

Photoreduction of Aromatic Ketones by Amines in Aqueous and Alcoholic Solution

By **R. S. Davidson,* P. F. Lambeth, and (Mrs.) F. A. Younis**, Department of Chemistry, The University, Leicester, LE1 7RH,
R. Wilson, Division of Molecular Science, National Physical Laboratory, Teddington, Middlesex

Photolysis of fluorenone in an ethanolic solution of triethylamine and of benzophenone in aqueous and alcoholic solutions of isobutylamine and *t*-butylamine gave the radical-anion of the ketone which was, in each case, characterised by e.s.r. With fluorenone, the products included 9-hydroxyfluorene and 9,9'-bisfluorenyl-9,9'-diol. Photolysis of benzophenone in aqueous and alcoholic solutions of a number of aliphatic amines usually gave 1,1,2,2-tetra-phenylethane-1,2-diol. 4-Phenylbenzophenone, and 2-acetylnaphthalene, on photolysis in ethanolic triethylamine, gave the corresponding diols. Fluorenone is thermally reduced by solutions of sodium isopropoxide in isopropyl alcohol to give its radical-anion which subsequently gives 9-hydroxyfluorene.

THERE have been several reports of the photoreduction of aromatic ketones by aliphatic¹ and *N*-alkylaryl-amines.² Tertiary amines have been found to be effective in reducing ketones, in which the excited state of lowest energy is of the $\pi \rightarrow \pi^*$ type (*e.g.* fluorenone,^{2,3}

4-phenylbenzophenone,⁴ and 2-acetylnaphthalene⁴), and also of a charge-transfer type (*e.g.* *p*-aminobenzophenone^{5a,b}). Such ketones are not effectively photo-reduced by alcohols and alkanes since intramolecular

³ S. G. Cohen and J. B. Guttonplan, *Tetrahedron Letters*, 1968, 5353.

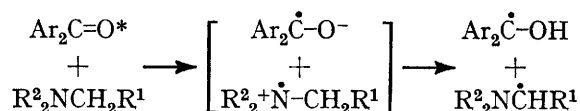
⁴ R. S. Davidson and P. F. Lambeth, unpublished results.

⁵ (a) S. G. Cohen and J. I. Cohen, *J. Amer. Chem. Soc.*, 1967, **89**, 164; (b) S. G. Cohen and J. I. Cohen, *J. Phys. Chem.*, 1968, **72**, 3782.

¹ S. G. Cohen and H. M. Chao, *J. Amer. Chem. Soc.*, 1968, **90**, 165.

² R. S. Davidson and P. F. Lambeth, *Chem. Comm.*, 1967, 1265.

energy-transfer from the $n \rightarrow \pi^*$ triplet to the $\pi \rightarrow \pi^*$ triplet state is faster than the bimolecular hydrogen abstraction reaction. Cohen has suggested^{5a} that reduction by amines occurs by electron transfer from the amine to the excited carbonyl group. The excited complex (I), so formed, gives an α -hydroxydiarylmethyl radical and an amine radical by proton transfer and electron redistribution. Evidence in favour of this



mechanism includes (a) the lack of specificity of attack of the excited carbonyl group upon the C-H bonds of alkylated amines,² (b) the quenching of benzophenone

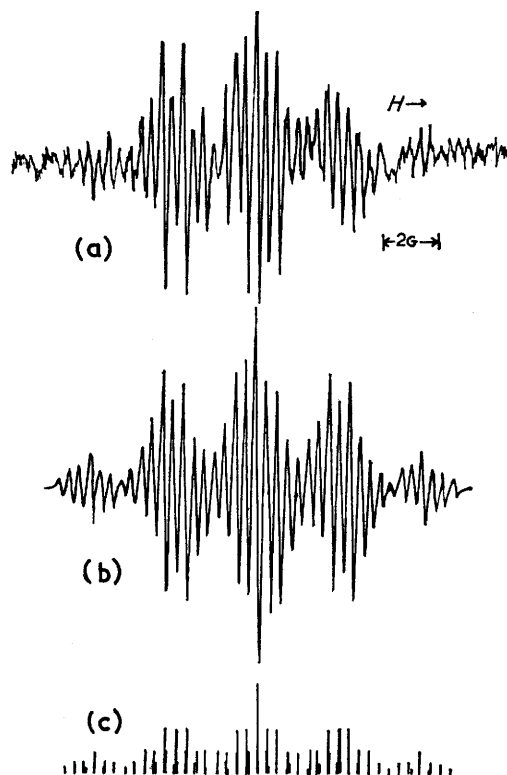


FIGURE (a) Spectrum of fluorenone radical-anion in ethanolic triethylamine solution; (b) computed spectrum; (c) 'stick' spectrum

