and P. v. R. Schleyer, Ed., Wiley Interscience, 1973, p 1734, and references cited therein.

(38) A further possible difference between these protonated aldehydes and ketones could possibly derive from differences in their preferred ground state conformations. The formation of the protonated oxete would take place from a s-cis conformation, and this is probably not the preferred conformation of the protonated aldehydes.

(39) A. Devaquet, *J. Am. Chem. Soc.*, **94**, 5160 (1972); R. R. Birge and P. A. Leermakers, *ibid.*, **94**, 8105 (1972); A. Devaquet and L. Salem, *Can. J. Chem.*, **49**, 977 (1971); J. J. McCullough, H. Ohorodnyk, and D. P. Santry, *Chem. Commun.*, 570 (1969).

(40) G. J. Brealey and M. Kasha, *J. Am. Chem. Soc.*, **77**, 4462 (1955); R. Rusakowicz, G. W. Byers, and P. A. Leermakers, *ibid.*, **93**, 3263 (1971).

(41) J. Bacon and R. J. Gillespie, *J. Am. Chem. Soc.*, **93**, 6914 (1971); G. A. Olah, J. R. DeMember, R. H. Schlosberg, and Y. Halpern, *ibid.*, **94**, 156 (1972).

Radical Ions in Photochemistry. 3. Photosensitized (Electron Transfer) Cleavage of β-Phenethyl Ethers[1]

D. R. Arnold*[2] and A. J. Maroulis

Contribution from the Photochemistry Unit, Department of Chemistry,
University of Western Ontario, London, Ontario, N6A 5B7, Canada.

Received January 5, 1976

Abstract: The photosensitized (electron transfer) irradiation of some β-phenethyl ethers led to cleavage of the α-carbon-carbon bond. For example, the photosensitized irradiation of 2,2-diphenylethyl isopropyl ether (IIb) in acetonitrile-methanol solution gave diphenylmethane (III) and the methyl isopropyl acetal of formaldehyde (IVb). Photosensitizers which were effective include methyl *p*-cyanobenzoate (V), *p*-dicyanobenzene (VI), and 1,4-dicyanonaphthalene (VIII); 1-cyanonaphthalene (VII) was not effective. Electrochemical and photophysical evidence was obtained which supports the proposed mechanism. The primary process is an electron transfer which gives the sensitizer radical anion and the ether radical cation. Fluorescence studies indicated that the singlet states of the sensitizers V, VI, and VIII were quenched by IIb. The singlet state of VII was not quenched by IIb. Triplet-triplet transfer photosensitized experiments indicate that the triplet of VI does not bring about reaction. The relationship involving the reduction potential of the sensitizer, the oxidation potential of the ether, the available electronic-excitation energy, and the energy associated with the electron-transfer process has been used to correlate the results.

Introduction

In part 1 of this series we described the photosensitized (electron transfer) additions of alcohols to 1,1-diphenylethylene (I) (reaction 1 (eq 1)).[3a] This reaction, which yields the

$$\underset{\text{I}}{(C_6H_5)_2C{=}CH_2} + ROH \xrightarrow[CH_3CN]{h\nu,\,\text{sens}} \underset{\text{II}}{(C_6H_5)_2CHCH_2OR} \qquad (1)$$

	R	% yield
IIa	$-CH_3$	36
b	$-CH(CH_3)_2$	49
c	$-C(CH_3)_3$	17

Sens: methyl *p*-cyanobenzoate (V)
p-dicyanobenzene (VI)
1-cyanonaphthalene (VII)

ethers IIa-c expected from anti-Markownikoff addition, has been studied in detail and, when the minor products were isolated and characterized, diphenylmethane (III) was found among them. In fact, under some conditions, III 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 1, we decided to focus some attention on it.

We found that diphenylmethane (III) was a secondary photolysis product which results from the photosensitized (electron transfer) decomposition of the initially formed ether (reaction 2 (eq 2)). The other product of this reaction was the acetal of formaldehyde (IV). In fact, by either prolonged irradiation starting with the olefin (I) or by starting with the ether (II), yields between 40 and 60% of III and IV can be realized under some conditions.

$$\underset{\text{IIa-c}}{(C_6H_5)_2CHCH_2OR} + R'OH \xrightarrow[CH_3CN]{h\nu,\,\text{sens}} \underset{\text{III}}{(C_6H_5)_2CH_2} + \underset{\text{IV}}{R'OCH_2OR} \qquad (2)$$

IVa, $R = R' = CH_3$
b, $R = CH(CH_3)_2$; $R' = CH_3$
c, $R = R' = CH(CH_3)_2$
d, $R = R' = C(CH_3)_3$

Sens: V, VI, 1,4-dicyanonaphthalene (VIII)
(VII was *not* effective)

Scheme I

(1) $A \xrightarrow{h\nu} A^*$

(2) (a) $A^* + II \longrightarrow II \ldots A^*$ (encounter complex)

(b) $II \ldots A^*$ (encounter complex) $\longrightarrow II^{\cdot +} \ldots A^{\cdot -}$ (radical ion pair or exciplex)

(c) $II^{\cdot +} \ldots A^{\cdot -}$ (radical ion pair or exciplex) $\longrightarrow II^{\cdot +}_{(s)} + A^{\cdot -}_{(s)}$

(3) $II^{\cdot +}_{(s)} \longrightarrow [(C_6H_5)_2CH]\cdot + [CH_2OR]^{+}_{(s)}$

