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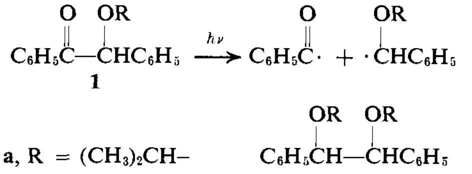
Photochemistry of Benzoin Ethers. Type I Cleavage by Low Energy Sensitization

Sir:

The photochemistry of benzoin ethers (α-alkoxy-α-phenylacetophenone derivatives) is of considerable interest, particularly in view of their extensive commercial usage as "photosensitizers" in "solventless" coatings and printing inks curable by ultraviolet radiation.[1,2] Recent studies on product quenching[3] and the utilization of radical trapping agents[4] have provided evidence for facile type I cleavage in this system (eq 1). The



$$C_6H_5\overset{\overset{O}{\|}}{C}-\overset{\overset{OR}{|}}{C}HC_6H_5 \xrightarrow{h\nu} C_6H_5\overset{\overset{O}{\|}}{C}\cdot + \cdot\overset{\overset{OR}{|}}{C}HC_6H_5 \qquad (1)$$

1

a, $R = (CH_3)_2CH-$

$$C_6H_5\overset{\overset{OR}{|}}{C}H-\overset{\overset{OR}{|}}{C}HC_6H_5$$

2

resulting radicals presumably initiate conventional polymerization of vinyl monomers,[3] although the reported incorporation of more than 12 benzoin methyl ether residues per poly(methyl methacrylate) molecule[5] remains unexplained. Herein, we wish to report the results of a mechanistic study on the photochemistry of benzoin isopropyl ether, which, we believe, provides the first example of low energy sensitization of type I cleavage.

Irradiation of benzoin ethers (**1**) in benzene provides α,α'-dialkoxybibenzyls (**2**) in high yield, together with benzaldehyde and benzil.[3] At low conversions in acetonitrile, benzoin isopropyl ether (**1a**) yields only **2a** and benzil in approximately equal amounts as evidenced by glc analysis, although several products, which were not identified, appeared with time at the expense of benzil. Quantum yields for the formation of **2a** ($<10\%$ conversions) were found to be 0.35 and 0.20 at 313 and 366 nm, respectively.[6] The phosphorescence spectrum of **1a**, obtained in an EPA glass at 77°K, exhibited 3 bands with vibrational spacings of 1200–1600 cm^{-1} and a lifetime of 30 msec, characteristic of an n,π^* state.[7] The short wavelength band corresponded to 73.4 kcal/mol.

Based on the lack of quenching of the photocleavage of benzoin ethers by naphthalene (<1 *M*) and 1,3-pentadiene (>1 *M*), Heine has suggested that reaction may occur *via* the excited singlet state of **1**.[3] Our analogous results with 1,3-cyclohexadiene support the intermediacy of a short-lived reactive state. However, we find that the formation of **2a** is sensitized by *m*-methoxyacetophenone (E_t = 72.4 kcal/mol).[9] The efficiency of sensitization exhibits a slight dependency on the concentration of *m*-methoxyacetophenone, increasing from 0.10 to 0.16 as the concentration of sensitizer decreases from 0.48 to 0.10 *M*. The corresponding yield of 0.35 in the direct reaction at 313 nm raises the possibility of a competitive singlet process. However, it appears as likely that the reduced yield may reflect inefficient energy transfer to **1a** (0.078 *M*) as a consequence of the equivalent triplet energies and self-quenching of the sensitizer.[10] The latter interpretation is more in accord with related findings on dibenzyl[11] and cyclic[12] ketones, particularly in view of the faster intersystem crossing rates of aryl ketones.[13]

Thus, the quenching and sensitization results indicate that the triplet-state lifetime of the benzoin ethers is considerably less than 10^{-10} sec, which may be attributed to facile type I cleavage. The absence of products resulting from intramolecular H abstraction, which has been reported to occur with rates on the order of 10^{10} sec^{-1} for α-alkoxyacetophenones,[14] is in accord with this conclusion.

