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EXCIPLEX AND RADICAL ION INTERMEDIATES IN THE PHOTOCHEMICAL REACTION OF 9-CYANOPHENANTHRENE WITH 2,3-DIMETHYL-2-BUTENE

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Abstract—The photochemical reaction of 9-cyanophenanthrene and 2,3-dimethyl-2-butene, first reported by Mizuno, Pac and Sakurai, has been reinvestigated. The formation of a [2+2]-cycloadduct via a singlet exciplex is the exclusive reaction in the nonpolar solvents benzene and ethyl acetate. Photochemical behavior in polar solvents is far more complicated than previously reported. Mechanisms consistent with the effects of solvent polarity, methanol concentration, methanol deuteration, and light intensity upon product yields are proposed. Formation of a 9-cyanophenthrene anion radical and 2,3-dimethyl-2-butene cation radical is the primary photoinitiated process in polar solvent. The cation radical can undergo deprotonation to yield an allyl radical or nucleophilic attack by methanol to yield a methoxyalkyl radical. Covalent bonding of these radicals and the 9-cyanophenanthrene anion radical gives rise to the acyclic adducts obtained in polar solvents. The anion radical can also be protonated, leading ultimately to the formation of 9,10-dihydro-9-cyanophenanthrene.

The importance of electron donor-acceptor (D–A) interactions in photochemical reactions has come clearly into focus during the last decade! The interaction of an excited molecule and ground state molecule ($A^* + D$ or $A + D^*$) can, under the proper circumstances, result in either the formation of a charge-transfer stabilized exciplex or in full electron transfer to yield a radical ion pair ($A^{-}D^{+\cdot}$).[2] In the course of our investigations of the singlet state [2+2]-cycloaddition reaction of *trans*-stilbene with electron-rich and electron-poor alkenes, it became clear that cycloaddition occurs more efficiently from relatively nonpolar exciplexes than from highly polar exciplexes or radical ion pairs.[3-5] The highest limiting quantum yields for cycloaddition are obtained with alkenes which are neither strong donors nor acceptors and are relatively inefficient quenchers of singlet stilbene (Fig. 1).[4] In addition, the quantum yields for both cycloaddition and exciplex fluorescence from highly polar exciplexes such as *trans*-stilbene-dimethyl fumarate decrease with increasing solvent polarity.[5] These results led us to conclude that singlet state [2+2]-cycloaddition reactions occur from a singlet exciplex and not from a radical ion pair (Scheme 1). The absence of products in polar nonhydroxylic solvents was attributed to rapid exothermic back electron transfer in the radical ion pair.[2] Radical ion pairs are, of course, intermediates in other photochemical reactions, including the addition of tertiary amines to singlet *trans*-stilbene.[3,6]

In contrast to our results for photochemical [2+2]-cycloaddition, many thermal [2+2]-cycloaddition reactions are accelerated by enhanced donor-acceptor interactions and by increased solvent polarity. Such reactions

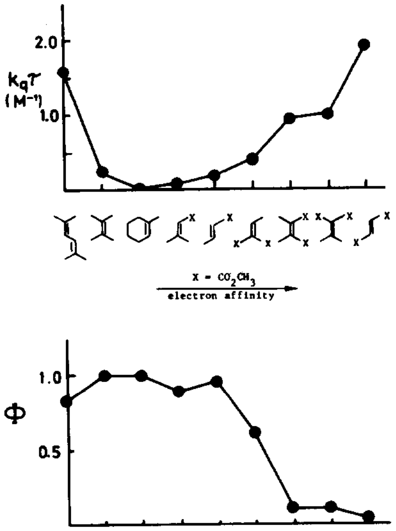
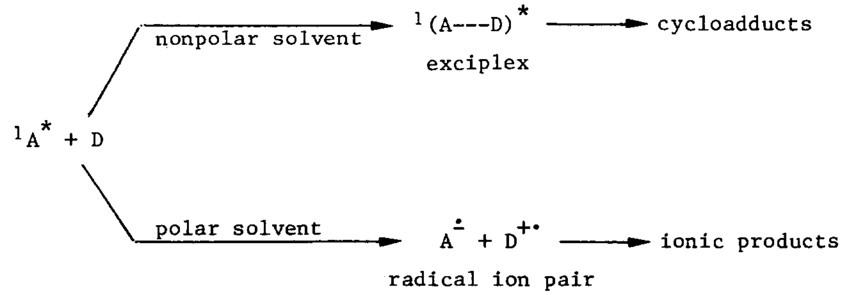


Fig. 1. *trans*-Stilbene Stern–Volmer quenching constants (upper curve) and limiting cycloaddition quantum yields (lower curve) vs alkene electron affinity (arbitrary scale).



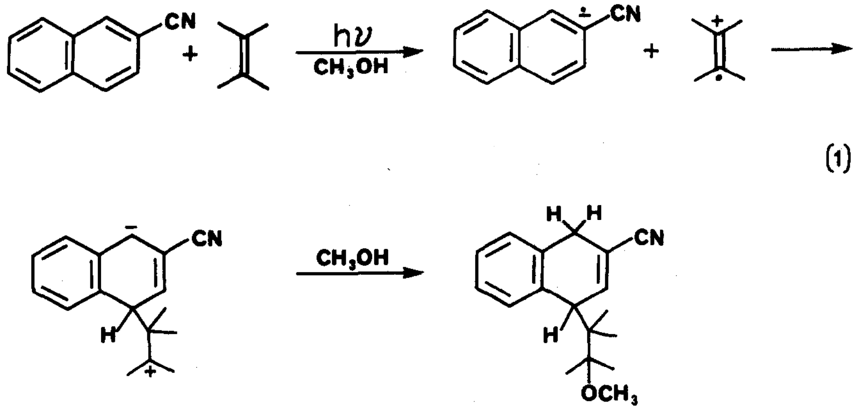
Scheme 1. Exciplex and radical ion pair formation.

occur in stepwise fashion via a 1,4-zwitterionic intermediate.[7] Several years ago Epiotis and Shaik[8] predicted the occurrence of photochemical ionic cycloaddition reactions and noted the absence of reported examples. This prediction prompted us to examine the photochemistry of several electron donor–acceptor pairs known to undergo thermal ionic cycloaddition reactions.[9] The photochemical [2 + 2]-cycloaddition reaction of N-isobutenylpyrrolidine with dimethyl fumarate was found to occur only in nonpolar solvents and to yield a different stereoisomer than the thermal reaction, the rate of which increases with increasing solvent polarity. This result supported our conclusion that singlet state [2 + 2]-cycloaddition occurs via a nonionic mechanism (Scheme 1).