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

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

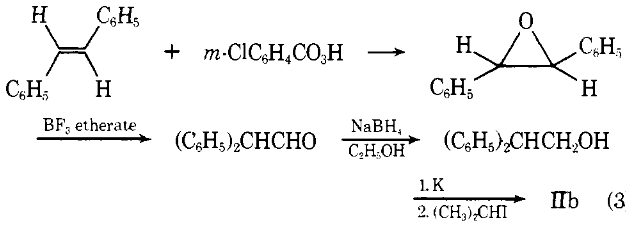
(6) $[CH_2OR]^{+}_{(s)} + R'OH \longrightarrow R'OCH_2OR + H^{+}_{(s)}$

The mechanism we propose for reaction 2 is summarized in Scheme I. 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 more 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 paper we report the characterization of the products from the photosensitized (electron transfer) cleavage of the ethers II (a and b) in methyl and isopropyl alcohol and the results of photophysical and electrochemical studies which support the proposed mechanism. We have found sensitizers which are effective in bringing about reaction 1, but will not induce reaction 2, so that secondary photolysis does not necessarily present an important limitation for the preparation of ethers. We point out that these examples of reaction 2 are the first of this type. If this reaction is general, it will have important synthetic applications, particularly since it can be used to photochemically remove a protecting group for the hydroxyl function under mild, neutral conditions.

Results

The ethers IIa and b, used in this study, were prepared by the photosensitized (electron transfer) addition of methyl and isopropyl alcohol to 1,1-diphenylethylene (I) (reaction 1).[3a] Sensitizers effective for this reaction are methyl p-cyanobenzoate (V), p-dicyanobenzene (VI), and 1-cyanonaphthalene (VII). The isopropyl ether (IIb) was also prepared by a multistep synthesis in low overall yield as outlined in eq 3.

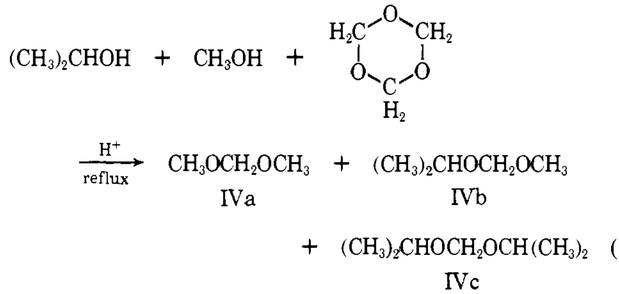


$$\xrightarrow{BF_3\ \text{etherate}} (C_6H_5)_2CHCHO \xrightarrow[C_2H_5OH]{NaBH_4} (C_6H_5)_2CHCH_2OH \xrightarrow[2.\ (CH_3)_2CHI]{1.\ K} \text{IIb} \quad (3)$$

Typical conditions for reaction 2 involve irradiation of a solution of II (0.2 M), alcohol (3.0 M), and the sensitizer (0.06 M) in acetonitrile through a Pyrex filter which absorbs wavelengths shorter than 280 nm. Under these conditions light is absorbed only by the sensitizer. The involvement of the sensitizer was easily confirmed; upon irradiation 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 (NMR), and/or by vapor-phase chromatography (VPC).

Diphenylmethane (III) 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 IVb, from the irradiation of IIa in isopropyl alcohol and the irradiation of IIb in methyl alcohol, was distilled from the reaction mixture along with the solvent upon bulb-to-bulb distillation at reduced pressure (70 mmHg). The initial indication of structure came from the NMR spectrum of this solution. All of the proton signals of the product were superimposed upon those from an authentic sample of IVb 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 mmp) precipitated.

The authentic sample of IVb necessary for comparison purposes was prepared by the acid-catalyzed exchange starting with paraformaldehyde, methyl alcohol, and isopropyl alcohol (eq 4). The resulting acetals were separated by distillation and VPC and were characterized by ir and NMR spectroscopy.



$$(CH_3)_2CHOH + CH_3OH + \cdots \xrightarrow[\text{reflux}]{H^+} \underset{\text{IVa}}{CH_3OCH_2OCH_3} + \underset{\text{IVb}}{(CH_3)_2CHOCH_2OCH_3} + \underset{\text{IVc}}{(CH_3)_2CHOCH_2OCH(CH_3)_2} \quad (4)$$

Some 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.

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

In an attempt to determine the nature of the excited state responsible for reaction 2, we have studied the fluorescence of the sensitizers (VI–VIII)[4] as a function of the ether (IIb) concentration in acetonitrile solution. The fluorescence intensity of VI and VIII decreased upon addition of the ether IIb. In contrast, the fluorescence intensity of VII was not affected by added IIb. The quenching rate constants gleaned from these Stern–Volmer plots and the measured fluorescence lifetime 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) = 1.82×10^{10} M^{-1} s^{-1}.[5] Therefore, the fluorescence of p-dicyanobenzene is quenched by both IIb and IX at essentially the diffusion-controlled rate. Since the addition of IIb (2×10^{-3} M) and IX (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 (II) and the reduction potential of the sensitizers. For this reason, we have studied the electrooxidation and/or reduction processes of these compounds. Half-wave oxidation and reduction potentials have been calculated from these data and are summarized in Table II.

Polarographic data were available in the literature for some of the compounds studied here; however, since variations can result from differences in solvent, electrode material, electrolyte, reference electrode, etc., the data in Table II were obtained under standardized conditions, so they are internally consistent.

