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Exciplex and Radical Ion Intermediates in the Photochemical Reaction of α-Phenylcinnamonitrile with 2,5-Dimethyl-2,4-hexadiene

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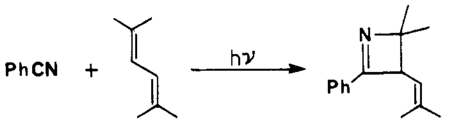
The photochemical reaction of α-phenylcinnamonitrile with 2,5-dimethyl-2,4-hexadiene has been investigated in several solvents. In nonpolar, nonhydroxylic solvents four isomeric [2 + 2] cycloadducts are formed. Cycloaddition is proposed to occur via a singlet exciplex intermediate. In acetonitrile solution a novel acyclic adduct is formed via an electron transfer–proton transfer–radical coupling mechanism. In alcohol solvents, reduced α-phenylcinnamonitrile, a solvent-incorporated adduct, and an oxidative coupling product of 2,5-dimethyl-2,4-hexadiene are formed. The two latter products are formed via nucleophilic trapping of the diene cation radical by solvent. The difference between electrochemical and photochemical oxidative addition of methanol to dienes and styrenes is discussed.

Investigations of the photochemical reactions of aryl nitriles with electron-rich alkenes and dienes have provided crucial evidence for the role of exciplexes and radical ion pairs in organic photochemistry.[1-8] Reactions of singlet aryl nitriles with alkenes or dienes in nonpolar solvents typically result in efficient cycloaddition via exciplex intermediates; however, the mode of cycloaddition is highly dependent upon aryl nitrile structure. For example, reaction of 2,5-dimethyl-2,4-hexadiene with benzonitrile (eq 1)[5b] or 1-naphthonitrile[6b] yields mainly a nitrile [2 + 2] adduct while reaction with 9-phenanthrenecarbonitrile (eq 2)[2a] or 9-anthracenecarbonitrile (eq 3)[4a] yields carbocyclic [2 + 2] and [4 + 2] adducts, respectively. In polar solvents, reactions take a different course, typically leading to redox products and/or solvent-incorporated acyclic adducts.[2a,3b,c,7,8] Unfortunately, there have been few quantitative studies of solvent effects on aryl nitrile–alkene reactions in both nonpolar and polar solvents. We report here on our investigation of the photochemical reactions of α-phenylcinnamonitrile with 2,5-dimethyl-2,4-hexadiene. The analysis of cycloadduct stereochemistry in both nonpolar and polar solvents supports an exciplex mechanism for cycloaddition in all solvents. The structures of the acyclic adducts formed in polar solvents are indicative of radical pair combination reactions. Finally, the photoredox reactions of dienes, styrenes, and alkenes in methanol solution are compared and found to diverge after nucleophilic attack of solvent on a cation radical intermediate.



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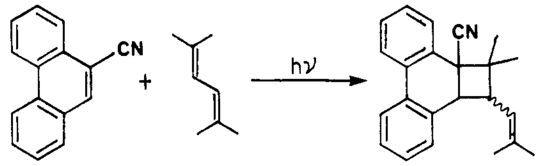

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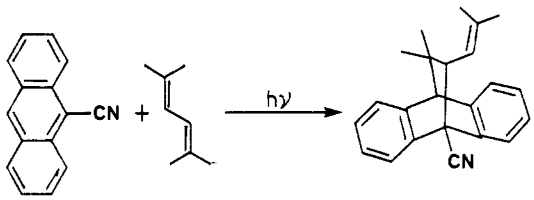

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Results and Discussion

Product Studies. Irradiation of *trans*-α-phenylcinnamonitrile (**1**, 0.025 M) and 2,5-dimethyl-2,4-hexadine (**2**, 0.5 M) in hexane or ether solution (Pyrex filter) results in the formation of all four possible isomeric [2 + 2] adducts having *trans*-phenyl stereochemistry (eq 4). The same products are obtained upon irradiation of *cis*-**1** with **2**, following an induction period required for the formation of *trans*-**1**. Thus cycloaddition occurs from an excited state of *trans*-**1** and not *cis*-**1**, as is the case for the cycloaddition

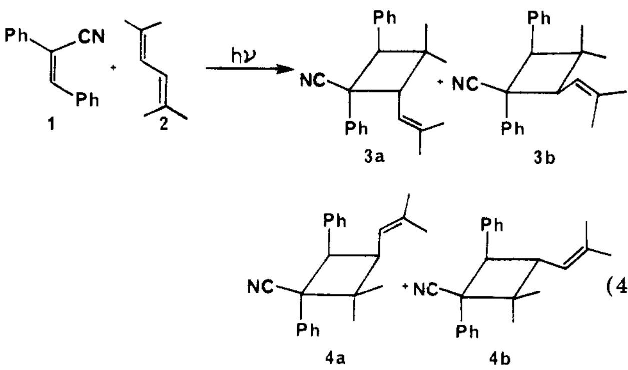

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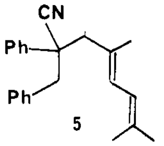
Table I. Product Distribution and Quantum Yields in Several Solvents[a]

solvent	adduct yield, % 3a	3b	4a	4b	5 or 6	Φ
hexane	22	38	13	27		0.14 (0.59)[b]
ether	30	37	15	18		0.05
methanol	47	16	14	10	13[c]	<0.001
acetonitrile	38	17	15	9	22[d]	<0.001

