptor. The next step (step 2), which may occur in several stages, leads ultimately to the solvent separated radical ions. Step 3 involves electrophilic attack by the radical cation on the ground state alkylated olefin. Step 4 is ring closure to form a nonstrained six membered ring and step 5 is back electron transfer from the radical anion of the sensitizer. The last step (step 6) is aromatization via a 1,3 hydrogen shift.

In this chater, we report the characterization of the products from the photosensitized (electron transfer) cross cycloaddition of phenylated olefins to alkylated olefins. We also present the results of the preliminary studies on the triplet-triplet sensitized addition of 2-methylpropene (XXXIX) to 2-phenylnorbornene (XXVIII).

b. Results

Typical conditions for all the photoreactions in this study involve irradiation of a solution of phenylated olefin (0.3 M), alkylated olefin (1.4 M) and sensitizer in acetonitrile through pyrex.


(1)
A
hν
A*
(2)
(a)
H
C6H5
+ A*
H
C6H5
...A*
(encounter complex)
(b)
H
C6H5
... A*
(encounter complex)
H+·
C6H5
...A-·
(radical ion pair or exciplex)
(c)
H+·
C6H5
... A-·
(radical ion pair or exciplex)
H+·
C6H5(s)
+ A-·(s)
(3)
H+·
C6H5(s)
+
CH3
CH3
H
CH3
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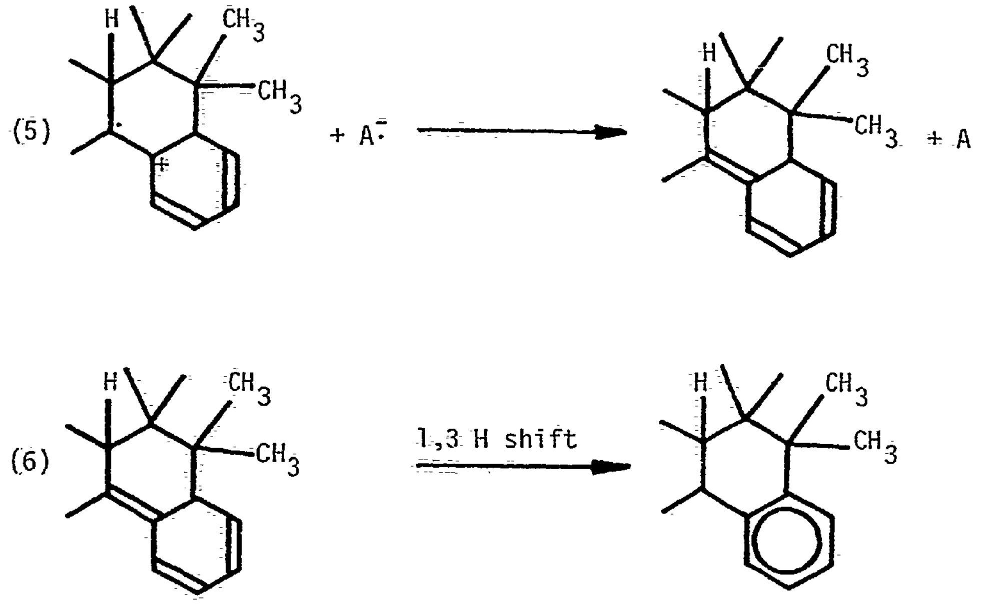
H
CH3
CH3
+



Scheme V. The proposed mechanism for the photosensitized (electron transfer) cross cycloaddition of olefins.

The structures of the products of reactions 15 and 17 rest upon analysis of their spectra (ir, ^{1}Hnmr, ms) and on their elemental analysis. The assignment of the structure of the product from reaction 16 was based in addition to the above (spectra and analysis) on the analysis of its ^{13}Cnmr spectrum.

The triplet signal at 4.13 ppm in the ^{1}Hnmr spectrum of 1,1-dimethyl-4-phenyl-1,2,3,4-tetrahydronaphthalene (LV, reaction 15) collapsed to a singlet when irradiating H_3 (δ 2.40 - ca. 1.8 ppm) it is therefore due to H_4 of LV. The ^{1}Hnmr spectrum of 1,1,2,2-tetramethyl-1,2,3,4-tetrahydronaphthalene (LVIII, reaction 17) exhibited a typical AMX pattern. The H_4 (X part of the AMX system) appeared as pair of doublets at 4.12 ppm. Upon irradiation at the M part of the system (δ 1.66 ppm) it collapsed to a doublet (J_{AX} = 11.5 Hz[51]). When the H_4 was irradiated (X part of the AMX system) the AM part collapsed to a doublet pair (J_{AM} = 12.5 Hz[52]). The structures of the byproducts 1,1,2,2-tetramethyl-3,3-diphenylcyclobutane (LIX) and 2,3-dimethyl-5,5-diphenyl-2-hexene (LX) were consistent with their spectra. 2,3,6,7-Tetramethylocta-2,6-diene (LXI) and 2,3,3,4,4,5-hexamethyl-1,5-diene (XII) were identified on the basis of their reported ^{1}Hnmr spectrum.[53] The major hydrocarbon byproduct of reaction 17, 1,1,4-triphenyl-1,2,3,4-tetrahydronaphthalene (XXIV) was identified by comparison of its ir spectrum with that of an authentic sample prepared as described in reference 19.

The only practical information offerred by the ^{1}Hnmr spectrum with respect to the structure of 1,2,3,4,4aα,9,10,10aα-octahydro-9,9-dimethyl-1β,4β-methanophenantrene (LVI, reaction 16) is the ratio of the integration of the aromatic and the aliphatic hydrogens. Convincing evidence for its structure came from analysis of its ^{13}Cnmr spectrum. The assignment shows clearly six carbons in the region expected for sp^2 hybridized carbon. Two of the sp^2 hybridized carbons were quarternary (147.2 and 138.5 ppm) and the remaining four tertiary (127.8 - 123.4 ppm). The remaining eleven carbons were sp^3 hybridized. The signals at 29.8 and 29.5 ppm were assigned to the c_5 and c_6 nuclei.[54] It was noted that those shieldings were approximately the same as those for the corresponding nuclei of norbornane[54] (29.7 ppm). Since it was known that the presence of endo methyl substituents in the 2 and 3 positions of the norbornane system caused considerable shielding of the c_5 and c_6 shieldings,[54] we concluded that the junction with the norbornane system in the cross cycloadduct (LVI) was exo-exo.

The structures of the photosubstitution products 2,3-dimethyl-1-(4-cyanophenyl)-2-butene (LXIII) and 2,3-dimethyl-3-(4-cyanophenyl)-1-butene (LXIV) were consistent with their spectra.

In order to examine the possible involvement of the triple+ of the phenylated olefins in the photocycloaddition, we attempted to carry out a triplet sensitized reaction using p-methoxy acetophenone (LXV) and xanthone (LXVI) in acetonitrile. The yield of 1,2,3,4,4aα,9,-10,10aα-octahydro-9,9-dimethyl-1β,4β-methonophenanthrene (LVI) was less than 4% under comparable irradiation conditions after equal or larger irradiation times than those for the electron transfer experiments. We have had some success with triplet sensitization in benzene. When 2-phenylnorbornene (XXVIII) and 2-methylpropene (XXXIX), in benzene, were irradiated in the presence of p-methoxy acetophenone (LXV), small yield (8%) of 1,2,3,4,4aα,9,10,10aα-octahydro-9,9-dimethyl-1β,4β-methanophenanthrene (LVI) was obtained.

c. Discussion

The proposed mechanism for the cross photocycloaddition reaction is basically similar to that proposed for the photosensitized (electron transfer) dimerization of 1,1-diphenylethylene (XX).[19] The first step is the excitation of the sensitizer and the second step leads ultimately to the solvent separated radical ions. We calculated the free-energy change (ΔG) associated with the electron transfer process, using Eq. 4. Since we were unable to find the oxidation potentials of the alkylated olefins we used the available[53] ionization potentials to calculate them by the use of Eq. 5.[55]

$$E_{1/2}^{ox} = 0.827\ \mathrm{IP} - 5.40\ \mathrm{V} \qquad (5)$$

The oxidation potentials of the olefins and the reduction potentials of the sensitizers used are summarized in Table IV. The calculated free-energy changes (ΔG) for electron transfer are summarized in Table V.

It can be seen from Table V that electron transfer to the electron acceptor sensitizers is spontaneous for both of the phenylated olefins (XX and XXVIII) and also for 2,3-dimethyl-2-butene (LVII). The significance of this fact is that we are unable to exclude the possibility of formation of the 2,3-dimethyl-2-butene radical cation; consequently, the alternative of having the latter radical cation attacking electrophilically a ground state 1,1-diphenylethylene (XX) molecule must be seriously considered. However, the same mechanism, depicted in Scheme V, can account, with only minor changes, for that portion of the reaction

Table IV. Half-wave oxidation and reduction potentials and ionization potentials.

Compound	IP eV	$E^{red}_{1/2}$[a,b] V	$E^{ox}_{1/2}$[a,b] V
methyl p-cyanobenzoate (XXII)		2.10	
1,4-dicyanobenzene (XXI)		2.00	
1,1-diphenylethylene (XX)			1.48[c]
2-phenylnorbornene (XXVIII)			1.07[c]
2-methylpropene (XXXIX)	9.3[d]		2.3 [e]
2,3-dimethyl-2-butene (LVII)	8.5[d]		1.6 [e]

a. Cyclic voltammetry on Pt electrode, tetraethylammonium perchlorate (TEAP, 0.1 M) in acetonitrile solution, vs Ag/0.1 M $AgNO_3$.

b. Taken as 0.028 V before the anodic peak potential and 0.029 V before the cathodic peak potential (R.S. Nicholson and I. Shain, Anal. Chem., 36, 706 (1964)).

c. The oxidative process was not reversible, the half-wave potential was estimated using the 100 mV/s sweep rate.

d. From reference 53.

e. Obtained from the IP by the use of Eq. 5 ($E^{ox}_{1/2}$ = 0.827 IP - 5.40 V, W.C. Neikam, G.R. Dimeler and M.M. Desmond, J. Electrochem. Soc. 111, 1190 (1964)).

Table V. Calculated ΔG for the electron transfer process using Equation (4).

Sensitizer	Singlet and Triplet Energy kcal mol^{-1}		Calculated ΔG,[a,b] kcal mol^{-1} Singlet (Triplet) XX	XXVIII	XXXIX	LVII
XXII	95.3	72.0[d]	-14.0	-23.5	+4.7	-10.5
			(+8.3)	(-0.17)	(+27.96)	(+12.74)
XXI	97.6	70.1	-18.7	-28.1	0.0	-15.2
			(+8.8)	(-0.6)	(+27.5)	(+12.3)

a. The energy required for the electron transfer process (step 2b), assuming the encounter distance to be 7 Å and the dielectric constant of acetonitrile, $\varepsilon_{25^\circ} = 36.7$.

b. The singlet and the triplet energy of the sensitizer was used. The singlet energies of the olefins were estimated to be higher than those of the sensitizers. The triplet energies of the olefins (XX, XXVIII) while not known, are certainly less than the triplet energies of the sensitizers XXII and XXI and therefore the electron transfer process cannot be more favourable than calculated here. The triplet energies of the olefins XXXIX and LVII are much higher than the triplet energies of the sensitizers and therefore cannot be obtained by triplet-triplet energy transfer.

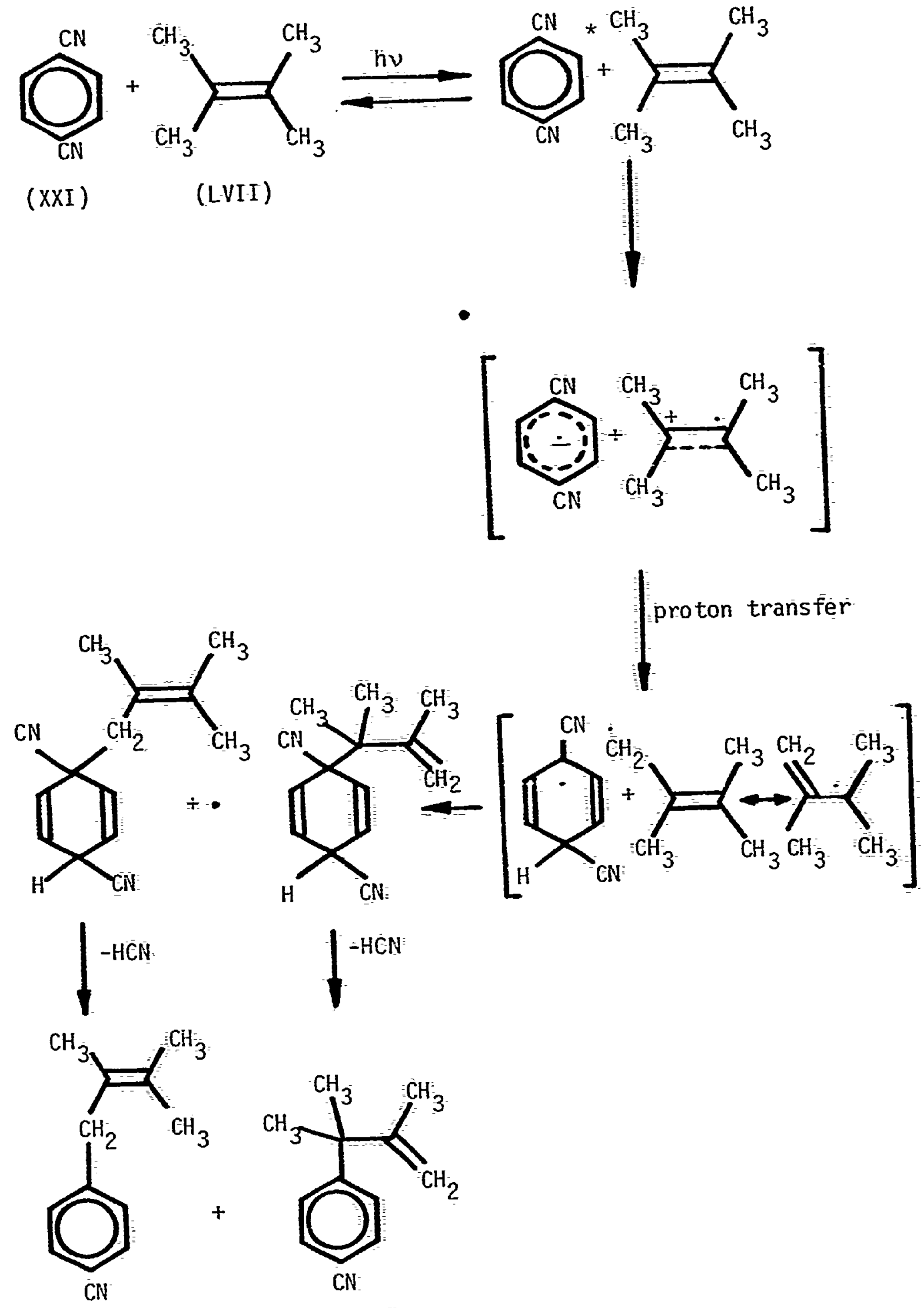
c. D.R. Arnold, J.R. Bolton, G.E. Palmer and K.V. Prabhu, Can. J. Chem., 55, 2728 (1977).

which comes about via the formation of 2,3-dimethyl-2-butene radical cation.

An evidence for the formation of the radical cation of 2,3-dimethyl-2-butene (LVII) in the course of the reaction is the formation of the photosubstitution products. These products are presumably formed by the coupling of the 2,3-dimethyl-2-butene radical cation with the radical anion of the sensitizer after proton transfer and subsequent rearomatization by elimination of hydrogen cyanide, in analogy with known similar cases[56,57] (Scheme VI).

As can be seen from the data in Table V, electron transfer to the triplet of the sensitizers is in all cases but two a non-spontaneous process. Furthermore, separate control experiments showed that triplet-triplet energy transfer from p-methoxyacetophenone (LXV) to 1,1-diphenylethylene (XX) does not lead to the products; upon prolonged irradiation, the olefin remains almost intact. In the case of 2-phenylnorbornene (XXVIII) however, the triplet-triplet sensitization experiments using p-methoxyacetophenone (LXV) and xanthone (LXVI) showed that a small amount (up to 4%) of the [2+4] cross cycloadduct was produced. We feel that the low chemical yield of the triplet reaction in this medium[58] (acetonitrile), in connection with the quenching of the fluorescence of the sensitizers by 2-phenylnorbornene (XXVIII) at the diffusion controlled rate, supports an electron transfer mechanism for the reaction under our conditions.

Step 3 in the proposed mechanism involves electrophilic attack by the radical cation of the phenylated olefin on a ground-state olefin. As expected,[13c,d,19] some of the radical cations attack ground state phenylated olefins with concomitant formation of dimers


CN
CN
CH3
CH3
CH3
CH3
hν
(XXI)
(LVII)
*
proton transfer
-HCN
-HCN
H
CH2
(LXIII)
(LXIV)

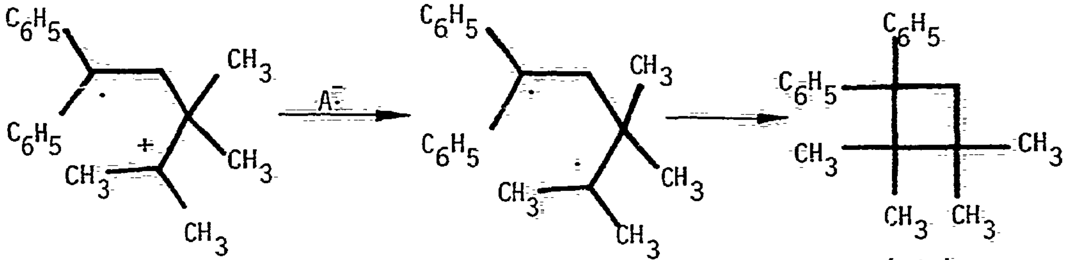
Scheme VI.

as by-products. The possibility of the 2,3-dimethyl-2-butene radical cation attacking a ground state phenylated olefin is in principle possible and could account for part of the reaction.

In step 4, the newly formed radical cation cyclizes to give the more stable six membered ring.

Step 5 is the back electron transfer. During this step, an electron is transferred from the radical anion of the sensitizer to the cyclized (Scheme V) or open chain cation radical (Scheme VII). Back electron transfer to the cyclized radical cation gives the tetrahydronaphthalene-type cross cycloadducts, while back electron transfer to the open chain radical cation gives the cyclobutane adduct.[59] The latter was observed only in the case of 1,1-diphenylethylene (XX) addition to 2,3-dimethyl-2-butene (LVII).

Scheme VII



(LIX)

Step 6 is the rearomatization step. The triene, formed during step 5, can rearomatize via a 1,3 hydrogen shift completing the mechanistic sequence. This 1,3 hydrogen shift can, in principle, be a concerted process; it could proceed suprafacially, if it is induced by light, or antarafacially in a thermal process. Alternatively, it could be an acid catalyzed reaction. We have no evidence for any of the above mechanistic possibilities. The minor product 2,3-dimethyl-5,5-diphenyl-2-hexene (LX, reaction 17) most likely results from the coupling of the two radicals produced by hydrogen atom abstraction by the 1,1-diphenylethylene triplet from 2,3-dimethyl-2-butene (LVII). Hydrogen abstraction by the 1,1-diphenylethylene $\pi \rightarrow \pi^*$ triplet has been previously demonstrated.[60]

CHAPTER IV

THE PHOTOSENSITIZED (ELECTRON TRANSFER) CLEAVAGE OF BETA-PHENETHYL ETHERS

a. Introduction

In Chapter II of this work, we described the photosensitized (electron transfer) addition of alcohols to 1,1-diphenylethylene (XX), reaction 5. This reaction, which yields the ethers (XXV, XXVI, XXX) expected from anti-Markovnikov addition, has been studied in detail; and, when the minor products were isolated and characterized diphenylmethane (LXVII) was found among them. In fact, under some conditions, LXVII was formed in quite significant amounts (> 15%). Diphenylmethane was not an expected product, the mechanism of its formation under these conditions was not obvious, and, since this reaction could represent an important limitation of the synthesis of ethers by reaction 5, we decided to focus attention on it.

We found that diphenylmethane (LXVII) was a secondary photolysis product which results from the photosensitized (electron transfer) decomposition of the initially formed ether (reaction 18). The other product of this reaction was the acetal of formaldehyde (LXVIII). In fact, by either prolonged irradiation starting with the olefin (XX), or by starting with the ether (XXV, XXVI, XXX), yields between 40 - 60% of LXVII and LXVIII can be realized.

Reaction 18

$$(C_6H_5)_2CH\text{-}CH_2\text{-}OR + R'\text{-}OH \xrightarrow[CH_3CN]{h\nu,\ Sens.} (C_6H_5)_2CH_2 + R'\text{-}O\text{-}CH_2\text{-}O\text{-}R$$

(XXV, XXVI, XXX) (LXVII) (LXVIII)

a-$R=R'=CH_3$
b-$R=CH(CH_3)_2$; $R'=CH_3$
c-$R=R'=CH(CH_3)_2$
d-$R=R'=C(CH_3)_3$

Sens: XXII, XXI, 1,4-dicyanonaphthalene (LXIX)
(XXIX was not effective)

The mechanism we propose for reaction 18 is summarized in Scheme VIII. The first step involves excitation of the sensitizer which is potentially an electron acceptor (A). Step 2 may occur in several stages but leads ultimately to the solvent separated radical ions. The ether radical cation cleaves (step 3) in the direction which yields the most stable fragments, in this case the diphenylmethyl radical and the α-oxycarbonium ion. The radical is then reduced to the anion by the radical anion of the sensitizer (step 4) and protonated (step 5). Step 6 represents the reaction of the α-oxycarbonium ion with alcohol present in the solvent, which gives the formaldehyde acetal.

In this chapter, we report the characterization of the products from the photosensitized (electron transfer) cleavage of the ethers (XXV, XXVI) in methyl and isopropyl alcohol; and, the results

1. $$A \xrightarrow{h\nu} A^*$$

2. (a) $$A^* + (C_6H_5)_2CHCH_2OR \rightarrow \underset{\text{encounter complex}}{(C_6H_5)_2CHCH_2OR \ldots A^*}$$

(b) $$\underset{\text{encounter complex}}{(C_6H_5)_2CHCH_2OR \ldots A^*} \rightarrow \underset{\text{radical ion pair or exciplex}}{(C_6H_5)_2CHCH_2OR^{\cdot+} \ldots A^{\cdot-}}$$

(c) $$\underset{\text{radical ion pair or exciplex}}{(C_6H_5)_2CHCH_2OR^{\cdot+} \ldots A^*} \rightarrow (C_6H_5)_2CHCH_2OR^{\cdot+}{}_{(s)} + A^{\cdot-}{}_{(s)}$$

3. $$(C_6H_5)_2CHCH_2OR^{\cdot+}{}_{(s)} \rightarrow [(C_6H_5)_2CH]^{\cdot} + [CH_2OR]^{+}{}_{(s)}$$

4. $$[(C_6H_5)_2CH]^{\cdot} + A^{\cdot-}{}_{(s)} \rightarrow [(C_6H_5)_2CH]^{-}{}_{(s)} + A$$

5. $$[(C_6H_5)_2CH]^{-}{}_{(s)} + H^{+}{}_{(s)} \rightarrow (C_6H_5)_2CH_2$$

6. $$[CH_2OR]^{+}{}_{(s)} + R'OH \rightarrow R'OCH_2OR + H^{+}{}_{(s)}$$

Scheme VIII. The proposed mechanism for the photosensitized (electron transfer) cleavage of β-phenethyl ethers.

of photophysical and electrochemical studies which support the proposed mechanism. We have found sensitizers which are effective in bringing about reaction 5, which will not induce reaction 18 so that secondary photolysis does not necessarily present an important limitation for the preparation of ethers. We point out that these examples of reaction 18 are the first of this type. If this reaction is general, it will have important synthetic applications, particularly since it can be used to remove photochemically a protecting group for the hydroxyl function under mild, neutral conditions.

b. Results

The ethers XXV and XXVI used in this study, were prepared by the photosensitized (electron transfer) addition of methanol and isopropanol to 1,1-diphenylethylene (XX) (reaction 5) (see also chapter II, part A). Sensitizers effective for this reaction are methyl p-cyanobenzoate (XXII), 1,4-dicyanobenzene (XXI), and 1-cyanonaphthalene (XXIX).