Discussion

The first step in the proposed mechanism (Scheme I) for reaction 2 involves excitation of the sensitizer (A). The ultraviolet absorption spectra of mixtures of the ether and sensitizers (IIb, 1.44×10^{-4} and VI, 1.01×10^{-2} M; IIb, 1.83×10^{-2} and VIII, 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. Several intermediate stages may be involved in this process; for example, sequential formation of an encounter complex, an exciplex, a radical ion pair, and finally the solvent-separated radical ions. We have little evidence per-

Table I. Fluorescence Quenching of the Sensitizers Studied by 2,2-Diphenylethyl Isopropyl Ether (IIb) and 1,1-Diphenylethane (IX) in Acetonitrile Solution at 20 °C

		k_q, s^{-1} M^{-1}	
Fluorophor	τ (ns)	IIb	IX
p-Dicyanobenzene (VI)	9.732	1.29×10^{10} [a]	1.86×10^{10} [b]
1,4-Dicyanonaphthalene (VIII)	10.057	5.37×10^{9} [c]	
1-Cyanonaphthalene (VII)	8.923	$<1.9 \times 10^{9}$ [d]	$<1.3 \times 10^{8}$ [d]

Exciting the fluorophore at: [a] 280; [b] 289; [c] 311; [d] 313 nm.

Table II. Half-wave Oxidation and Reduction Potentials[a] Obtained by Cyclic Voltammetry[e]

Compd	$E_{1/2}{}^{red}$, V	$E_{1/2}{}^{ox}$, V
Methyl *p*-cyanobenzoate (V)	2.10	*c*
p-Dicyanobenzene (VI)	2.00	*c*
1-Cyanonaphthalene (VII)	2.33	*c*
1,4-Dicyanonaphthalene (VIII)	1.67	*c*
2,2-Diphenylethyl isopropyl ether (IIb)	*d*	1.81[b]
1,1-Diphenylethane (IX)	*d*	1.81[b]
1,1-Diphenylethylene (I)	*d*	1.48[b]

[a] Taken as 0.028 V before the anodic peak potential and 0.029 V before the cathodic peak potential (R. S. Nicholson, *Anal. Chem.*, **38**, 1406 (1966)). [b] The oxidative process was not reversible, the half-wave potential was estimated using the 100 mV/s sweep rate. [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] Pt electrode, tetraethylammonium perchlorate (TEAP, 0.1 M) in acetonitrile solution, vs. Ag/0.1 M $AgNO_3$.

Table III. Comparison of Calculated and Observed Fluorescence-Quenching Rate Constants

Fluorophor	Singlet energy, kcal mol^{-1}	Calculated ΔG,[b,c] kcal mol^{-1} for IIb and IX	Obsd (calcd)[c,d] $k_q \times 10^{-10}$	
			IIb	IX
V	95.3[a]	−6.41		
VI	97.6	−11.01	1.29	1.86 (1.26)
VII	89.4	4.80	<0.19	<0.01 (0.0003)
VIII	86.4	−7.42	0.54	(1.00)

[a] Estimated from the absorption spectrum; no fluorescence was observed from V. [b] The energy required for the electron-transfer process (step 2b), assuming the distance to be 7 Å and the dielectric constant of acetonitrile ($\epsilon_{25}° = 36.7$). [c] Using eq 5, these values are the same for IIb and IX, since they have the same oxidation potential. [d] Using eq 6 and 7 (see ref 6b).

taining to these various stages; nevertheless, it is useful to consider the dissection, since at some point during this step the reaction progresses from an electronic excited-state reaction to become a reaction of ground-state intermediates. Furthermore, using reasoning originally proposed to relate fluorescence emission quenching, exciplex formation, oxidation and reduction potentials, and singlet energy,[6-8] the energetics of the various stages can be considered.

The free-energy change (ΔG) associated with the electron-transfer process which occurs within an encounter complex (step 2b) is represented by

$$\Delta G\ (\text{kcal mol}^{-1}) = 23.06\left[E(\text{D/D}^+)_\text{V} - E(\text{A/A}^-)_\text{V} - \frac{e_0{}^2}{\epsilon\alpha}\right] - \Delta E_{0\text{-}0}\ (\text{kcal mol}^{-1}) \quad (5)$$

applied by Weller to explain fluorescence quenching.[6b] The term in brackets represents the energy required for the electron transfer and contains the oxidation potential of the donor ($E(\text{D/D}^+)$) and the reduction potential of the acceptor ($E(\text{A/A}^-)$). Usually half-wave potentials determined by polarography are used here; we have chosen cyclic voltammetry to obtain these data.[9] There are advantages and disadvantages to both methods. A major problem with either method is the inability to obtain thermodynamically significant oxidation or reduction potentials when the electron-transfer process is not reversible. If the electron-transfer process was not reversible, the peak potential was a funtion of sweep rate and the half wave was estimated using the 100 mV/s sweep; nevertheless, meaningful correlations can be obtained from them.[10]

In this polar medium (acetonitrile, $\epsilon_{25}° = 36.7$), when the separation is within the encounter distance (ca. 7 Å), the Coulombic attraction term is small (1.3 kcal mol^{-1}) and we believe the radical ions can dissociate before the reaction.

The amount of energy available for the electron-transfer process is the excited-state energy of the donor or acceptor, whichever is lowest. The sensitizer fluorescence-quenching studies indicate that the excited state involved in these reactions is the sensitizer singlet. We will return to the question of whether the triplet state might, in these or other cases, be involved.