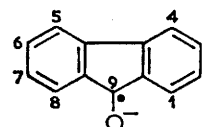
triplets by amines which do not contain abstractable hydrogens,⁶ (c) the ineffectiveness of known triplet quenchers upon the reduction by amines,^{1,6} and (d) the relatively small kinetic deuterium isotope effect shown in reduction by amines.¹

Photolysis of fluorenone either neat or in benzene solutions of triethylamine has been shown, by e.s.r. spectroscopy, to give the 9-hydroxyfluorenyl radical.⁷ When ethanolic solutions of triethylamine (from 1.25 to

10% amine) were used, asymmetric spectra were obtained which were of lower quality on the high-field side. The use of low amine-concentrations gave spectra of the highest quality and these were essentially the same as those obtained at higher amine concentrations. An example is given in Figure 1a. The spectrum in Figure 1b and the 'stick' spectrum in Figure 1c were calculated from the proton hyperfine coupling-constants in Table 1. Lorentzian line-shape functions for the

TABLE 1

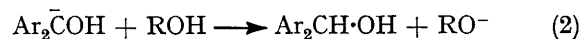
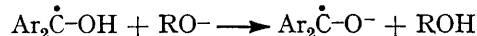
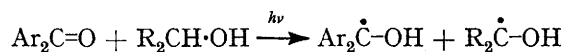
Isotropic proton hyperfine coupling constants (G) for the fluorenone radical-anion



	a_1, a_8	a_3, a_7	a_5, a_6	a_4, a_2
Fluorenone-Et ₃ N-EtOH	2.59	0.40	3.33	0.73

hyperfine lines with a peak-to-peak width of 62 mg were used. The coupling constants in Table 1 are in very close agreement with the values measured by Ayscough and Wilson⁸ for the fluorenone radical-anion generated by the photolysis of fluorenone in ethanol which contained sodium ethoxide. The asymmetry in the spectrum could well arise from distortion by a superimposed spectrum, possibly that of the 9-hydroxyfluorenyl radical, or from incomplete averaging of the anisotropic hyperfine and g -tensor interactions.

The photoreduction of aromatic carbonyl compounds in basic solution has, in many cases, been found to give secondary alcohols.⁹ Cohen has proposed¹⁰ that the initial product of reaction is an α -hydroxydiarylmethyl radical which dissociates to give the radical-anion of the ketone. Reaction of an α -hydroxydiarylmethyl radical with a radical-anion gives, by electron transfer and protonation, ketone and secondary alcohol.



Since triethylamine is a strong base ($\text{p}K_a$ 10.7) it is reasonable to suggest that 9-hydroxyfluorenyl radicals produced by reduction by the amine, dissociate to give the radical-anion. One cannot rule out that these radicals are produced directly by electron transfer from the amine to the excited ketone. Since the radical-anion was formed the products of the reaction were examined to see if any secondary alcohol was produced. Photoreduction of fluorenone in solutions of triethyl-

⁶ R. S. Davidson and P. F. Lambeth, *Chem. Comm.*, 1968, 511.

⁷ R. S. Davidson and R. Wilson, *J. Chem. Soc. (B)*, in the press.

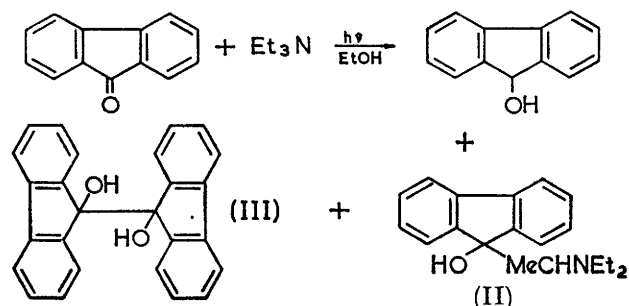
⁸ P. B. Ayscough and R. Wilson, *J. Chem. Soc.*, 1963, 5412.

⁹ W. F. Bachmann, *J. Amer. Chem. Soc.*, 1933, 55, 355, 391.

¹⁰ S. G. Cohen and W. V. Sherman, *J. Amer. Chem. Soc.*, 1963, 85, 1642.

Org.