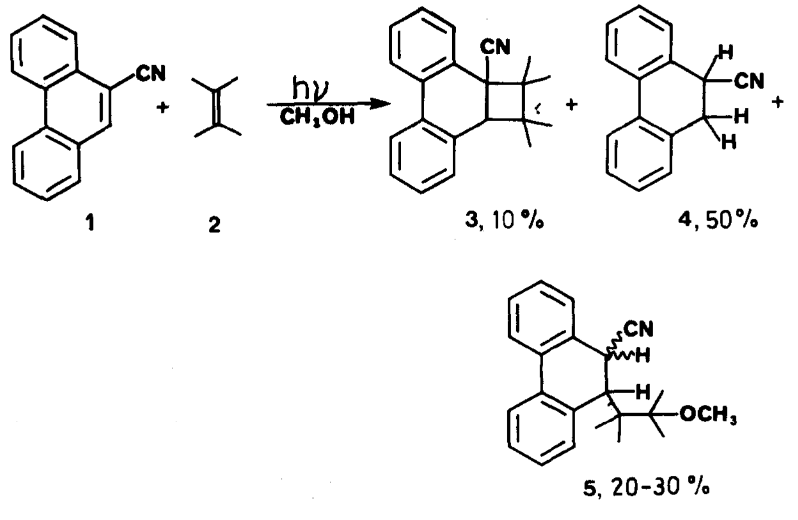
Our failures to observe photochemical ionic cycloaddition reactions could, of course, be attributed to unfortunate choices of reactants and reaction conditions. Definitive evidence for the intermediacy of 1,4-zwitterions in thermal [2 + 2]-cycloaddition reactions was provided by their interception with alcohols.[7] Thus we were attracted by the mechanism proposed by McCullough *et al.*[10] for the formation of methanol-incorporated adducts of 2-naphthonitrile and 2,3-dimethyl-2-butene (eqn 1). A similar solvent-incorporated adduct was reported by Pac *et al.*[11] as one of three products obtained upon irradiation of 9-cycanophenanthrene with 2,3-dimethyl-2-butene in methanol solution (eqn 2). The exclusive formation of cycloadduct 3 in benzene solution was attributed to reaction via a singlet exciplex.[11] The formation of dihydrophenanthrene 4 and solvent-incorporated adduct 5 in methanol was attributed to reaction via a radical ion pair;[11] however, the mechanism of bond formation was not addressed. We thought it might be possible to determine if 3 and/or 5 are formed via a 1,4-zwitterionic intermediate simply by determining the effect of methanol concentration on the yields of products in a polar nonhydroxylic solvent. What was intended as a simple investigation developed into a most fascinating and complicated mechanistic problem.

RESULTS AND DISCUSSION

Irradiation in nonhydroxylic solvents. The exclusive product of irradiation of 9-cyanophenanthrene (1, 2 × 10^{-2} M) and 2,3 - dimethyl - 2 - butene (2, 1.7 M) in degassed benzene or ethyl acetate solution is cycloadduct 3. The intercept and slope of a plot of Φ^{-1} vs [2] (eqn 3) provide a limiting quantum yield $\Phi_\infty = 0.19 \pm 0.03$ and a Stern–Volmer quenching constant $k_q\tau = 0.37 \pm 0.06\ M^{-1}$ for benzene solution. Quenching of the fluorescence of 1 by added 2 in benzene solution provides a value of $k_q\tau = 0.31 \pm 0.01\ M^{-1}$ similar to that reported by Pac *et al.*[11] for cyclohexane solution. The



(1)



(2)

agreement of $k_q\tau$ values obtained from product formation and fluorescence quenching data confirms that formation of **3** occurs via the singlet state of **1**. The

$$\Phi^{-1} = \Phi_\infty^{-1}(1 + 1/k_q\tau\,[\mathbf{2}]) \qquad (3)$$

rate constant for quenching of singlet **1** by **2** is calculated to be $k_q = 2.1 \times 10^7\ \text{M s}^{-1}$ using the value for $\tau = 15$ ns reported by Caldwell *et al.*[12] for nondegassed benzene solution.

Irradiation of **1** and **2** in acetonitrile solution results in the formation of cycloadduct **3**, dihydrophenanthrene **4**, acyclic adduct **6**, and dienes **7a**, **7b** (eqn 4). The mass balance for formation of **3**, **4** and **6** vs disappearance of **1** is satisfactory. While there have been numerous reports of arene-olefin cycloaddition reactions involving olefin **2**,[3,10,11] dienes **7a** and **7b** have not previously been reported as products of such reactions[13] and allylic addition products such as **6** have but rarely been observed.[14,15] The structure of adduct **6** is based upon spectral data (Experimental). Only one stereoisomer of **6** was evident from the NMR spectrum of the isolated adduct or the GC-MS of the total product mixture. *cis*-Stereochemistry is tentatively assigned on the basis of comparison of the vicinal coupling constant ($J_{c,x} = 4.9$ Hz) with the reported values for *cis* and *trans* - 9 - acetoxy - 10 - chloro - 9,10 - dihydrophenanthrene.[16]

Plots of Φ^{-1} vs $[\mathbf{2}]^{-1}$ (eqn 3) for the products of irradiation in acetonitrile solution are shown in Fig. 2. The linear plot of the data for cycloadduct **3** provides values of $\Phi_\infty = 0.11 \pm 0.04$ and $k_q\tau = 0.40 \pm 0.15\ \text{M}^{-1}$, similar to those for benzene solution. A substantially higher value of $k_q\tau = 35 \pm 1\ \text{M}^{-1}$ is obtained from a linear fluorescence quenching Stern–Volmer plot. The plots shown in Fig. 2 for dienes **7a** and **7b** display slight upward curvature. Limiting quantum yields $\Phi_\infty = 0.20 \pm 0.02$ and 0.16 ± 0.02 and quenching constants $k_q\tau = 1.9 \pm 0.2$ and $1.2 \pm 0.2\ \text{M}^{-1}$ are obtained for **7a** and **7b**, respectively, from the data for low olefin concentration [**2**]. Marked upward curvature at high olefin concentrations is observed for product **4** and **6** (Fig. 2). It is unlikely that this curvature results from the reaction of both singlet and triplet states of **1** with **2**, as the fluorescence quenching data indicates that the lowest concentration of **2** employed is sufficient to quench 94% of singlet **1**. The rate constant for quenching of singlet **1** by **2** in acetonitrile solution obtained from the fluorescence quenching data and the reported value of $\tau = 24$ ns in degassed acetonitrile solution[17] is $k_q = 1.5 \times 10^9\ \text{M}^{-1}\ \text{s}^{-1}$. This value is 70-fold larger than the value for benzene solution, yet slower than the rate of diffusion in acetonitrile.