The singlet energies of the sensitizers were obtained from the fluorescence emission and/or absorption spectra. A distinct 0–0 band was observed with 1,4-dicyanonaphthalene and 1-cyanonaphthalene. The point of intersection of the absorption and emission spectra was taken as the singlet energy. 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 III are listed the singlet energies of the sensitizers and the calculated values of ΔG for the donors IIb and IX, using eq 5. The electron-transfer process (step 2) is spontaneous when the donor is the isopropyl ether (IIb) or 1,1-diphenylethane (IX) and the sensitizer is *p*-dicyanobenzene (VI), methyl *p*-cyanobenzoate (V), and 1,4-dicyanonaphthalene (VIII); it is *not* spontaneous when 1-cyanonaphthalene (VII) is the sensitizer. This is in complete agreement with the observed ability of these sensitizers to bring about reaction 2. Furthermore, the sensitizer fluorescence-quenching results are qualitatively consistent; IIb and IX quench the fluorescence of VI and VIII, but do *not* quench the fluorescence of VII.

Weller has developed a semiempirical approach for estimating the fluorescence-quenching rate constants if the electron-transfer process pertains.

$$\Delta G^{\ddagger} = [(\Delta G/2)^2 + (\Delta G^{\ddagger}(0))^2]^{1/2} + \Delta G/2 \quad (6)$$

$$k_q = \frac{20 \times 10^9\ \text{M}^{-1}\ \text{s}^{-1}}{1 + 0.25[\exp(\Delta G^{\ddagger}/RT) + \exp(\Delta G/RT)]} \quad (7)$$

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

We have used eq 6 and 7 to obtain calculated values for the fluorescence-quenching process. The agreement with the observed values summarized in Table III can be taken as prima facia evidence for the electron-transfer mechanism (step 2b).

Other methods for calculating fluorescence-quenching rate constants, based on ionization potential and electron affinity, have been developed.[7,8] 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 and reduction potentials of the fluorescer and quencher. The difference in the donor and acceptor properties of the sensitizers and the ether IIb (or IX), based on oxidation- and reduction-potential differences, is >0.4eV (Table II).

1,1-Diphenylethane (IX) was chosen as a model compound to determine what part of the ether molecule (II) was important for the electron-transfer process (step 2b). This was particularly important in order to gain some idea of the scope of reaction 2; that is, will the reaction occur with aliphatic ethers or possibly with other types of β-phenethyl compounds. The oxidation potential of the ether IIb 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 IX (Table II) is essentially identical with that of the ether IIb. The conclusion that the ether oxygen atom in IIb plays a minor role in the photosensitized electron-transfer process (step 2) is confirmed by the result that IX is able to quench the fluorescence emission of p-dicyanobenzene (VI) with a rate constant comparable to that of the ether IIb. Similarly, the fluorescence-emission intensity of 1-cyanonaphthalene is not affected by the addition of IX. These results lead us to predict that α cleavage (step 3) of other β-phenethyl compounds will occur.

During step 2 of the proposed mechanism (Scheme I) 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 implicate the involvement of an exciplex is to study the emission from it. Usually exciplex emission, which is common in nonpolar solvents, is quenched by the addition of polar solvents (e.g., acetonitrile). This quenching process is due to the rapid dissociation of the exciplex to give the radical ions. Nevertheless, weak exciplex emission has been observed in some cases even in acetonitrile solution.[6d,8b] 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 (>0.4eV) difference in the donor and acceptor properties of the sensitizers and ethers II and IX, and high dielectric constant of acetonitrile.[6a]

The question of the possible involvement of the sensitizer triplet in reaction 2 is interesting. There is evidence in other systems that triplet excited states are capable of electron-transfer processes and triplet-exciplex formation.[6a,11] 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 5. The triplet energies of the sensitizers V-VII were obtained from the phosphorescence emission spectra in ethanol-methanol (4:1) glass at 77 K. In the case of 1,4-dicyanonaphthalene (VIII) 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 VIII was esasily obtained when ethyl iodide was added to the solution (4:1 mixed alcohol solution-ethyl iodide).[12] The phosphorescence emission spectrum of VII 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.

Table IV. Triplet Energies of the Sensitizers and Calculated ΔG Values, Using Equation 5, for the Electron-transfer Process Involving the Triplet of the Sensitizer and IIb

Sensitizer (acceptor)	E_T, kcal mol^{-1}	ΔG, kcal mol^{-1}
p-Dicyanobenzene (VI)	70.1[a]	16.5
Methyl p-cyanobenzoate (V)	72.0[a]	15.7
1-Cyanonaphthalene (VII)	57.4,[a] 57.2[b]	36.8
1,4-Dicyanonaphthalene (VIII)	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 (J. J. Graham-Bryce and J. M. Corkill, *Nature (London)*, **186**, 965 (1960)).

Table V. 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 (X)	74.1	2.49	2.34	28.7
p-Methoxyacetophenone (XI)	71.7	2.68	1.60	11.6
p-Methylacetophenone (XII)	72.8	2.60	2.12	23.6

[a] Taken from D. R. Arnold, *Adv. Photochem.*, **6**, 301 (1968). The maximum 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 5 and considering the ketone as the donor and the triplet of VI as the acceptor. [d] The oxidative process was not reversible. The half-wave potential was estimated using the 100 mV/s sweep rate.