Typical conditions for reaction 18 involve irradiation of a solution of ether (0.2 M), alcohol (4.0 M), and the sensitizer (0.12 M) in acetonitrile, through a Pyrex filter. The ultraviolet absorption spectra of the ether XXVI, and the model compound, 1,1-diphenylethane (XLVI, the reasons for choosing this model compound will be discussed later), in acetonitrile solution, are shown in Fig. 6. The absorption and fluorescence emission spectra of the sensitizers XXI and LXIX, also in acetonitrile solution, are shown in Figs. 7 and 8.[61] The involvement of the sensitizer was easily confirmed; upon irradiation

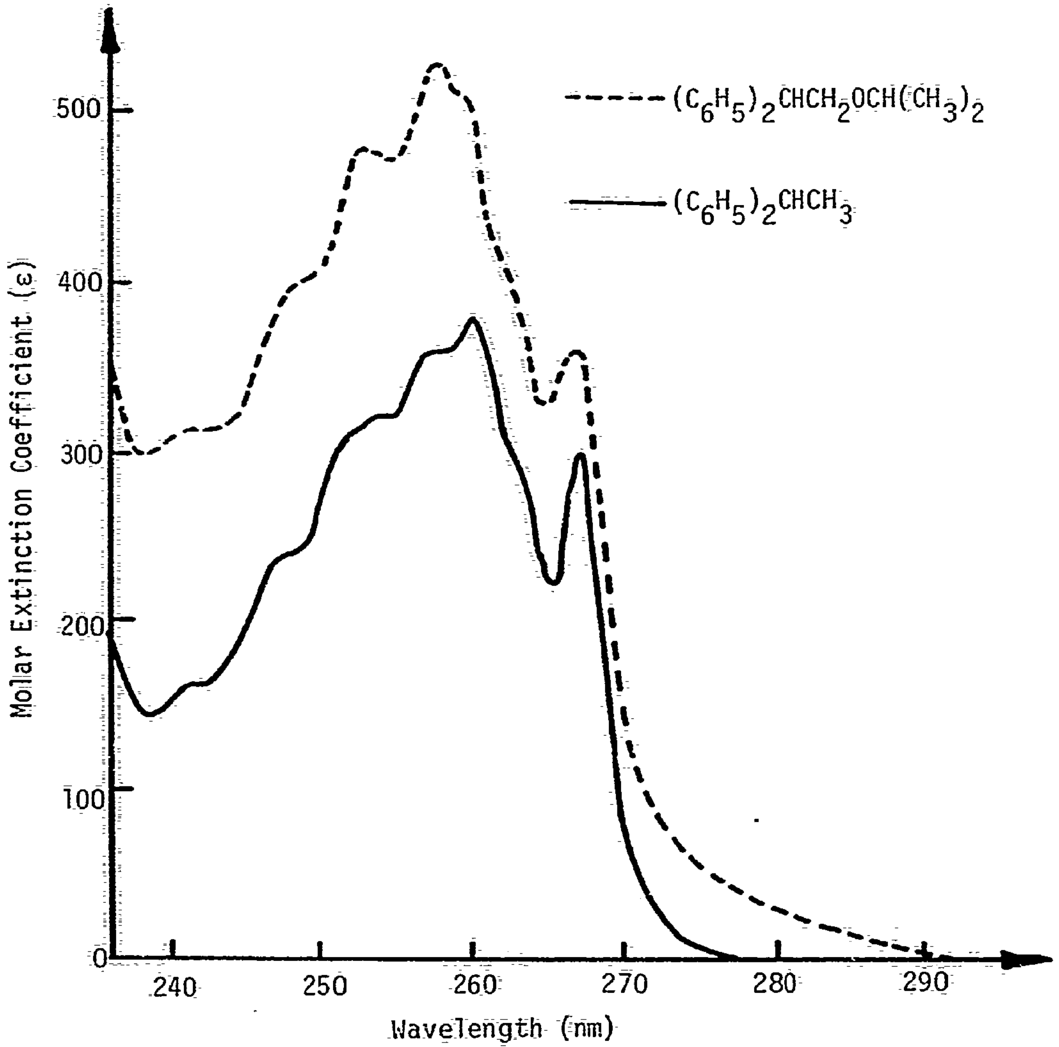


Figure 6. The ultraviolet absorption spectra of 2,2-diphenylethyl isopropyl ether (XXVI, ---), and 1,1-diphenylethane (XLVI, ——) in acetonitrile.

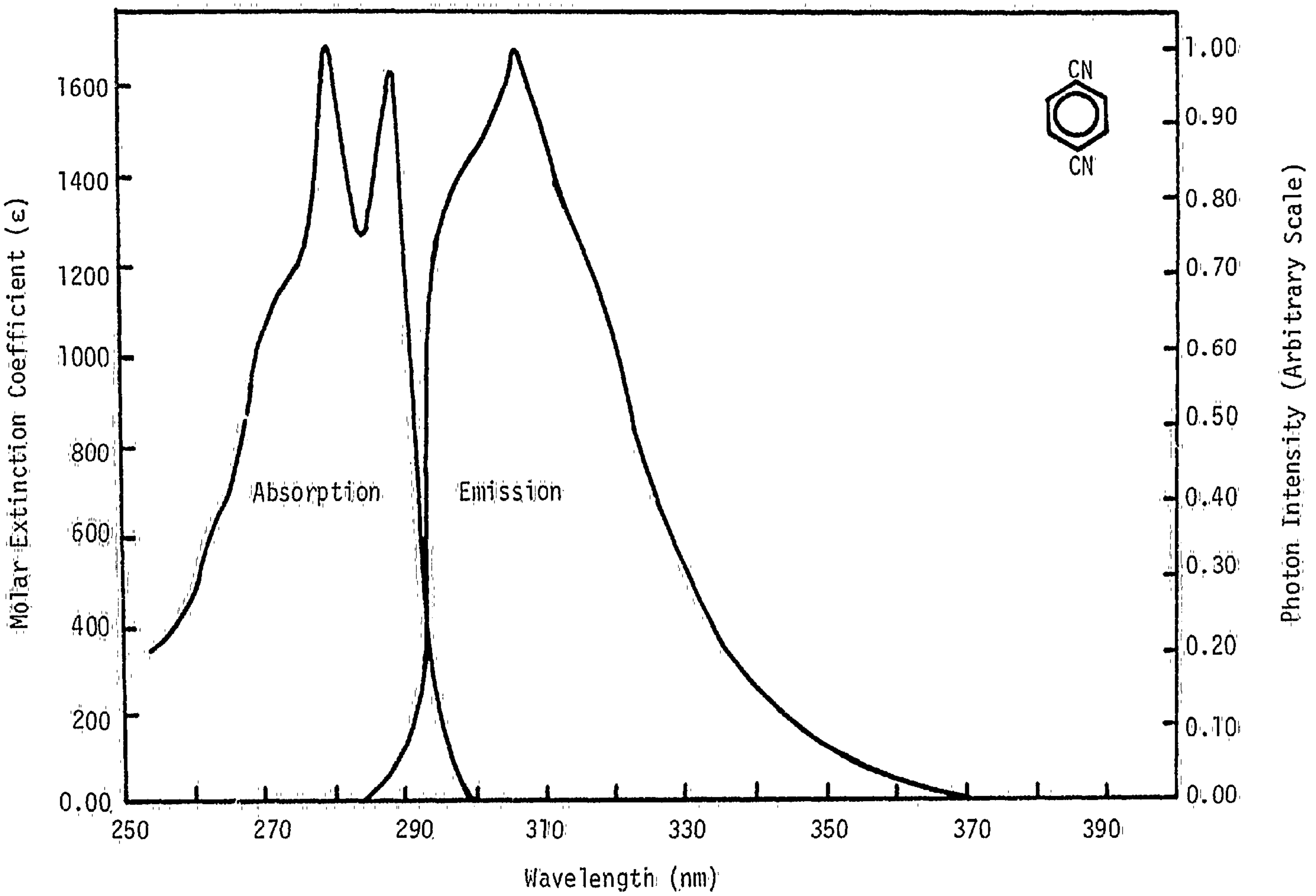
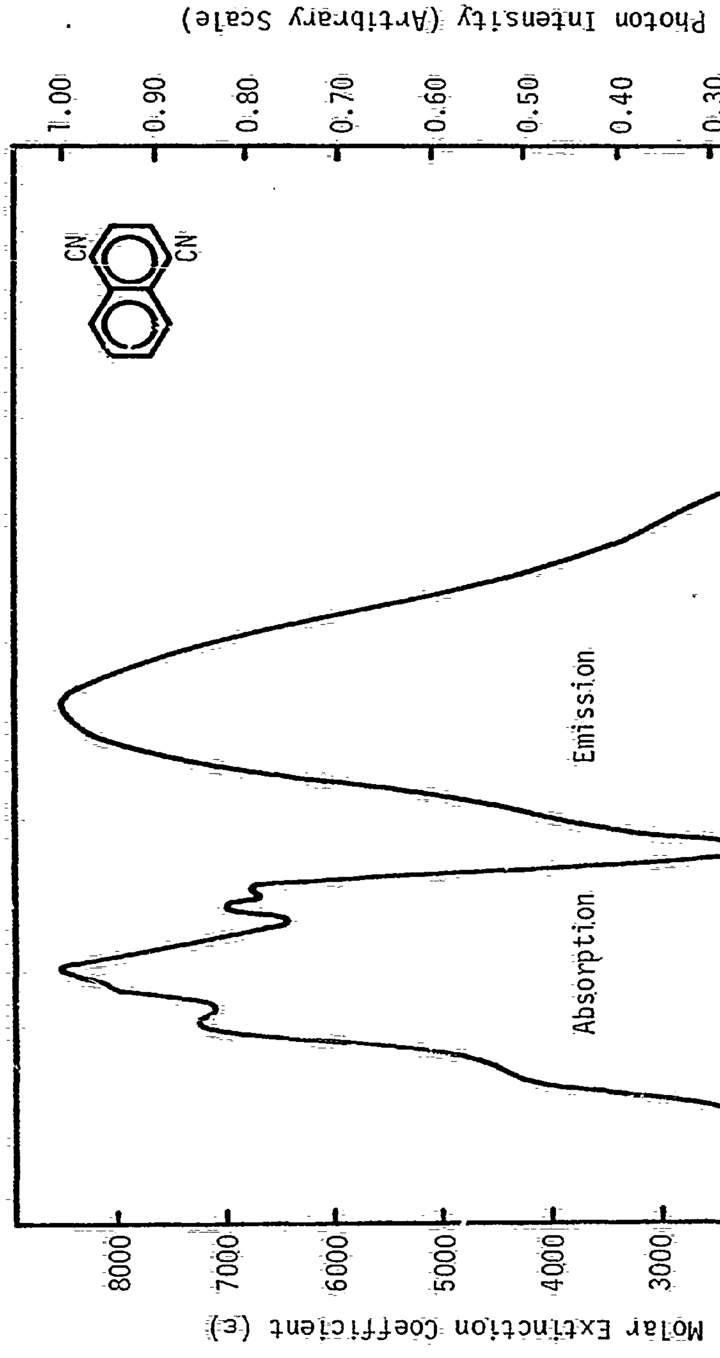


Figure 7. The absorption and fluorescence emission spectra of 1,4-dicyanobenzene (XXI) in acetonitrile.

Figure 8. The absorption and fluorescence emission spectra of 1,4-dicyanonaphthalene (LXIX) in acetonitrile.


Photon Intensity (Artibrary Scale)
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
CN
CN
Emission
Absorption
250
290
330
370
410
450
490
Wavelength (nm)
8000
7000
6000
5000
4000
3000
2000
1000
0.00
Molar Extinction Coefficient (ε)

under identical conditions but in the absence of a sensitizer, no reaction occurred.

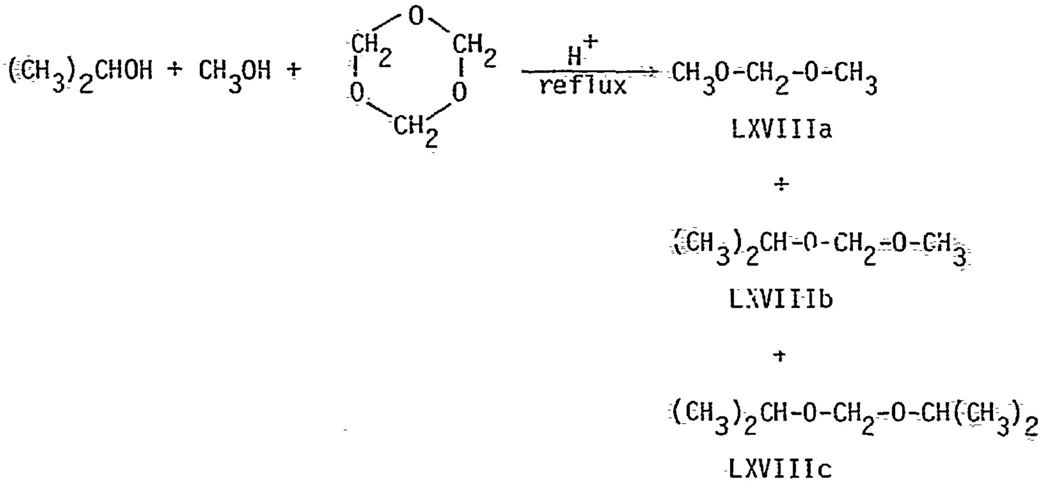
The progress of the reaction was followed by nuclear magnetic resonance spectroscopy (^{1}Hnmr), and/or by vapour phase chromatography (vpc). The pairs of methylene protons in the products LXVII and LXVIII (a and b) and the AB_2 pattern from the coupled protons of the starting ether (XXV and XXVI) can be seen in the reaction mixture. When the starting ether was consumed, the yield of acetal (LXVIII) was determined from the integrated ^{1}Hnmr spectrum after the addition of an internal standard (triphenylmethane). The peak due to the methylene protons of LXVII was too close to those due to the solvent to allow use of this method, so the yield of LXVII was determined by quantitative vpc using the same internal standard.

Diphenylmethane (LXVII) was isolated from the reaction mixture by preparative vpc (10% SE-30 column). The structure was established by comparison of the infrared (ir) spectrum with that of an authentic sample. The acetal LXVIIIb, from the irradiation of XXV in isopropyl alcohol and from the irradiation of XXVI in methyl alcohol, was distilled from the reaction mixture along with the solvent upon bulb-to-bulb distillation at reduced pressure (70 mm Hg). The initial indication of structure came from the ^{1}Hnmr spectrum of this solution. All of the proton signals of the product were superimposable upon those from an authentic sample of LXVIIIb added to the solution. The vpc retention time, on several columns, was also identical with that of the authentic sample. Furthermore, when the distillate from the reaction mixture was added to 2,4-dinitrophenylhydrazine in dilute aqueous sulfuric acid, the hydrazone of formaldehyde (identical ir, undepressed mixed mp) precipitated.

The authentic sample of LXVIIIb, necessary for comparison purposes, was prepared by the acid catalyzed exchange starting with paraformaldehyde, methanol, and isopropyl alcohol (reaction 19). The resulting acetals were separated by distillation and vpc and were characterized by ir and ^{1}Hnmr spectroscopy.

Most of the sensitizer always remained after the ether was consumed; however, in some cases the sensitizer was partially consumed. The products incorporating the sensitizer were not identified.

Reaction 19



As part of our study of the sensitizers effective for reaction 5, we noticed that, while 1-cyanonaphthalene (XXIX) did cause ether formation, no diphenylmethane (LXVII) was detected when this sensitizer was used. In a separate experiment the ether XXV was found to be stable to irradiation using XXIX as a potential sensitizer. Prolonged irradiation did result in some consumption of XXIX but no LXVII was detected.

In an attempt to determine the nature of the excited state responsible for reaction 18, we have studied the fluorescence of the sensitizers (XXI, LXIX and XXIX)[61] as a function of the ether (XXVI) concentration in acetonitrile solution. The fluorescence intensity of LXIX and XXI decreased upon addition of the ether XXVI. In contrast, the fluorescence intensity of XXIX was not affected by added XXVI. These results are illustrated with Stern-Volmer plots shown in Figs. 9, 10 and 11. The quenching rate constants, gleaned from these plots, and the measured fluorescence lifetime in the absence of quencher (τ), are summarized in Table VI.

The calculated diffusion limited rate constant for acetonitrile solution at 20° is kq (diffusion) = $1.8 \times 10^{10}\ M^{-1}sec^{-1}$.[26] Therefore, the fluorescence of 1,4-dicyanobenzene is quenched by both XXVI and by XLVI at essentially the diffusion-controlled rate. Since the addition of XXVI (2×10^{-3} M) and XLVI (1×10^{-2} M) did not decrease the fluorescence intensity (experimental error ca. 2%) of 1-cyanonaphthalene, the upper limit of these quenching rate constants has been calculated.

An indication of the energetics of the electron transfer step (step 2) can be obtained from knowledge of the oxidation potential of the ether (XXV, XXVI and XXX) and the reduction potential of the sensitizers. For this reason, we have studied the electro-oxidation and/or reduction processes of these compounds, on a platinum electrode, in acetonitrile solution, by cyclic voltametry. The results are presented in Table XII (experimental). Half-wave oxidation and reduction potentials have been calculated from these data and are summarized in Table VII.

Polarographic data were available in the literature for some

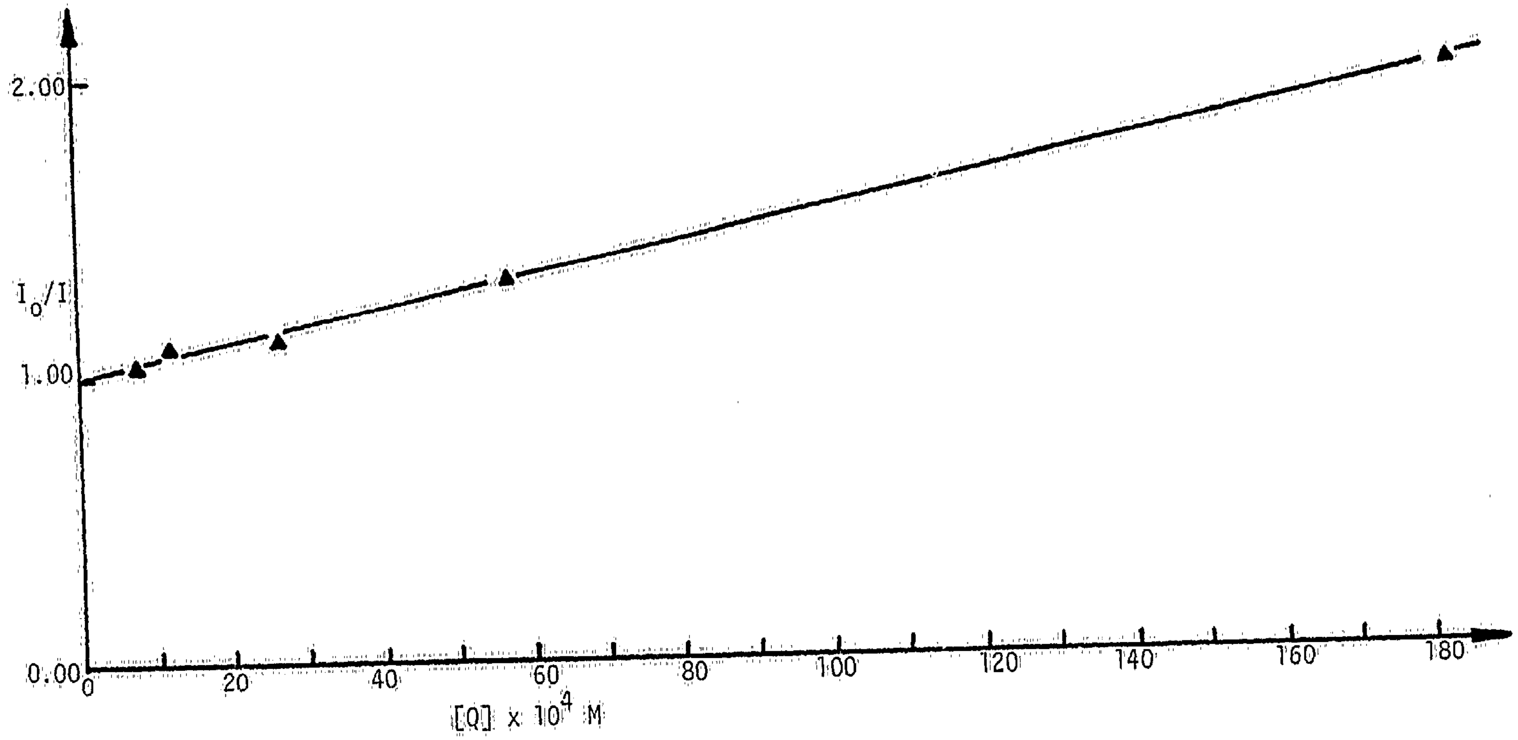


Figure 9. Stern-Volmer plot for the fluorescence quenching of 1,4-dicyanonaphthalene (LXIX) by 2,2-diphenylethyl isopropyl ether (XXVI).

Figure 10. Stern-Volmer plots for the fluorescence quenching of 1,4-dicyanobenzene (XXI) by a) 2,2-diphenylethyl isopropyl ether (XXVI, ▲), b) 1,1-diphenylethane (XLVI, ●).