The olefin concentrations employed for the quantum yield measurements shown in Fig. 2 are sufficiently high to influence the bulk solvent dielectric constant. For example the calculated dielectric constants for 0.84 and 2.5 M **2** in acetonitrile are 35 and 28, respectively. The effect of solvent dielectric constant on the yields of products at constant olefin concentration is shown in Fig. 3. The rapid increase in yields of products **4**, **6**, **7a** and **7b** at high solvent dielectric constant indicates that the

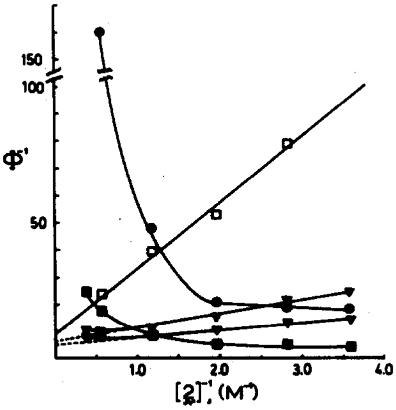


Fig. 2. Dependence of quantum yields for product formation upon concentration of 2,3 - dimethyl - 2 - butene (**2**) in acetonitrile solution: **3** (□), **4** (■), **6** (●), **7a** (▽), **7b** (▼).

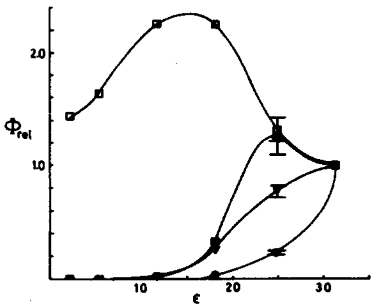
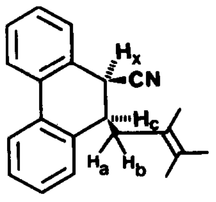


Fig. 3. Solvent dependence of quantum yields for product formation in benzene and ethyl acetate-acetonitrile mixed solvents relative to value in acetonitrile. Dielectric constant $\epsilon = \Sigma_i \epsilon_i V_i$, where V_i is the volume fraction of component i ($V_i = 0.20$ for 1.68 M **2**): **3** (□), **4** (■), **6** (●), **7a** + **7b** (▽).

$$\mathbf{1} + \mathbf{2} \xrightarrow[\text{CH}_3\text{CN}]{h\nu} \mathbf{3} + \mathbf{4} + \mathbf{6} + \mathbf{7a} + \mathbf{7b} \qquad (4)$$

Φ = 0.048 0.057 0.006 0.13 0.10



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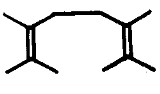
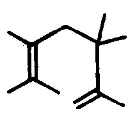


7a



7b

curvature seen in Fig. 2 for these products may arise from a change in the solvent polarity.

The effects of solvents on product yields are indicative of the formation of cycloadduct **3** via a singlet exciplex and products **4**, **6**, **7a** and **7b** via a radical ion pair.[3] The data for **3** in Fig. 3 is reminiscent of that for the cycloaddition product of the diphenylvinylene carbonate - 2,5 - dimethyl - 2,4 - hexadiene exciplex;[18] while the data for the other products is reminiscent to that for the products of the *trans* - stilbene - triethylamine radical ion pair.[6] The free energy for electron transfer from **2** to singlet **1** in acetonitrile solution can be calculated from Weller's equation (eqn 5)[19]

$$\Delta G_{ET} = -E_S - E_{A^-/A} + E_{D/D^+} - \frac{e_0^2}{\epsilon a} \qquad (5)$$

where Es is the singlet energy of **1** obtained from the onset of fluorescence (3.43 eV), $E_{A^-/A}$ is the reduction potential of **1** (−1.91 V vs Ag/AgCl[20]), E_{D/D^+} is the oxidation potential of **2** (1.6 V vs Ag/AgCl[15b]), and the last term is the ionic attraction (*ca.* 0.06 V[19]). The calculated value of $\Delta G_{ET} = 0.0$ eV is consistent with the formation of a radical ion pair in polar solvents with a rate constant slightly less than the rate of diffusion.[2,19] The mechanisms of product formation will be discussed in detail following the presentation of the results obtained upon irradiation of **1** and **2** in methanol solution.

Irradiation in methanol solution. Irradiation of **1** and **2** in methanol solution results in formation of all of the products of irradiation in acetonitrile solution (eqn 4) and, in addition, the methyl ethers **5**, **8a**, **8b** and **9** (eqn 6). Both the absolute and relative quantum yields are dependent upon olefin concentration, thoroughness of degassing, and light intensity (*vide infra*). Thus it is not surprising that the relative yields of products **3**, **4** and **5** are different from those reported by Pac *et al.*[11] We observe the formation of a single stereoisomer of **5**, not the previously reported *cis*, *trans*-mixture.[11] *cis*-Stereochemistry is tentatively assigned on the basis of the vicinal coupling constant ($J_{a,x} = 4.5$ Hz).[16]

The effect of increasing methanol concentration upon the relative quantum yields for product formation in acetonitrile solution is shown in Fig. 4. The yields of methanol-containing products **5**, **8a** and **8b** increase rapidly at low methanol concentration (< 5 mole %) and gradually at higher concentration (Fig. 4). The yield of cycloadduct **3** is relatively insensitive to methanol concentration; however, the yields of **4** and **6** display extraordinary methanol dependence (Fig. 4). The methanol dependence of the product quantum yields does not by itself provide definitive evidence for or against a 1,4-zwitterionic intermediate in the formation of **5** and/or **3**. It does provide a yardstick against which any proposed mechanism must be measured. It should be noted that the yields of all products save **3** are lower in 93 vs 30 mole % methanol in acetonitrile (Fig. 4). This decrease is probably related to the decrease in solvent polarity (Fig. 3) for 93 mole % ($\epsilon = 26.6$) vs 30 mole % ($\epsilon = 30.2$) methanol in acetonitrile.