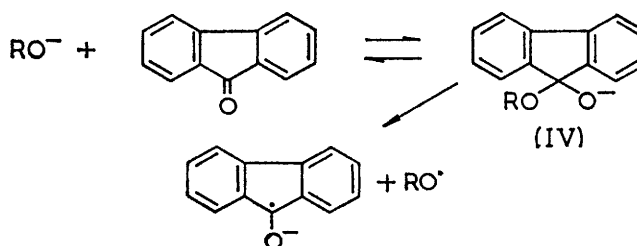
amine in aqueous ethanol, ethanol, and isopropyl alcohol gave 9-hydroxyfluorene in each case. In ethanol and isopropyl alcohol solutions the diol (III) was also formed. The mixed product (II) was formed in each case with the



exception of the reaction carried out in aqueous ethanol. Formation of (II) also occurs when fluorenone is reduced in neat triethylamine³ or in a benzene solution of triethylamine.^{3,4}

Although it has been known for some time⁸ that photolysis of fluorenone in alcoholic solutions which contain alkoxide anions produces the radical-anion, the products of the reaction have not been previously studied. Photolysis of fluorenone in isopropyl alcohol which contains sodium isopropoxide has now been found to give 9-hydroxyfluorene and fluorenone. It was shown, by following the change in u.v. absorption spectrum of the reaction mixture that the fluorenone was completely utilised in the reaction. The fluorenone in the product must therefore have been formed in the work up by reactions (1) and (2). The fluorenone radical-anion is particularly stable and a solution of it in isopropyl alcohol was found to be stable, in the absence of moisture, for several days. It was found that when fluorenone is added to a boiling solution of sodium isopropoxide in isopropyl alcohol a brown colour, typical of the radical-anion, was produced. The u.v. absorption and e.s.r. spectrum of the solution confirmed that this radical was produced. If the addition of fluorenone is made at room temperature (20°) the radical is produced only after the solution has been set aside in the dark for 24 hr. It was also found that addition of fluorenone to potassium t-butoxide in t-butyl alcohol at 20° leads to the immediate formation of the radical-anion which was easily detected by e.s.r. A similar result has been reported by Russell and his co-workers¹¹ who found that addition of potassium t-butoxide to a solution of fluorenone in t-butyl alcohol and dimethyl sulphoxide produces the radical-anion. The results described lead to the speculation that formation of the radical-anion in the photochemical reactions was a purely thermal process and that an excited state of fluorenone is not involved in the reaction. It was found that photolysis of a solution of fluorenone in isopropyl alcohol and sodium isopropoxide at -196° did not produce any radical-anion. The same solution when heated under reflux, without

illumination, gave the radical-anion. These results confirm that radical-anion formation from the reaction of fluorenone with alkoxide anions is a thermal reaction and therefore rules out such suggested mechanisms as electron transfer from alkoxide anions to fluorenone.¹² A possible mechanism for radical-anion formation is that nucleophilic attack of an alkoxide anion upon fluorenone produces the anion (IV) which undergoes homolytic fission. The stability of the radical-anion will facilitate such a fission.



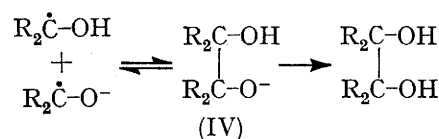
Photolysis of benzophenone in aqueous and ethanolic solutions of isobutylamine and t-butylamine produces the radical-anion, presumably by ionisation of the initially formed α -hydroxydiphenylmethyl radical. The radical-anion was identified from its e.s.r. spectrum; coupling constants are given in Table 2 and the values

TABLE 2
Isotropic proton hyperfine coupling constants (G) for the benzophenone radical-anion

	a_o	a_m	a_p
$\text{Ph}_2\text{CO}-\text{Bu}^t\text{NH}_2-\text{H}_2\text{O}$	2.81	1.02	3.50
$\text{Ph}_2\text{CO}-\text{Bu}^t\text{NH}_2-\text{EtOH}$	2.82	1.02	3.45

should be compared with the values of 2.80, 1.03, and 3.46 G reported for the benzophenone radical-anion in an ethanolic solution of sodium ethoxide.⁸

The photoreduction of benzophenone in aqueous and ethanolic solutions of primary, secondary, and tertiary aliphatic amines was found to give 1,1,2,2-tetraphenyl-ethane-1,2-diol. Only when an aqueous solution of isobutylamine was used, was diphenylmethanol produced and this in only low yield. Reaction of an α -hydroxy-diarylmethyl radical with its related radical-anion need not necessarily give secondary alcohol plus ketone [equations (1) and (2)]. Combination of the two radicals



on protonation will give a diol. This is probably the

¹¹ G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Amer. Chem. Soc.*, 1964, **86**, 1807.

¹² P. B. Ayscough and F. P. Sargent, *Proc. Chem. Soc.*, 1963, 94.

mechanism by which the diol is formed in the benzophenone-amine systems. Stocker and Kern have found¹³ that diol formation occurs on photolysis of acetophenone in isopropyl alcohol which contained sodium isopropoxide. The preferential formation of the (\pm)-isomer in this reaction was attributed to the more favourable conformation of the (\pm)-isomer of the anion (V) which allows hydrogen bonding between the O⁻ and OH groups. Schenck¹⁴ has also reported that photolysis of benzophenone in isopropyl alcohol which contained sodium isopropoxide gives 1,1,2,2-tetraphenylethane-1,2-diol.