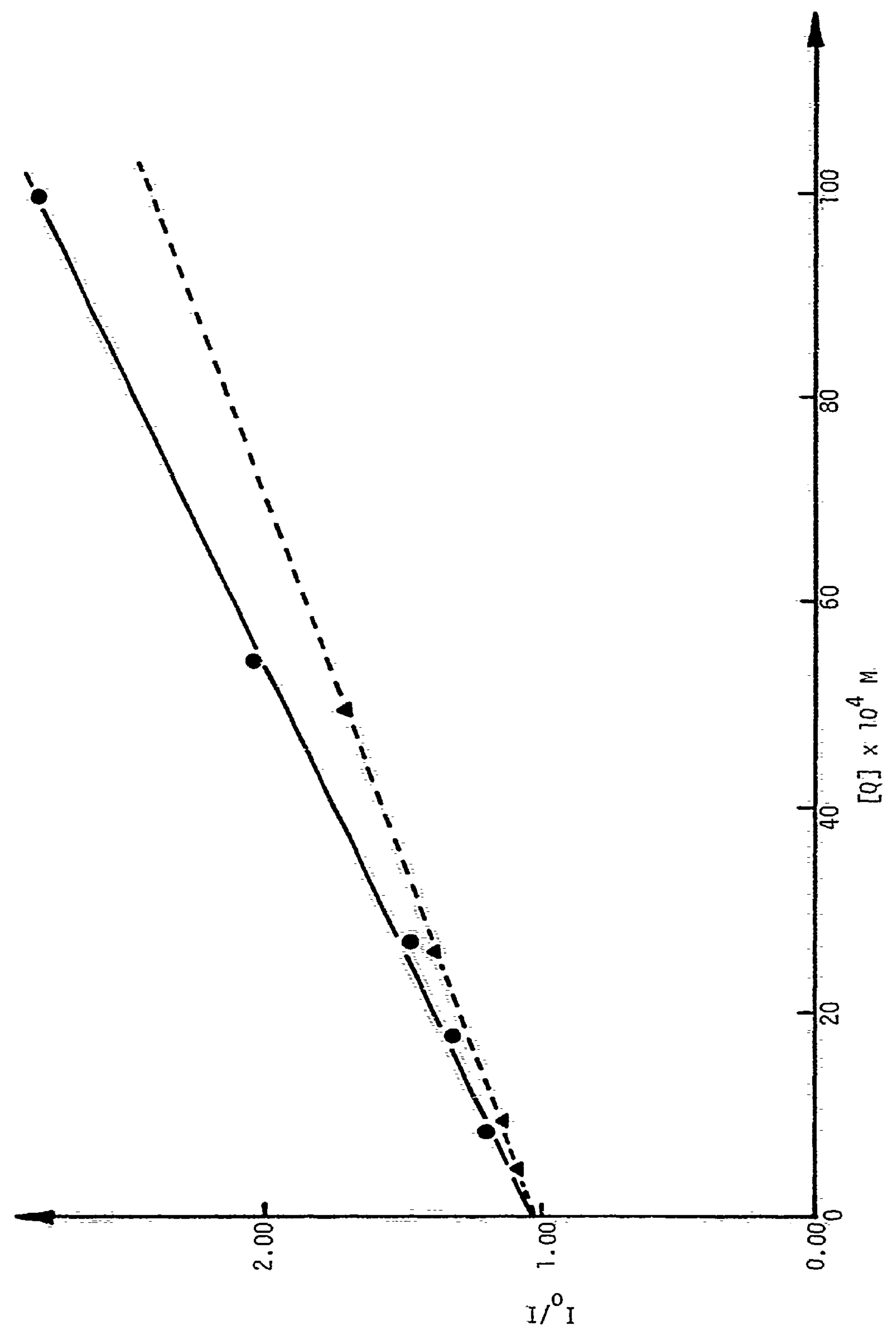

I_0/I
2.00
1.00
0.00
0
20
40
60
80
100
$[Q] \times 10^4$ M

Figure 11. Stern-Volmer plots for the fluorescence quenching of 1-cyanonaphthalene (XXIX) by, a) 2,2-diphenylethyl isopropyl ether (XXVI, ▲), b) 1,1-diphenylethane (XLVI, ●).

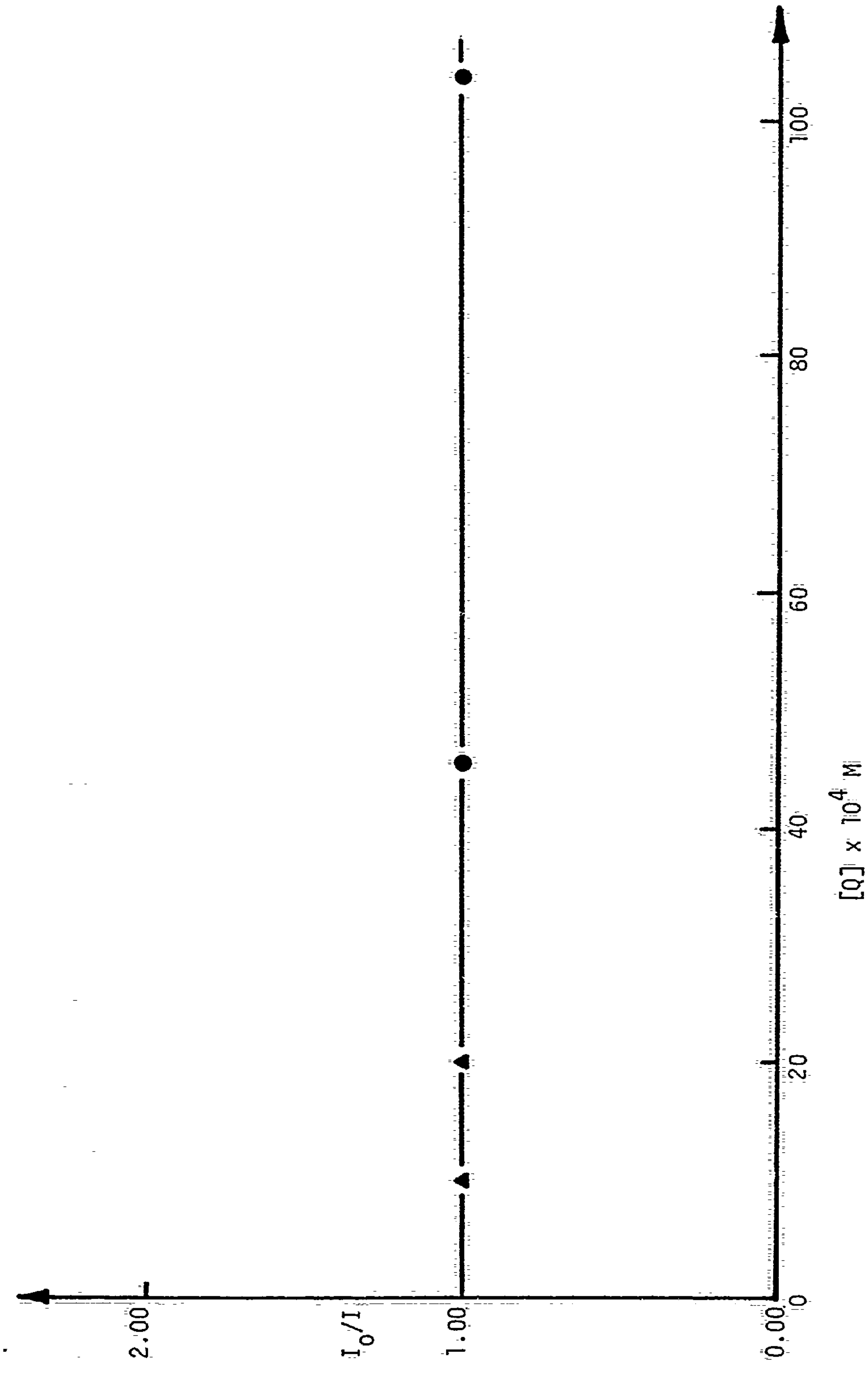

2.00
I_o/I
1.00
0.00
0
20
40
60
80
100
$[Q] \times 10^4$ M

Table VI. Fluorescence quenching of the sensitizers studied by 2,2-diphenylethyl isopropyl ether (XXVI) and 1,1-diphenylethane (XLVI) in acetonitrile solution at 20°.

Fluorophor	Measured Fluorescence Lifetimes τ (nsec)	XXVI k_q(sec^{-1}M^{-1})	XLVI k_q(sec^{-1}M^{-1})
1,4-dicyanobenzene (XXI)	9.7	1.3×10^{10}[a]	1.9×10^{10}[b]
1,4-dicyanonaphthalene (LXIX)	10.1	5.4×10^{9}[c]	-
1-cyanonaphthalene (XXIX)	8.9	$<1.9 \times 10^{9}$[d]	$<1.3 \times 10^{8}$[d]

Exciting the fluorophor at: a) 280; b) 289; c) 311; d) 313 nm.

Table VII. Half-wave oxidation and reduction potentials (Pt electrode, TEAP (0.1 M) in acetonitrile solution, vs. Ag/0.1 M $AgNO_3$).

Compound	$E_{1/2}^{red}$ (V)	$E_{1/2}^{ox}$ (V)
methyl p-cyanobenzoate (XXII)	2.10	b
1,4-dicyanobenzene (XXI)	2.00	b
1-cyanonaphthalene (XXIX)	2.33	b
1,4-dicyanonaphthalene (LXIX)	1.67	b
2,2-diphenylethyl isopropyl ether (XXVI)	c	1.81[a]
1,1-diphenylethane (XLVI)	c	1.81[a]
1,1-diphenylethylene (XX)	c	1.48[a]

a. The oxidative process was not reversible, the half-wave potential was estimated using the 100 mV/sec sweep rate.

b. In these cases, the oxidation wave was not observed, i.e. > 2.0 V.

c. In these cases, the reduction wave was not observed, i.e. < 2.2 V.

of the compounds studied here; however, since variations can result from differences in solvent, electrode material, electrolyte, reference electrode, etc., the data in Table XII (experimental) were obtained under standardized conditions, so they are internally consistent.

c. Discussion

The first step in the proposed mechanism (Scheme VIII) for reaction 18 involves excitation of the sensitizer (A). The ultraviolet absorption spectra of the ether XXVI and the sensitizers are shown in Figs. 6, 7 and 8. The ultraviolet absorption spectra of mixtures of the ether and sensitizers (XXVI, 1.44×10^{-2} M and XXI, 1.01×10^{-4} M; XXVI, 1.83×10^{-2} M and LXIX, 1.15×10^{-4} M) in acetonitrile, were the composite of the individual spectra; there was no evidence of complex formation between the ground state molecules. Step 2 represents the overall process during which an electron is transferred from the ether molecule to the excited state of the sensitizer. This step is completely analogous to the step 2 of the mechanism involved in the photosensitized (electron transfer) addition of oxygen centered nucleophiles to phenylated olefins, and has been to some extent presented there (Chapter II). We have used Eq. 4 in order to calculate the free-energy change (ΔG) associated with the electron transfer process which occurs within an encounter complex (step 2b).

Half-wave potentials were determined by cyclic voltametry and the singlet energies of the sensitizers were obtained from the fluorescence emission and/or absorption spectra (Figs. 7 and 8). A distinct 0-0 band was observed with 1,4-dicyanonaphthalene (LXIX). The point of intersection of the absorption and emission spectra was taken as the singlet energy of 1,4-dicyanobenzene (XXI). In the case of methyl *p*-cyanobenzoate no fluorescence emission was observed, so the singlet energy was estimated from the onset of the long wavelength absorption band. In Table VIII are listed the singlet energies of the sensitizers and the calculated values of ΔG for the donors XXVI and XLVI, using Eq. 4. The electron transfer process (step 2) is spontaneous when the donor is the isopropyl ether (XXVI) or 1,1-diphenylethane (XLVI) and the sensitizer is 1,4-dicyanobenzene (XXI), methyl *p*-cyanobenzoate (XXII), and 1,4-dicyanonaphthalene (LXIX); and, it is *not* spontaneous when 1-cyanonaphthalene (XXIX) is the sensitizer. This is in complete agreement with the observed ability of these sensitizers to bring about reaction 18. Furthermore, the sensitizer fluorescence quenching results are qualitatively consistent; XXVI and XLVI quench the fluorescence of XXI and LXIX, but do *not* quench the fluorescence of XXIX.

Weller has developed an empirical approach for estimating the fluorescence quenching rate constants if the electron transfer process pertains. This approach, using Eqs. 6 and 7, while not rigorously derived, nevertheless did provide calculated quenching rate constants in agreement with experimental values (within a factor of two) for a large number of donor-acceptor systems having a variation in ΔG between -60 and $+6$ kcal mol^{-1}.[11b]

$$\Delta G^{\neq} = \left[\left(\frac{\Delta G}{2}\right)^2 + \left(\Delta G^{\neq}(0)\right)^2\right]^{1/2} + \frac{\Delta G}{2} \tag{6}$$

$$kq = \frac{20 \times 10^{9}\ M^{-1}\text{sec}^{-1}}{1 + 0.25\left[\exp\left(\frac{\Delta G^{\neq}}{RT}\right) + \exp\left(\frac{\Delta G}{RT}\right)\right]} \tag{7}$$

Table VIII. The comparison of calculated and observed fluorescence quenching rate constants.

Fluorophor	Singlet Energy (kcal mol^{-1})	Calculated $\Delta G^{b,c}$ (kcal mol^{-1}) for XXVI and XLVI	Quenching Rate Constants kq x 10^{-10} Obs (Calcd)^{c,d}		
			XXVI	XLVI	
(XXII)	95.3^{a}	- 6.41	-	-	
(XXI)	97.6	-11.01	1.3	1.9	(1.3)
(XXIX)	89.4	+ 4.80	<0.2	0.0	(0.0)
(LXIX)	86.4	- 7.42	0.5	-	(1.00)

a. Estimated from the absorption spectrum; no fluorescence was observed from XXII.

b. The energy required for the electron transfer process (step 2b) assuming the distance to be 7 Å and the dielectric constant of acetonitrile ($\varepsilon_{25^{\circ}}$ = 36.7).

c. Using Eq. 4, these values are the same for XXVI and XLVI since they have the same oxidation potential.

d. Using Eqs. 6 and 7 (see Ref. 11b).

The activation energy ($\Delta G^{\neq}$) is obtained from Eq. 6. $\Delta G^{\neq}(0)$ represents the activation energy when the electron transfer process is isoenergetic and was determined experimentally ($\Delta G^{\neq}(0) = 2.4$ kcal mole^{-1}, acetonitrile solution).[11b]

We have used Eqs. 6 and 7 to obtain calculated values for the fluorescence quenching process. The agreement with the observed values, summarized in Table VIII, can be taken as <u>prima facia</u> evidence for the electron transfer mechanism (step 2b).

Other methods for calculating fluorescence quenching rate constants, based on ionization potential and electron affinity, have recently been developed.[27,28] It is apparent that factors in addition to oxidation and reduction potential (e.g. steric effects, molecular orbital overlap and symmetry) must be important in some cases. The utility of the approach used here, which emphasizes the electron transfer aspects of the quenching process, may be limited to very polar solvents and to systems where there is a large difference in the oxidation potentials and reduction potentials of the fluorescer and quencher. The difference between the donor XXVI (or XLVI) and acceptor reduction potentials ($ED/D^{+} - EA/A^{-}$) is < 4 V (Table VIII).

1,1-Diphenylethane (XLVI) was chosen as a model compound to determine what part of the ether molecule was important for the electron transfer process (step 2b). This was particularly important in order to gain some idea of the scope of reaction 18; that is, will the reaction occur with aliphatic ethers or possibly with other types of β-phenethyl compounds. The oxidation potential of the ether XXVI is considerably lower than that of aliphatic ethers, which suggests the donor site is largely, if not exclusively, the phenyl rings. Support for this argument comes from the observation that the oxidation potential of XLVI (Table VII) is essentially identical with that of the ether XXVI. The conclusion that the ether oxygen atom in XXVI plays a minor rôle in the photosensitized electron transfer process (step 2) is confirmed by the result that XLVI is able to quench the fluorescence emission of 1,4-dicyanobenzene (XXI) with a rate constant comparable to that of the ether XXVI. Similarly, the fluorescence emission intensity of 1-cyanonaphthalene (XXIX) is not affected by the addition of XLVI. These results lead us to predict that α-cleavage (step 3) of other β-phenethyl compounds will occur.[62]

During step 2 of the proposed mechanism (Scheme VIII) the reaction progresses from an excited state reaction to one of ground state intermediates. When this transition occurs is an interesting and difficult question. In particular, is an excited state complex (exciplex) involved as an intermediate preceding the complete electron transfer? The best way to prove the involvement of an exciplex is to study the emission from it.

We have been unable to detect any emission from an exciplex in the cases studied here in acetonitrile solution. The lack of observable emission is not unexpected in view of the large difference in the donor and acceptor properties of the sensitizers, and the ethers and XLVI, and high dielectric constant of acetonitrile.[11a]

The question of the possible involvement of the sensitizer triplet in reaction 18 is interesting. There is evidence in other systems that triplet excited states are capable of electron transfer processes and triplet exciplex formation.[11a,63] An indication of the ability of the triplet state of the sensitizer to participate in the electron transfer process (step 2) can be obtained by substituting the corresponding sensitizer triplet energy in Eq. 4. The triplet energies of the sensitizers, XXII, XXI, XXIX, were obtained from the phosphorescence emission spectra in ethanol-methanol (4:1) glass at 77° K. In the case of 1,4-dicyanonaphthalene (LXIX) in the mixed alcohol solvent, the phosphorescence emission intensity was too weak to measure with our instrument; strong fluorescence emission was observed. The phosphorescence emission spectrum of LXIX was easily obtained when ethyl iodide was added to the solution (4 parts mixed alcohol solution: 1 part ethyl iodide).[64] The phosphorescence emission spectrum of XXIX was essentially the same shape and was shifted only slightly in the mixed alcohol solution with and without ethyl iodide; therefore, we conclude that the addition of the ethyl iodide has little effect on the triplet energy.

The triplet energies of the sensitizers and the free energy change (ΔG) for the electron transfer process with XXVI, calculated using Eq. 4, are given in Table IX. In all cases, ΔG is significantly positive. Nevertheless, we have made an attempt to triplet sensitize reaction 18, with 1,4-dicyanobenzene (XXI) as the electron transfer sensitizer and XXVI as the donor. The choice of XXI as the electron transfer sensitizer was made upon consideration of its triplet energy (which is well below that of XXVI and yet relatively high) and of the calculated ΔG for the electron transfer process; with XXI this process is nonspontaneous by a relatively small amount ($\Delta G = + 16.5$ kcal mol^{-1}). The choice of a triplet sensitizer to produce the triplet of XXI was more difficult. Some of the characteristics required of the triplet sensitizer are: (1) the triplet energy of the triplet sensitizer must be above that of XXI, i.e., > 70.1 kcal mol^{-1}; (2) the triplet sensitizer must have ultraviolet absorption extending to long enough wavelength to allow exclusive excitation in solutions containing XXI; (3) the triplet sensitizer should have an efficient and rapid intersystem crossing

Table IX. Triplet energies of the sensitizers and calculated ΔG values, using Eq. 4, for the electron transfer process involving the triplet of the sensitizer and XXVI.

Sensitizer (Acceptor)	E_T (kcal mol^{-1})	ΔG (kcal mol^{-1})
1,4-dicyanobenzene (XXI)	70.1[a]	+ 16.5
methyl p-cyanobenzoate (XXII)	72.0[a]	+ 15.7
1-cyanonaphthalene (XXIX)	57.4[a], 57.2[b]	+ 36.8
1,4-dicyanonaphthalene (LXIX)	55.5[b]	+ 23.5

a. ethanol:methanol (4:1) at 77° K.

b. The mixed alcohol solution: ethyl iodide (4:1) at 77° K (I.J. Graham-Bryce and J.M. Corkill, Nature, 186, 965 (1960)).

process; (4) the triplet of the triplet sensitizer should be unreactive; (5) the triplet of the triplet sensitizer should not be self-quenched at the concentrations which will allow exclusive excitation; (6) the oxidation and reduction potentials of the triplet sensitizer must be such as to make it unlikely that competitive electron transfer processes involving it will occur.[65,66]

Acetophenone (LXX), p-methoxyacetophenone (LXV), and p-methylacetophenone (LXXI) satisfy these criteria to varying degrees. The triplet energies of LXX, LXV and LXXI are all above that of XXI (Table X. However, the triplet energies of LXV and LXXI are so close to that of XXI that reversible triplet transfer is probable. This problem is minimized with LXX where the triplet transfer is favoured by ca. 4 kcal mol^{-1}. 2) The carbonyl $n \rightarrow \pi^*$ transition of LXX, LXV and LXXI extends to long enough wavelengths to allow selective excitation in solutions containing XXI. 3) All three ketones have an efficient intersystem crossing process; the quantum yields for phosphorescence are: 0.74 (LXX), 0.68 (LXV) and 0.61 (LXXI) and fluorescence has not been observed.[67] 4) A photochemical reaction, likely to occur with these ketones, is hydrogen atom abstraction, probably from the benzylic position of the ether. The rate constant for hydrogen atom abstraction by the triplet of the ketones will decrease in the order LXX, LXXI, LXV.[67,68] However, even with LXX the rate constant will be ca. 10^6, which is three powers of ten less than the rate constant for exothermic triplet energy transfer.[69] With this large difference in rate constant the concentration of the triplet quencher (in this case XXI) can be adjusted, relative to the potential hydrogen atom donor (ether), so that hydrogen atom abstraction will not be an important competing process. 5) None of these ketones should suffer from self-quenching at the concentrations required to assure exclusive excitation.[66,70] 6) In order to consider competitive electron transfer processes involving the ketones, we require their oxidation and reduction potentials. The reduction potentials for LXX, LXV and LXXI have been reported[71] but the oxidation potentials were not available; in fact, the electrolytic oxidation of ketones has received very little attention.[72] The results of our study, using cyclic voltametry, of LXX, LXV and LXXI are summarized in Table XII (experimental) and the oxidation and reduction potentials obtained from these data are listed in Table X.

The electron transfer process where the ketone excited state (singlet or triplet) acts as the acceptor and XXVI as the donor can easily be ruled out in view of the relatively large magnitude (negative) of the reduction potential of the ketones. For all three ketones, using Eq. 4, we calculate $\Delta G > + 20$ kcal mol^{-1} for this process. Electron transfer where the triplet of XXI accepts an electron from the ground state ketone is not so easily dismissed; particularly with LXV where the oxidation potential is in fact below that of XXVI. The ΔG for this process is + 11.65 kcal mol^{-1} for this case.

The triplet sensitizer experiments were carried out by irradiation of an acetonitrile solution of XXVI (0.2 M), XXI (0.12 M), and the triplet sensitizers LXX, LXV and LXXI (0.62 M) and methanol (4 M), for prolonged periods through a filter solution which allowed excitation of the triplet sensitizer only. No reaction was observed, under these conditions. These results, while complicated by the factors discussed above, are consistent with the prediction based on Eq. 4, that the electron transfer between XXVI and the triplet of XXI will not be

Table X. Characteristics of the triplet sensitizers used.

	E_T (kcal mol^{-1})[a]	$E_{1/2}^{red}$ (V)[b]	$E_{1/2}^{ox}$ (V)[d]	ΔG (kcal mol^{-1})[c]
acetophenone (LXX)	74.1	2.49	2.34	+ 28.7
p-methoxyacetophenone (LXV)	71.7	2.68	1.60	+ 11.6
p-methylacetophenone (LXXI)	72.8	2.60	2.12	+ 23.6

a. Taken from D.R. Arnold, Adv. in Photochem., 6, 301 (1968). The max of the 0-0 band in EtOH:MeOH (4:1) at 77° K.

b. R.O. Loutfy and R.O. Loutfy, Tetrahedron, 29, 2251 (1973). Using a dropping mercury electrode and Ag/AgCl reference electrode. The values given have been converted to Ag/AgNO$_3$. We were unable to observe a reduction wave with the Pt electrode (i.e. $E_{1/2}^{red} < -2.2$ V).

c. Calculated using Eq. 4 and considering the ketone as the donor and the triplet of XXI as the acceptor.

