dom since it is not sterically hindered, and internal as well as overall molecular motion would determine $\Delta\nu_Q$ of the 1-2′ lines. Assuming this to be the case, then if overall molecular rotation slowed at $\chi_{\text{CHOL}} = 0.33$ one might expect the 2-2′ lines to disappear before the 1-2′ lines. The disappearance of the 1 chain lines at $\chi_{\text{CHOL}} \simeq 0.2$ would then reflect a retardation of internal molecular motion of the chains.

Other experimental data can be interpreted to support this hypothesis. In the x-ray experiment of Engelman and Rothman it was observed that the in plane 4.15 Å spacing was replaced by a 4.7 Å spacing at $\chi_{\text{CHOL}} \simeq 0.33$ at 20 °C. Such an increase would facilitate molecular rotation about the bilayer perpendicular. Note, in addition, that our data predict this break point will be rather temperature dependent.

The spin-label data of Shimshick and McConnell[11] were obtained with a label at the 8 position of the 2 acyl chain. Thus, our hypothesis concerning the chain motion freezing at $\chi_{\text{CHOL}} \simeq 0.2$ is consistent with the spin-label results.

Finally, we should mention that we have studied the concentration and temperature dependence of the $^2$H spectra of [3-$\alpha$-D]CHOL in the range $\chi_{\text{CHOL}} = 0.1$-$0.5$ and $T = 20$-$60$ °C. In the case of DMPC we observe an essentially constant $\Delta\nu_Q \approx 50$ kHz at $T \sim 23$ °C over the entire concentration range, while at $T = 60$ °C $\Delta\nu_Q$ increases from 38 to 47 kHz in going from $\chi_{\text{CHOL}} = 0.1$ to 0.5. To date we have not observed two components in these spectra, as has been reported in $^{13}$C spectra of [4-$^{13}$C]CHOL,[18] but this could be due to one species simply having a very broad spectrum. We will report more complete results in a future publication.

**Acknowledgment.** Thanks are accorded to A. Pines for his assistance in obtaining some of the [3-$\alpha$-D]cholesterol spectra. This work was supported in part by the National Science Foundation (Grant PCM 76-01491) and the National Institutes of Health (Grants HL-19481, GM-23289). The Francis Bitter National Magnet Laboratory is supported primarily by Contract NSF-C670 from the National Science Foundation.

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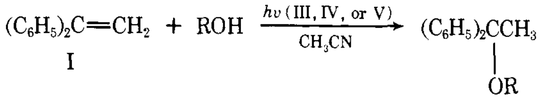
*Received May 19, 1977*

## Radical Ions in Photochemistry. 4. The 1,1-Diphenylethylene Anion Radical by Photosensitization (Electron Transfer)[1]

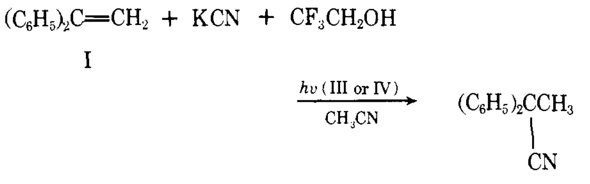
*Sir:*

A few years ago we described the formation of the 1,1-diphenylethylene (I) cation radical by photosensitization (electron transfer) using electron-accepting sensitizers (e.g., 1-cyanonaphthalene, II).[2a] Subsequent studies have shown that this procedure has synthetic utility; products formally derived from anti-Markownikoff addition of alcohols, carboxylic acids, water, and hydrogen cyanide to several aryl olefins are readily prepared by this reaction.[2] We now report that the corresponding anion radical can also be prepared by the photosensitized (electron transfer) technique through the use of electron-donating sensitizers (e.g., 1-methoxynaphthalene (III), 1,4-dimethoxynaphthalene (IV), and 1-methylnaphthalene (V)). The resulting products are those expected from Markownikoff addition to the olefin under *mild, nonacidic conditions.* Reactions 1 and 2 are illustrative.



$$\underset{\text{I}}{(C_6H_5)_2C{=}CH_2} + ROH \xrightarrow[CH_3CN]{h\nu\,(\text{III, IV, or V})} (C_6H_5)_2\underset{\substack{|\\ OR}}{C}CH_3 \qquad (1)$$