Of considerable significance was the finding that Michler's ketone (4,4′-bis(dimethylamino)benzophenone) (E_t = 61.0 kcal/mol)[15] sensitized the formation of **2a** with ϕ = 0.05 at 366 nm in acetonitrile. This experiment was undertaken as part of an investigation of synergism in radiation curing, as, for example, has been implied for combinations of Michler's ketone and benzophenone.[16] Recently, Hammond has clarified this interaction by providing evidence for an exciplex, derived from the triplet state of Michler's ketone, in

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(1) For a discussion of the economic and ecological aspects of ultraviolet radiation curing, see S. B. Levinson, *J. Paint. Technol.*, **44**, 28 (1972).

(2) For a review on photopolymerization, see G. Oster and N.-L. Yang, *Chem. Rev.*, **68**, 125 (1968).

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(6) Irradiations of degassed solutions of **1a**, 0.078 *M* in acetonitrile, were conducted in a merry-go-round apparatus with a 450-W Hanovia medium-pressure mercury lamp. The 313 and 366 nm lines were isolated by a potassium chromate solution and a Corning 7-83 filter combination, respectively. Quantum yields for the formation of **2a**, monitored by glc analysis, were determined by 0.05 *M* benzophenone–0.20 *M* benzhydrol actinometry, for which ϕ was taken as 0.85. The quantum yield values in the text account for the requirement of 2 photons per molecule of **2a** formed. The wavelength effect on quantum yields probably reflects higher light intensity at 313 nm, rather than incomplete vibrational equilibration in the excited state manifold of **1a**.

(7) Emission and excitation spectra were obtained on a Perkin-Elmer MFP-3 fluorescence spectrophotometer with a phosphorescence attachment. A relatively weak emission ($\phi \approx 0.01$, benzophenone standard)[8] with the same general appearance and band positions of the low-temperature spectrum, although broader, was also observed at room temperature in carbon tetrachloride solution (0.01 *M* **1a**). Based on studies with several benzoin ether derivatives as well as sensitization by *m*-methoxyacetophenone and lack of quenching by 1,3-cyclohexadiene, we suspect that the room temperature emission is predominately short-lived phosphorescence of **1a**. This aspect of our study will be discussed in a full report.

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(14) F. D. Lewis and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 311 (1970).

(15) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *ibid.*, **86**, 4537 (1964).

(16) J. F. Ackerman, J. Weisfield, R. G. Savageau, and G. Beerli, U. S. Patent 3,673,140 (1972); *Chem. Abstr.*, 77, 890223 (1972).

which benzophenone abstracts hydrogen from the *N*-methyl groups of Michler's ketone.[17] The present results are also explicable in terms of a triplet exciplex which leads to type I cleavage of the benzoin ether; *i.e., in this case the photochemistry is independent of the sensitizer.* Triplet energy transfer is clearly excluded by kinetic arguments. Thus, utilizing the 12 kcal/mol endothermicity, the specific rate for energy transfer may be calculated[18] to be more than 8 powers of 10 lower than the diffusional rate, *i.e.*, on the order of 10^2 M^{-1} sec^{-1}. Furthermore, taking into account the initial concentration of **1a** (0.078 *M*), the initial rate of energy transfer is predicted to be 3 orders of magnitude lower than the rate of radiationless decay of triplet Michler's ketone, taken as 10^4 sec^{-1}.[17] While the nature of the exciplex is a matter for speculation at present, the finding that 61 kcal/mol shared by Michler's ketone and **1a** may be utilized specifically for C–C bond cleavage of the ether in as high efficiency as observed (25% of the direct yield) is considered noteworthy. Indeed, the bond dissociation energy in question may be estimated as 63 ± 2 kcal/mol.[19] The potential importance of the concept of low energy sensitization for efficient energy utilization is particularly exemplified by dye sensitized photoimaging processes.[20]

Acknowledgment. We wish to express our appreciation to the Alcoa Foundation for financial assistance and to Dr. Fred D. Lewis for helpful discussions.