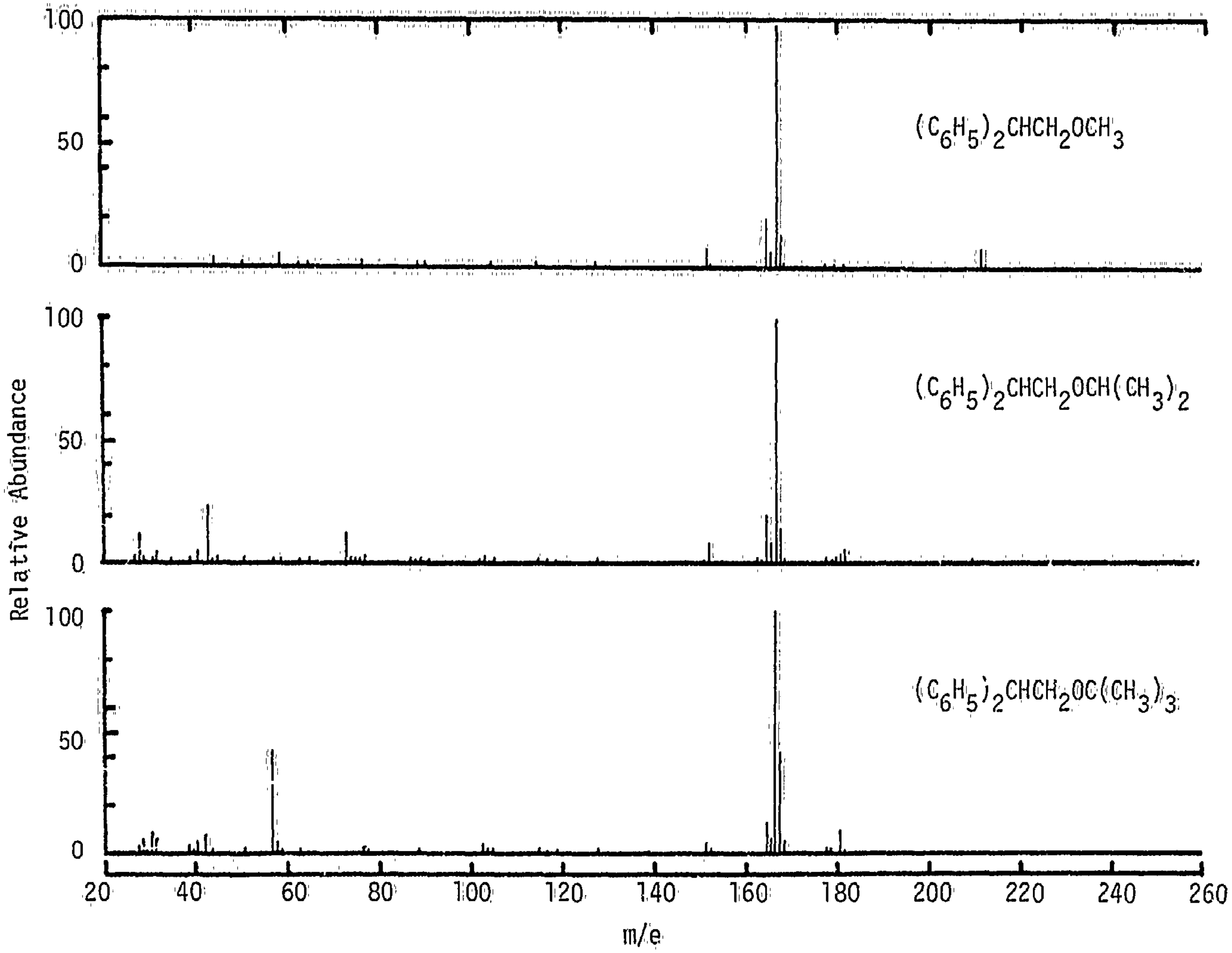
d. The oxidative process was not reversible, the half-wave potential was estimated using the 100 mV/sec sweep rate.

spontaneous.

Before leaving the discussion of the electron transfer process (step 2) we mention that it is at this point that selectivity between reaction 5 and reaction 18 can be obtained. The oxidation potential of 1,1-diphenylethylene (XX) is considerably lower than that of the ether XXVI; 1.48 and 1.81 V respectively (Table VIII . The oxidation potential of XX is low enough so that the electron transfer process, according to Eq. 4, should be spontaneous with 1-cyanonaphthalene (XXIX) as the sensitizer (electron transfer). This calculation is in good agreement with the experimental results; the fluorescence emission of XXIX is quenched by XX, and XXIX is an effective sensitizer for reaction 5. Thus, by taking advantage of the lower oxidation potential of the olefin, relative to the ether, a sensitizer may be chosen which will bring about reaction 5 (*anti*-Markovnikov addition of alcohol) without causing reaction 18 (ether cleavage).

We envision step 3 as a cleavage of the ether radical cation into the more stable fragments; in this case, the diphenylmethyl radical and the α-oxycarbonium ion. This type of fragmentation is commonly observed when the radical cation is produced in the mass spectrometer and accounts for the usual absence of a parent-peak in the mass spectrum of ethers.[73]

The mass spectra of the ethers XXV, XXVI and XXX are shown in Fig. 12. The parent-peaks are not observed. Furthermore, the major fragments, leading to the base peaks, in all three cases are those resulting from the cleavage of the same carbon-carbon bond as that which is involved in step 3; however, the positive charge is associated with the diphenylmethyl fragment. Cleavage of the radical cation to



<u>Figure 12</u>. The mass spectra of the β-diphenylethyl ethers (XXV, XXVI and XXX).

give the diphenylmethyl radical and the α-oxycarbonium ion is not a dominant process in the mass spectra of XXV, XXVI or XXX. In contrast, neither diphenylmethyl methyl ether nor diphenylmethyl isopropyl ether were detected (vpc and ^{1}Hnmr) as products from reaction 18 carried out in the presence of methanol or isopropanol.

The lack of correspondence between these two fragmentation processes, while interesting, is perhaps not surprising in view of the vastly different conditions that prevail. The explanation may be that the more highly delocalized cation (diphenylmethyl carbonium ion) is more stable in the gas phase, but in solution solvation serves to stabilize the more localized α-oxycarbonium ion.

Another fragmentation process of the radical cation in the mass spectrometer is alkyl-oxygen fission. As expected, this process becomes more prominent in the series XXV < XXVI < XXX, which reflects the increasing stability of the carbonium ion. This process apparently does not occur in competition with the cleavage illustrated in step 3. For example, we were unable to detect (^{1}Hnmr and vpc) isopropyl methyl ether (an authentic sample of this ether was prepared in the crude reaction mixture of reaction 18 with XXVI in acetonitrile-methanol solution. We conclude therefore that knowledge of the favoured modes of radical cation fragmentation gleaned from mass spectroscopy will not allow predictions of products upon photochemical generation of the same species in solution.

In step 4 of the proposed reaction sequence, the diphenylmethyl radical is reduced by the radical anion of the sensitizer to give the diphenylmethyl anion. This type of electron transfer process has been discussed in some detail in Chapter II (discussion section).

Step 5 (protonation of the diphenylmethyl anion) and step 6 (the reaction of the α-oxycarbonium ion with alcohol to give the acetal) are, or course, well known reactions.

CHAPTER V

THE PHOTOSENSITIZED (ELECTRON TRANSFER) MARKOVNIKOV ADDITION OF NUCLEOPHILES TO 1,1-DIPHENYLETHYLENE

a. Introduction

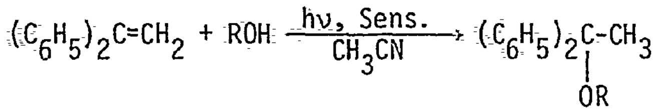
In the previous chapters (II to IV), we have focused our attention on the reactions of radical cations generated by photosensitization (electron transfer). The reason for the extra emphasis which has been placed upon the study of the radical cation lies in the fact that we get, upon addition of nucleophiles, products having the anti-Markovnikov orientation. Naturally, at some later point of our research efforts, we decided to examine the preparation and reactivity of radical anions generated by photosensitization (electron transfer).

Photoaddition of protic solvents to olefinic compounds depends upon the nature of the double bond, the solvent and the sensitizer.[2] When six- and seven-membered cycloalkenes are irradiated directly or in the presence of a triplet sensitizer in an alcoholic (acidic) solution, ethers, arising from the Markovnikov addition of the alcohol to the double bond, are obtained.[16,17] The reaction is thought to involve the twisted triplet olefin or a highly-strained trans ground state of olefin.[16,17] Cyclooctenes, being also able to isomerize to the less strained trans cyclooctenes, upon irradiation, undergo this polar addition with less efficiency.[16a,c,17b,74]

In the acyclic series, 2,3-dimethyl-2-butene (LVII) gave upon direct irradiation in hydroxylic medium, both hydrocarbon and ether products. These results were interpreted in terms of nucleophilic trapping of the Rydberg excited state or the radical cation intermediate.[16b]

We found that when 1,1-diphenylethylene (XX) was irradiated in acetonitrile-alcohol solution in the presence of an electron donating sensitizer such as 1-methoxynaphthalene (LXXII), 1,4-dimethoxynaphthalene (LXXIII), or 1-methylnaphthalene (LXXIV) good yields (between 50 and 90%) of the ethers having the Markovnikov orientation (LXXV and LXXVI) were obtained. (Reaction 20) When 1,1-diphenylethylene (XX) and an electron donor sensitizer were irradiated in acetonitrile-water solution, a good yield (68%) of 1,1-diphenylethyl alcohol (LXXVII) was obtained (reaction 20). Irradiation of 1,1-diphenylethylene (XX) and potassium cyanide in acetonitrile-2,2,2-trifluoroethanol solution with an electron donor sensitizer resulted in 10% yield of the 2,2-diphenylpropanonitrile (LXXVIII) (reaction 21).

Reaction 20



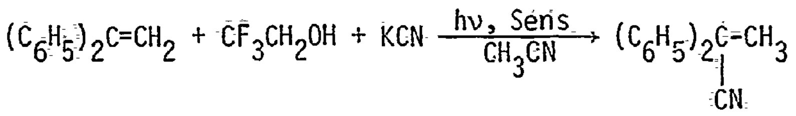
$$(C_6H_5)_2C{=}CH_2 + ROH \xrightarrow[CH_3CN]{h\nu,\ Sens.} (C_6H_5)_2\underset{\displaystyle OR}{\underset{|}{C}}{-}CH_3$$

(XX)

	R	Yield (%)
LXXV	CH_3-	88
LXXVI	CF_3CH_2-	64
LXXVII	H-	68

Sens: 1-methoxynaphthalene (LXXII), 1,4-dimethoxynaphthalene (LXXIII), 1-methylnaphthalene (LXXIV).

Reaction 21



$$(C_6H_5)_2C{=}CH_2 + CF_3CH_2OH + KCN \xrightarrow[CH_3CN]{h\nu,\ Sens} (C_6H_5)_2\underset{CN}{\underset{|}{C}}{-}CH_3$$

(XX) (LXXVIII)

Yield (%)
10

Sens: 1-methoxynaphthalene (LXXII), 1,4-dimethoxynaphthalene (LXXIII).

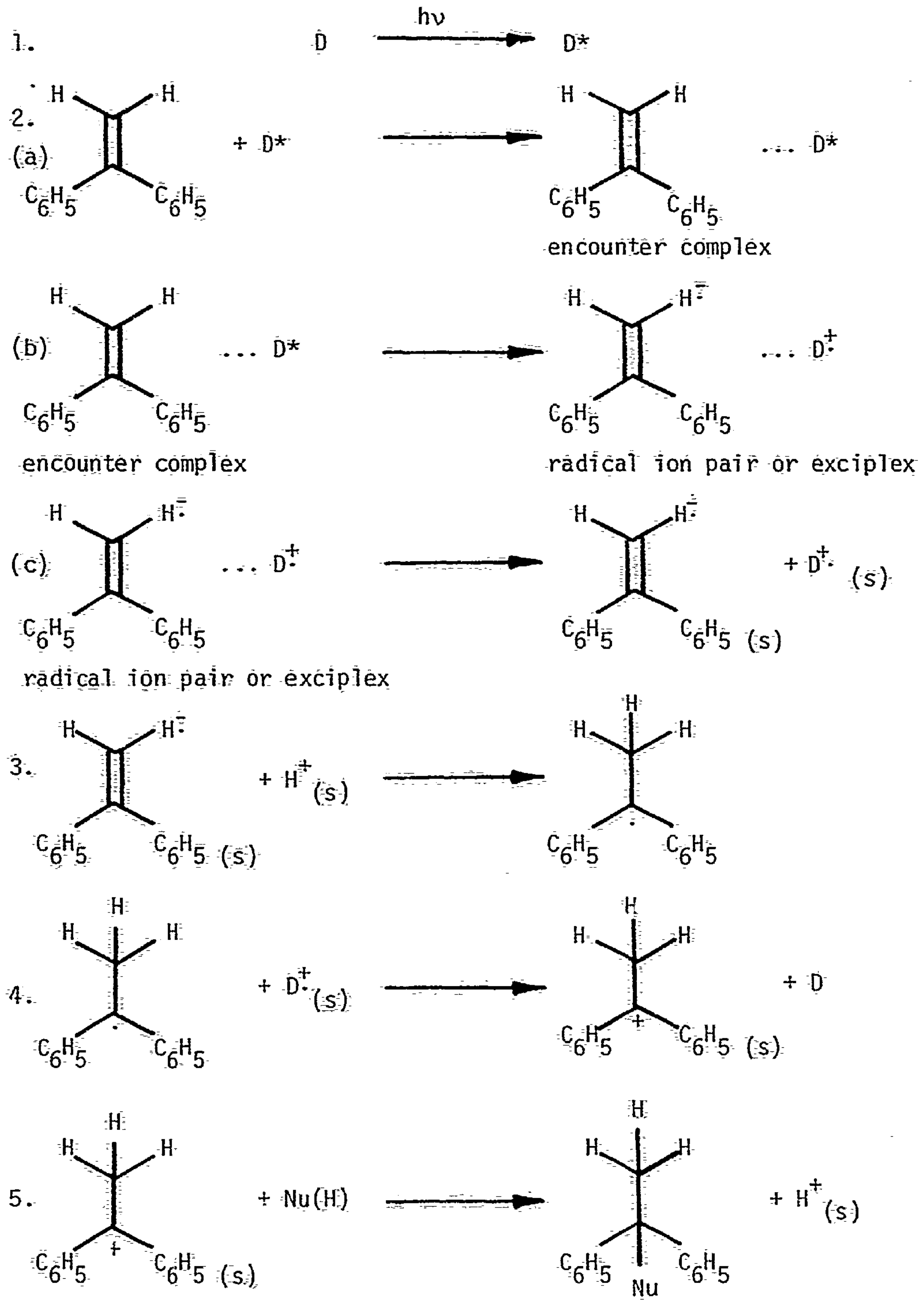
The mechanism we propose for the photosensitized (electron transfer) Markovnikov addition of nucleophiles to 1,1-diphenylethylene (XX) is summarized in Scheme IX.

In this chapter, we report the characterization of the products from the photosensitized (electron transfer) Markovnikov addition of oxygen centered nucleophiles and cyanide ion to 1,1-diphenylethylene (XX) in acetonitrile-alcohol solutions and the results of photophysical studies which support the proposed mechanism (Scheme IX).

b. Results

Typical conditions employed for the photosensitized (electron transfer) Markovnikov-type addition of oxygen nucleophiles to 1,1-diphenylethylene (XX) (reaction 20) involve irradiation of a solution of olefin (0.15 M), sensitizer (0.08 M) and nucleophilic solvent (15 M) in acetonitrile through a Pyrex filter. For the Markovnikov cyanation (reaction 21) a solution of olefin (0.15 M), sensitizer (0.08 M),

<u>Scheme IX</u>. The mechanism proposed for the photosensitized (electron transfer) Markovnikov addition of nucleophiles to 1,1-diphenylethylene (XX).


1.
D
hν
D*
2.
(a)
+ D*
... D*
encounter complex
(b)
... D*
encounter complex
... D+·
radical ion pair or exciplex
(c)
... D+·
radical ion pair or exciplex
+ D+· (s)
(s)
3.
+ H+ (s)
(s)
4.
+ D+· (s)
+ D
(s)
5.
+ Nu(H)
(s)
Nu
+ H+ (s)
H
C6H5

2,2,2-trifluoroethanol (0.15 M) and potassium cyanide (0.3 M) in acetonitrile was irradiated through Pyrex. The absorption and fluorescence emission spectra of the sensitizers (LXXII, LXXIII and LXXIV), are shown in Figs. 13, 14 and 15.

The structure of the products from reaction 20 except for 1,1-diphenyl 2,2,2-trifluoroethyl ether (LXXVI) rests on comparison of their infrared (ir) and nuclear magnetic resonance (^{1}Hnmr) spectra with those of authentic samples. The structure of 1,1-diphenyl 2,2,2-trifluoroethyl ether (LXXVI) was deduced from its spectra and its precise mass.

2,2-Diphenylpropanonitrile (LXXVIII), from reaction 21, was identified by comparison of its infrared (ir) spectrum with that of an authentic sample prepared as described by M. Makosza and B. Serafin.[75]

When reaction 20 was carried out using methanol-O-d, after ca. 50% conversion, analysis of the nuclear magnetic resonance (^{1}Hnmr) and mass spectrum (ms) of the starting material indicated incorporation of deuterium (29% D_1, 1% D_2) in the vinyl position. Deuterium (81% D_1, 13% D_2, 0.1% D_3) was also incorporated in the methyl position of 1,1-diphenylethyl methyl ether (LXXV).

In order to identify the excited state responsible for the reaction, we have studied the fluorescence of the sensitizers as a function of the 1,1-diphenylethylene (XX) concentration. The quenching rate constants obtained from these Stern-Volmer plots (Figs. 16, 17 and 18) and the measured fluorescence lifetimes in the absence of quencher (τ) are summarized in Table X.

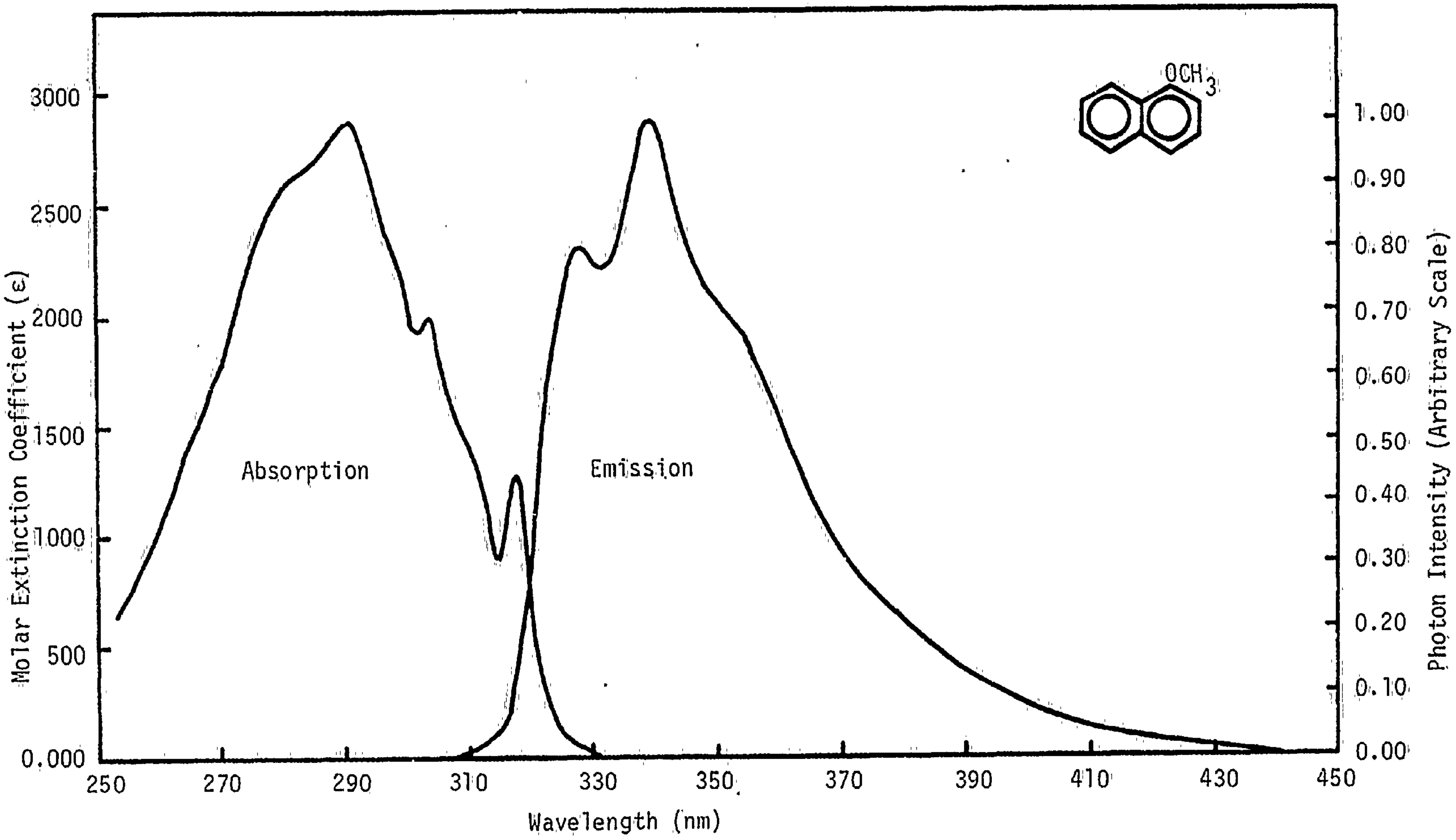
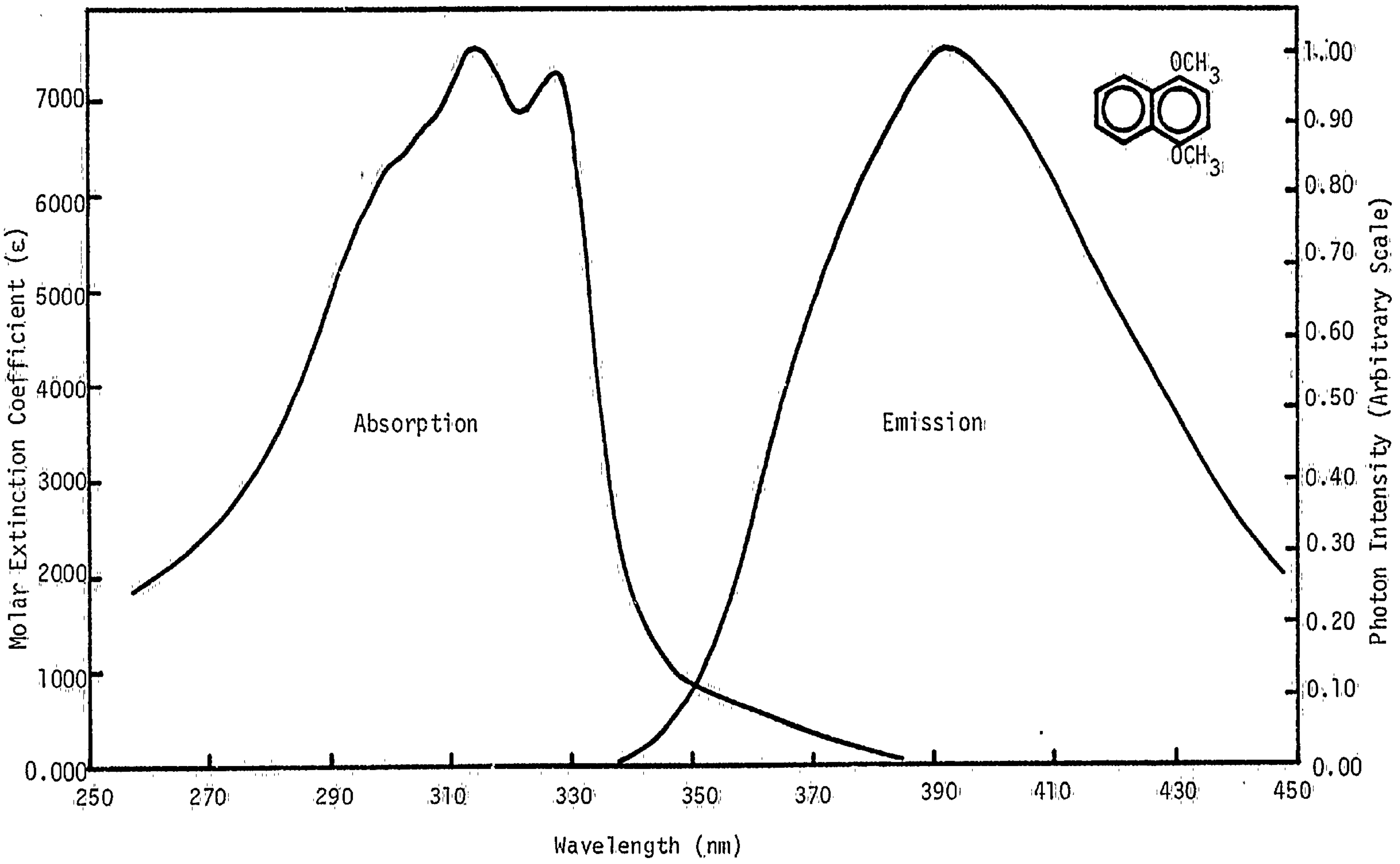


Figure 13. The absorption and fluorescence emission spectra of 1-methoxynaphthalene (LXXII).