The triplet energies of the sensitizers and the free energy (ΔG) of the electron-transfer process with IIb, calculated using eq 5, are given in Table IV. In all cases ΔG is significantly positive. Nevertheless, we have made an attempt to triplet sensitize reaction 2, with p-dicyanobenzene (VI) as the electron-transfer sensitizer and IIb as the donor. The choice of VI as the electron-transfer sensitizer was made upon consideration of its triplet energy (which is well below that of IIb and yet relatively high) and the calculated ΔG for the electron-transfer process; with VI this process is nonspontaneous by a relatively small amount ($\Delta G = 16.5$ kcal mol^{-1}).

Acetophenone (X), p-methoxyacetophenone (XI), and p-methylacetophenone (XII) were chosen as sensitizers to produce the triplet of VI. The triplet energies and oxidation and reduction potentials of X-XII are summarized in Table V. The triplet-sensitizer experiments were carried out by irradiation of an acetonitrile solution of IIb (0.2 M), VI (0.12 M), and the triplet sensitizers X-XII (0.62 M) and methanol (4 M) for prolonged periods through a filter solution which allowed excitation of X-XII only. No reaction was observed under these conditions. These results are consistent with the prediction, based on eq 5, that the electron transfer between IIb and the triplet of VI will not be spontaneous.

The importance of the electron-transfer process as a complication in photosensitized (excitation energy transfer) reactions has largely been ignored.[13] The process where the ketone excited state (singlet or triplet) acts as the acceptor and IIb as the donor can easily be ruled out in view of the relatively large magnitude of the reduction potential of the ketones. For all three ketones, using eq 5, we calculate $\Delta G > 20$ kcal mol^{-1} for this process. Electron transfer where the triplet of VI accepts an electron from the ground-state ketone is not so easily dismissed, particularly with XI, where the oxidation potential is in fact below that of IIb. The ΔG for this process is 11.65 kcal mol^{-1} for this case.

Before leaving the discussion of the electron-transfer process (step 2) we mention that it is at this point that selectivity between reaction 1 and 2 can be obtained. The oxidation potential of 1,1-diphenylethylene (I) is considerably lower than that of the ether IIb: 1.48 and 1.81 V, respectively (Table II). The oxidation potential of I is low enough so that the electron-transfer process, according to eq 5, should be spontaneous with 1-cyanonaphthalene (VII) as the sensitizer (electron transfer). This calculation is in good agreement with the experimental results; the fluorescence emission of VII is quenched by I and VII is an effective sensitizer for reaction 1. 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 1 without causing reaction 2.

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.[14]

The mass spectra of the ethers IIa–c are shown in Figure 1. 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 give the diphenylmethyl radical and the α-oxycarbonium ion is not a dominant process in the mass spectra of IIa, b, or c. In contrast, neither diphenylmethyl methyl ether nor diphenylmethyl isopropyl ether was detected (VPC and NMR) as products from reaction 2 carried out in the presence of methyl or isopropyl alcohol.

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 (diphenylmethylcarbonium 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 IIa < IIb < IIc, 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 (NMR and VPC) isopropyl methyl ether (an authentic sample of this ether was prepared) in the crude reaction mixture of reaction 2 with IIb in acetonitrile–methanol solution. We conclude therefore that knowledge of the favored 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 received some attention. Particularly relevant is the reduction of alkyl halides upon treatment with alkali naphthalenes.[15] While it seems reasonable that the electron transfer involved in step 4 (Scheme I) 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 (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 reaction 2 and reaction 1, where a similar process is also involved.

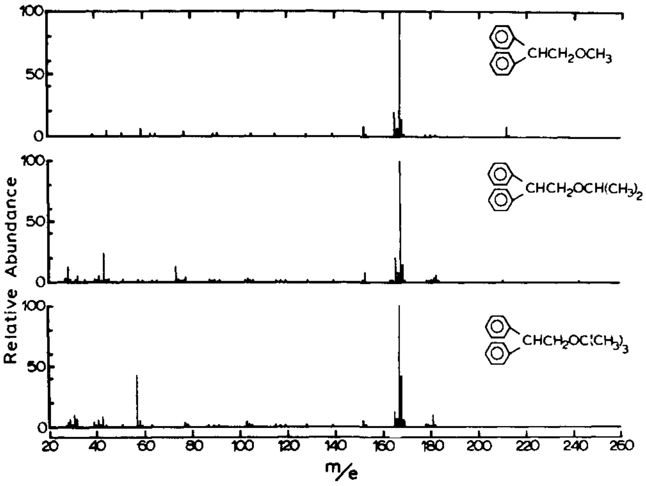


Figure 1. The mass spectra of IIa–c (70 eV).

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.[15] This type of reaction may account for the consumption of the sensitizer during reaction 2. However, since the sensitizers are largely recovered, electron transfer must be favored over coupling with the diphenylmethyl radical and the sensitizer radical anions we have used in reaction 2.