[a] 0.025 M α-phenylcinnamonitrile and 0.5 M dimethylhexadiene. Quantum yield is for cyclobutane formation. [b] Limiting quantum yield from a Φ^{-1} vs. $[\text{diene}]^{-1}$ plot. [c] Percent yield of adduct 6. [d] Percent yield of adduct 5.

of singlet stilbene with 2.[9] Irradiation of 1 and 2 in acetonitrile or alcohol solvents also leads to the formation of cycloadducts. In addition, the acyclic adducts 5 and 6 are



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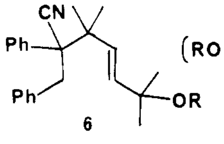

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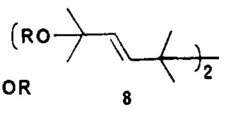

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formed in acetonitrile and alcohol (methanol, ethanol, or propanol) solution, respectively. Also formed in alcohol solution are 2,3-diphenylpropionitrile (7) and the diether 8. All products were isolated and characterized spectroscopically and, in the case of 7 and 8, by comparison with independently synthesized samples. Assignment of regiochemistry is based on NMR coupling constants and mass spectral retro-[2 + 2] fragmentation of **3a,b** to yield ionized 2 (100%) and β,β-dimethylstyrene (*m/e* 132, 40%) and of **4a,b** to yield 2 (100%) and 1-phenyl-4-methyl-1,3-pentadiene (*m/e* 158, 60%). Cycloadduct stereochemistry is assigned on the basis of NMR data, including lanthanide shift studies (see Experimental Section) and comparison with published data for *trans*-stilbene–diene adducts.[9]

The percent yields of nitrile-containing products determined by chromatographic analysis at <10% conversion of 1 are reported in Table I along with the total adduct quantum yields for several solvents. The yields of solvent-incorporated products vs. cycloadducts decrease in the order methanol > ethanol > propanol. Irradiation of 1 and 2 in methanol-*O-d* results in quantitative deuteration of 5 at the benzylic carbon and dideuteration of 7.

Nitrile 1 is nonfluorescent in fluid solution. At -196 °C in a methylcyclohexane glass both *cis*- and *trans*-1 are fluorescent: $\lambda_{\max}$ = 380 and 375 nm for *trans*- and *cis*-1, respectively.[10] No fluorescence is observed at intermediate temperatures. No exciplex fluorescence is observed from solutions of *trans*-1 or *cis*-1 when 2 is added.[11] A least-squares fit to the data from the plot of Φ^{-1} for cycloadduct formation vs. $[2]^{-1}$ shown in Figure 1, according to eq 5,

$$\Phi^{-1} = \Phi^{-1}_{\infty}\,(1 + (k_q\tau[2])^{-1}) \qquad (5)$$

provides an extrapolated quantum yield $\Phi_\infty = 0.59 \pm 0.02$ and a Stern–Volmer quenching constant $k_q\tau = 0.64 \pm 0.03$ M^{-1}. The quantum yield reported in Table I is lower than Φ_∞ due to incomplete quenching of singlet 1 by 0.5 M 2. A lower limit for the singlet lifetime of 1 can be estimated from the Stern–Volmer quenching constant and the assumption that quenching occurs near the rate of diffusion in hexane solution (3.3×10^{10} M^{-1} s^{-1}). The value obtained, 19 ps, is smaller than the most recently measured values for the planar singlet state of *trans*-stilbene (50–110 ps).[13]

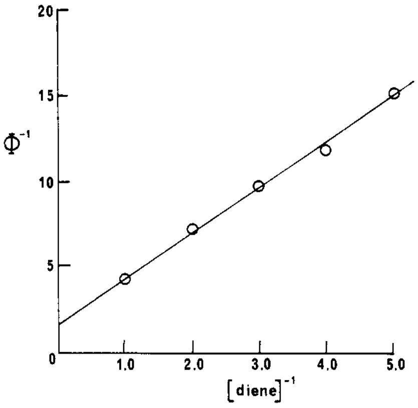
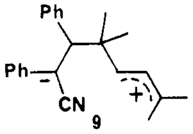


Figure 1. Variation in the quantum yield for total adduct formation (**3a,b** + **4a,b**) with diene concentration.

Mechanism of Cycloaddition. The short singlet lifetime of 1 precluded attempts to obtain spectroscopic or kinetic evidence for an exciplex intermediate in the cycloaddition process. Ample precedent exists for the formation of singlet exciplexes between both aryl nitriles[1-7] and stilbenes[12] with electron-rich alkenes and dienes. The preferred regiochemistry for cycloaddition of 1 and 2 is head-to-head (**3a,b**) in all solvents, as is the case for cycloaddition of 9-phenanthrenecarbonitrile with β-methylstyrenes[1] but not with 2 (eq 2).[2a] Stereoisomers **3a** and **4a**, which had adjacent isobutenyl and phenyl groups in a cis relationship, are favored in polar but not in nonpolar solvents. The low stereoselectivity and absence of pronounced solvent effects on isomer ratios is similar to the results for singlet *trans*-stilbene–diene exciplex cycloaddition.[9,12]

Several years ago Epiotis and Shaik[14] predicted the occurrence of ionic photochemical cycloaddition reactions via a 1,4-zwitterionic intermediate. The reaction of 1 and 2 was selected to test this prediction on the basis of expectation that the intermediate 1,4-zwitterion 9 would be



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unusually stable. The absence of enchanced regioselectivity or quantum yields in polar vs. nonpolar solvents as well as the absence of solvent trapping products for zwitterion 9 (vide infra) argue against its formation.