<u>Figure 14</u>. The absorption and fluorescence emission spectra of 1,4-dimethoxynaphthalene (LXXIII) in acetonitrile.

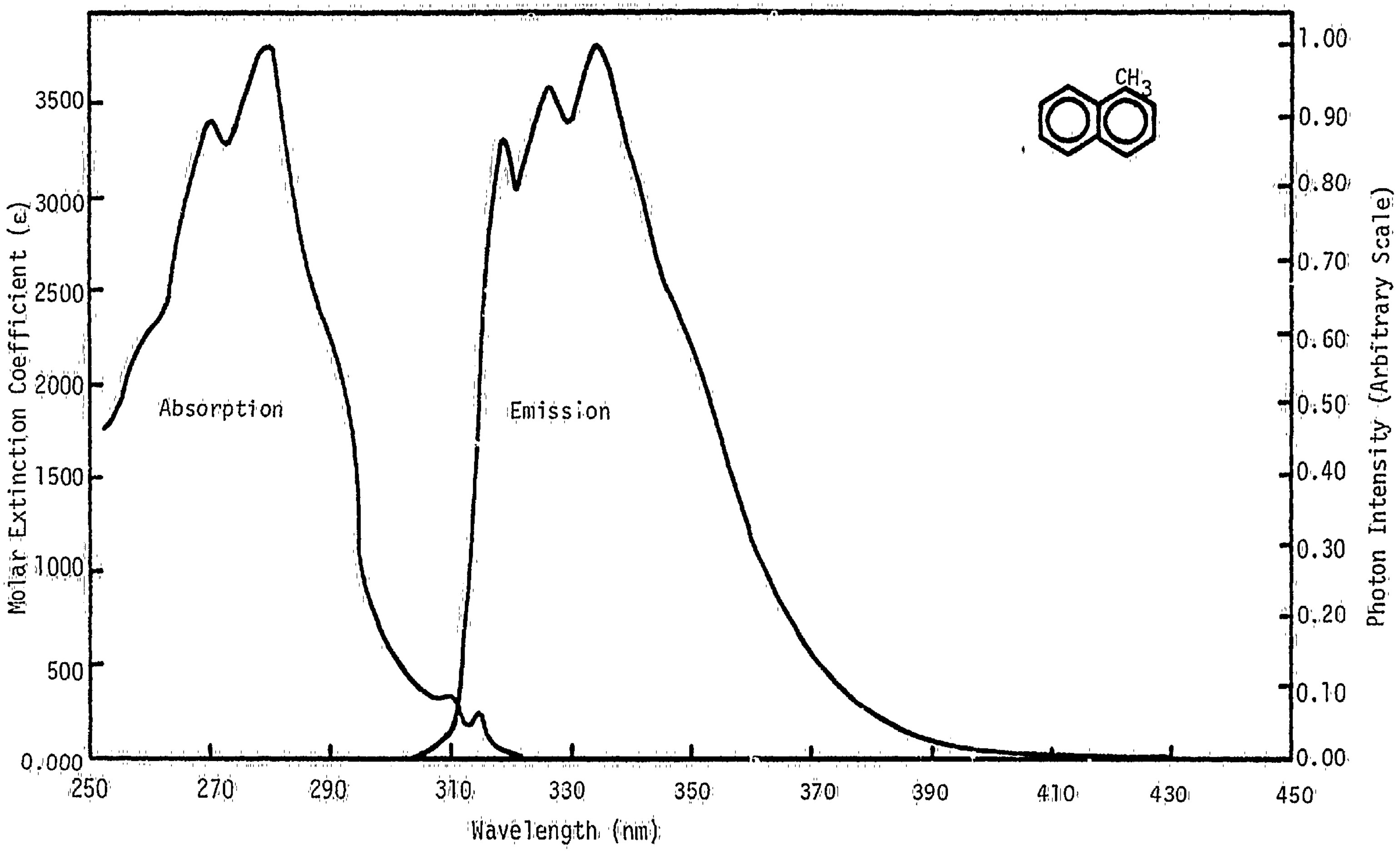


Figure 15. The absorption and fluorescence emission spectra of 1-methylnaphthalene (LXXIV).

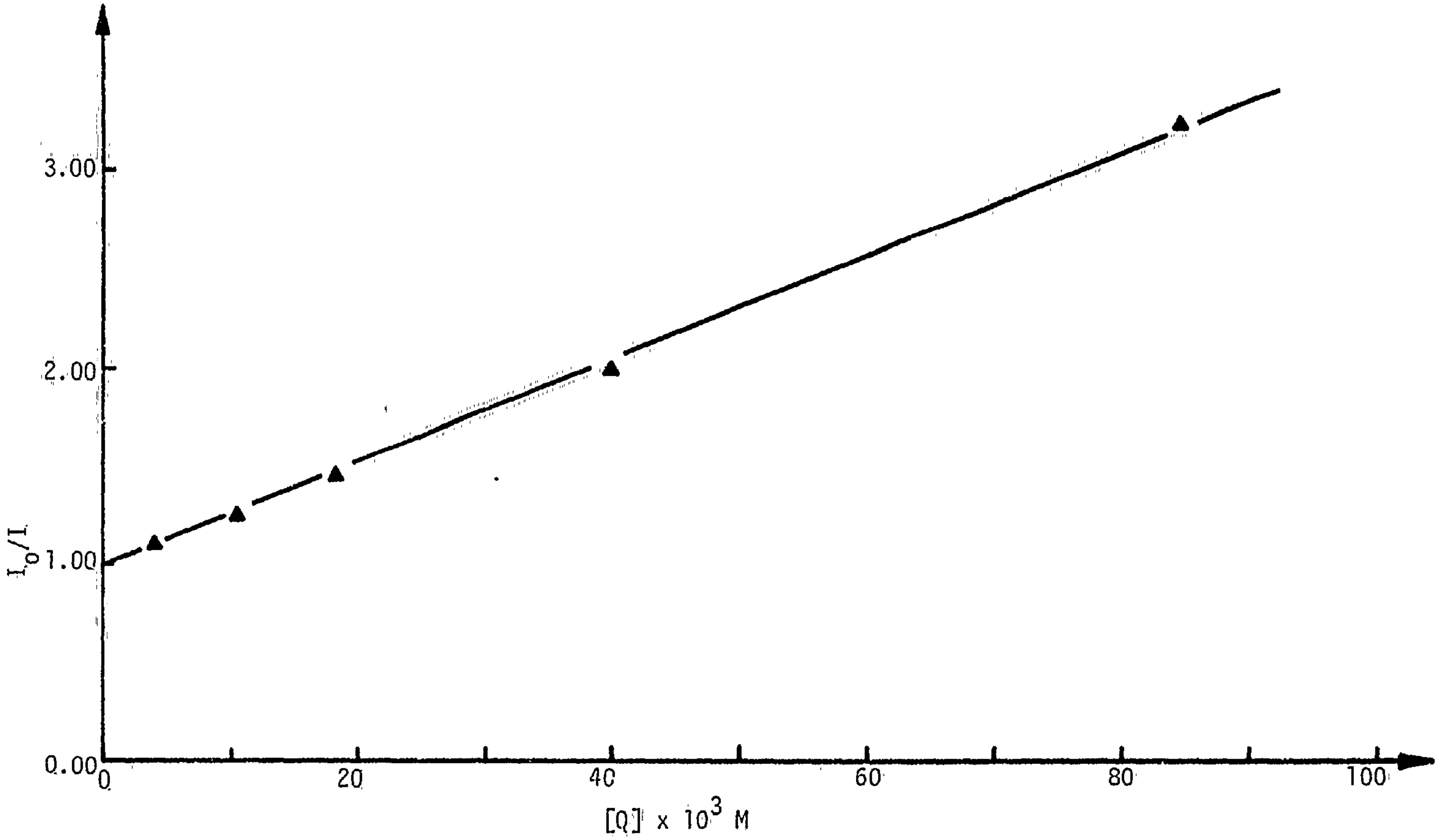


Figure 16. Stern-Volmer plot for the fluorescence quenching of 1-methoxynaphthalene (LXXII) by 1,1-diphenylethylene (XX).

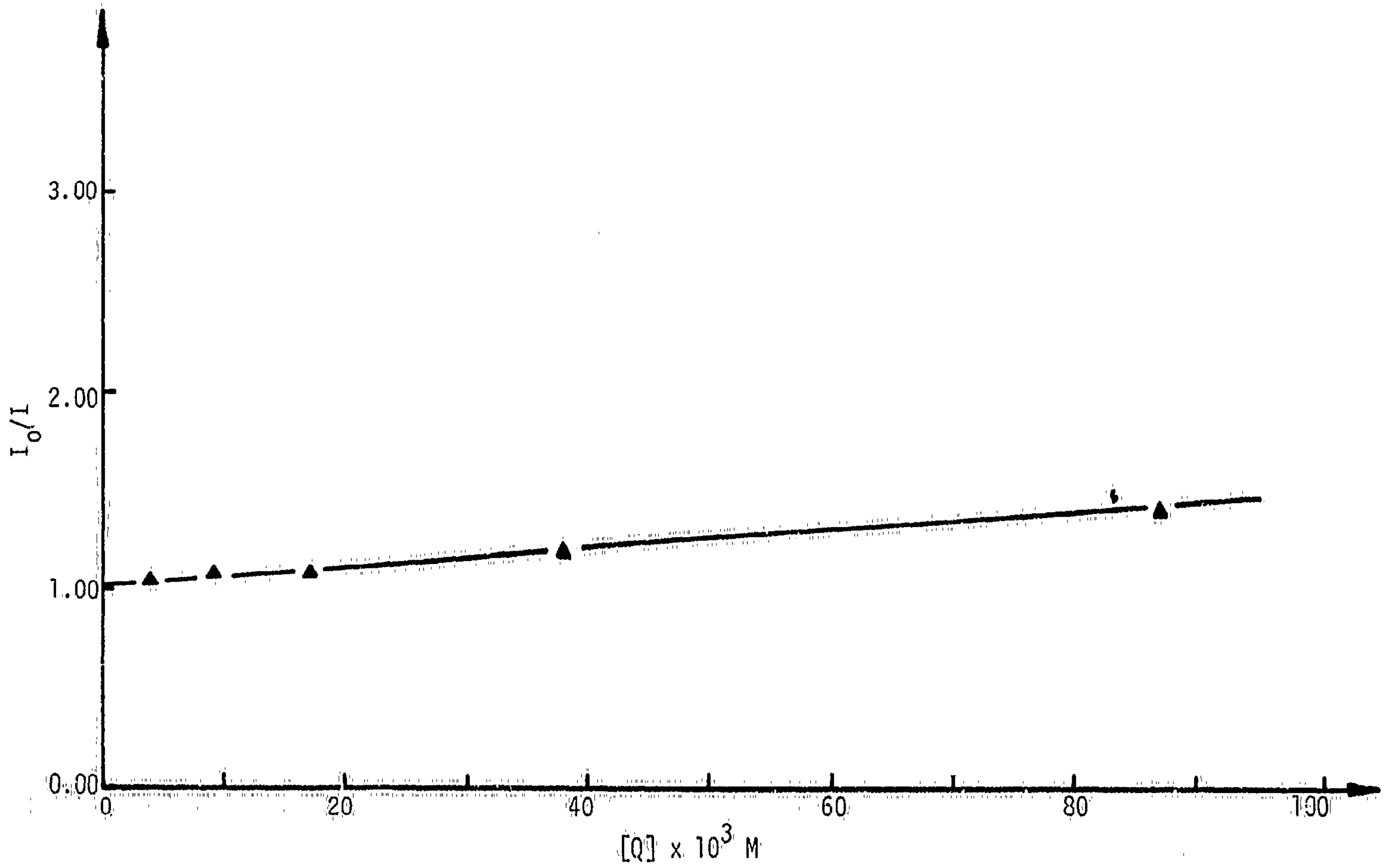


Figure 17. Stern-Volmer plot for the fluorescence quenching of 1,4-dimethoxynaphthalene (LXXIII) by 1,1-diphenylethylene (XX).

Figure 18. Stern-Volmer plot for the fluorescence quenching of 1-methylnaphthalene (LXXIV) by 1,1-diphenylethylene (XX).

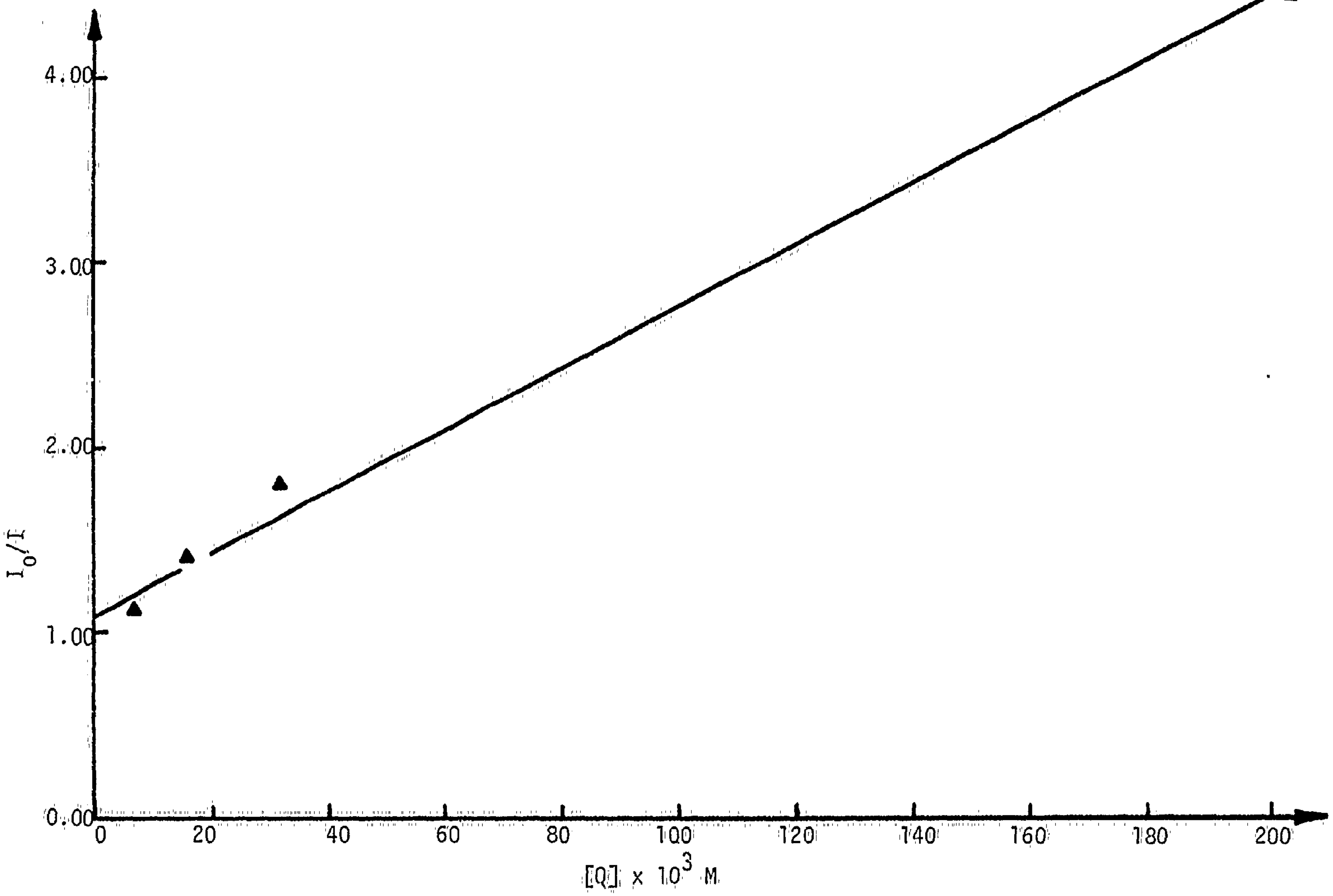

4.00
3.00
2.00
1.00
0.00
I_0/I
0
20
40
60
80
100
120
140
160
180
200
[Q] x 10^3 M

Table XI. Fluorescence quenching of some naphthalene derivatives by 1,1-diphenylethylene (XX) in acetonitrile solution at 20°.

Fluorophor	τ(ns)	Singlet Energy kcal mol^{-1}	k_q M^{-1} s^{-1}	ΔG kcal mole^{-1} (Calc.)[a]
1-cyanonaphthalene (XXIX)	8.9	89.4	1.3×10^{10}	- 2.8[b]
1-methoxynaphthalene (LXXII)	13.5	89.9	2.0×10^{9}	- 6.3[c,d]
1,4-dimethoxynaphthalene (LXXIII)	8.4	81.7	5.0×10^{8}	- 4.6[c,e]
1-methylnaphthalene (LXXIV)	72.3	90.8	1.4×10^{8}	- 6.0[c,f]

a. Using Eq. 4.

b. With XX as the donor.

c. With XX as the acceptor; using the reduction potential ($E_{red}^{1/2}$ = - 2.3 V vs. SCE) reported by P.G. Grodzka and P.J. Elving, J. Electrochem. Soc., 110, 231 (1963).

d. Using the oxidation potential ($E_{ox}^{1/2}$ = 1.38 V vs. SCE) reported by A. Zweig, A.H. Maurer and B.G. Roberts, J. Org. Chem., 32, 1322 (1967).

e. Using the oxidation potential ($E_{ox}^{1/2}$ = 1.10 V vs. SCE) reported by A. Zweig, A.H. Maurer and B.G. Roberts, J. Org. Chem. 32, 1322 (1967).

f. Using the oxidation potential ($E_{ox}^{1/2}$ = 1.43 vs. SCE) reported by E.S. Pysh and N.C. Yang, J. Am. Chem.

Table XI (Continued)

Soc., 85, 2124 (1963).

c. Discussion

The mechanism of the photosensitized (electron transfer) reaction of 1,1-diphenylethylene (XX) with nucleophiles in the presence of an electron donor sensitizer is similar to the mechanism described for those cases where an electron acceptor sensitizer is used. The only significant difference is that the electron transfer steps are reversed.

The first step in the proposed mechanism (Scheme IX) involves excitation of the sensitizer. We had no evidence of charge transfer complex formation between the ground-state molecules. Step 2 is the electron transfer step. It may involve, as in the case of the electron acceptor sensitizers, the sequential formation of an encounter complex, an exciplex, a radical ion pair and finally the solvent-separated radical ions.

An estimate of the free-energy associated with the electron transfer step can be obtained using Eq. 4.

The singlet energies of the sensitizers were obtained from the fluorescence emission spectra (Figs. 13, 14 and 15). 1-Methoxynaphthalene (LXXII) and 1-methylnaphthalene (LXXIV) exhibited a distinct 0-0 band. The point of intersection of the emission and absorption spectra was taken as the singlet energy of 1,4-dimethoxynaphthalene (LXXIII).

Table X includes 1-cyanonaphthalene (XXIX) which is an electron acceptor sensitizer. It is worth noting that the calculated ΔG values are consistent with the observed reactivity toward addition to the olefin (anti-Markovnikov and Markovnikov). 1-Cyanonaphthalene (XXIX) is an effective electron acceptor and Eq. 4 indicates that the electron transfer step should be spontaneous. Indeed, its fluorescence was quenched by 1,1-diphenylethylene (XX) and the anti-Markovnikov addition product was formed upon irradiation with this sensitizer via the 1,1-diphenylethylene radical cation. With 1-methoxynaphthalene (LXXII), 1,4-dimethoxynaphthalene (LXXIII) and 1-methylnaphthalene (LXXIV), Eq. 4 indicates that the electron transfer step should be spontaneous with 1,1-diphenylethylene (XX) as the acceptor. In agreement with this, the fluorescence of 1-methoxynaphthalene (LXXII), 1,4-dimethoxynaphthalene (LXXIII) and 1-methylnaphthalene (LXXIV) was quenched by 1,1-diphenylethylene (XX), and the Markovnikov addition product was obtained with these sensitizers.

The fluorescence quenching rate constants do not correlate with the calculated ΔG values (Table XI), a fact which illustrates the importance of factors other than electron transfer for the fluorescence quenching process.[28a]

The fluorescence quenching studies (summarized in Table XI) are indicative of the involvement of the singlet excited state of the sensitizers (LXXII, LXXIII or LXXIV).