Irradiation of **1** and **2** in 93 mole % CH_3OD results in essentially quantitative deuterium incorporation in products **4** (9,10-d_2),[11] **5** (9-d) and **6** (9-d) by GC-MS analysis (Table 1). Product **8a** and recovered starting material (> 90% conversion) display low levels of D incorporation, while products **3**, **7a** and **7b** are undeuterated. Only partial deuteration of products **4**, **5** and **6** is observed for 2.6 or 6.5 mole % MeOD in acetonitrile (Table 1). The effect of isotopic substitution (MeOH vs MeOD) upon product quantum yields is reported in Table 2. The quantum yields for formation of cycload-

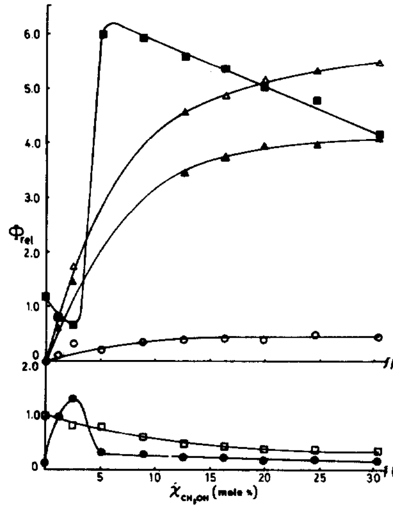


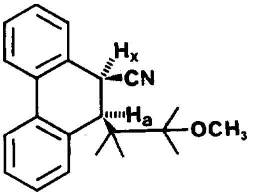
Fig. 4. Solvent dependence of relative quantum yields for product formation in methanol-acetonitrile mixed solvent relative to the yield of cycloadduct **3** in acetonitrile solution: **3** (□), **4** (■), **5** (○), **6** (●), **8a** (△), **8b** (▲).

$$\underset{\sim}{1} + \underset{\sim}{2} \xrightarrow[CH_3OH]{h\nu} \underset{\sim}{3} + \underset{\sim}{4} + \underset{\sim}{5} + \underset{\sim}{6} + \underset{\sim}{7a} + \underset{\sim}{7b} +$$

$$\Phi = 0.027 \quad 0.022 \quad 0.009 \quad 0.001 \quad 0.008 \quad 0.007 \qquad (6)$$

$$\underset{\sim}{8a} + \underset{\sim}{8b} + \underset{\sim}{9}$$

$$\Phi = 0.079 \quad 0.052 \quad 0.007$$



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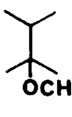
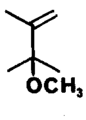
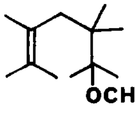


8a



8b



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duct **3** and dienes **7a** and **7b** are relatively insensitive to solvent deuteration, in accord with the absence of D in these products. The yields of adducts **5** and **6** are lower in MeOH vs MeOD (inverse isotope effect) while the yields of **4** and **8a** are distinctly higher (normal isotope effect). Isotope effects are more pronounced at low vs high methanol concentrations.

The final piece of evidence pertaining to the reaction mechanism is provided by the effect of light intensity upon product quantum yields in 6.5 mole % methanol–acetonitrile solution (Table 3). A 5.8-fold increase in light intensity has no effect on the quantum yield for formation of **3**. The quantum yield for formation of **8a** is slightly lower and the quantum yields for formation of **4**, **5** and **6** distinctly higher at the higher light intensity. An increase in yield with light intensity implicates the reaction of two intermediates formed by different photons in the formation of **4**, **5** and **6**.

Electron transfer mechanism. The results obtained for irradiation of **1** and **2** in methanol solution further support an exciplex cycloaddition mechanism (Scheme 1) for the formation of **3** and rule out the formation of **3** and **5** via a common 1,4-zwitterionic intermediate (eqn 1). A common intermediate would require the same light intensity dependence (Table 3) and either similar or complementary responses to methanol concentration (Fig. 4) and deuteration (Table 2). The results show the formation of **3** and **5** to be mechanistically unrelated processes. The effects of solvent polarity (Fig. 3) and composition (Fig. 4) provide prima facia evidence for the formation of products **4–9** via the radical ions $1^{\cdot-}$ and $2^{+\cdot}$, which are formed by photostimulated one-electron transfer in polar solvents. A possible mechanism for the formation of **4–9** is outlined in Scheme 2 (eqns 7–15).

Table 1. Product deuterium incorporation (%)[a]

	Mole % CH_3OD		
Product	2.6	6.5	93
5	53	65	100
6	64	85	b
8a	11	5	6

[a] Data for 2 x 10^{-2} M 9-cyanophenanthrene and 1.7M 2,3-dimethyl-2-butene in deoxygenated methanol-acetonitrile solution.

[b] Yield of 6 too low for accurate analysis.

Table 2. Isotope effects on quantum yields: Φ_H/Φ_D[a]

	Mole % $CH_3OH(D)$		
Product	2.6	6.5	93
3	0.93	0.96	0.77
4	3.9	2.8	1.6
5	0.79	0.65	1.4
6	0.61	0.43	b
7a	0.95	0.81	1.1
7b	0.85	0.90	0.90
8a	2.44	1.71	0.95

[a, b] See footnotes to Table I.

Table 3. Effect of light intensity on quantum yields[a]

Product	Φ_{high}/Φ_{low}[b]
3	1.02 ±0.05
4	4.38
5	1.68
6	1.66
8a	0.85

[a] Data for 2 x 10^{-2} M 9-cyanophenanthrene and 1.7M 2,3-dimethyl-2-butene in deoxygenated 6.5 mole % methanol-acetonitrile solution.