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

Experimental Section

General. Acetonitrile (Aldrich Gold Label) was refluxed overnight over calcium hydride under a dry nitrogen atmosphere and fractionated. 1-Cyanonaphthalene was sublimed three times under vacuum and stored in a freezer. Methyl *p*-cyanobenzoate and 1,4-dicyanobenzene were recrystallized four times from ethanol. 1,4-Dicyanonaphthalene was prepared by reaction of 1,4-dibromonaphthalene with cuprous cyanide and was purified by sublimation (two times) under vacuum and 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. 1,1-Diphenylethane was prepared by catalytic hydrogenation of 1,1-diphenylethylene using platinum on charcoal as catalyst and was purified by VPC (5% Apiezon M liquid phase). 1,1-Diphenylethylene was obtained from Eastman Kodak Co. and was purified by distillation under vacuum. Tetramethylammonium perchlorate was recrystallized from water four times and dried under vacuum at 65 °C. Silver nitrate, for the reference electrode, was purified by recyrstallization from water. NMR spectra were obtained in deuteriochloroform solution with tetramethylsilane as internal standard, using a Varian HA-100 spectrometer.

Spectroscopic Studies. Fluorescence spectra were measured on a conventional 90° two-monochromator spectrofluorimeter at room temperature. Stern-Volmer plots were obtained, using the same instrument, from the intensity of the spectra at the maximum. Fluorescence decay measurements were made on a time-correlated single-photon counting instrument, details of which have been described elsewhere.[16-18] The excitation source was a Photochemical Research Associates nanosecond flash-lamp system. The decay curves were deconvoluted by iterative convolution.[16,18] 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 using a spectrometer described elsewhere.[19]

Oxidation- and Reduction-Potential Measurements. Cyclic voltammetric data were obtained using a three-electrode cell with a Princeton Applied Research Electrochemistry System Model 170. The working electrode was a platinum sphere (≈1 mm diameter) 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 as supporting electrolyte.

Irradiation of 1,1-Diphenylethylene in Acetonitrile–Alcohol Solution with a Photosensitizer (Electron Transfer): Reaction 1. A solution of 1,1-diphenylethylene (I, 360 mg, 2 mmol), photosensitizer (electron transfer, 0.8 mmol) in alcohol (40 mmol), and acetonitrile (12 ml) was purged with argon for 30 min and irradiated through a Pyrex filter with a 1-kW medium-pressure mercury-vapor lamp, at 10 °C. The progress of the reaction was followed by NMR (disappearance of the signal due to the vinyl proton) 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 (II), 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 (IIa). In addition to IIa (36.1%, colorless 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. The structure proof for these products rests upon direct comparison (ir, NMR) with authentic samples prepared by established procedures (IIa has been described previously).[20]

2,2-Diphenylethyl Isopropyl Ether (IIb). IIb was obtained by the above procedure in 48.5% yield; methyl *p*-cyanobenzoate was the sensitizer. In addition, diphenylmethane (7.2%) was isolated. A sample of IIb (colorless liquid) was purified by VPC (10% SE-30 on Chromosorb W): ir (neat) ν 1610, 1500, 1370, 1140, 1090, 700 cm^{-1}.

The NMR spectrum of IIb consists of absorption in the aromatic region centered at 7.42 ppm, an AB_2 pattern for the benzylic and methylene protons (A, 4.24 ppm; B, 3.93 ppm; $J_{AB} = 7.53$ Hz), and the signal due to the protons of the isopropyl group (1.12 ppm doublet, 3.57 ppm heptet, $J = 6.5$ Hz).

The mass spectrum of IIb is shown in Figure 1.

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

Alternative Synthesis of 2,2-Diphenylethyl Isopropyl Ether (IIb). *trans*-Stilbene oxide was prepared by epoxidation of *trans*-stilbene with *m*-chloroperbenzoic acid[21] and the epoxide was isomerized to 2,2-diphenylacetaldehyde using boron trifluoride etherate.[22] 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 (IIb). The yield of the last step was 3.5%. The spectra (NMR, ir) of the ether obtained in this synthesis were identical with those of the ether (IIb) obtained from the photoreaction (eq 1).

2,2-Diphenylethyl *tert*-Butyl Ether (IIc). The general procedure for reaction 1 using methyl *p*-cyanobenzoate as the sensitizer (electron transfer) and *tert*-butyl alcohol as the alcohol gave IIc (17%) and diphenylmethane (III, 35%). A sample of IIc (colorless liquid) for spectral characterization and analysis was purified by VPC (column, 10%, SE-30 on Chromosorb W): ir (neat) ν 1604, 1495, 1374, 1197, 1080, 695 cm^{-1}; the mass spectrum is shown in Figure 1.

The NMR spectrum of IIc had the singlet for the *tert*-butyl group at 1.15 ppm, the benzylic and methylene protons appear as an AB_2 pattern (A, 4.18 ppm; B, 3.87 ppm; $J_{AB} = 7.46$ Hz), and the aromatic protons absorb as a broad singlet centered at 7.40 ppm.

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

Irradiation of 2,2-Diphenylethyl Isopropyl Ether (IIb) in the Presence of 1,4-Dicyanobenzene (Electron-Transfer Sensitizer) and Methyl Alcohol in Acetonitrile Solution. A solution of 2,2-diphenylethyl isopropyl ether (24 mg, 0.1 mmol), 1,4-dicyanobenzene (electron-acceptor sensitizer, 8 mg, 0.06 mmol), in 80 µl (2.0 mmol) of methyl alcohol and 400 µl of acetonitrile was purged with argon for 30 min and irradiated through a Pyrex filter with a 1-kW medium-pressure mercury-vapor lamp at 10 °C. The progress of the reaction was followed by NMR (disappearance of the signal due to the methyl groups of the ether) and VPC. After 21 h of irradiation, a known amount of an internal standard (triphenylmethane) was added and the yield of the methyl isopropyl acetal of formaldehyde (67.4%) was determined by integration of the methylene proton vs. the proton of the internal standard. The yield of the diphenylmethane (29.4%) 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.[23] The 2,4-dinitrophenylhydrazone was identified as the 2,4-dinitrophenylhydrazone of formaldehyde by comparison (ir spectrum, mmp) 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 Wuyts and Docquier,[24] 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 as the sensitizer with similar results; 1-cyanonaphthalene, under the same conditions, did not lead to reaction. Control experiments showed that in the absence of the sensitizer the reaction does not occur.