The possibility that the triplet excited state of 1,1-diphenylethylene (XX) is responsible for the observed reaction is ruled out by the observation that 1-benzoylnaphthalene (LXXIX) or benzophenone (LXXX) failed to sensitize the reaction. Besides, the triplet of 1,1-diphenylethylene (XX) is relatively rapidly deactivated by the free-rotor effect.[10]

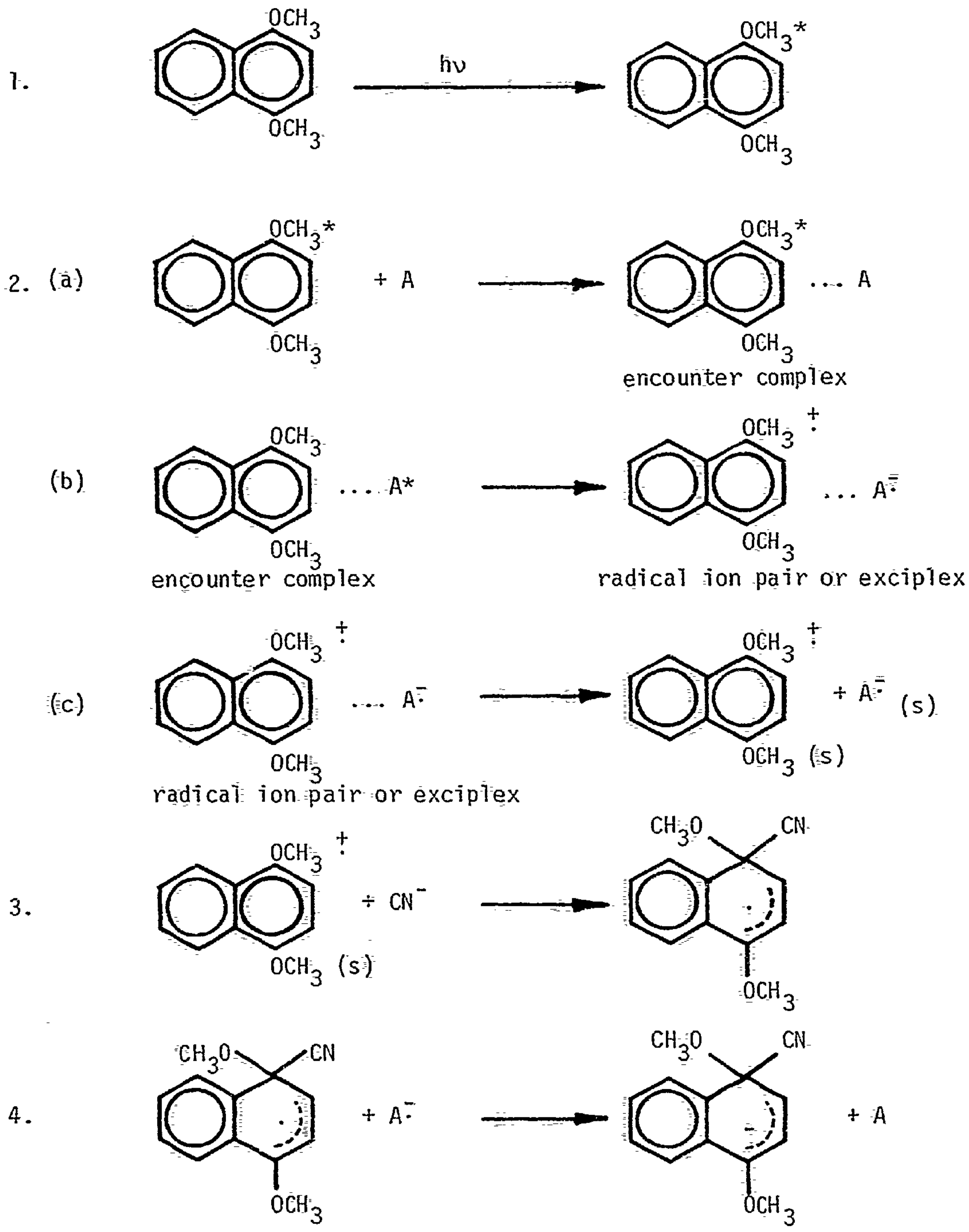
Step 3 is the protonation of the anion radical. It proceeds in such a manner as to give the more stable radical. When methanol-O-d was used as the proton source the product incorporated deuterium in the methyl position (81% D_1, 13% D_2, 0.1% D_3).

Step 4 is the oxidation of the 1,1-diphenylethyl radical by the radical cation of the sensitizer to give the corresponding carbonium ion. Deprotonation of this carbonium ion should be competitive with reaction with nucleophile (step 5) and accounts for the deuterium incorporation in the vinyl position of the starting material.

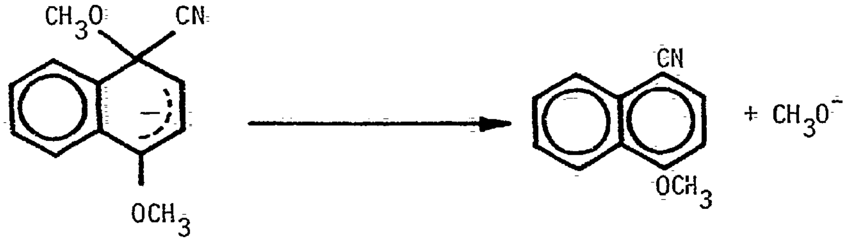
Step 5, the reaction of the 1,1-diphenylethyl carbonium ion with the nucleophile, is a well known reaction. In the case of the cyanation reaction (reaction 21) the virtue of 2,2,2-trifluoroethanol as a non-nucleophilic proton source[33a,b] was evident: a relatively small amount of the 1,1-diphenylethyl 2,2,2-trifluoroethyl ether (LXXVI) was formed, in competition with the nitrile (LXXVIII), upon irradiation of 1,1-diphenylethylene (XX) with either 1-methoxynaphthalene (LXXII) or 1,4-dimethoxynaphthalene (LXXIII). Also, in the cyanation reaction, a major portion of the sensitizers was consumed. When 1,4-dimethoxynaphthalene (LXXIII) was the sensitizer, 1-cyano-4-methoxynaphthalene (LXXXI) was found amongst the products of the reaction. This photochemical nucleophilic substitution is a known process.[38a,76] The mechanism we postulate as occurring under our conditions is depicted in Scheme X.

Steps 1 and 2 are the excitation of the sensitizer and the electron transfer step. They have been discussed earlier. Step 3 is attack of the radical cation of 1,4-dimethoxynaphthalene by cyanide ion and it is analogous to step 3 of the cyanation scheme presented in part B of Chapter II.

Step 4, the back electron transfer, which gives a carbanion next to a methoxy group, should not be a particularly favourable process.


1.
OCH3
OCH3
hν
OCH3*
OCH3
2. (a)
OCH3*
OCH3
+ A
OCH3*
OCH3
.... A
encounter complex
(b)
OCH3
OCH3
.... A*
encounter complex
OCH3 +·
OCH3
... A-·
radical ion pair or exciplex
(c)
OCH3 +·
OCH3
.... A-·
radical ion pair or exciplex
OCH3 +·
OCH3 (s)
+ A-· (s)
3.
OCH3 +·
OCH3 (s)
+ CN-
CH3O
CN
OCH3
4.
CH3O
CN
OCH3
+ A-·
CH3O
CN
OCH3
+ A

5.



Scheme X. The proposed mechanism for the formation of 1-cyano-4-methoxynaphthalene (LXXXI).

The inefficiency of this step could provide a rationale for the low yield of the photosubstitution. Step 5 is rearomatization. The methoxide ion, being a better leaving group than cyanide ion, preferentially leaves.

We expect this type of reaction will be general for aryl olefins (at least) and other nucleophiles and that the mild non-acidic conditions may offer considerable synthetic utility.

CHAPTER VI

REACTIONS OF RADICAL IONS GENERATED BY PHOTOSENSITIZATION (ELECTRON TRANSFER). EXPERIMENTAL.

General

Acetonitrile (Aldrich Gold Label) was refluxed over calcium hydride under dry nitrogen atmosphere and fractionated. Methanol (Fisher, Spectro), methanol-O-d (Aldrich, 99.5% +) and isopropyl alcohol (Fisher Spectro) were used without further purification. tert-Butyl alcohol was distilled over calcium hydride. 2,2,2-Trifluoroethanol (Aldrich Gold Label) was used after distillation. Acetic acid (glacial) was first distilled from anhydrous copper sulfate and then fractionally distilled. Pyridine (Eastman Spectro) was distilled from barium oxide. 1-Cyanonaphthalene was sublimed under vacuum, once for the study of the photoreactions and three times for the quenching experiments. 1,4-Dicyanobenzene (Aldrich) was recrystallized from ethanol four times. 1,4-Dicyanonaphthalene was prepared by the reaction of 1,4-dibromonaphthalene with cuprous cyanide and was purified by sublimation under vacuum (two times) and recrystallization from ethanol. Methyl p-cyanobenzoate was prepared by acid catalyzed esterification of p-cyanobenzoic acid and purified by recrystallization from ethanol (four times). 1-Methoxynaphthalene was prepared via a Williamson synthesis using 1-naphthol and dimethyl sulfate[77] and was purified by distillation under vacuum. 1,4-Dimethoxynaphthalene was similarly prepared from 1,4-naphthalenediol and was purified first by column chromatography on neutral alumina and then by recrystallization from ethanol. Acetophenone, p-methylacetophenone, and p-methoxyacetophenone were purified by distillation and column chromatography on silica gel until only one peak was observed upon vpc. Xanthone was purified by recrystallization from ethanol. 1-Benzoylnaphthalene was prepared by Friedel-Crafts benzoylation of naphthalene and was purified by recrystallization from ethanol. 1,1-Diphenylethylene (Eastman Kodak Co.), 2-phenylnorbornene (Aldrich) and 1-phenylcyclohexene (Aldrich) were purified by distillation under vacuum; further purification for the quenching experiments and for the measurement of their oxidation potentials was carried out by preparative vpc (10% DEGS, ChrW, Non Acid Washed, 60/80 mesh) and subsequent bulb-to-bulb distillation prior to their use. 2-Methylpropene (Matheson Research Grade, 99.8%) and 2,3-dimethyl-2-butene (Aldrich, 98%) were used without purification. 1,1-Diphenylethane was obtained by catalytic hydrogenation (Pt on C) of 1,1-diphenylethylene. 2,2-Diphenylethyl acetate was prepared by acetylation of 2,2-diphenylethyl alcohol with acetic anhydride. 2,2-Diphenylethyl alcohol was prepared by reduction of 2,2-diphenylacetaldehyde with sodium borohydride. 2,2-Diphenylacetaldehyde was prepared by acid catalyzed opening and rearrangement of trans stilbene oxide, which was in turn prepared from trans stilbene by epoxidation with m-chloroperbenzoic acid. 3,3-Diphenylpropanonitrile was prepared as described by A.D. Grebenyuk and I.P. Tsukervanik.[79] 2,2-Diphenylpropanonitrile was prepared by alkylation of 2,2-diphenylacetonitrile with methyl chloride in 50% aqueous sodium hydroxide, in the presence of catalytic amounts of benzyltriethylammonium chloride.[75] 1,1,4-

Triphenyl-1,2,3,4-tetrahydronaphthalene was made as described by R.A. Neunteufel and D.R. Arnold.[19] 18-Crown-6-ether was prepared and purified as described by G.W. Gokel and coworkers.[80] The dipotassium salt of azodicarboxylic acid (PADA) was prepared and purified as described by B.M. Trost.[81] Tetraethylammonium perchlorate (Eastman Kodak Co.) was recrystallized from water four times and dried under vacuum at 65° C. Silver nitrate, for the reference electrode, was purified by recrystallization from water. All irradiations were carried out using a General Electric Co. 1 kw medium-pressure mercury vapour lamp, through a Pyrex filter, at 10° C. All the samples, except for those in Chapter III, were purged with argon for 20 minutes, prior to their irradiation. The progress of the reaction was followed by ^{1}Hnmr and/or vpc. ^{1}Hnmr spectra were obtained in deuterochloroform solution with tetramethylsilane (TMS) as internal standard, using a Varian HA-100 spectrometer. Ir spectra were recorded on a Beckman IR-5A spectrometer and/or on a Perkin Elmer 621 grating spectrometer. Calibration of the ir spectra was done using the 1601.8 cm^{-1} absorption band of polystyrene. The combustion analyses were performed by Chemalytics, Inc., Tempe, Arizona. All reported yields are based on isolated products except if it is otherwise stated.

Spectroscopic studies. Fluorescence spectra were measured on a conventional 90° two-monochromator spectrofluorimeter or on a Perkin-Elmer Fluorescence Spectrophotometer (MPF-4) at room temperature. "Quenching" values were obtained, with the same instruments, from the spectra. The Stern-Volmer slopes were found by using the least squares method. The correlation coefficients were always > 0.99. Fluorescence decay measurements were made on a time-correlated single photon counting instrument, details of which have been described elsewhere.[82,83,84] The excitation source was a Photochemical Research Associates nanosecond flash lamp system. The decay curves were deconvoluted by iterative convolution.[82,84] All measurements were done at room temperature. In all cases (transient and steady-state measurements) the solutions were degassed on a mercury-free vacuum line.

The phosphorescence spectra were obtained on a spectrometer comprised of a Hanovia 150-W xenon source, the light from which was passed through a Bausch and Lomb 0.25 m monochromator and focused onto the sample by a quartz lens. The sample was in a quartz Dewar kept at liquid nitrogen temperature. The emission at right angles from the sample was passed through a Jarrel-Ash spectrophotometer into an EMI 9558 QD photomultiplier (S-20 response), cooled with dry ice-methanol. The output from the photomultiplier was fed, via a timing amplifier (Ortec Model 454) and a fast discriminator (Ortec Model 417), to a multichannel analyzer (Geos Model 7010) with 1024 channels. The signal was displayed on an oscilloscope and then recorded on an Infotronic stepping recorder.

Oxidation and Reduction Potential Measurements. Cyclic voltametric data were obtained using a three-electrode cell with a Princeton Applied Research Electrochemistry System Model 170. The working electrode was a platinum sphere sealed into glass and the counter electrode was a platinum wire. A Ag/Ag^+ (0.1 M) electrode was used as a reference electrode and 0.1 M tetraethylammonium perchlorate was the cupporting electrolyte (0.1 M).

The solutions were purged with nitrogen prior to each measurement and a nitrogen atmosphere was maintained throughout the experiment.

Half-wave oxidation potentials were taken as 0.028 V before the anodic peak potential and half-wave reduction potentials 0.029 V before the cathodic peak potential.[29] If the electron transfer process were not reversible, the peak potential was a function of sweep rate; the half-wave was then estimated using the 100 mV/sec sweep and these values were therefore less reliable.

The results are summarized in Table XII.

Irradiation of 1,1-Diphenylethylene in Acetonitrile-Alcohol Solution with a Photosensitizer (Electron Transfer). A solution of 1,1-diphenylethylene (XX, 360 mg, 2 mmole), photosensitizer (electron transfer, 0.8 mmole) in alcohol (40 mmol) and acetonitrile (12 ml) was purged with argon for 30 minutes and irradiated through a Pyrex filter with a 1 kw medium-pressure mercury vapour lamp, at 10°. The progress of the reaction was followed by ^{1}Hnmr (disappearance of the signal due to the vinyl protons and/or vpc). After approximately 60 h of irradiation (depending upon the alcohol used), the solvent was evaporated and the residue was chromatographed on a silica gel (60-200 mesh) column, using solvents of varying polarity. In addition to the major products, alkyl 2,2-diphenylethyl ethers, a large portion of the sensitizer (ca. 80%) was usually recovered. According to the above general procedure, the following ethers were prepared.

2,2-Diphenylethyl Methyl Ether (XXV). In addition to XXV (36.1%,

Table XII. Cyclic voltametric data using platinum electrode, tetraethylammonium perchlorate (TEAP) 0.1 M, in acetonitrile solution vs. Ag/0.1 M $AgNO_3$.

Sweep rate mV/sec	Anodic ip, mA	Cathodic ip, mA	$ip/V^{1/2}$ µA $sec^{1/2}/V^{1/2}$	Anodic Ep, V vs Ag/Ag^+ (0.1 M)	Cathodic Ep, V vs Ag/Ag^+ (0.1 M)
		1-cyanonaphthalene (XXIX) 1.0 mM			
50	2.8[a]	2.8	12.5	2.28	2.36
100	2.9[a]	2.9	9.2	2.28	2.36
500	9.0[a]	8.4	11.9	2.28	2.36
	2,2-diphenylethyl isopropyl ether (XXVI) 0.88 mM				
20	7.2	-	51.1	1.80	-
50	11.0	-	49.3	1.82	-
100	15.0	-	47.5	1.84	-
200	21.2	-	47.4	1.85	-
		1,1-diphenylethane (XLVI) 1.72 mM			
50	40.0	-	179.4	1.82	-
100	57.0	-	180.4	1.84	-
200	82.0	-	183.4	1.87	-
		1,1-diphenylethylene (XX) 1.0 mM			
100	6.3	-	19.9	1.48	-
200	8.5	-	19.0	1.50	-

Table XII (Continued)

5000	16.5	-	7.4	1.52	-
2-phenylnorbornene (XXVIII)					
200	-	-	-	1.10	-
1-phenylcyclohexene (XXVII)					
100	-	-	-	1.29	-
1,4-dicyanobenzene (XXI) 1.03 mM					
20	3.6	3.6	25.5	1.96	2.03
50	5.4	5.6	24.1	1.96	2.03
100	7.6	7.6	24.0	1.96	2.03
1,4-dicyanonaphthalene (LXIX) 0.95 mM					
20	2.1	2.3	14.9	1.63	1.70
50	3.3	3.3	14.7	1.63	1.70
100	4.6	4.6	14.6	1.63	1.70
methyl *p*-cyanobenzoate (XXII) 1.0 mM					
20	3.3	3.7	26.2	2.02	2.10
50	4.7[a]	5.2	23.2	2.02	2.09
100	6.6[a]	7.0	22.2	2.01	2.08
p-methylacetophenone (LXXI) 2.18 mM					
20	13.0	-	91.9	2.10	-

Table XII (Continued)

50	18.0	-	80.5	2.12	-
100	23.9	-	75.6	2.15	-
200	31.3	-	70.0	2.16	-
			p-methoxyacetophenone (LXV) 0.95 mM		
20	13.5	-	95.5	1.61	-
50	18 5	-	82.7	1.61	-
100	25.5	-	80.6	1.63	-
200	33.5	-	74.9	1.64	-
			acetophenone (LXX) 1.01 mM		
20	20.0	-	141.4	2.33	-
50	27.1	-	121.2	2.33	-
100	34.5	-	109.1	2.37	-
200	45.0	-	100.6	2.38	-

a. Calculated using the semiempirical procedure reported by R.S. Nicholson, Anal. Chem. 38, 1406 (1966).

colourless liquid), 1,1-diphenylethyl methyl ether (9.1%), and 1,1-diphenylethane (1.6%) were obtained. The sensitizer for this irradiation was methyl p-cyanobenzoate (XXII). The structure proof for these products rests upon direct comparison (ir, ^{1}Hnmr) with authentic samples prepared by established procedures (XXV has been described previously).[20]

2,2-Diphenylethyl Isopropyl Ether (XXVI). 2,2-Diphenylethyl isopropyl ether (XXVI) was obtained by the above procedure in 48.5% yield; methyl p-cyanobenzoate (XXII) was the sensitizer. In addition, diphenylmethane (LXVII, 7.2%) was isolated. A sample of XXVI (colourless liquid) was purified by vpc (10% SE-30 on Chromosorb W).

Ir (neat) ν_{max} 1610, 1500, 1370, 1140, 1090, 700 cm^{-1}.

^{1}Hnmr $\delta_{TMS}^{CDCl_3}$ 7.42 (broad singlet, ArH); the benzylic and methylene protons appeared as an AB$_2$ pattern; part A 4.24, part B 3.93, J_{AB} = 7.5 Hz; 3.57 (heptet, methyl H's, J = 6.5 Hz), 1.12 (doublet, methine H).

Mass spectrum (70 eV), m/e (rel. intensity) 240 (1, M^{+}), 168 (15), 167 (100), 165 (21), 73 (13), 43 (24) (shown in Fig. 12).

Anal. Cald. for XXVI ($C_{17}H_{20}O$): C, 84.95; H, 8.39. Found: C, 85.23; H, 8.44.

Alternative Synthesis of 2,2-Diphenylethyl Isopropyl Ether (XXVI). Trans-stilbene oxide was prepared by epoxidation of trans-stilbene with meta-chloroperbenzoic acid[85] and the epoxide was isomerized to 2,2-diphenylacetaldehyde, using boron trifluoride etherate.[86] The aldehyde was reduced to 2,2-diphenylethanol with sodium borohydride. The potassium alcoholate was treated with isopropyl iodide to give 2,2-diphenylethyl isopropyl ether (XXVI). The yield of the last step was 3.5%. The spectra (^{1}Hnmr, ir) of the ether obtained in this synthesis were identical with those of the ether (XXVI) obtained from the photoreaction (reaction 5).

2,2-Diphenylethyl tert-butyl ether (XXX). The general procedure for reaction 5, using methyl p-cyanobenzoate (XXII) as the sensitizer (electron transfer) and tert-butanol as the alcohol, gave XXX (17%) and diphenylmethane (LXVII, 35%). A sample of XXX (colourless liquid), for spectral characterization and analysis, was purified by vpc (column, 10%, SE-30 on Chromosorb W).

Ir (neat) ν_{max} 1604, 1495, 1374, 1197, 1080, 695 cm^{-1}.

^{1}Hnmr $\delta_{TMS}^{CDCl_3}$ 7.40 (broad singlet, ArH); the benzylic and methylene protons appeared as an AB_2 pattern; part A 4.18, part B 3.87, J_{AB} = 7.5 Hz, 1.15 (singlet, tert-butyl H's).

Mass spectrum (70 eV), m/e (rel. intensity) 168 (42), 167 (100), 165 (14), 57 (42) (shown in Fig. 12).

Anal. Calcd. for XXX ($C_{18}H_{22}O$): C, 84.99; H, 8.72. Found: C, 85.03; H, 8.74.

Irradiation of 1,1-Diphenylethylene in Acetonitrile-Water Solution with Methyl p-Cyanobenzoate (Electron Transfer Photosensitizer). A solution of 1,1-diphenylethylene (XX, 1.8 g, 10 mmol) and methyl p-cyanobenzoate (XXII, 0.8 g, 5 mmol) in acetonitrile (30 ml) and water (4.5 ml) was irradiated for 70 h. The solvent was evaporated from the resultant solution and the residue was extracted with ether. Evaporation of the dried ethereal extracts led to an oily residue which upon chromatography on silica gel (60-200 mesh), using solvents of varying polarity, gave the following products: diphenylmethane (LXVII, 322 mg, 19%), 1,1-diphenylethane (XLVI, 86 mg, 5%), 2,2-diphenylethyl alcohol (XXXIV, 487 mg, 25%) and sensitizer (XXII, 458 mg, 57% recovery). The structure proof for these products rests upon direct comparison (ir and/or ^{1}Hnmr) with authentic samples prepared by established procedures.

Irradiation of 1,1-Diphenylethylene in Acetonitrile-Acetic Acid Solution with Methyl p-Cyanobenzoate (Electron Transfer Photosensitizer). A solution of 1,1-diphenylethylene (XX, 360 mg, 2 mmol) and methyl p-cyanobenzoate (XXII, 128 mg, 0.8 mmol) in acetonitrile (12 ml) and glacial acetic acid (2.4 ml) was irradiated for 350 h. The solvent was evaporated from the resultant yellow solution and the residue upon chromatography on a silica gel column (60-200 mesh), using solvents of varying polarity, gave the following compounds: unreacted olefin (XX, 40 mg, 89% conversion), 1,1-diphenylethane (XLVI, 20 mg, 6%), 1,1,4-triphenyl-1,2,3,4-tetrahydronaphthalene (XXIV, 137 mg, 43%) and methyl 2,2-diphenylethyl acetate (XXXV, 11 mg, 5%). All the sensitizer was consumed.

Irradiation of 1-Phenylcyclohexene in Acetonitrile-2,2,2-Trifluoroethanol Solution with 1-Cyanonaphthalene (Electron Transfer Photosensitizer). A solution of 1-phenylcyclohexene (XXVII, 79 mg, 0.5 mmol) and 1-cyanonaphthalene (XXIX, 31 mg, 0.2 mmol) in acetonitrile (2 ml) and 2,2,2-trifluoroethanol (1.6 ml) was irradiated for 4 h. The solvent was evaporated from the resultant solution and the residue was chromatographed on a silica gel column (60-200 mesh) using solvents of varying polarity. The following compounds were obtained: trans-2-phenyl-1-(2,2,2-trifluoroethoxy)-cyclohexane (XXXII, 16 mg, 12%), cis-2-phenyl-1-(2,2,2-trifluoroethoxy)-cyclohexane (XXXI, 10 mg, 8%) and 1-cyanonaphthalene (XXIX, 9 mg, 29% recovery).

trans-2-Phenyl-1-(2,2,2-trifluoroethoxy)-cyclohexane (XXXII). Ir (neat) ν_{max} 2940, 2862, 1446, 1277, 1162, 1147, 1106, 970, 761, 698 cm^{-1}.