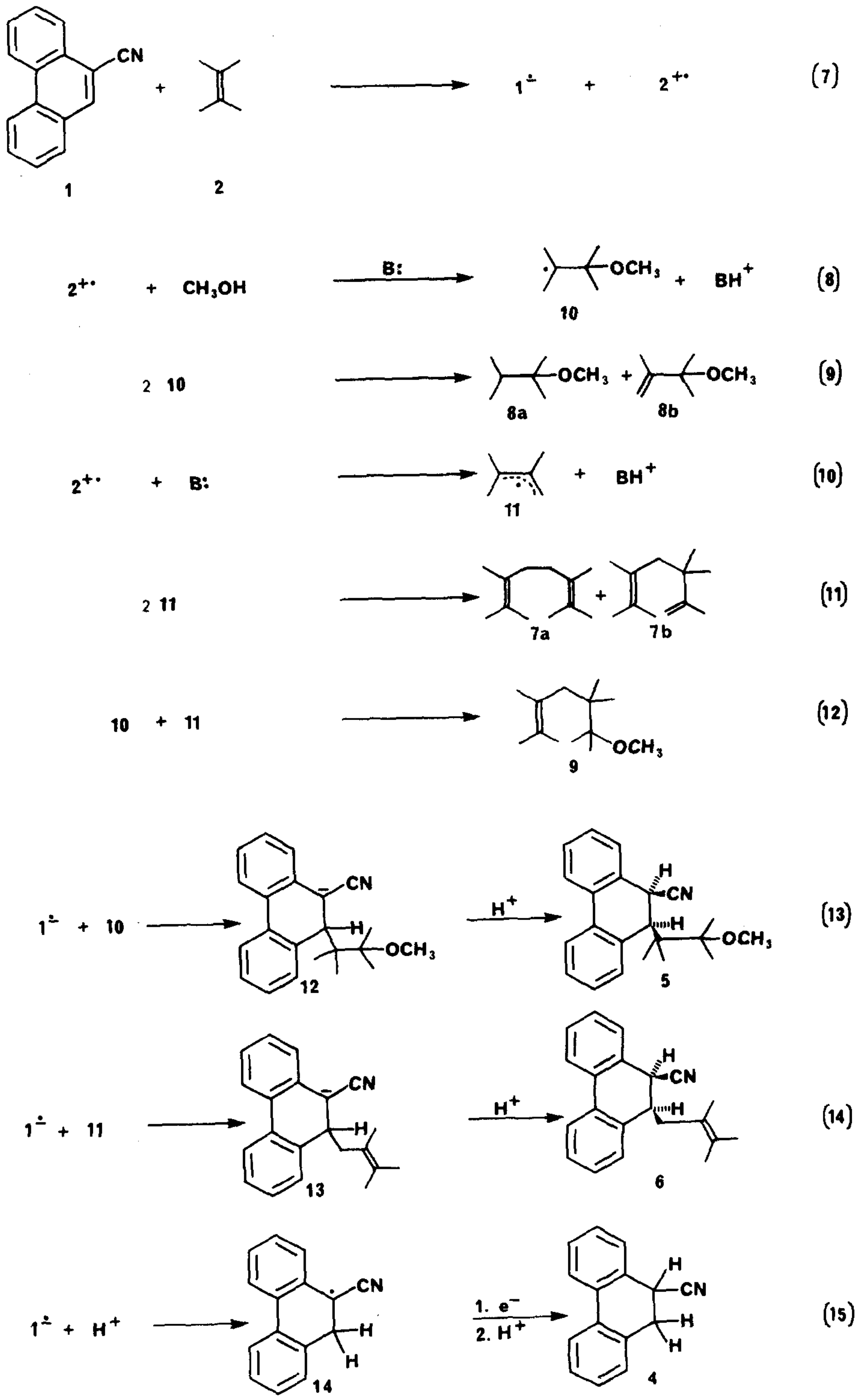
[b] $I_{high} = 2.47 \times 10^{-7}$ Einstein s^{-1}, $I_{low} = 4.25 \times 10^{-8}$ Einstein s^{-1}, $I_{high}/I_{low} = 5.8$.

The formation of ethers **8a** and **8b**, the major products of irradiation of **1** and **2** in methanol solution (eqn 6), is proposed to occur via nucleophilic attack of methanol on $2^{+\cdot}$ to yield the free radical **10** followed by autodisproportionation of **10** to yield **8a** and **8b** (eqns 8 and 9). The absence of the auto-coupling product of **10** in the reaction mixture is consistent with the known preference of tertiary radicals for disproportionation vs combination.[21] MacBlane[20] has observed that **8a** and **8b** are the major products obtained upon irradiation of several aryl nitriles with **2** in methanol solution; the yield increasing with increasing electron affinity of the aryl nitrile singlet state (eqn 5). Kropp[22] has also reported the formation of **8a** and **8b** upon direct irradiation of **2** in methanol solution; however, no light is absorbed by **2** under the conditions of our reactions. It is interesting to compare the products of the reaction of methanol with $2^{+\cdot}$ to those obtained in the reactions of aryl olefin cation radicals with methanol. The mechanism proposed by Arnold[23] for anti-Markovnikov addition of methanol to 1,1-diphenylethylene is given in Scheme 3. The small excess of **8a** vs **8b** (eqn 6) and extent of D incorporation in 8a (Table 1) indicate that the reaction pathway shown in Scheme 3 is at best a minor one for olefin **2**. A possible explanation for the reduction of the methoxydiphenylethyl radical (Scheme 3) but not radical **10** is provided by the reported high gas phase electron affinity of the benzyl radical (*ca.* 20 kcal/mole).[24] Thus electron transfer from $ArCN^{\cdot-}$ to free radical intermediates may be exothermic for benzyl radicals but endothermic for t-alkyl radicals.

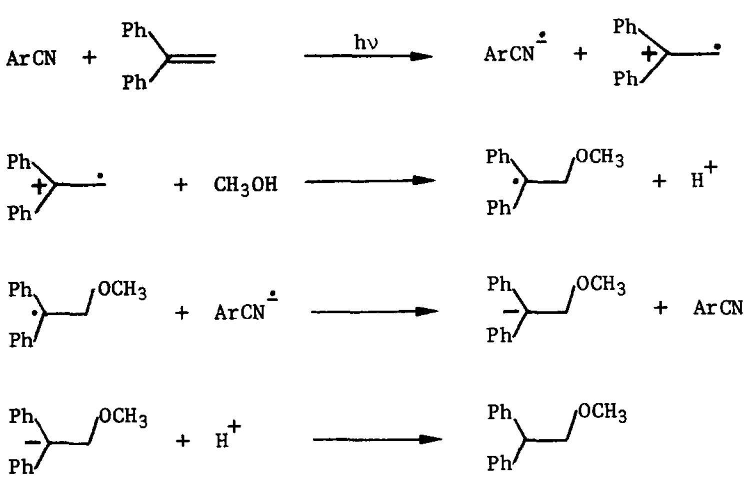
The formation of dienes **7a** and **7b**, the major products of irradiation of **1** and **2** in acetonitrile solution (eqn 4), is proposed to occur via deprotonation of $2^{+\cdot}$ to yield allyl radical **11** followed by tail-to-tail and head-to-tail combination of two allyl radicals to yield **7a** and **7b**, respectively (eqns 10 and 11). Engel *et al.*[25] have reported that thermolysis of azoalkane **15** yields exclusively allyl radical autocombination products, the tail-to-tail product predominating (eqn 16). The formation of product **9** in methanol can occur by cross-combination of radicals **10** and **11**. Engel[25] reports that cross-termination of Me and allyl radicals displays a marked preference for combination vs disproportionation.