The rapid decrease in cycloaddition quantum yields with increasing solvent polarity may be attributed to radical ion pair formation.[2,3,7,15] The free energy for electron transfer from singlet 1 to 2 in acetonitrile solution can be calculated by using Weller's equation (eq 6),[16] where E_S and $E_{A^-/A}$ are

$$\Delta G_{ET} = -(E_S + E_{A^-/A}) + E_{D/D^+} - 0.06\ \text{eV} \qquad (6)$$

the singlet energy and reduction potential of 1 (Table II),

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[9] Lewis, F. D.; Hirsch, R. H. *Tetrahedron Lett.* **1973**, 4947–4950.

[10] Similar observations have been reported for α- and α,α′-substituted stilbenes: (a) Wismontski-Knittel, T.; Muszkat, K. A.; Fischer, E. *Mol. Photochem.*, **1979**, *9*, 217–225. (b) Fischer, G.; Seger, G.; Muszkat, K. A.; Fischer, E. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1569–1576.

[11] Exciplex emission previously reported from 1 and 2[12] is due to the formation of 9-phenanthrenecarbonitrile upon irradiation of 1 in the presence of oxygen.

[12] Lewis, F. D. *Acc. Chem. Res.* **1979**, *12*, 152–158.

[13] (a) Sumitani, M.; Nakashima, K.; Yoshihara, K.; Nagakura, S. *Chem. Phys. Lett.* **1977**, *51*, 183–185. (b) Teschke, O.; Ippen, E. P.; Holtom, G. R. *Ibid.* **1977**, *52*, 233–235. (c) Greene, B. I.; Hochstrasser, R. M.; Weisman, R. B. *Ibid.* **1979**, *62*, 427–430.

[14] Epiotis, N. D.; Shaik, S. *J. Am. Chem. Soc.* **1978**, *100*, 9–17.

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Table II. Quantum Yields for Formation of Diether 8 and Aryl Nitrile Electron Affinities

aryl nitrile	Φ [a]	$E_{A^-/A}$,[b] V	E_S,[c] eV	ΔG_{ET},[d] eV
α-phenylcinnamonitrile	<0.001	−1.58	3.54	−0.93
9-cyanoanthracene	0.012	−1.50	3.04	−0.51
9-cyanophenanthrene	0.017	−1.91	3.43	−0.49
2-cyanonaphthalene	0.019	−2.12	3.75	−0.61
1-cyanonaphthalene	0.033	−2.01	3.84	−0.80

[a] Quantum yield for formation of 8 from 0.1 M aryl nitrile and 1.0 M diene in degassed methanol solution by using monochromatic 313-nm irradiation. [b] Half-wave reduction potential in acetonitrile solution vs. Ag/AgCl. [c] Singlet energy taken from the onset of fluorescence. [d] Calculated by using eq 6.

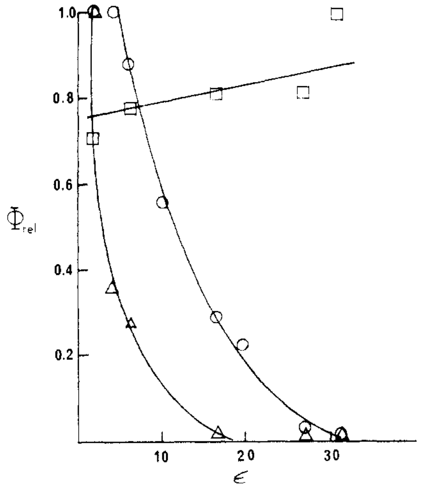
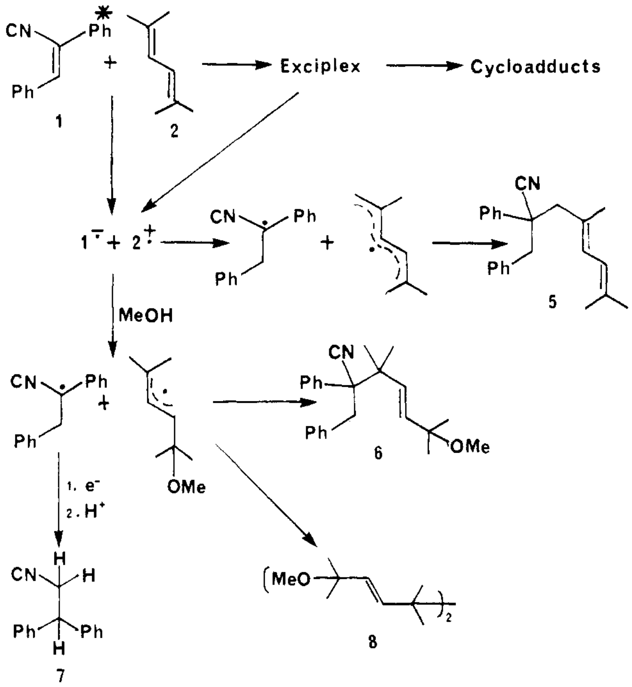


Figure 2. Solvent dependence of the relative quantum yields for reaction of α-phenylcinnamonitrile (△), *trans*-stilbene (○), and diphenylvinylene carbonate (□) with 2,5-dimethyl-2,4-hexadiene.