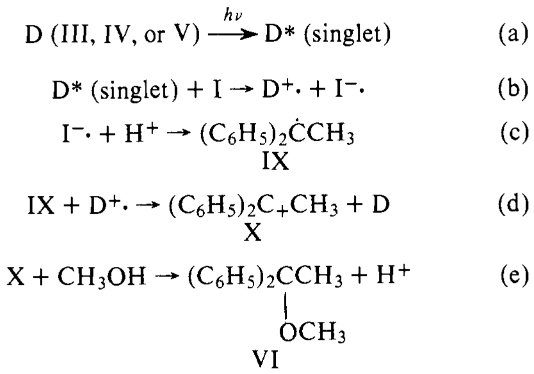
VI, R = $CH_3$
VII, R = H



$$\underset{\text{I}}{(C_6H_5)_2C{=}CH_2} + KCN + CF_3CH_2OH \xrightarrow[CH_3CN]{h\nu\,(\text{III or IV})} \underset{\text{VIII}}{(C_6H_5)_2\underset{\substack{|\\ CN}}{C}CH_3} \qquad (2)$$

Irradiation[3] of I (0.5 mmol) in acetonitrile-methanol (2 and 1.6 mL, respectively) with III, IV, or V (0.22 mmol) present as photosensitizer (electron donor) resulted in formation of 1,1-diphenylethyl methyl ether[4] (VI, 50-80%). When the irradiation was carried out using methanol-*O-d*, after ~50% conversion, analysis of the nuclear magnetic resonance and mass spectrum of the starting material indicates incorporation of deuterium (29% $d_1$, 1% $d_2$) in the vinyl position. Deuterium (81% $d_1$, 13% $d_2$, 0.1% $d_3$) was also incorporated in the methyl position of product VI. The photosensitizer (III, IV, or V) was largely recovered (50-60%). Scheme I accounts for these observations.

**Scheme I**



$$\mathrm{D\ (III, IV, or\ V)} \xrightarrow{h\nu} \mathrm{D^*\ (singlet)} \qquad \text{(a)}$$

$$\mathrm{D^*\ (singlet) + I \rightarrow D^{+\cdot} + I^{-\cdot}} \qquad \text{(b)}$$

$$\mathrm{I^{-\cdot} + H^+ \rightarrow \underset{IX}{(C_6H_5)_2\dot{C}CH_3}} \qquad \text{(c)}$$

$$\mathrm{IX + D^{+\cdot} \rightarrow \underset{X}{(C_6H_5)_2C^+CH_3} + D} \qquad \text{(d)}$$

$$\mathrm{X + CH_3OH \rightarrow \underset{VI}{(C_6H_5)_2\underset{OCH_3}{\underset{|}{C}}CH_3} + H^+} \qquad \text{(e)}$$

Step a, excitation of the photosensitizer, is assured by the use of an appropriate filter. Furthermore, no reaction is observed upon irradiation of I under identical conditions except for the absence of a sensitizer.

Step b, which may involve several intermediate stages (exciplex, radical-ion pair, etc.) leads ultimately to the radical ions. The extent to which the radical ions become separated is as yet unknown; however, in this polar medium the calculated coulombic attraction between the ions is quite small (1.3 kcal mol$^{-1}$ at 7 Å separation in acetonitrile). Involvement of the singlet state of the sensitizer (III, IV, or V) is indicated by the fluorescence quenching studies summarized in Table I. The possibility that the triplet state of I is responsible for the observed reaction is ruled out by the observation that 1-benzoylnaphthalene or benzophenone do not sensitize the reaction. Besides, the triplet of I is undoubtedly rapidly deactivated by the free-rotor effect.[5]

An estimate of the free-enthalpy associated with the electron-transfer step can be obtained using eq 3 developed by Weller and coworkers to account for fluorescence quenching by the electron-transfer mechanism.[6]

$$\Delta G\ (\mathrm{kcal\ mol^{-1}}) = 23.06\ [E(\mathrm{D/D^+})_\mathrm{v} - E(\mathrm{A/A^-})_\mathrm{v} - (e_0{}^2/\epsilon\alpha)] - \Delta E_{0,0}\ (\mathrm{kcal\ mol^{-1}}) \qquad (3)$$