The formation of products **7a**, **7b**, **8a**, **8b** and **9** via radical-radical termination (eqns 9, 11 and 12) suggests the possibility that adducts **5** and **6** might be formed via combination of radicals **10** and **11** with the 9 - cyano - 9 - hydrophenanthryl radical **16**. This mechanism can be excluded from consideration for at least two reasons. First, radical **16** should be less stable than its isomer **14**.[26] Investigations by Correa[27] in this laboratory have established that **14** is the exclusive intermediate radical formed in the photoreduction of **1** by amines. Second, radical combination of **16** with **10** or **11** should be stereorandom; whereas, **5** and **6** are formed stereospecifically.

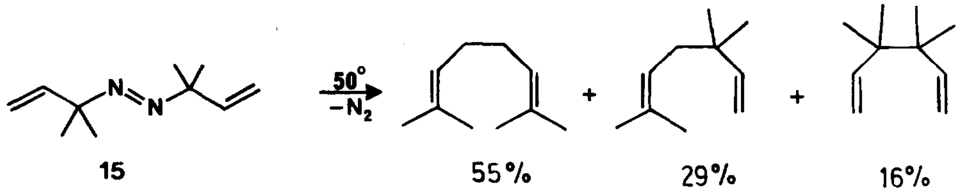
Having rejected a 1,4-zwitterion mechanism for the formation of **5** and a radical coupling mechanism for the formation of **5** and **6**, we propose that the formation of **5** and **6** results from covalent bond formation between



Scheme 2. Electron transfer mechanism for product formation



Scheme 3. Electron transfer mechanism for anti-Markovnikov addition of methanol to 1,1-diphenylethylene



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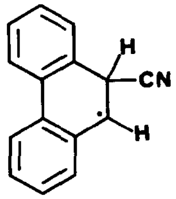

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radicals **10** and **11** and anion radical 1^{-} to yield carbanions **12** and **13** (eqns 13 and 14). An indication of the stability of these carbanions is provided by the relatively high acidity of 9,10 - dihydro - 9 - cyanophenanthrene ($pK_a = 21.9$ in DMSO).[28] Precedent for the stereospecific protonation of carbanions **12** and **13** is provided by the stereospecific cis reduction of 9,10-dialkyl phenanthrenes by lithium in ammonia[29] and stereoselective exchange of benzylic protons in a rigid N-nitrosodibenzazepine.[30] The extent of deuterium incorporation in adducts **5** and **6** (Table 1) indicates that methanol is the dominant proton donor at high methanol concentrations, but that a second protom donor (probably $2^{+\cdot}$, eqn 10) is involved at low methanol concentrations. The formation of **5** and **6** via the combination of two reactive intermediates, which are not necessarily formed by a single photon, accounts for the increased yield of **5** and **6** at higher light intensities (Table 3).

The mechanism proposed for reduction of **1** to dihydrophenanthrene **4** (eqn 15) is the same as that for electrochemical[31] and alkali metal[29] reduction of phenanthrenes: namely, two sequential electron transfer-proton transfer reactions. As is the case for carbanions **12** and **13**, protonation can involve either solvent or $2^{+\cdot}$. At high methanol concentrations solvent predominates, thus accounting for the extensive dideuteration of **4** in 93 mole % CH_3OD. The only possible source of the second electron required in the reduction process is 1^{-}. The pronounced effect of light intensity on the quantum yield for the formation of **4** (Table 3) is consistent with a mechanism requiring the reaction of a free radical derived from 1^{-} with a second 1^{-} (eqn 15). We were at first reluctant to propose the formation of radical **14** in view of the absence of either free radical coupling products of **14** with **10** or **11** or auto-termination products. No dimer of radical **14** was detected and disproportionation can be ruled out by the absence of deuterium incorporation in recovered **1**. A possible explanation of the absence of products other than **4** derived from radical **14** is provided by its anticipated stability[26] and high electron affinity.[24,28]

Having presented mechanisms for all of the products formed upon irradiation of **1** and **2** in methanol solution (Scheme 2) we can now account for the highly complex dependence of product yields upon methanol concentration (Fig. 4) and deuteration (Tables 1, 2). Cation radical $2^{+\cdot}$ undergoes two competing reactions; nucleophilic addition of methanol (eqn 8) and deprotonation by methanol or anion radical 1^{-} (eqn 10). Anion radical 1^{-} also undergoes two competing reactions; free radical addition of **10** or **11** (eqns 13 and 14) and protonation by methanol or cation radical $2^{+\cdot}$. Protonation of 1^{-} promotes the formation of **4** and inhibits the formation of **5** and **6**. Protonation of 1^{-} should be slower in MeOD vs MeOH, accounting for the lower yields of **4** and **8a** (normal isotope effect) and higher yields of **5** and **6** (inverse isotope effect) in MeOD (Table 2).

The effects of methanol concentration on product yields (Fig. 4) can be explained if it is assumed that a methanol concentration of *ca.* 5–10 mole % is sufficient to scavenge all $2^{+\cdot}$ prior to its diffusion away from 1^{-}.

This assumption accounts for the nearly constant yields of **5** and **6** from 5–30 mole% methanol. The slow decrease in the yield of **4** and increase in the yields of **8a** and **8b** in this concentration range indicate that the protonation of $\mathbf{1}^{\dot{-}}$ by methanol is much slower than the reactions of $\mathbf{2}^{+\cdot}$ with methanol. Formation of **4** requires electron transfer from $\mathbf{1}^{\dot{-}}$ to radical **14** (eqn 15) resulting in an optimum yield of **4** at 5–10 mole% methanol. At low methanol concentrations (< 5 mole %) deprotonation of $\mathbf{2}^{+\cdot}$ (eqn 10) is apparently favored over nucleophilic attack (eqn 8). An increase in the concentration of radical **11** can account for the increased yield of **6** (eqn 14) and decreased yield of **4** (eqn 15). Low concentrations of methanol may allow $\mathbf{1}^{\dot{-}}$ and $\mathbf{2}^{+\cdot}$ to diffuse apart prior to reaction of $\mathbf{2}^{+\cdot}$ with methanol. Diffusion away from $\mathbf{1}^{\dot{-}}$ should substantially increase the acidity of $\mathbf{2}^{+\cdot}$, thus accounting for an increased rate of deprotonation vs nucleophilic attack (eqn 10 vs 8).[32] We are currently engaged in kinetic modeling of Scheme 2 in order to test the assumption that the rate of diffusion of the radical ion pair $\mathbf{1}^{\dot{-}}\mathbf{2}^{+\cdot}$ is larger than the rate of reaction of $\mathbf{2}^{+\cdot}$ with methanol at low methanol concentrations (< 5 mole %).