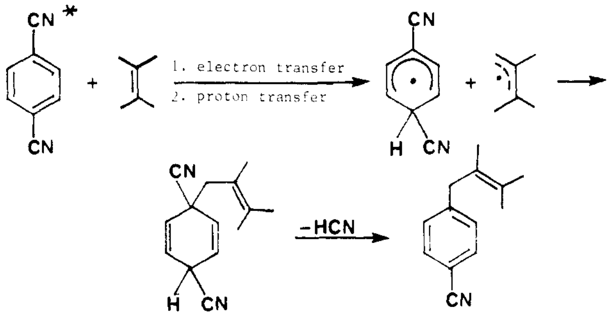
E_{D/D^+} is the oxidation potential of 2 (1.09 V),[17a] and the constant term is the coulombic attraction energy in acetonitrile solution. The calculated value of $\Delta G = -0.93$ eV is more exothermic than the values for the aryl nitriles listed in Table II. The effects of solvent polarity upon the cycloaddition quantum yields for 1, *trans*-stilbene, and diphenylvinylene carbonate with 2[12] are shown in Figure 2. Quantum yields decrease rapidly in the case of 1 for which radical ion pair formation is highly exothermic, gradually in the case of diphenylvinylene carbonate for which radical ion pair formation is moderately exothermic (−0.39 eV), and not at all in the case of *trans*-stilbene for which radical ion pair formation is only slightly exothermic (−0.24 eV).

On the basis of evidence available from this and related studies, we conclude that cycloaddition occurs via an exciplex intermediate and not via a radical ion pair or zwitterion (Scheme I).

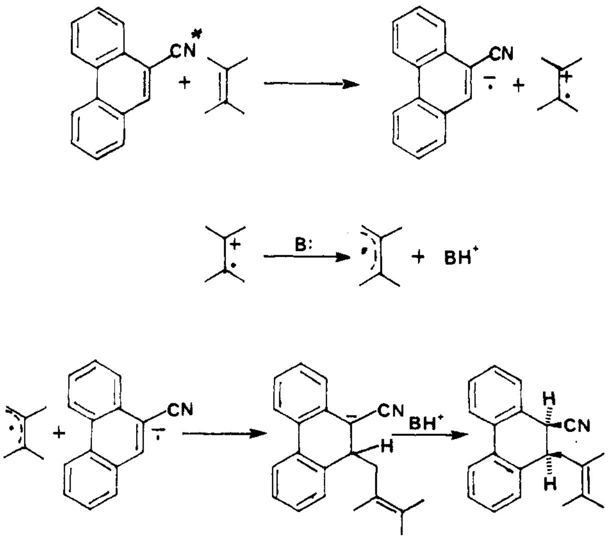
Scheme I



Scheme II



Scheme III



Mechanism of Acyclic Adduct Formation. Acyclic adducts such as 5 and 6 have not previously been reported for photochemical reactions of dienes; however, analogous products have been observed for the reactions of aryl nitriles with alkenes.[2,3,7,8] Arnold and co-workers[8d] have proposed the radical coupling mechanism shown in Scheme II for the reaction of 1,4-dicyanobenzene with 2,3-dimethyl-2-butene, and we[7] have proposed the radical–radical anion coupling mechanism shown in Scheme III for the reaction of 9-phenanthrenecarbonitrile with 2,3-dimethyl-2-butene. A radical coupling mechanism is consistent with the observed regioselectivity of bond formation

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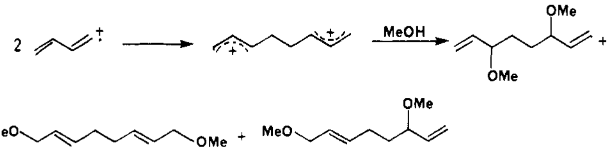
(17) (a) Baltes, H.; Steckhan, E.; Schäfer, H. J. *Chem. Ber.* **1978**, *111*, 1294–1314. (b) Schäfer, H.; Steckhan, E. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 518. (c) Schäfer, H. *Chem.-Ing.-Tech.* **1970**, *42*, 164–170. (d) Schäfer, H.; Steckhan, E. *Ibid.* **1972**, *44*, 186–187.

Scheme IV



in 5 (Scheme I); whereas a radical–radical anion reaction should yield the cyano-stabilized carbanion intermediate leading to the wrong regioisomer. The kinetic basicity of the anion radical most likely determines whether it (Schemes I and II) or the solvent (Scheme III) deprotonates the cation radical.