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Diethyl Ether Soluble Aluminum Hydride[1]

Sir:

We would like to report the preparation of diethyl ether soluble aluminum hydride prepared by three different reactions: (1) the reaction of lithium aluminum hydride and beryllium chloride, (2) the reaction of 100% H_2SO_4 with lithium aluminum hydride, and (3) the reaction of lithium aluminum hydride and zinc chloride. The yield in all three cases is quantitative.

$$2LiAlH_4 + BeCl_2 \xrightarrow{Et_2O} Li_2BeH_2Cl_2\downarrow + 2AlH_3 \tag{1}$$

$$2LiAlH_4 + H_2SO_4 \xrightarrow{Et_2O} H_2\uparrow + Li_2SO_4\downarrow + 2AlH_3 \tag{2}$$

$$2LiAlH_4 + ZnCl_2 \xrightarrow{Et_2O} 2\,LiCl\downarrow + ZnH_2\downarrow + 2AlH_3 \tag{3}$$

Previous to this report soluble aluminum hydride could only be prepared in tetrahydrofuran. All attempts to prepare aluminum hydride in diethyl ether according to the method of Schlesinger (eq 4) resulted

$$3LiAlH_4 + AlCl_3 \xrightarrow{Et_2O} LiCl\downarrow + 4AlH_3\downarrow \tag{4}$$

in significant precipitation of the aluminum hydride within 20 min after the rapid addition of reactants.[2,3]

To 20 mmol of $LiAlH_4$ in 150 ml of ether was added 10 mmol of $BeCl_2$ The solution was stirred for 2 hr and filtered. Analysis of the filtrate gave an Al:H:Li ratio of 1.0:2.97:0.002. No beryllium or chlorine was detected in the solution. Reversing the order of addition of the reactants yielded the same results. No precipitate of AlH_3 from solution was observed after 24 hr. The concentration of the solution dropped 4% in 1 week and 20% in 2 weeks. The infrared spectrum of the resulting solution[3] of AlH_3 (before precipitation) prepared by the Schlesinger method showed an Al–H stretching vibration at 1801 cm^{-1}. The AlH_3 which we have prepared has absorption bands at 1788 cm^{-1} owing to the Al–H stretching vibration and at 765 cm^{-1} owing to the Al–H deformation vibration.

Removal of the solvent under vacuum yields a white solid which was shown by elemental analysis to have the empirical formula of $AlH_3 \cdot 0.24(C_2H_5)_2O$. The X-ray powder diffraction pattern of this solid shows five main lines: 11.5 Å (s); 4.55 Å (m); 3.85 Å (m); 2.85 Å (m); and 2.32 Å (m). Bousquet, Choury, and Claudy,[4] have reported a powder pattern for $AlH_3 \cdot 0.25(C_2H_5)_2O$. Their lines match ours with the exception of the line at 3.85 Å.

DTA-TGA analysis of the solid AlH_3 etherate prepared from $LiAlH_4$ and $BeCl_2$ shows that evolution of ether begins at 50°. Evolution of hydrogen begins at 90° and is centered at 110°. Molecular association studies on a freshly prepared sample of AlH_3 in ether indicate that AlH_3 prepared from $LiAlH_4$ and $BeCl_2$ is monomeric at a concentration of 0.13–0.16 *m*.

The reduction of ketones was investigated in order to evaluate ether soluble AlH_3 as a stereoselective reducing agent. With 4-*tert*-butylcyclohexanone, AlH_3 in diethyl ether gave 46% axial alcohol, compared with 13% axial alcohol using AlH_3 in THF and 12% axial alcohol using $LiAlH_4$ in ether.

The preparation of soluble AlH_3 in diethyl ether provides an opportunity to prepare compounds that normally disproportionate in THF solvent. For example, we have prepared HBeCl by reaction of AlH_3 with $BeCl_2$ (eq 5). HBeCl was prepared unequivocally from

$$AlH_3 + BeCl_2 \longrightarrow HBeCl + H_2AlCl \tag{5}$$

BeH_2 and $BeCl_2$ in diethyl ether establishing the infrared bands for HBeCl at 1330, 1050, 970, 908, 840 (sh), 790, and 700 cm^{-1}. The infrared spectrum of DBeCl showed the band at 1330 cm^{-1} shifted to 985 cm^{-1} and the band at 970 cm^{-1} in HBeCl had disappeared in DBeCl. Molecular weight determination of HBeCl in ether shows the compound to be dimeric indicating that the BeH frequency at 1330 cm^{-1} is a bridge stretching mode.[5]

Exactly why stable ether solutions of AlH_3 are so

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(1) We are indebted to the Office of Naval Research (Contract No. N00014-67A-0159-0005 and Contract Authority No. NR-93-050/12-5-67-429) for support of this work.

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