Irradiation of 2,2-Diphenylether Methyl Ether in the Presence of 1,4-Dicyanobenzene and Isopropyl Alcohol in Acetonitrile Solution. A solution of 2,2-diphenylethyl methyl ether (IIa, 21 mg, 0.1 mmol), 1,4-dicyanobenzene (8 mg, 0.06 mmol) in 55 µl (2.0 mmol) of isopropyl alcohol, and 400 µl of acetonitrile was irradiated and worked up as described above. The yield of the methyl isopropyl acetal of formaldehyde was 16.6% and the yield of diphenylmethane 35.3%.

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

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

References and Notes

(1) Contribution No. 153 from the Photochemistry Unit.
(2) Alfred P. Sloan Fellow 1972–1974.
(3) (a) R. A. Neunteufel and D. R. Arnold, *J. Am. Chem. Soc.*, **95**, 4080 (1973), Part 1; (b) Y. Shigemitsu and D. R. Arnold, *J. Chem. Soc., Chem. Commun.*, 407 (1975), Part 2.
(4) The fluorescence emission from methyl *p*-cyanobenzoate (V) in acetonitrile was too weak to measure with our apparatus.
(5) Using the viscosity ($\eta_{20} = 0.35891$ cP) reported by S. Minc and L. Werblan, *Rocz. Chem.*, **40**, 1537 (1966).
(6) (a) A. Weller in "Exciplex", M. S. Gordon and W. R. Ware, Ed., Academic Press, New York, N.Y., 1975, Chapter 2; (b) D. Rehm and A. Weller, *Isr. J. Chem.*, 8, 259 (1970); (c) A. Weller, *Fast React. Primary Processes Chem. Kinet., Proc. Nobel Symp. 5th.* 413 (1967); (d) H. Beens and A. Weller, *Acta Phys. Pol.*, **34**, 593 (1968).
(7) (a) C. Lewis and W. R. Ware, *Mol. Photochem.*, **5**, 261 (1973); (b) W. R. Ware, D. Watt, and J. D. Holmes, *J. Am. Chem. Soc.*, **96**, 7853 (1974).
(8) (a) D. A. Labianca, G. N. Taylor, and G. S. Hammond, *J. Am. Chem. Soc.*, **94**, 3679 (1972); (b) G. N. Taylor, *Chem. Phys. Lett.*, **10**, 355 (1971).
(9) R. S. Nicholson, *Anal. Chem.*, **38**, 1406 (1966).
(10) "We are in the position of using what we have to seek correlations that may be suggestive, if not definitive". ref 8a.
(11) (a) J. G. Guttenplan and S. G. Cohen, *J. Am. Chem. Soc.*, **94**, 4040 (1972); (b) *Tetrahedron Lett.*, 2163 (1972).
(12) I. J. Graham-Bryce and J. M. Corkill, *Nature* (*London*), **186**, 965 (1960).
(13) P. S. Engel and B. M. Monroe, *Adv. Photochem.*, 8, 245 (1971).
(14) J. H. Beynon, "Mass Spectrometry and Its Application to Organic Chemistry", Elsevier, Amsterdam, 1960, pp 362–367.
(15) (a) J. F. Garst in "Free Radicals", Vol. 1, J. K. Kochi, Ed., Wiley-Interscience, New York, N.Y., 1973, Chapter 9; (b) J. F. Garst, *Acc. Chem. Res.*, **4**, 400 (1971).
(16) W. R. Ware, "Creation and Detection of the Excited State", Vol. IA, A. Lamola, Ed. Marcel Dekker, New York, N.Y., 1971, pp 213–302.
(17) C. Lewis, W. R. Ware, L. J. Doemeny, and T. L. Nemzek, *Rev. Sci. Instrum.*, **44**, 107 (1973).
(18) W. R. Ware, L. J. Doemeny, and T. L. Nemzek, *J. Phys. Chem.*, **77**, 2038 (1973).
(19) D. R. Arnold and R. J. Birtwell, *J. Am. Chem. Soc.*, **95**, 4599 (1973).

(20) W. A. Bonner and F. D. Mango, *J. Org. Chem.*, **29**, 430 (1964).

(21) An analogous preparation is described by D. J. Reif and H. O. House, "Organic Syntheses", Collect. Vol. IV, Wiley, New York, N.Y., 1963, p 860.

(22) D. J. Reif and H. O. House, ref 21, p 375.

(23) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds", 5th ed, Wiley, New York, N.Y., 1964, p 253.

(24) H. Wuyts and P. Docquier, *Bull. Soc. Chim. Belg.*, **44**, 297 (1935).

Formation and Thermal Rearrangements of Some Dimers of Butadiene and Piperylene. Tests of the Validity of Thermochemical-Kinetic Arguments for Identification of Common Biradical Intermediates[1,2]

Jerome A. Berson,* Peter B. Dervan,[3] Roger Malherbe,[4] and Jerry A. Jenkins[5]

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06520.