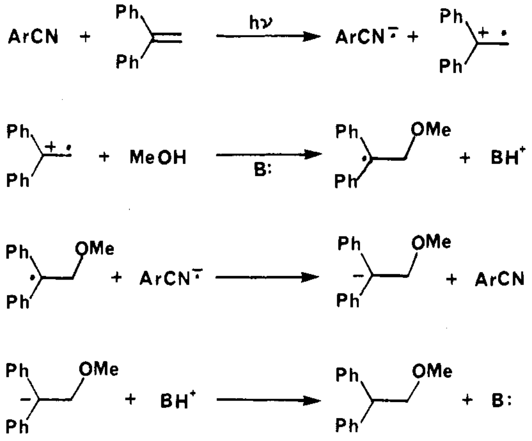
The formation of adduct **6** may occur via nucleophilic trapping of the diene cation radical to yield a methoxyallyl radical, which couples with the 1-cyano-1,2-diphenylethyl radical (Scheme I). Both radical–radical anion coupling and solvent trapping of zwitterion **9** would yield the wrong regioisomer. Formation of the methoxyallyl radical by nucleophilic attack of solvent on the diene cation radical is also consistent with the decrease in the relative yield of **6** vs. cyclobutanes with decreasing solvent nucleophilicity (methanol > ethanol > propanol). Complete deuteration at the benzylic carbon of adduct **6** in methanol-*O-d* is indicative of protonation of the anion radical of **1** by solvent.

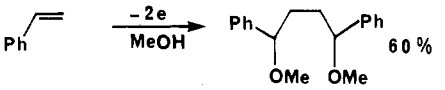
Photooxidative Addition Methanol to Dienes and Alkenes. The formation of products **7** and **8** plausibly occurs via the radical pair precursor of adduct **6** (Scheme I). Diffusion of the radical pair followed by autocoupling of the methoxyallyl radical would yield **8**. The formation of **7** from the 1-cyano-1,2-diphenylethyl radical is more complicated, since the incorporation of 2 equiv of deuterium in methanol-*O-d* solution rules out autodisproportionation and hydrogen atom abstraction from the solvent or **2**. Reduction of the 1-cyano-1,2-diphenylethyl radical (presumably by the anion radical of **1**) would yield a stable carbanion, protonation of which would account for incorporation of a second equivalent of deuterium.[2a,7] Reduction of **1** via two sequential electron transfer–proton transfer reactions finds analogy in the alkali metal[17] and electrochemical[18] reduction of aromatic hydrocarbons.

Mizuno, Pac, and Sakurai[2a] previously observed the formation of diether **8** and 9,10-dihydrophenanthrene-9-carbonitrile in 90% yield upon irradiation of 9-phenanthrenecarbonitrile and **2** in methanol solution. While a radical ion pair intermediate was proposed, no mechanistic details were advanced. In support of an electron-transfer mechanism, we find that the quantum yield for formation of **8** with a series of aryl nitriles and **2** increases as ΔG_{ET} becomes more exothermic (Table II). Under the reaction conditions, all the incident 313-nm light is absorbed by the aryl nitrile, and the diene concentration is sufficiently high to quench all (>95%) of the aryl nitrile singlets. Formation of **8** is not observed in the absence of aryl nitrile or when the triplet sensitizer Michler's ketone is employed with 365-nm irradiation. The low quantum yield for formation of **8** with **1** (Table II) may be due either to inefficient quenching of singlet **1** (lifetime unknown) by 1.0 M **2** or to rapid back electron transfer in the radical ion pair.

Diethers similar to **8** are also formed upon oxidation of dienes at graphite electrodes in methanol solution.[19] The mechanism proposed by Schäfer and Steckhan involves coupling of two cation radicals followed by solvent trapping of the dication (Scheme IV). Coupling of cation radicals prior to nucleophilic attack by methanol is plausible under electrochemical but not photochemical reaction conditions due to their high concentration in the former but not the latter reaction. Evidence that electrochemical and photochemical oxidations proceed via different mechanisms is provided by the reactions of styrenes, which form dimeric ethers electrochemically (eq 7) and monoethers upon

Scheme V





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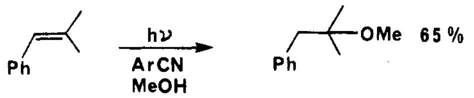
irradiation in the presence of aryl nitriles.[8] For example, irradiation of a methanol solution of 2-methyl-1-phenylpropene (0.15 M) in the presence of 9-phenanthrenecarbonitrile (0.007 M) results in efficient formation of 2-methoxy-2-methyl-1-phenylpropane (eq 8).



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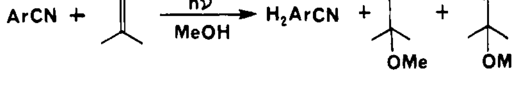
Arnold and co-workers[8] have proposed the mechanism shown in Scheme V for the aryl nitrile sensitized addition of methanol to styrenes. In Scheme V, the methoxybenzyl radical is reduced to the carbanion by the aryl nitrile anion radical; whereas, the anion radical is protonated in Scheme I. As a consequence, the aryl nitrile is a photocatalyst in Scheme V but is consumed in Scheme I. A possible explanation for this divergence of mechanism is that the benzyl radical is more readily reduced than the allyl radical. This conclusion is supported by the reported gas-phase electron affinities of benzyl (20.4 kcal/mol) and allyl (12.7 kcal/mol) radicals.[20] Alkyl radicals should have even lower electron affinities than allyl radicals, in accord with the observation of free-radical autodisproportionation products from the photooxidation of 2,3-dimethyl-2-butene (eq 9).[7] The formation of radical disproportionation