CONCLUSIONS

The initial objective of this investigation was to establish the mechanism of bond formation for the methanol-incorporated adduct **5** observed by Pac *et al.*[11] We have presented evidence for the formation of both **5** and **6** via reaction of an aryl nitrile anion radical $\mathbf{1}^{\dot{-}}$ with an alkyl radical (**10** or **11**). The failure of $\mathbf{1}^{\dot{-}}$ and $\mathbf{2}^{+\cdot}$ to form a 1,4-zwitterionic intermediate, as proposed by McCullough[10] (eqn 1), adds to our previous failures to establish the occurrence of photo-initiated ionic cycloaddition reactions.[4,9] The failure to observe ionic addition of $\mathbf{1}^{\dot{-}}$ and $\mathbf{2}^{+\cdot}$ probably reflects the slow inherent rate of such a process (resulting from a low pre-exponential factor) when compared to the rates of exothermic back electron transfer, proton transfers (eqns 10 and 15), or nucleophilic trapping (eqn 8). The proposed mechanism for formation of **5** and **6** via anion radical-radical coupling is quite similar to the $S_{RN}1$ mechanism for addition of free radicals to enolates.[33] Radical ion-radical coupling mechanisms have been proposed for several other electron-transfer initiated photochemical reactions and it is likely that such mechanisms may prove to be rather common.[34] Evidence for radical ion-radical coupling in the reaction of 2-naphthonitrile and 2,3 - dimethyl - 2 - butene (eqn 1) is provided by the stereospecific cis addition of the tertiary alkyl radical **10** and deuterium in CH_3OD.[10]

A final word is in order concerning the efficiency of product formation via the electron transfer mechanism shown in Scheme 2. A lower limit for the quantum yield for formation of $\mathbf{2}^{+\cdot}$ in acetonitrile solution can be established from the limiting quantum yields for formation of dienes **7a** and **7b** (eqn 17). The value obtained from the intercepts in

$$\Phi_{\mathbf{2}^{+\cdot}} \geq \Phi_{\mathbf{11}} = 2(\Phi_{\mathbf{7a}} + \Phi_{\mathbf{7b}}) + \Phi_{\mathbf{6}} \qquad (17)$$

Fig. 2 is $\Phi \geq 0.83$. Thus electron-transfer derived products account for nearly all of singlet **1** which does not undergo cycloaddition ($\Phi_3 = 0.11$). Apparently back electron transfer from $\mathbf{1}^{\dot{-}}$ to $\mathbf{2}^{+\cdot}$ does not compete effectively with the chemical reactions of $\mathbf{1}^{\dot{-}}$ and $\mathbf{2}^{+\cdot}$.[2] Our results also indicate that exciplex and radical ion pair formation are competitive rather than sequential processes (Scheme 1). Thus, the value of $k_q\tau$ obtained from fluorescence quenching is 70-fold higher in acetonitrile vs benzene; whereas, the $k_q\tau$ values obtained from cycloaddition quantum yields are viturally the same in both solvents. The unusual observation of concurrent exciplex cycloaddion and radical ion chemistry in polar solvents is most likely a consequence of the isoergonic nature of the electron transfer process (eqn 5). Arene-olefin exciplexes for which electron transfer is endoergonic yield only cycloadducts in polar solvents;[18] whereas, only radical ion chemistry is observed when electron transfer is exergonic.[10,15a,32]

EXPERIMENTAL

General. Benzene (Aldrich, gold label) was distilled from P_2O_5 and from sodium/benzophenone under N_2 prior to use. Acetonitrile (Burdick and Jackson) was distilled under N_2 from CaH_2 prior to use. Methanol (Burdick and Johnson) was distilled under N_2 from $Mg(OCH_3)_2$ prior to use. EtOAc (Aldrich, gold label) was used as received. Gas chromatographic analyses employed Hewlett–Packard 5750 and Varian 3700 gas chromatographs, each equipped with flame ionization detectors. Products **8a** and **8b** were analyzed on a 10 ft × $\frac{1}{8}$ in. GC column of 8% carbowax 1000/1% KOH on chromosorb G. Product **5** was analyzed on a 3 ft × $\frac{1}{8}$ in. GC column of 5% SF96 on chromasorb G. All other products were analyzed on a 6 ft × $\frac{1}{8}$ in. 3% OV101 on Supercoport GC column. Fluorescence spectra were obtained on a Perkin–Elmer MPF-44A fluorescence spectrometer equipped with a corrected spectra unit. NMR spectra were recorded using Varian EM360 (60 MHz), CFT-20 (80 MHz), and Perkin–Elmer R20B (60 MHz) NMR spectrometers. IR spectra were obtained on a Perkin–Elmer 283 IR spectrometer and a Nicolet 7199 Fourier-transform IR spectrometer interfaced with a Varian 3700 gas chromatograph. Mass spectra were obtained on a Hewlett–Packard 5985 GC/MS system.

Materials. Compound **2** (Aldrich, 99 + %, or Chemical Samples Co., ≥ 98%) was stored under N_2 at 5° prior to use. Compound **1** (Aldrich) was recrystallized four times from EtOH and vacuum sublimed. *trans*-Stilbene (Aldrich) was recrystallized from benzene and from EtOH. Benzophenone (Aldrich) was recrystallized three times from EtOH. Benzohydrol (Aldrich) was recrystallized four times from benzene/hexane mixtures.

Quantum yields were measured at 313 nm using a 450 W or 200 W Hanovia medium pressure mercury arc in a water-cooled Pyrex immersion well. Monochromatic light was provided using a $K_2Cr_2O_7$ filter soln. Samples in 13 mm o.d. Pyrex ampules were vacuum line degassed five freeze-pump-thaw cycles. Samples were irradiated on a merry-go-round apparatus immersed in a water bath. Light intensities were measured by chemical actinometry using benzophenone/benzhydol reduction[35] or *trans*-stilbene isomerization ($\varphi_{trans \to cis} = 0.44$).[5] Product formation was measured by gas chromatography (≤ 10% conversion) with octane, tetradecane, hexadecane or octadecane as internal standard.