^{1}Hnmr $\delta_{TMS}^{CDCl_3}$ 7.36 (broad singlet, ArH), 3.35 (quartet, $O-CH_2-CF_3$, $J_{F,H}$ = 9.0 Hz), 2.24 - 0.72 (multiplet, aliphatic hydrogens of the cyclohexane ring).

Mass spectrum (70 eV), m/e (rel. intensity) 258 (62, M^+), 215 (100), 158 (21), 115 (40), 91 (24).

Anal. cald. for XXXII ($C_{14}H_{17}F_3O$): C, 65.10; H, 6.63. Found: C, 65.37; H, 6.62.

cis-2-Phenyl-1-(2,2,2-trifluoroethoxy)-cyclohexane (XXXI). Ir (neat) ν_{max} 2940, 2867, 1284, 1161, 970, 700 cm^{-1}.

^{1}Hnmr $\delta_{TMS}^{CDCl_3}$ 7.25 (broad singlet, ArH), 3.68 (broad singlet, H_1), 3.29 (quartet, $O-CH_2-CF_3$, $J_{F,H}$ = 9.0 Hz), 2.66 (broad doublet, H_2, J = 12 Hz), 2.50 - 0.70 (multiplet, aliphatic hydrogens of the cyclohexane ring).

Mass spectrum (70 eV), m/e (rel. intensity) 258 (87, M^+), 130 (77), 129 (51), 117 (100), 104 (72), 91 (87).

Anal. cald. for XXXI ($C_{14}H_{17}F_3O$): C, 65.10; H, 6.63. Found; C, 65.18; H, 6.42.

Irradiation of 2-Phenylnorbornene in Acetonitrile-*tert*-Butyl Alcohol Solution with Methyl *p*-Cyanobenzoate (Electron Transfer Photosensitizer).

A solution of 2-phenylnorbornene (XXVIII, 0.7 g, 4 mmol) and methyl *p*-cyanobenzoate (XXII, 256 mg, 1.6 mmol) in acetonitrile (24 ml) and *tert*-butyl alcohol (80 ml) was irradiated for 55 h. After removal of the solvents from the resultant solution, vpc analysis of a small portion of the reaction mixture showed that it contained: starting material (76 mg, 89% conversion), 2-phenylnorbornanes (68 mg, 11%), 2-*exo*-*tert*-butoxy-3-*endo*-phenylnorbornane (XXXIII, 212 mg, 24%), 2-*exo*-cyanomethyl-3-*endo*-phenylnorbornane (LXXXII, 147 mg, 19%) and essentially all of the photosensitizer. The major portion of the reaction mixture was chromatographed on silica gel (60-200 mesh) using solvents of varying polarity. The compounds isolated in this manner were further purified by vpc (10% DEGS, chromosorb W, NAW, 60/80 mesh) in order to obtain analytical samples and/or their spectra.

2-*exo*-*tert*-Butoxy-3-*endo*-phenylnorbornane (XXXIII). Ir (KBr disc) ν_{max} 3076, 3038, 3970, 2883, 1602, 1394, 1363, 1198, 1116, 1059, 1018, 767, 757, 738, 708 cm^{-1}.

^{1}Hnmr $\delta_{TMS}^{CDCl_3}$ 7.44 - 7.00 (multiplet, ArH), 3.66 (doublet of doublets, H_2, $J_{2,3}$ = 3.5, $J_{2,7a}$ = 1.5 Hz), 2.98 (triplet, H_3, $J_{3,4}$ = 4.0 Hz), 2.22 (multiplet, H_1, H_4), 1.93 (broad doublet, H_{7s}), 1.74 - 0.85 (multiplet, H_5, H_6, H_{7a}).

Mass spectrum (70 eV) m/e (rel. intensity) 244 (2, M^+), 188 (33), 170 (19), 93 (21), 92 (68), 53 (100).

Anal. Cald. for XXXIII ($C_{17}H_{24}O$): C, 83.55; H, 9.90. Found: C, 83.56; H, 10.22.

2-exo-Cyanomethyl-3-endo-phenylnorbornane (LXXXII). Ir (neat) ν_{max} 3067, 3037, 2959, 2882, 2252, 1605, 1501, 743, 703 cm^{-1}.

^{1}Hnmr $\delta_{TMS}^{CDCl_3}$ 7.50 - 7.08 (multiplet, ArH), 2.74 (triplet, exo H_2, J = 4.5 Hz).

Mass spectrum (70 eV) m/e (rel. intensity) 211 (27, M^+), 170 (59), 143 (54), 115 (90), 92 (100), 67 (100), 65 (50).

Anal. Cald. for LXXXII ($C_{15}H_{17}N$): C, 85.26; H, 8.11. Found: C, 85.55; H, 8.26.

Irradiation of 1,1-Diphenylethylene Potassium Cyanide and 18-Crown-6-Ether in Acetonitrile - 2,2,2-Trifluoroethanol Solution with 1-Cyanonaphthalene (Electron Transfer Photosensitizer). A solution of 1,1-diphenylethylene (XX, 450 mg, 2.5 mmol), potassium cyanide (650 mg, 10 mmol), 18-crown-6-ether (2.64 g, 10 mmol), and 1-cyanonaphthalene (XXIX, 382 mg, 2.5 mmol) in 2,2,2-trifluoroethanol (1.5 ml) - acetonitrile (20.0 ml) was irradiated for 90 h. After irradiation, the mixture was poured into water and the organic products extracted with diethyl ether. Column chromatography of the etheral extracts on silica gel (60-200 mesh), using solvents of varying polarity gave the products: 3,3-diphenylpropanonitrile (XLI, 48%) and 1,1-diphenylethane (XLVI, 18%). The structure proof for these compounds rests upon direct comparison (ir, ^{1}Hnmr) with authentic samples prepared by established procedures.

Irradiation of 2-Phenylnorbornene and Potassium Cyanide in Acetonitrile-2,2,2-Trifluoroethanol Solution with 1-Cyanonaphthalene (Electron Transfer Photosensitizer). A solution of 2-phenylnorbornene (XXVIII, 680 mg, 4 mmol), potassium cyanide (650 mg, 10 mmol) and 1-cyanonaphthalene (XXIX, 308 mg, 2 mmol) in 2,2,2-trifluoroethanol (16 ml) - acetonitrile (20 ml) was irradiated. After 2.5 h of irradiation, the solvent was evaporated and the residue was extracted with a benzene-pentane mixture. The mixture obtained, upon chromatography on a silica gel (60-200 mesh) column using solvents of varying polarity, gave the following products: 2-*exo*-cyano-3-*endo*-phenylnorbornane (XLII, 29%), 2-*exo*-cyano-3-*exo*-phenylnorbornane (XLIII, 10%), 2-*exo*-(2,2,2-trifluoroethoxy)-3-*endo*-phenylnorbornane (XLVIII, 7%), and a small amount (< 5%) of an impure product which we believe is 2-cyano-3-phenylnorbornene (XLVII). Further purification of the products XLII, XLIII and XLVIII by vpc (10% DEGS, ChrW, NAW, 60/80 mesh) and/or column chromatography was carried out in order to obtain samples for analysis and spectra.

2-*exo*-cyano-3-*endo*-phenylnorbornane (XLII). Ir (neat) ν_{max} 2980, 2890, 2250, 1620, 1510, 1465, 745, 710 cm^{-1}.

^{1}Hnmr $\delta_{TMS}^{CDCl_3}$ 7.67 - 7.25 (multiplet, ArH), 3.52 (triplet, *exo* H_3), 2.84 - 2.52 (multiplet, H_1, H_2, H_4), 1.96 (broad doublet H_{7s}), 1.74 - 1.14 (multiplet, H_5, H_6, H_{7a}).

Mass spectrum (70 eV), m/e (rel. intensity) 197 (100, M^+), 131 (71), 91 (95).

Anal. Cald. for XLII ($C_{14}H_{15}N$): C, 85.23; H, 7.66; N, 7.10. Found: C, 85.31; H, 7.40; N, 7.35.

2-*exo*-Cyano-3-*exo*-phenylnorbornane (XLIII). Ir (neat) ν_{max} 2930, 2900, 2260, 1508, 1468, 1312, 740, 710 cm^{-1}.

^{1}Hnmr $\delta_{TMS}^{CDCl_3}$ 7.33 - 7.08 (multiplet, ArH), 3.10 - 2.84 (multiplet, H_2, H_3, $J_{2,3}$ = 9, $J_{2,7a}$ = 1.8, $J_{3,7a}$ = 2.0 Hz), 2.75 - 2.59 (multiplet, H_1, H_4), 2.08 (multiplet center, H_{7s}), 1.77 - 1.18 (multiplet, H_5, H_6, H_{7a}).

Mass spectrum (70 eV), m/e (rel. intensity) 197 (100, M^+), 131 (52), 91 (62).

Anal. Cald. for XLIII ($C_{14}H_{15}N$): C, 85.23; H, 7.66; N, 7.10. Found: C, 85.14; H, 7.62; N, 7.26.

2-exo(2,2,2-Trifluoroethoxy)-3-endo-phenylnorbornane (XLVIII). Ir (neat) ν_{max} 2980, 1295, 1175, 1130, 980, 750, 710 cm^{-1}.

^{1}Hnmr $\delta_{TMS}^{CDCl_3}$ 7.66 - 7.22 (multiplet, ArH), 3.19 (triplet, H_3, $J_{2,3}$ = 3.5, $J_{3,4}$ = 4.0 Hz), 3.86 (quartet, methylene $J_{F,H}$ = 8.5 Hz), 3.5 (multiplet, H_2, $J_{2,7a}$ = 1.5 Hz), 2.46 - 2.41 (multiplet, H_1, H_4), 1.91 (broad doublet, H_{7s}), 1.7 - 0.93 (multiplet, H_5, H_6, H_{7a}).

Mass spectrum (70 eV) m/e (rel. intensity) 270 (100, M^+), 139 (45), 117 (65).

Anal. Cald. for XLVIII ($C_{15}H_{17}F_3O$): C, 66.66; H, 6.34. Found: C, 66.77; H, 6.18

Irradiation of 2-Phenylnorbornene and Potassium Cyanide in Acetonitrile-Methanol-0-d Solution with 1-Cyanonaphthalene (Electron Transfer Photosensitizer). A solution of 2-phenylnorbornene (XXVIII, 25 mg, 1.5 mmol), potassium cyanide (243 mg, 3.75 mmol) and 1-cyanonaphthalene (XXIX, 115 mg, 0.75 mmol) in methanol-O-d (10 ml) - acetonitrile (13 ml), was irradiated for 2 h. After irradiation, the solvent was evaporated and the residue extracted with diethyl ether. Column chromatography of the ethereal extract, using silica gel (60-200 mesh) and solvents of varying polarity, gave the following products: 2-*exo*-cyano-3-*exo*-deutero-3-*endo*-phenylnorbornane (XLIX, 18%), 2-*exo*-cyano-3-*endo*-deutero-3-*exo*-phenylnorbornane (L, 5%) and 2-*exo*-methoxy-3-*exo*-deutero-3-*endo*-phenylnorbornane (LI, 54%). Further purification of samples for spectral characterization was carried out using vpc (10% DEGS, ChrW, NAW, 60/80 mesh).

2-*exo*-Cyano-3-*exo*-deutero-3-*endo*-phenylnorbornane (XLIX). Ir (neat) ν_{max} 2998, 2910, 2262, 1515, 1465, 750, 712 cm^{-1}.

^{1}Hnmr $\delta_{TMS}^{CDCl_3}$ 7.66 - 7.26 (multiplet, ArH), 2.84 - 2.58 (multiplet, H_1, H_2, H_4), 1.97 (multiplet center, H_{7s}), 1.75 - 1.10 (multiplet, H_5, H_6, H_{7a}).

Mass spectrum (70 eV) m/e (rel. intensity) 198 (100, M^+), 132 (90), 92 (99).

2-*exo*-Cyano-3-*endo*-deutero-3-*exo*-phenylnorbornane (L). Ir (neat) ν_{max} 2970, 2880, 2240, 1500, 1460, 700 cm^{-1}.

^{1}Hnmr $\delta_{TMS}^{CDCl_3}$ 7.60 - 7.22 (multiplet, ArH), 3.00 (broad singlet, H_2), 2.80 - 2.66 (multiplet, H_1, H_4), 2.11 (multiplet center, H_{7s}), 1.8 - 0.79 (multiplet, H_5, H_6, H_{7a}).

2-*exo*-Methoxy-3-*exo*-deutero-3-*endo*-phenylnorbornane (LI). Ir (neat) ν_{max} 2960, 2880, 1500, 1455, 1126, 1105, 740, 700 cm^{-1}.

^{1}Hnmr $\delta_{TMS}^{CDCl_3}$ 7.60 - 7.30 (multiplet, ArH), 3.5 (sharp doublet, H_2, $J_{2,7a}$ = 1.5 Hz), 3.36 (singlet, methoxy H), 2.54 - 2.36 (multiplet, H_1, H_4), 1.82 (broad doublet, H_{7s}), 1.7 - 0.9 (multiplet, H_5, H_6, H_{7a}).

Mass spectrum (70 eV) m/e (rel. intensity) 203 (100, M^+), 171

(58), 118 (43), 92 (69), 71 (97).

Preparation of 2-*exo*-Cyano-3-*endo*-Phenylnorbornene (LII) and 2-*endo*-Cyano-3-*exo*-Phenylnorbornene (LIII) (Diels Alder Reaction). A solution of *trans*-cinnamonitrile (1.3 g, 0.01 mol) and freshly distilled cyclopentadiene (0.66 g, 0.01 mmol) in 5 ml toluene was heated in a sealed glass tube at 154° for 65 h. The resultant mixture contained unreacted starting materials and a one to one ratio of the products LII and LIII (conversion 50%). Repeated chromatography on silica gel (60-200 mesh) using solvent of varying polarity gave 2-*exo*-cyano-3-*endo*-phenylnorbornene (LII) and 2-*endo*-cyano-3-*exo*-phenylnorbornene (LIII). Further purification of the adducts was carried out using vpc (10% DEGS, ChrW, NAW, 60/80 mesh) in order to obtain their spectra.

2-*exo*-Cyano-3-*endo*-phenylnorbornene (LII). Ir (neat) ν_{max} 3062, 3030, 2980, 2944, 2875, 2232, 2200, 1600, 1620, 1495, 1450, 1336, 1196, 1080, 1030, 905, 868, 745, 720, 698 cm^{-1}.

^{1}Hnmr $\delta_{TMS}^{CDCl_3}$ 7.40 - 7.00 (multiplet, ArH), 6.24, 6.01 (multiplet center, olefinic H, $J_{5,6}$ = 6.0 Hz), 3.68 (doublet pair, H_3, $J_{2,3}$ = 5.0 Hz, $J_{3,4}$ = 3.2 Hz), 3.28 (broad singlet, H_1, H_4), 2.40 (doublet pair, H_2, $J_{2,7a}$ = 2 Hz), 1.96 - 1.56 (multiplet, H_{7a}, H_{7s}).

Mass spectrum (70 eV) m/e (rel. intensity) 195 (7, M$^+$), 130 (60), 67 (21), 66 (100).

Exact mass cald. for LII ($C_{14}H_{13}N$): 195.1048; found (ms): 195.1044.

2-*endo*-Cyano-3-*exo*-Phenylnorbornene (LIII). Ir (neat) ν_{max} 3065, 3030, 2980, 2880, 2238, 2200, 1500, 1450, 1340, 1160, 1035, 850, 792, 750, 728, 700 cm^{-1}.

^{1}Hnmr $\delta_{TMS}^{CDCl_3}$ 7.58 - 7.04 (multiplet, ArH), 6.56, 6.36 (multiplet center, olefinic H, $J_{5,6}$ = 6.0 Hz), 3.31 (broad singlet, H_1), 3.15 (broad singlet, H_4), 3.03 (broad doublet, coupled to 7_a, H_3, $J_{2,3}$ = 5.0 Hz), 2.85 (doublet pair, H_2), 1.6 (multiplet center, H_{7a}, H_{7s}).

Mass spectrum (70 eV) m/e (rel. intensity) 195 (3, M^+), 130 (19), 129 (22), 66 (100).

Exact mass cald. for LIII ($C_{14}H_{13}N$): 195.1048; found (ms): 195.1045.

Preparation of 2-exo-Cyano-3-endo-Phenylnorbornane (XLII) (Diimide Reduction of LII). 25 mg (0.13 mmol) of the dipotassium salt of azodicarboxylic acid (PADA) and 10 mg (0.05 mmol) of 2-exo-cyano-3-endo-phenylnorbornene (LII) were stirred in 0.4 ml of pyridine under nitrogen atmosphere. 0.1 g (0.1 ml) of glacial acetic acid in 0.2 ml of pyridine was added dropwise over a period of 30 min. The mixture was stirred at room temperature for 6 h. This mixture was poured into water and extracted with ether. The ether layers were washed with dilute aqueous hydrochloric acid and then saturated aqueous sodium bicarbonate. After drying, evaporation gave 10 mg (100% yield) of a colourless liquid with ir and ^{1}Hnmr spectra identical to those obtained for the photoproduct XLII.

Preparation of 2-endo-Cyano-3-exo-Phenylnorbornane (LIV) (Diimide Reduction of LIII). The procedure outlined above was used also for the reduction of LIII to LIV. The product was further purified using column chromatography on silica gel (60-200 mesh) in order to obtain its spectra.

2-endo-Cyano-3-exo-phenylnorbornane (LIV). Ir (neat) ν_{max} 3060, 3030, 2963, 2882, 2238, 1600, 1493, 1478, 1450, 1300, 1181, 1080, 1032, 752, 730, 700 cm^{-1}.

^{1}Hnmr $\delta_{TMS}^{CDCl_3}$ 7.26 (singlet, ArH), 2.96 (broad doublet, H_3), 2.80 - 2.47 (multiplet, H_1, H_2, H_4), 1.90 - 1.34 (multiplet, H_5, H_6, H_7).

Mass spectrum (70 eV) m/e (rel. intensity) 197 (31, M^+), 131 (53), 115 (34), 91 (100).

Exact mass cald. for LIV ($C_{14}H_{15}N$): 197.1204; found (ms): 197.1202.

Base Catalyzed Isomerization of 2-exo-Cyano-3-exo-Phenylnorbornane (XLIII) to 2-endo-Cyano-3-exo-Phenylnorbornane (LIV). 6 mg of 2-exo-cyano-3-exo-phenylnorbornane (XLIII) were dissolved in 1 ml of tert-butyl alcohol under nitrogen atmosphere and trace of potassium metal was added. After 3 h stirring at room temperature, the reaction mixture was poured in water and extracted with ether. After drying, evaporation gave 4 mg of product whose ir spectrum was identical to that of LIV.

Irradiation of 1-Phenylcyclohexene and Potassium Cyanide in Acetonitrile-2,2,2-Trifluoroethanol Solution with 1-Cyanonaphthalene (Electron Transfer Photosensitizer). A solution of 1-phenylcyclohexene (XXVII, 790 mg, 5 mmol), potassium cyanide (650 mg, 10 mmol) and 1-cyanonaphthalene (XXIX, 308 mg, 2 mmol) in 2,2,2-trifluoroethanol (16 ml) -

acetonitrile (20 ml) was irradiated. After 80 h or irradiation, the solution was poured in water and the organic part extracted with diethyl ether. Column chromatography of the etheral extract, using silica gel (60-200 mesh) and solvents of varying polarity, gave the following products: cis-1-cyano-2-phenylcyclohexane (XLIV, 20%), trans-1-cyano-2-phenylcyclohexane (XLV, 19%), cis-2-phenyl-1-(2,2,2-trifluoroethoxy)-cyclohexane (XXXI, 1.5%), and trans-2-phenyl-1-(2,2,2-trifluoroethoxy)-cyclohexane (XXXII, 1.6%). Further purification of the above products was carried out using vpc (10% DEGS, ChrW, NAW, 60/80 mesh) and/or column chromatography, in order to obtain analytical samples and spectra.

cis-1-Cyano-2-phenylcyclohexane (XLIV). Ir (neat) ν_{max} 2949, 2874, 2237, 1497, 1449, 893, 855, 772, 745, 697 cm^{-1}.

^{1}Hnmr $\delta_{TMS}^{CDCl_3}$ 7.32 (singlet, ArH), 3.08 (broad singlet, H α-to CN group), 2.9 - 2.6 (multiplet, benzylic H), 2.3 - 1.2 (multiplet, methylene H).

Mass spectrum (70 eV), m/e (rel. intensity) 185 (48, M$^+$), 117 (100), 91 (97).

Anal. cald. for XLIV ($C_{13}H_{15}N$): C, 84.28; H, 8.16; N, 7.56. Found: C, 84.32; H, 7.93; N, 7.74.

trans-1-Cyano-2-phenylcyclohexane (XLV). Ir (neat) ν_{max} 2920, 2850, 2230, 1486, 1440, 1062, 1013, 750, 692 cm^{-1}.

^{1}Hnmr $\delta_{TMS}^{CDCl_3}$ 7.46 - 7.1 (multiplet, ArH), 2.82 - 1.1 (multiplet, aliphatic H).

Mass spectrum (70 eV), m/e (rel. intensity) 185 (47, M$^+$), 117 (100), 91 (98).

Anal. cald. for XLV ($C_{13}H_{15}N$): C, 84.28; H, 8.16, N, 7.56. Found: C, 84.57; H, 8.11; N, 7.48.

Irradiation of 1,1-Diphenylethylene and 2-Methylpropene in Acetonitrile with Methyl p-Cyanobenzoate (Electron Transfer Photosensitizer). A solution of 1,1-diphenylethylene (XX, 72 mg, 0.4 mmol) and methyl p-cyanobenzoate (XXII, 32 mg, 0.2 mmol) in acetonitrile (1.25 ml) was purged with 2-methylpropene (XXXIX) until saturation (ca. 100 mg, 1.8 mmol) and irradiated for 28 h. The solvent was evaporated from the resultant yellow solution and the residue upon chromatography on a silica gel (60-200 mesh) solumn, using solvents of varying polarity gave 1,1-dimethyl-4-phenyl-1,2,3,4-tetrahydronaphthalene (LV, 11 mg, 12%). The sensitizer was largely recovered. Further purification of the adduct was carried out using vpc (10% DEGS, Chromosorb W, NAW, 60/80 mesh) in order to obtain samples for analysis and spectra.

1,1-Dimethyl-4-phenyl-1,2,3,4-tetrahydronaphthalene (LV). Ir (neat) ν_{max} 3064, 3029, 2964, 2936, 2865, 1602, 1492, 1452, 1386, 1363, 759, 738, 700 cm^{-1}.

^{1}Hnmr $\delta_{TMS}^{CDCl_3}$ 7.50 - 6.75 (multiplet, ArH), 4.13 (triplet, benzylic H, J = 7.5 Hz), 2.40 - ca. 1.8 (multiplet, $3CH_2$), ca. 1.8 - 1.56 (multiplet, $2CH_2$), 1.37 and 1.34 (singlet, methyl H's).

Mass spectrum (70 eV) (rel. intensity) 236 (26, M^+), 180 (43), 143 (85), 128 (45), 115 (31), 91 (100).

Anal. cald. for LV ($C_{18}H_{20}$): C, 91.47; H, 8.53. Found: C, 91.80; H, 8.71.