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products in this case and coupling products for methoxyallyl radicals is consistent with the known propensity of tertiary alkyl radicals toward disproportionation and of allyl radicals toward combination.[21]

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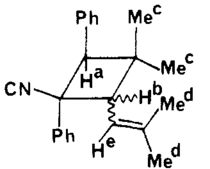
Table III. ^{1}H NMR Data for Cycloadducts Including Lanthide Induced Shifts [a]



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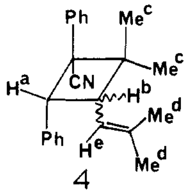

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adduct	Eu, equiv	shift H(a)	shift H(b)	shift H(c)	shift H(d)	shift H(e)
3a	0	4.04	3.62 (10.5)	1.47, 1.14	1.64, 1.56	4.71 (10.5)
	0.1	4.37	4.14	1.85,	1.73, 1.64	4.94
	0.2	4.63	4.52	2.03, 1.45	1.80, 1.71	5.11
3b	0	3.72	3.19 (10.5)	1.19, 1.27	1.63, 1.84	5.71 (10.5)
	0.1	4.00	3.44	1.41, 1.50	1.75, 1.86	6.20
	0.2	4.24	3.67	1.54, 1.75	1.81, 1.88	6.55
4a	0	4.07 (9.0)	3.40	0.70, 1.45	1.74	5.13 (10.5)
	0.1	4.46	4.07			5.35
	0.2	4.72	4.45			5.52
4b	0	4.56 (9.2)	3.25	0.93, 1.30	1.60, 1.70	5.47 (11.2)

[a] All spectra in $CDCl_3$ with chemical shifts in parts per million from Me_4Si and coupling constants (parentheses) in hertz. Lanthanide-induced shifts with Eu(fod)$_3$.

In summary, the interaction of 2,5-dimethyl-2,4-hexadiene with the excited states of 1 and aryl nitriles can lead to the formation of exciplex and/or radical ion pair intermediates. Exciplex intermediates are favored in nonpolar solvents and give rise to cycloadducts by a mechanism which does not involve charge separation. Radical ions are favored in polar solvents and give rise to several products, all of which are formed via proton transfer or solvent nucleophilic trapping of the radical ions. The fate of the radical ion and free-radical intermediates is largely determined by their electron and/or proton affinities.

Experimental Section

General Methods. Melting points were measured on a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer 283 infrared spectrometer, NMR spectra on a Perkin-Elmer R20B NMR spectrometer, and mass spectra on a Hewlett-Packard 5985 GC/MS system. Gas chromatographic analyses were obtained by using a 3 ft × $^1/_8$ in. or 10 ft. × $^1/_8$ in. GC column of 5% SF96 on Chromosorb G with a Hewlett-Packard 5750 gas chromatograph equipped with dual flame-ionization detectors. Satisfactory elemental analyses were obtained for adducts **3a,b** and **4a,b**.

Quantum yield measurements were carried out by using a Hanovia 450-W medium-pressure mercury lamp in a water-cooled Pyrex immersion well. Monochromatic light (313 nm) was provided by a potassium chromate filter solution in a Pyrex lamp well. Light intensities were measured by chemical actinometry using benzophenone/benzyhydrol reduction.[22] Samples were prepared by using solutions (3 mL) of 1 (0.025 M) and 2 in 13-mm-o.d. Pyrex ampules which were degassed by three freeze–pump–thaw cycles and sealed under vacuum. Samples were irradiated on a merry-go-round apparatus, maintained at a temperature of 23 ± 2 °C, and analyzed by gas chromatography.

Oxidation potentials were determined by differential pulse polarography using a Princeton Applied Research 374 polarograph vs. Ag/AgCl in acetonitrile solution containing tetra-*n*-butylammonium iodide as the electrolyte.

Materials. Methanol (Burdick and Jackson) was distilled from $Mg(OCH_3)_2$ under nitrogen immediately prior to use. Acetonitrile (Burdick and Jackson) was distilled from CaH_2 under nitrogen prior to use. Hexanes (Aldrich, Gold Label) and ethyl ether (Mallinkrodt, anhydrous) were used as received. The 2,5-dimethyl-2,4-hexadiene (Aldrich) was distilled under nitrogen prior to use. α-Phenylcinnamonitrile was prepared by the method of Frost,[23] recrystallized twice from ethanol, and vacuum sublimed. 2,3-Dimethyl-2-butene (Chemical Samples Co.) was used as received. β,β-Dimethylstyrene was synthesized by Grignard addition of phenylmagnesium bromide to isobutyraldehyde and subsequent dehydration.