Received October 6, 1975

Abstract: The mechanisms of the dimerization of butadiene and piperylene and the thermal rearrangements of the corresponding dimers are investigated by kinetic and stereochemical techniques. Particular attention is given to the question whether, in the Diels-Alder dimerization of the dienes **1a** or **1b**, intermediates are involved that are common to the 1,3-sigmatropic rearrangements of the corresponding [2 + 2] dimers **3a** and **3b**. Substituents on the terminal vinyl position of *cis*-1,2-divinylcyclobutane (**5a**) retard the normal stereospecific boat-like Cope rearrangement to 3,4-dimethyl-*cis,cis*-cycloocta-1,5-diene and permit the detection of a new "nonboat" process, which leads to a stereoisomeric product. The boat-like rate constant declines with increasing terminal cis-methyl sustitution in the series **5a** > cTT-**8** > cCT-**8** > cCC-**8**. The total range of the effect amounts to a factor of 1.81×10^5. The *trans*-1,2-dipropenylcyclobutanes also give Cope rearrangement products, but this reaction occurs exclusively by an indirect mechanism: prior epimerization to the cis isomer followed by Cope rearrangement of the latter. The rearrangement of *trans*-3,4-dimethyl-*cis,trans*-cycloocta-1,5-diene (**16**) to *cis*-3,4-dimethyl *cis,cis*-cycloocta-1,5-diene (**10**), involving overall epimerization at one asymmetric center and geometric isomerization at one olefinic site, proceeds by a two-step mechanism in which *cis*-1,2-*trans,trans*-dipropenylcyclobutane (cTT-**8**) is an intermediate. The 1,3-sigmatropic rearrangement of (1*R*,2*R*)-(+)-*trans*-1,2-divinylcyclobutane (**3a**) gives (*R*)-(+)-4-vinylcyclohexene (**2a**) with 7.7% preservation of enantiomeric purity (corrected for competing racemization of **3a**). This corresponds to 54% inversion and 46% retention of configuration of the migrant carbon. By attaching stereochemical labels to the terminal vinyl positions as in optically active tTT-**9** and tCT-**9**, the stereochemistry of the 1,3-sigmatropic rearrangement can be subdivided into the four possible pathways (Schemes IX and X), suprafacial inversion, antarafacial retention, suprafacial retention, and antarafacial inversion. In this way, it can be shown that relative rates through these four pathways are, respectively, 50.2, 6.0, 41.1, and 2.7 from tTT-**9**, and 49.5, 2.8, 46.8, and 0.9 from tCT-**9**. These results can be fitted by a biradical mechanism, but are more fruitfully interpreted as mainly the outcome of two competing concerted reactions, one allowed (suprafacial inversion) and one forbidden (suprafacial retention). The absence of any substantial antara contribution in the dipropenyl systems rules out a stereorandom biradical intermediate in the tTT-**9** and tCT-**9** rearrangements and makes it unlikely in the divinyl system **3a**. The Diels-Alder dimerization of *trans*-penta-1,3-diene-*trans-1-d* (**45**, Scheme XIV) in both the exo and endo orientations gives exclusively the product of reaction cis-on-the-diene,cis-on-the-dienophile. This is consistent with a concerted [4s + 2s]cycloaddition and rules out common intermediates in the formation of product tT-**13** and cT-**12** from the two alternative pathways of Diels-Alder dimerization of piperylene and 1,3-sigmatropic rearrangement of tTT-**9**.

Although historical documentation is sparse and scattered, we suspect that many of the early proposals of biradical intermediates in thermal reactions really were simple bookkeeping schemes devised to permit the authors to identify readily the molecular sites of bond making and bond breaking. In time, however, biradicals took on more clearly defined mechanistic significance, and with the advent of transition-state theory, the investigation of thermal reactions incorporated as one of its objectives the location of such species as intermediates on reaction energy surfaces.

It is obviously required of a biradical intermediate that its heat of formation ($\Delta H_f°$) be lower than that of the highest-energy transition state of the reaction. The heat of formation of the transition state usually is an experimental (or semiexperimental) quantity, being the sum of the measured activation energy ($\Delta H^{\ddagger}$) and the measured (or estimated) $\Delta H_f°$ of the reactant. The biradical $\Delta H_f°$ is nonexperimental and usually is estimated from bond-additivity tables, with certain additional assumptions.

However, to be plausible, any particular biradical intermediate also must be convertible to the rate-determining transition state by processes whose energies and entropies are reasonable and predictable. The development of methods for making such predictions has come from the examination of large collections of data on the rates and activation parameters of many thermal reactions.[6,7] As a result of such studies, biradical intermediates and transition states leading to them have been shown to have heats and entropies of formation that permit them to be placed on reaction energy surfaces. The existence of these correspondences has led to the postulation of biradical mechanisms for a wide variety of thermal reactions.[6,7]

In support of such mechanisms, it has been noted that some hypothetical biradical intermediates might be formed from two or more different reactants or be converted to two or more different products, and that the values of $\Delta H_f°$ of the transition states flanking the biradical all can be derived by the same additivity schemes.[6,7] Within the framework of the thermochemical-kinetic approach, the thermodynamic properties of such biradical *common intermediates* have provided an important check on the internal consistency of the method.

Stereochemical experiments can provide a supplementary

Berson et al. / Rearrangements of Some Dimers of Butadiene and Piperylene