Irradiation of 1,1-Diphenylethylene and 2-Methylpropene in Acetonitrile with 1,4-Dicyanobenzene (Electron Transfer Photosensitizer). A solution of 1,1-diphenylethylene (XX, 720 mg, 4 mmol) and 1,4-dicyanobenzene (XXI, 200 mg, 1.6 mmol) in acetonitrile (12.5 ml) was purged with 2-methylpropene (XXXIX) until saturation (ca. 1 g, 18 mmol) and irradiated for 66 h. The solvent was evaporated from the resultant yellow solution and the residue was subsequently treated with ether. The separated colourless crystals of the sensitizer were recovered (184 mg, 92% recovery) by filtration. The ether was removed from the filtrate and the oily residue upon chromatography, as described above, gave unreacted starting material (XX, 371 mg, 48% conversion) and 1,1-dimethyl-4-phenyl-1,2,3,4-tetrahydronaphthalene (LV, 142 mg, 24%).

Irradiation of 1,1-Diphenylethylene and 2,3-Dimethyl-2-Butene in Acetonitrile with 1,4-Dicyanobenzene (Electron Transfer Photosensitizer). A solution of 1,1-diphenylethylene (XX, 720 mg, 4 mmol), 2,3-dimethyl-2-butene (LVII, 840 mg, 10 mmol) and 1,4-dicyanobenzene (XXI, 200 mg, 1.6 mmol) in acetonitrile (12.5 ml) was irradiated for 40 h. The solvent was evaporated from the resultant yellow solution and the residue was subsequently treated with ether. The separated colourless crystals of the sensitizer were recovered (59 mg, 30% recovery) by filtration. The ether was removed from the filtrate and the oily residue upon chromatography on silica gel (60-200 mesh), using solvents of varying polarity, gave a variety of products in the following order of elution: a 4:1 mixture of 2,3,6,7-tetramethylocta-2,6-diene and 2,3,3,4,4,5-hexamethylhexa-1,5-diene (LXI, LXII, 20 mg, 2.3%, based on the amount of 2,3-dimethyl-2-butene); their identification was based on the comparison of ^{1}Hnmr spectrum of the mixture with the ^{1}Hnmr spectra reported for these compounds;[53] unreacted starting material (XX, 277 mg, 61% conversion), 2,3-dimethyl-5,5-diphenyl-2-hexene (LX, 29 mg, 4%), 1,1,2,2-tetramethyl-3,3-diphenylcyclobutane (LIX, 38 mg, 6%), 1,1,2,2-tetramethyl-4-phenyl-1,2,3,4-tetrahydronaphthalene (LVIII, 15 mg, 15%), 1,1,4-triphenyl-1,2,3,4-tetrahydronaphthalene (XXIV, 84 mg, 19%), 2,3-dimethyl-1-(4-cyanophenyl)-2-butene (LXIII, 70 mg, 34%, based on the amount of consumed 1,4-dicyanobenzene), and 2,3-dimethyl-3-(4-cyanophenyl)-1-butene (LXIV, 44 mg, 22%). Further purification of the products by vpc (10% DEGS, Chromosorb W, NAW, 60/80 mesh) was carried out in order to obtain samples for analysis and spectra.

2,3-Dimethyl-5,5-diphenyl-2-hexene (LX). Ir (neat) ν_{max} 3090, 3060, 3030, 2975, 2920, 2865, 1598, 1493, 1442, 1320, 1028, 769, 752, 696 cm^{-1}.

^{1}Hnmr $\delta^{CDCl_3}_{TMS}$ 7.04 (singlet, ArH), 3.00 (broad singlet, CH$_2$), 1.61 (singlet, 6H, gem methyl H's), 1.54 (broad singlet, 3-CH$_3$), 1.00 (broad singlet, methyl H's).

Mass spectrum (70 eV) (rel. intensity) 264 (5, M$^+$), 182 (64), 181 (100), 166 (65), 165 (66), 103 (69), 77 (64).

Exact mass cald. for LX ($C_{20}H_{24}$): 264.1878. Found (ms): 264.1881.

1,1,2,2-Tetramethyl-3,3-diphenylcyclobutane (LIX). Ir (neat) ν_{max} 3086, 3058, 2965, 2868, 1592, 1488, 1443, 761, 740, 703, 690 cm^{-1}.

^{1}Hnmr $\delta^{CDCl_3}_{TMS}$ 7.46 - 6.92 (multiplet, ArH), 2.75 (singlet, CH$_2$), 1.44 singlet, 2-CH$_3$'s), 0.88 (singlet, 1-CH$_3$).

Mass spectrum (70 eV) (rel. intensity) 264 (1, M$^+$), 181 (31), 180 (100), 165 (45), 85 (88), 70 (71).

Exact mass cald. for LIX ($C_{20}H_{24}$): 264.1878. Found (ms): 264.1876.

1,1,2,2-Tetramethyl-4-phenyl-1,2,3,4-tetrahydronaphthalene (LVIII). Ir (neat) ν_{max} 3069, 3033, 2978, 2878, 1601, 1498, 1381, 773, 751, 702 cm^{-1}.

^{1}Hnmr $\delta^{CDCl_3}_{TMS}$ 7.52 - 6.71 (multiplet, ArH); an AMX system was attributed to the protons at the 4 and 3 positions; 4.12 (doublet pair, benzylic H, H_X, J_{AX} = 11.5 Hz, J_{MX} = 7.0 Hz), 2.00 (doublet pair, H_A, J_{AM} = 12.5 Hz), 1.66 (doublet pair, H_M), 1.37, 1.31 (singlet, 1-CH_3), 1.02 (singlet, 2-CH_3's).

Mass spectrum (70 eV) (rel. intensity) 264 (32, M^+), 193 (100), 180 (42), 178 (47), 105 (46), 91 (77), 77 (33).

Anal. cald. for LVIII ($C_{20}H_{24}$): C, 90.85; H, 9.15. Found: C, 90.91; H, 9.31.

2,3-Dimethyl-1-(4-cyanophenyl)-2-butene (LXIII). Ir (neat) ν_{max} 2994, 2922, 2864, 2232, 1606, 1504, 844, 815 cm^{-1}.

^{1}Hnmr $\delta^{CDCl_3}_{TMS}$ AB quartet, centered at 7.40 (ArH), 3.44 (broad singlet, CH_2), 1.74 (broad singlet, gem CH_3's), 1.56 (broad singlet, 2-CH_3's).

Mass spectrum (70 eV) (rel. intensity) 185 (51, M^+), 171 (13), 170 (100), 143 (16), 142 (34), 116 (17).

Anal. cald. for LXIII ($C_{13}H_{15}N$): C, 84.28; H, 8.16. Found: C, 84.03; H, 8.34.

2,3-Dimethyl-3-(4-cyanophenyl)-1-butene (LXIV). Ir (neat) ν_{max} 2977, 2233, 1607, 1502, 1095, 900, 843 cm^{-1}.

^{1}Hnmr $\delta_{TMS}^{CDCl_3}$ AB quartet, centered at 7.49 (ArH), 4.95 (multiplet, Hx AB part of an ABX_3 system, which collapses to a pair of doublets, upon irradiation at the 2-CH_3; J_{AB} = 1.4 Hz, J_{AX} = 0.7, J_{BX} = 1.4 Hz), 1.48 (doublet pair, 2-CH_3), 1.40 (singlet, gem CH_3's).

Mass spectrum (70 eV) (rel. intensity) 185 (43, M^+), 170 (100), 144 (22), 142 (33), 116 (40).

Anal. cald. for LXIV ($C_{13}H_{15}N$): C, 84.28; H, 8.16. Found: C, 84.08; H, 8.31.

Irradiation of 2,3-Dimethyl-2-Butene in Acetonitrile with 1,4-Dicyanobenzene (Electron Transfer Photosensitizer). A solution of 2,3-dimethyl-2-butene (LVII, 420 mg, 5 mmol) and 1,4-dicyanobenzene (XXI, 100 mg, 0.8 mmol) in acetonitrile (6.25 ml) was irradiated for 42 h. The solvent was evaporated on a rotary evaporator and the oily residue obtained was divided in two parts; one part was used for the determination of the yields using vpc (10% DEGS, Chromosorb W, NAW, 60/80 mesh, internal standard triphenyl methane), and the other for the isolation of the products by semipreparative vpc. The crude reaction mixture was found thus to contain: recovered sensitizer (XXI, 12 mg, 88% conversion), 2,3-dimethyl-1-(4-cyanophenyl)-2-butene (LXIII, 12 mg, 10%) and 2,3-dimethyl-3-(4-cyanophenyl)-1-butene (LXIV, 24 mg, 19%). The spectra (ir, ^{1}Hnmr of the products were identical with those obtained for the corresponding compounds in the previous reaction.

Irradiation of 2-Phenylnorbornene and 2-Methylpropene in Acetonitrile with Methyl p-Cyanobenzoate (Electron Transfer Photosensitizer). A solution of 2-phenylnorbornene (XXVIII, 680 mg, 4 mmol) and methyl p-cyanobenzoate (XXII, 320 mg, 2 mmol) in acetonitrile (12.5 ml) was purged with 2-methylpropene (XXXIX) until saturation (ca. 1 g, 18 mmol) and irradiated for 140 h. The solvent was evaporated from the resultant yellow solution and the residue upon chromatography on a silica gel column (60-200 mesh), using solvents of varying polarity, gave the following products: 1,2,3,4,4aα,9,10,10aα-octahydro-9,9-dimethyl-1β,4β-methanophenanthrene (LVI, 368 mg, 45%) and 2-phenylnorbornene dimers (95 mg, 15%). The latter were characterized as such on the basis of their mass spectrum and by comparison of their ^{1}Hnmr spectrum with the corresponding spectrum of the products obtained upon irradiation of 2-phenylnorbornene (XXVIII) with methyl p-cyanobenzoate (XXII). 2-Phenylnorbornene (XXVIII, 61 mg, 91% conversion) and methyl p-cyanobenzoate (XXII, 315 mg, 98% recovery) were also isolated from the reaction mixture. Further purification of 1,2,3,4,4aα,9,10,10aα-octahydro-9,9-dimethyl-1β,4β-methanophenanthrene was carried out using vpc (10% DEGS, Chromosorb W, NAW, 60/80 mesh) in order to obtain a pure sample for analysis and spectra.

1,2,3,4,4aα,9,10,10aα-Octahydro-9,9-dimethyl-1β,4β-methanophenanthrene (LVI). Ir (neat) ν_{max} 3062, 3030, 2957, 2872, 1487, 1363, 1054, 760, 735, 709 cm^{-1}.

^{1}Hnmr $\delta_{TMS}^{CDCl_3}$ 7.40 - 6.96 (multiplet, ArH), 2.68 (Broad singlet, H_1), 2.62 (broad doublet, H_2, $J_{2,3}$ ca. 7.0 Hz), 2.28 - 2.02 (multiplet, H_3), 1.96 (broad singlet, H_4), 1.84 - 0.88 (multiplet, rest of the aliphatic H's), 1.35, 1.10 (singlets, CH_3's).

^{13}Cnmr $\delta^{CDCl_3}_{TMS}$ 147.2, 138 quarternary aromatic nuclei, 127.8, 125.6, 125.2, 123.4 remaining aromatic nuclei. 29.8, 29.5, C_5 and C_6 (not necessarily in this order), 29.3 and 28.7 methyl carbons, 44.8, 43.4, 42.6, 42.3, 40.3, 33.4, 33.3 remaining of aliphatic carbons.

Mass spectrum (70 eV) (rel. intensity) 226 (41, M^+), 211 (36), 143 (100), 128 (39), 87 (48), 74 (71).

Anal. cald. for LVI ($C_{17}H_{22}$): C, 90.20; H, 9.80. Found: C, 90.24; H, 10.18.

Irradiation of 2-Phenylnorbornene and 2-Methylpropene in Benzene with p-Methoxy acetophenone (Triplet Photosensitizer). 2-Phenylnorbornene (XXVIII, 680 mg, 4 mmol) and p-methoxy acetophenone (LXV, 300 mg, 2 mmol) in benzene (12.5 ml) was purged with 2-methylpropene (XXXIX) until saturation (ca. 1.1 g, 20 ml) and irradiated for 98 h. The solvent was evaporated from the resultant yellow solution and the residue upon chromatography on a silica gel column (60-200 mesh) using solvents of varying polarity gave 1,2,3,4,4aα,9,10,10aα-octahydro-9,9-dimethyl-1β,4β-methanophenanthrene (LVI, 61 mg, 8%, based on the amount of consumed olefin) and 26 mg of an unidentified product. The sensitizer was completely recovered.

Irradiation of 2,2-Diphenylethyl Isopropyl Ether in the Presence of 1,4-Dicyanobenzene (Electron Transfer Photosensitizer) and Methanol in Acetonitrile Solution. A solution of 2,2-diphenylethyl isopropyl ether (XXVI, 24 mg, 0.1 mmole), 1,4-dicyanobenzene (electron acceptor sensitizer), (XXI, 8 mg, 0.06 mmole), in 80 μl (2.0 mmoles) methyl alcohol and

400 µl acetonitrile was irradiated for 21 h. After the end of the irradiation, a known amount of an internal standard (triphenylmethane) was added and the yield of methyl isopropyl acetal of formaldehyde (LXVIIIb, 67%) was determined by integration of the methylene proton vs the proton of the internal standard. The yield of the diphenylmethane (LXVII, 29%) was determined by vpc using the internal standard technique. In other experiments the irradiation mixture was distilled under reduced pressure and the distillate, trapped using a dry-ice acetone bath, was treated with a solution of 2,4-dinitrophenyhydrazine.[87] The 2,4-dinitrophenylhydrazone was identified as the 2,4-dinitrophenylhydrazone of formaldehyde by comparison (ir spectrum, mixed mp) with an authentic sample. The characterization of the mixed acetal was done by comparing the chemical shifts of the various protons, with those of an authentic sample, prepared in a method analogous with that described by H. Wuyts and P. Docquier,[88] and also by comparison of the vpc retention times using several columns (poropac Q, 10% SE-30 on Chromosorb W, and Apiezon M). The characterization of diphenylmethane was done by isolating it from the reaction mixture by vpc (10% SE-30 on Chromosorb W column) and comparing its ir spectrum with an authentic one. Similar experiments were carried out using methyl p-cyanobenzoate (XXII) as the sensitizer with similar results; 1-cyanonaphthalene (XXIX), under the same conditions, did not lead to reaction. Control experiments showed that in the absence of the sensitizer the reaction does not occur.

<u>Irradiation of 2,2-Diphenylethyl Methyl Ether in the Presence of 1,4-Dicyanobenzene and Isopropyl Alcohol in Acetonitrile Solution.</u> A solution of 2,2-diphenylethyl methyl ether (XXV, 21 mg, 0.1 mmole),

1,4-dicyanobenzene (XXI, 1 mg, 0.06 mmole), in 55 µl (2.0 mmole) isopropyl alcohol and 400 µl acetonitrile, was irradiated and worked up as described above. The yield of methyl isopropyl acetal of formaldehyde (LXVIIIb) was 17% and the yield of diphenylmethane (LXVII) 35%.

Attempted Triplet Sensitization of Reaction 18 (Ether Cleavage). A solution of 2,2-diphenylethyl isopropyl ether (XXVI, 12 mg, 0.05 mmole), 1,4-dicyanobenzene (XXI, 4 mg, 0.03 mmole) and ketone (triplet sensitizer, 0.156 mmole), in 40 µl (1.0 mmole) methyl alcohol and 200 µl acetonitrile was purged with argon and was irradiated through a filter solution consisting of sodium bromide (120 g) and lead nitrate (0.75 g) in 250 ml water, which absorbed wavelengths < 330 nm (75% transmission at 360 nm). No reaction occurred even after prolonged irradiation (1 day). When acetophenone (LXX) was used under the same conditions as above, except in the absence of 1,4-dicyanobenzene (XXI), both the ether XXVI and the acetophenone (LXX) were consumed.

Irradiation of 1,1-Diphenylethylene in Acetonitrile-Methanol Solution with 1-Methoxynaphthalene (Electron Transfer Photosensitizer). A solution of 1,1-diphenylethylene (XX, 90 mg, 0.5 mmol) and 1-methoxynapthalene (LXXII, 31 mg, 0.2 mmol) in acetonitrile (2 ml) and methanol (1.6 ml) was irradiated for 30 h. The solvent was evaporated from the resultant yellow solution and the residue upon chromatography on a silica gel column (60-200 mesh), using solvents of varying polarity, gave the following compounds: 1,1-diphenylethyl methyl ether (LXXV, 43 mg, 45%) and 1-methoxynaphthalene (unreacted sensitizer, LXXII, 20 mg, 64% recovery). The ether was identified by comparison of its ir spectrum with that of an authentic sample, prepared by acid catalyzed addition of methanol to 1,1-diphenylethylene (XX).

Irradiation of 1,1-Diphenylethylene in Acetonitrile-Methanol-O-d Solution with 1-Methoxynaphthalene (Electron Transfer Photosensitizer). A solution of 1,1-diphenylethylene (XX, 90 mg, 0.5 mmol) and 1-methoxynaphthalene (LXXII, 31 mg, 0.2 mmol) in acetonitrile (2 ml) and methanol-O-d (1.6 ml) was irradiated for 18 h. The solvent was evaporated from the resultant yellow solution and the residue upon chromatography on a silica gel column (60-200 mesh), using solvents of varying polarity, gave the following compounds: 1,1-diphenylethylene (XX, 14 mg, 62% conversion), 1-methoxynaphthalene (LXXII, 23 mg, 74% recovery) and 1,1-diphenylethyl methyl ether (LXXV, 27 mg, 30%). Analysis of the ^{1}Hnmr and the mass spectra of the starting material indicated incorporation of deuterium (29% D_1, 1% D_2) in the vinyl position. Deuterium (81% D_1, 13% D_2, 0.1% D_3) was also incorporated in the methyl position of 1,1-diphenylethyl methyl ether (LXXV).

Irradiation of 1,1-Diphenylethylene in Acetonitrile-Methanol Solution with 1,4-Dimethoxynaphthalene (Electron Transfer Photosensitizer). A solution of 1,1-diphenylethylene (XX, 90 mg, 0.5 mmol) and 1,4-dimethoxynaphthalene (LXXIII, 38 mg, 0.2 mmol) in acetonitrile (2 ml) and methanol (1.6 ml) was irradiated for 4 h. The solvent was evaporated from the resultant yellow solution and the residue was divided into two portions. From the first portion, a pure sample of the product, 1,1-diphenylethyl methyl ether (LXXV) was isolated, using vpc (10% SE-30, Chromosorb W, NAW, 60/80 mesh) and was identified by comparison of its ir spectrum with that of an authentic sample prepared by acid catalyzed addition of methanol to 1,1-diphenylethylene (XX). In the second portion, a known amount of triphenylmethane was added, as internal standard, and the yield of the product was determined using vpc (10% SE-30, Chromosorb W, NAW, 60/80 mesh). Thus, the reaction mixture was found to contain 1,1-diphenylethyl methyl ether (LXXV, 88%) and unreacted sensitizer (LXXIII, 63%).

Irradiation of 1,1-Diphenylethylene in Acetonitrile-2,2,2-Trifluoroethanol Solution with 1,4-Dimethoxynaphthalene (Electron Transfer Photosensitizer). A solution of 1,1-diphenylethylene (XX, 360 mg, 2 mmol) and 1,4-dimethoxynaphthalene (LXXIII, 152 mg, 0.8 mmol) in acetonitrile (8 ml) and 2,2,2-trifluoroethanol (6.4 ml) was irradiated for 12 h. The solvent was evaporated from the resultant slightly yellow solution and the residue was divided into two portions. From the first portion, pure samples of the products, 1,1-diphenylethyl 2,2,2-trifluoroethyl ether (LXXVI) and 1,1-diphenylethyl alcohol (LXXVII) were isolated using vpc (10% DEGS, Chromosorb W, NAW, 60/80 mesh). The alcohol was identified by comparison of its ir spectrum with that of an authentic sample, and resulted in from the addition of water present in acetonitrile and/or 2,2,2-trifluoroethanol via the photosensitized (electron transfer) route. In the second portion, a known amount of triphenylmethane was added, as internal standard, and the yields of the products were determined using vpc (10% DEGS, Chromosorb W, NAW, 60/80 mesh). Thus, the reaction mixture was found to contain 1,1-diphenylethyl 2,2,2-trifluoroethyl ether (LXXVI, 359 mg, 64%), 1,1-diphenylethyl alcohol (LXXVII, 139 mg, 35%) and 1,4-dimethoxy=

naphthalene (LXXIII, 150 mg, 99% recovery).

1,1-Diphenylethyl-1-2,2,2-trifluoroethyl ether (LXXVI). Ir (neat) ν_{max} 3088, 3062, 3029, 2984, 2940, 1600, 1493, 1447, 1372, 1276, 1164, 1112, 1053, 970, 897, 711, 758, 700 cm^{-1}.

^{1}Hnmr $\delta_{TMS}^{CDCl_3}$ 7.52 - 6.96 (multiplet, ArH), 3.54 (quartet, O-CH_2-CF_3, $J_{F,H}$ = 9 Hz), 1.8 (singlet, methyl H's).

Mass spectrum (70 eV) m/e (rel. intensity) 280 (1%, M^+), 265 (100), 203 (30), 181 (20), 165 (19), 105 (35), 77 (26).

Exact mass cald. for LXXVI ($C_{16}H_{15}F_3O$): 280.1075. Found (ms): 280.1078.

Irradiation of 1,1-Diphenylethylene in Acetonitrile-Water Solution with 1-Methoxynaphthalene (Electron Transfer Photosensitizer). A solution of 1,1-diphenylethylene (XX, 90 mg, 0.5 mmol) and 1-methoxynaphthalene (LXXII, 31 mg, 0.2 mmol) in acetonitrile (2 ml) and water (0.3 ml) was irradiated for 10 h. The solvent was partially evaporated from the resultant yellow solution and in the residue a known amount of triphenylmethane was added, as internal standard for the determination of the yields by the use of vpc (10% SE-30, Chromosorb W, NAW, 60/80 mesh). The reaction mixture was found thus to contain unreacted starting material (XX, 47 mg, 48% conversion), 1,1-diphenylethyl alcohol (LXXVII, 28 mg, 68%) and 1-methoxynaphthalene (LXXII, 28 mg, 90% recovery). The characterization of the alcohol was done by comparing the chemical shifts of the protons with those of an authentic sample, and also by comparison of its vpc retention time with that of an authentic sample.

Irradiation of 1,1-Diphenylethylene and Potassium Cyanide in Acetonitrile-2,2,2-Trifluoroethanol Solution with 1,4-Dimethoxynaphthalene (Electron Transfer Photosensitizer). A solution of 1,1-diphenylethylene (XX, 900 mg, 5 mmol), potassium cyanide (650 mg, 10 mmol) and 1,4-dimethoxynaphthalene (LXXIII, 380 mg, 2 mmol) in acetonitrile (20 ml) and 2,2,2-trifluoroethanol (16 ml) was irradiated for 114 h. The solvent was evaporated from the resultant solution and the residue upon chromatography on a silica gel (60-200 mesh) column, using solvents of varying polarity, gave the following compounds listed in their respective order of elution: unreacted starting material (XX, 13 mg, 99% conversion), 1,1-diphenylethane (XLVI, 26 mg, 3%), 1,1-diphenylethyl 2,2,2-trifluoroethyl ether (LXXVI, 303 mg, 22%), unreacted sensitizer (LXXIII, 95 mg, 25% recovery), 2,2-diphenylpropanonitrile (LXXVIII, 103 mg, 10%) and 1-cyano-4-methoxynaphthalene (LXXXI, 65 mg, 18%). All products were identified by comparison of their spectra (ir and/or ^{1}Hnmr) with those of authentic samples.

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