Irradiation in acetonitrile. A 100 ml soln containing 0.40 g **1** (2.0 mmole) and 18 g **2** (220 mmole) in acetonitrile was placed in a Pyrex annulus, bubbled with N_2 for 10 min, and then irradiated with a 450 W Hanovia medium pressure mercury arc for 7 hr. Solvent and unreacted **2** were removed by distillation (13 g **2** recovered). The residue was washed twice with pentane to remove **7a**, **7b** and some **4**. The washings were combined, the pentane removed under reduced pressure and the residue distilled in a Kugelrohr apparatus 98–110°/21 mm to yield 0.33 g (7% based on consumed **2**) of a colorless oil. The oil was identified as a 57:43 mixture of **7a**:**7b** by comparison with literature NMR and IR spectra.[13]

Approximately 30% of the residue remaining after washing with pentane was chromatographed on two preparative thin layer plates (silica gel) eluting with 2% EtOAc in hexane. The sections enriched in product **6** ($0.27 \leq R_f \leq 0.33$) were combined and rechromatographed under similar conditions to afford pure **6**: ^{1}H NMR δ ($CDCl_3$) 1.07 (s, 3H); 1.55 (s, 6H); ABCX: 2.19 (H_A), 2.38 (H_B), 3.22 (H_C), 4.33 (H_X), $J_{AB} = 13.6$ Hz, $J_{AC} = 9.8$ Hz, $J_{BC} = 4.9$ Hz, $J_{CX} = 4.9$ Hz; 6.93–7.85 (m, 8H) (see text for structure and discussion). Coupling constants and chemical shifts of the ABCX system were assigned with the aid of computer-synthesized spectra. IR spectrum (CCl_4): 2860–3110 cm^{-1} (s), 2245 (w), 1484 (s), 1453 (s), 1445 (s), 1376 (m). GC/MS (15 eV): *m/e* 287 (M^+, 5.6%), 204 (27.9%), 178 (100%), 83 (41.6%).

Products **3** and **4** ($0.20 \leq r_f \leq 0.24$ and $0.08 \leq R_f \leq 0.16$) were identified by comparing the GC/MS with that of samples isolated from methanol (see below).

Irradiation in methanol. A 235 ml soln containing 1.00 g **1** (4.9 mmole) and 7.1 g **2** (85 mmole) in MeOH was placed in a Pyrex annulus, the soln degassed by bubbling with N_2 for 10 min, and irradiated using a 450 W Hanovia medium pressure mercury arc for 21 hr. Products **8a** and **8b** were identified by comparing GC/MS with those of authentic samples.[20] Product **9** was identified by comparing the GC/MS with that of an independently synthesized sample (see below). Product **6** was identified by comparing the GC/MS with a sample of **6** from acetonitrile (see above). The solvent, unreacted **2**, and volatile products were removed under reduced pressure and the residue chromatographed on alumina eluting with 15% EtOAc in hexane using the flash chromatography technique of Still *et al.*[36] Addition of hexane to the fractions containing **3** caused crystallization of **3** (48 mg, 3.4%). The mother liquor, containing significant quantities of **3**, **4** and **5**, was rechromatographed using flash chromatography on silica gel eluting with 3% EtOAc. Additional **3** was recovered from these fractions upon concentration by solvent removal for a combined yield of 72 mg (5.1%): m.p. (uncorrected): 193–194° (lit. 186–188°).[11] ^{1}H NMR δ ($CDCl_3$): 0.52 (s, 3H), 0.83 (s, 3H), 1.16 (s, 3H), 1.60 (s, 3H), 3.86 (s, 1H), 6.8–8.05 (m, 8H). IR (KBr): 2875–3070 cm^{-1} (s); 2223 (m); 1488, 1479 (m); 1449–1440 (s); 1395 (w); 1380, 1375 (m); 1156 (m); 1138 (m); 758 (s); 733 (s). This sample showed the same GC/MS as a sample obtained from irradiation of **1** and **2** in benzene. GC/MS (30 eV): *m/e* 203 (39%), 84 (100%).

Subsequent fractions from the silica gel column contained **4**, which was identified by comparing the ^{1}H NMR with that reported in the literature.[16b]

Attempts to isolate **5** by column chromatography were unsuccessful. An NMR sample was obtained, however, by chromatographing a portion of the mother liquor from the isolation of **3** (**3** and **5** co-elute under all column chromatography conditions attempted) on a preparative thick layer plate (silica gel), eluting with 4% EtOAc in hexane ($0.25 \leq R_f \leq 0.30$). ^{1}H NMR δ ($CDCl_3$): 0.49 (s, 3H), 0.70 (s, 3H), 1.18 (s, 3H), 1.25 (s, 3H), 3.30 (s, 3H), 3.80 (d, J = 4.5 Hz, 1H), 4.42 (d, J = 4.5 Hz, 1H), 7.2–7.8 (m, 8H). (See text for discussion.) GC/MS (CH_4 chemical ionization): *m/e* 320 (MH^+, 25.0%), 288 (1.0%), 204 (100%).

Synthesis of 2,3,3,5,5,6-*hexamethyl* - 6 - *methoxy* - 1 - *heptene* (**9**). A 5 ml soln containing 0.71 g **2** (8.4 mmole) in MeOH was placed in a 13 mm o.d. quartz test tube, bubbled with N_2 for 3 min, and irradiated for 48 hr in a Rayonet reactor equipped with the 254 mm light source. The resulting mixture contained **7a**, **7b**, **8a**, **8b** and **9** by GC/MS analysis. Products **8a** and **8b** account for ≥ 75% of the products, the bulk of the remainder being **9**. The solvent, unreacted starting material, and all volatile products were removed using a rotary evaporator. The residue was distilled in a Kugelrohr apparatus at 65–70°, (4 mm), to yield **9** as a clear oil (~ 20 mg, 2%): ^{1}H NMR δ ($CDCl_3$): δ 0.87 (s, 6H), 1.13 (s, 6H), 1.67 (broad s, 9H), 2.17 (broad s, 2H), 3.20 (s, 3H). GC/IR (gas phase, cm^{-1}): 2982 cm^{-1} (s), 2923 (s), 2832 (m), 1473 (m), 1380 (s), 1147 (s), 1080 (s). GC/MS (CH_4 chemical ionization): *m/e* 199 (MH^+, 15%), 198 (M^+, 35%), 167 (83%), 165 (100%), 115 (74%), 111 (81%).

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