Irradiation of α-Phenylcinnamonitrile (1) and 2,5-Dimethyl-2,4-hexadiene (2) in Hexane. An 800-mL hexane solution containing 16.4 g of 1 and 25.5 g 2 was bubbled with nitrogen for 15 min and irradiated 9 h through Pyrex with a Hanovia 450-W medium-pressure mercury lamp. The solvent was removed under reduced pressure, and crude product was obtained as a crystalline mixture of isomers (7.8 g, 31%). A portion of the crude product was chromatographed on alumina by elution with 2% ethyl acetate in hexane. Cycloadduct **3a** elutes first and was obtained in crystalline form: mp 119–120 °C (hexane); NMR (Table III); IR (KBr) 2235, 1605 cm^{-1}. Adduct **3b** could not be separated from **3a** and **4b** by column chromatography and was identified by comparison with a sample isolated from the irradiation of 1 and 2 in 1-propanol. Adduct **4b** was obtained as a 3:1 mixture of **4b** and **4a**. This mixture was rechromatographed under the same conditions to yield pure **4b**: mp 96–98 °C (hexane); NMR (Table III); IR (KBr) 2230, 1605 cm^{-1}. Further elution on the original column afforded pure **4a**: mp 107–109 °C (hexane); NMR (Table III); IR (KBr) 2230, 1605 cm^{-1}.

Irradiation of 1 and 2 in 1-Propanol. Irradiation of 0.8 g of 1 and 3.1 g of 2 in 40 mL of 1-propanol for 9 h with a Hanovia 450-W medium-pressure mercury lamp through Pyrex after degassing with nitrogen resulted in the formation of products **3a,b**, **4a,b**, **6** (R = *n*-Pr), and **7**. Compound **6** (R = *n*-Pr) was identified by GC/MS (15 eV): *m/e* (relative intensity) 169 (90, $PrOC(CH_3)_2CH{=}CHC(CH_3)_2^+$), 110 (100, 2^+). Compound **7** was identified by comparison with an authentic sample. After removal of the solvent under reduced pressure, the crude product was fractionally crystallized from hexane, affording pure **3b** as prisms: mp 108–110 °C; NMR (Table III); IR (KBr) 2230, 1605 cm^{-1}.

Irradiation of 1 and 2 in Methanol. A 750-mL methanol solution containing 16 g of 1 and 29.7 g of 2 was degassed by bubbling nitrogen through the solution for 12 min and irradiated through Pyrex for 72 h with a Hanovia 450-W medium-pressure mercury lamp. The diether 8 (R = CH_3) was isolated by spinning-band distillation [81–83 °C (1 mm Hg)] and identified by comparison of the NMR with an authentic sample prepared by the method of Mizuno, Pac, and Sakurai:[2a] NMR ($CDCl_3$) δ 5.65 (d, *J* = 16 Hz, 2 H), 5.25 (d, *J* = 16 Hz, 2 H), 3.16 (s, 6 H), 1.25 (s, 12 H), 0.96 (s, 12 H); IR (film) 3050–2850, 1470, 1380, 1370, 1070, 910 cm^{-1}; GC/MS (70 eV) *m/e* (relative intensity) 141 (73), 110 (100), 109 (96), 73 (24). A 4.5-g sample of the crude product mixture was chromatographed on 350 g of alumina, eluting with

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2% ethyl acetate in hexane. The cyclobutanes eluted first and were identified by comparison with samples previously isolated (vide supra). Adduct **5** followed and was obtained as an oil. The structure assignment is based on the NMR and GC/MS data: NMR ($CDCl_3$) δ 1.10 (s, 3 H), 1.25 (s, 9 H), 3.10 (s) and 3.25, 3.38 (AB, J = 13.5 Hz, 5 H), 5.45, 5.70 (AB, J = 16 Hz, 2H), 7.10–7.50 (m, 10 H); GC/MS (15 eV) m/e (relative intensity) 206 (2, $PhCH_2CPhCN^+$), 141 (100, $MeOC(CH_3)_2CH{=}CHC(CH_3)_2^+$), 109 (90, $\mathbf{2}^+$), 92 (3, $PhCH_2^+$).

Irradiation of 1 and 2 in Ethanol. A 250-mL ethanol solution containing 5.1 g of **1** and 27.5 g of **2** was degassed by bubbling nitrogen through the solution for 15 min and irradiated 24 h through Pyrex with a Hanovia 450-W medium-pressure mercury lamp. The solvent was removed under reduced pressure. The crude product mixture was dissolved in heptane and extracted three times with acetonitrile and then three times with methanol. The methanol solutions were combined, and the solvent was removed under reduced pressure to yield **6** (R = C_2H_5) as an oil. The structure was assigned on the basis of the mass spectra and NMR data: NMR ($CDCl_3$) δ 5.6 (d, J = 16 Hz), 5.4 (d, J = 16 Hz), 3.3 (q, J = 6.8 Hz), 1.25 (s) 1.15 (t, obscured by singlets), 0.95 (s); GC/MS (15 eV) m/e (relative intensity) 155 (93, $EtOC(CH_3)_2CH{=}CHC(CH_3)_2^+$), 110 (100, $\mathbf{2}^+$), 109 (100). Cycloadducts were identified by comparison with previously isolated samples (vide supra).