The calculated $\Delta G$ values using eq 3 are consistent with the observed reactivity toward addition to the olefin (anti-Markownikoff and Markownikoff): 1-cyanonaphthalene (II) is an effective electron acceptor, the fluorescence of II is quenched by I, eq 3 indicates that the electron-transfer step should be spontaneous, and the anti-Markownikoff addition product formed upon irradiation with this sensitizer is diagnostic of the olefin cation radical. With III, IV, and V, eq 3 indicates that the electron-transfer step should be spontaneous with I as an acceptor, the fluorescence of III, IV, and V is quenched by I, and the Markownikoff addition product is obtained with these sensitizers. The fluorescence quenching rate constants do not correlate with the calculated $\Delta G$ values (Table I) which illustrates the importance of factors other than electron transfer for the fluorescence quenching process.[7]

Oxidation of the radical IX by the cation radical of the sensitizer gives the carbocation X (step d). Deprotonation of X should be competitive with reaction with nucleophile (step e) and can account for the observed deuterium incorporation in recovered I.

Step e, reaction of X with methanol should be a general reaction incorporating other nucleophiles. The alcohol VII[4] (68%) was obtained when aqueous acetonitrile was the solvent. When the irradiation was carried out in the presence of potassium cyanide and 2,2,2-trifluoroethanol (a nonnucleophilic proton source) the nitrile VIII[4] (10%) was obtained (reaction 2). The virtue of trifluoroethanol as a nonnucleophilic proton source was evident from the relatively small amount of the trifluoroethyl ethers formed in competition with the nitriles upon irradiation of I with either II or III as sensitizers.

**Table I.** Fluorescence Quenching of Some Naphthalene Derivatives by 1,1-Diphenylethylene (I) in Acetonitrile Solution at 20 °C

| Fluorophor | $\tau$, ns | $k_q$ M$^{-1}$ s$^{-1}$ | $\Delta G$, kcal mol$^{-1}$, calcd[b] |
|---|---|---|---|
| II | 8.923[a] | $1.26 \times 10^{10}$ | $-2.8$[c] |
| III | 13.6 | $1.98 \times 10^{9}$ | $-5.7$[d] |
| IV | 8.474 | $4.97 \times 10^{8}$ | $-4.6$[d] |
| V | 72.3 | $1.41 \times 10^{8}$ | $-5.2$[d] |

[a] Taken from ref 2c. [b] Using eq 3. Details will be reported in the full paper. [c] With I as the donor. [d] With I as the acceptor.

A major portion of the consumed sensitizer (III or IV) can be accounted for as photochemical nucleophilic substitution.[8]

We expect that this type of reaction will be general for aryl olefins (at least) and other nucleophiles and that the mild nonacidic conditions which can be used will offer considerable synthetic utility.[9]

**Acknowledgment.** This research was supported by a grant from the National Research Council of Canada.

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## A Model for an Intermediate in Pyridoxal Catalyzed γ-Elimination and γ-Replacement Reactions of Amino Acids

*Sir:*

Pyridoxal phosphate enzymes catalyze γ-elimination and γ-replacement reactions of amino acids and the reactions have been proposed to proceed through a series of Schiff base intermediates shown in Scheme I.[1-3] This report describes a spectral model for intermediate III.

A number of enzymatic and nonenzymatic studies have established that intermediates I and II absorb at ~420 and 500 nm, respectively.[2-4] Intermediate III has been predicted to absorb above 500 nm, since it has an extended conjugate system.[2] Miles[3] suggested that a transient absorption at 510 nm observed during tryptophan synthase catalyzed reaction of *trans*-L-2-amino-4-methoxy-3-butenoic acid might result from this structure.

Pyridoxal *N*-methochloride ($1 \times 10^{-4}$ M) and 2-aminobutanoic acid ($1 \times 10^{-3}$ M) were mixed in slightly alkaline