Irradiation of 1 and 2 in Acetonitrile. A 200-mL acetonitrile solution containing 6.7 g of **1** and 27.5 g of **2** was degassed by bubbling nitrogen through the solution for 15 min and irradiated through Pyrex for 52 h with a Hanovia 450-W medium-pressure mercury lamp. The solvent and other volatiles were removed under reduced pressure. A 1-g sample of the crude product was chromatographed on 350 g of alumina, eluting with 2% ethyl acetate in hexane. The cycloadducts eluted first and were identified by comparison with previously isolated samples (vide supra). These were followed by **5**, which was isolated as a mixture of cycloadducts and **5**. A sample of this mixture was chromatographed successively on two preparative thick-layer plates to yield pure **5** as an oil: NMR ($CDCl_3$), δ 6.9–7.4 (m, 10 H), 5.85 (br s, 2 H), 3.2 (s, 2 H), 2.8 (s, 2 H), 1.75 (s) and 1.60 (s) and 1.55 (s) (12 H); GC/MS (15 eV): m/e (relative intensity) 315 (9, $\mathbf{8}^+$), 109 (100, $\mathbf{2}^+$), 91 (3, $PhCH_2^+$).

Irradiation of 2-Methyl-1-phenylpropene with 9-Phenanthrenecarbonitrile. A 100-mL solution of 10% methanol in acetonitrile containing 0.15 g of 9-phenanthrenecarbonitrile and 2.0 g of 2-methyl-1-phenylpropene was degassed by bubbling nitrogen through the solution for 10 min and irradiated through Pyrex for 22 h with a Hanovia 450-W medium-pressure mercury lamp. The solvent was removed under reduced pressure and the residue distilled in a Kugelrohr apparatus. The middle fractions [bp 105–118 °C (14 mm)] were combined to yield 1.67 g (65%) of 2-methoxy-2-methyl-1-phenylpropane: NMR ($CDCl_3$) δ 1.13 (s, 6 H), 2.73 (s, 2 H), 3.23 (s, 3 H), 7.20 (s, 5 H).

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Registry No. *trans*-**1**, 16610-80-3; **2**, 764-13-6; **3a**, 80764-29-0; **3b**, 80795-29-5; **4a**, 80764-30-3; **4b**, 80795-30-8; **5**, 80764-31-4; **6** (R = *n*-Pr), 80764-32-5; **6** (R = C_2H_5), 80764-33-6; **7**, 2286-54-6; **8** (R = CH_3), 80764-34-7; β,β-dimethylstyrene, 768-49-0; 2-methoxy-2-methyl-1-phenylpropane, 69278-45-1; 9-cyanoanthracene, 1210-12-4; 9-cyanophenanthrene, 2510-55-6; 2-cyanonaphthalene, 613-46-7; 1-cyanonaphthalene, 86-53-3.

Nucleophilic Attacks on Carbon–Carbon Double Bonds. 28.[1,2] Complete and Partial Stereoconversion in the Substitution of Methyl (*E*)- and (*Z*)-β-Chloro-α-cyano-*p*-nitrocinnamates by Nucleophiles

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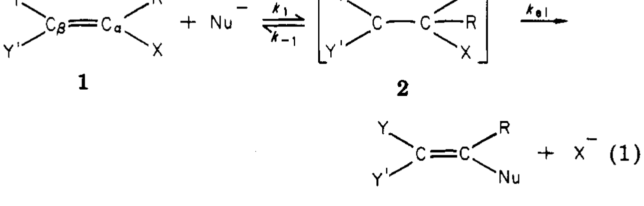
Methyl (*E*)- and (*Z*)-β-chloro-α-cyano-*p*-nitrocinnamates **5-E** and **5-Z** were prepared and separated. The stereochemistry of the substitution of the chlorine by nucleophiles was investigated in MeCN, MeOH, or their mixtures. Reaction with *p*-toluenethiolate ion gave only the *Z* substitution product **10-Z**. Reaction with MeO^- under kinetic control gave 67:33 and 33:67 mixtures of the (*E*)- to (*Z*)-methyl vinyl ethers on starting from **5-E** and **5-Z**, respectively. With excess MeO^- the MeOH adduct of the vinyl ether was obtained. Reaction with the *p*-cresolate ion gave 68:32 and 40:60 *E*/*Z* ratios of the corresponding ethers, on starting from **5-E** and **5-Z**, respectively. The thermodynamically controlled ratio of 77:23 *E*/*Z* ethers is obtained after longer reaction times. Both **5-E** and **5-Z** gave mutual isomerization to a 68:32 **5-E**/**5-Z** mixture with Et_4NCl in MeCN. $NaBH_4$ reduces both the chlorine and the double bond, N_3^- gives a nitrene-rearrangement product, and AcO^- and CF_3COO^- ions give methyl α-cyano-β-hydroxy-*p*-nitrocinnamate in their reactions with **5-E** and **5-Z**. The reactions with $p\text{-}MeC_6H_4S^-$, MeO^-, $p\text{-}MeC_6H_4O^-$, and Cl^- represent complete or partial stereoconversion in the substitution which differs from the usual stereochemical outcome of retention of configuration. This was predicted for a nucleophilic substitution of highly electrophilic olefins and indicates the intermediacy of relatively long-lived carbanionic intermediates which undergo internal rotation of 60°, 120°, and >120° before leaving-group expulsion.

An important question concerning the mechanism of nucleophilic vinylic substitution via addition–elimination[3,4] [eq 1; Y,Y′ = activating groups, X = nucleofuge (leaving group), Nu = nucleophile] is whether the reaction is a single-step or a multistep process. In the single-step process, C_α–Nu bond formation and C_α–X bond cleavage are concerted (and these bonds in **2** are partial), the C_α–C_β bond remains mainly a double bond throughout the sub-



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