Irradiation of 2-acetylnaphthalene in an ethanolic solution of triethylamine and of 4-phenylbenzophenone in aqueous and ethanolic solutions of triethylamine gave their corresponding diols.

The results reported in this paper contrast with those of Cohen, Stein and Mao¹⁵ who have found that photolysis of 4-benzoylbenzoic acid in aqueous triethylamine solution gives the secondary alcohol as the exclusive product. It would appear that, in general, photolysis of aromatic ketones in aqueous and alcoholic solution of amines gives a diol as the major product.

EXPERIMENTAL

Materials.—All the amines were redistilled under nitrogen prior to use. Ethanol (absolute) was heated under reflux with calcium hydride and then distilled under nitrogen to dry it. 4-Phenylbenzophenone was prepared according to the method of Long and Henze,¹⁶ with dry benzene instead of carbon disulphide as a solvent.

Spectra.—E.s.r. spectra were recorded with a Varian V-4500 spectrometer equipped with 100 Kc./sec. field modulation and with a Decca X3 spectrometer combined with Newport Instruments M5X magnet system. ¹H N.m.r. spectra were recorded on a Varian A-60 spectrometer and mass spectra on an A.E.I. MS 9 high resolution spectrometer.

Photolysis Conditions.—All solutions were purged with dry oxygen-free nitrogen prior to photolysis. A Hanovia 100 w medium-pressure mercury lamp was used. The photolysis apparatus was made with Pyrex glass. For details of conditions for photolysis in the cavity of the Decca e.s.r. spectrometer see ref. 7.

Photoreduction of Fluorenone in Alcoholic and Aqueous Solutions of Triethylamine.—Fluorenone (1.4 g.) dissolved in the solvent (150 ml.) was photolysed for 24 hr. The solvents were evaporated off under reduced pressure and the residue was chromatographed on alumina (150 g., Spence Type 'H' deactivated with 6% water). The products obtained, and their yields with the various solvent systems are shown in Table 3.

Elution of the column with benzene gave the mixed product (II), m.p. 128–129° (from light petroleum-benzene) (Found: C, 81.10, H, 8.24; N, 4.98. C₁₉H₂₃NO requires C, 81.11; H, 8.36; N, 5.04%). Elution with

benzene-ether (9:1) mixture gave 9-hydroxyfluorene, m.p. and mixed m.p. 152–153° [from light petroleum-ether (b.p. 60–80°)]. Elution with ether gave 9,9'-bifluorenyl-9,9'-diol, m.p. and mixed m.p. (from ethanol) 190–191°. 9,9'-Bifluorenyl-9,9'-diol (III) was found to be stable under the conditions of the chromatographic separation.

TABLE 3

Products obtained from photolysis of fluorenone in alcoholic and aqueous solutions of triethylamine

Solvent system	Yield of 9-hydroxy-fluorenone	Yield of diol (III)	Yield of mixed product (II)
Et ₃ N-EtOH (1:1)	31	28	10
Et ₃ N-H ₂ O (1:1)	29		21
Et ₃ N-EtOH-H ₂ O (7:2:7)	36		
Et ₃ N-PrOH (1:1)	14	5	17

Photolysis of Fluorenone in Isopropyl Alcohol-Sodium Isopropoxide at 20°.—Fluorenone (1.8 g.) was added to isopropyl alcohol (200 ml.) containing sodium (0.23 g.) and the mixture was photolysed for 24 hr. An i.r. spectrum of this solution showed the absence of any carbonyl-containing compound and u.v. spectrum showed the appearance of a new band at 452 nm. (fluorenone radical-anion as sodium salt λ_{max} 452 nm.¹⁷). Water (10 ml.) was added and the reaction mixture was evaporated under reduced pressure; the residual solid was chromatographed on alumina (100 g. Spence Type 'H'). Elution with benzene gave fluorenone (0.5 g.) m.p. and mixed m.p. 82–83° (from ethanol). Elution with ether gave 9-hydroxyfluorene (0.5 g.) m.p. and mixed m.p. 150–152° [from light petroleum (b.p. 60–80°)].

The Thermal Reaction of Fluorenone with Isopropyl Alcohol-Sodium Isopropoxide.—Fluorenone (1.8 g.) was added to isopropyl alcohol (150 ml.) containing sodium (0.23 g.) and the mixture was heated at 35–40° under nitrogen for 20 hr. Water (10 ml.) was added to the dark brown solution and the mixture was worked-up as previously described to give fluorenone (0.2 g.), m.p. and mixed m.p. 82–83° (from ethanol), and 9-hydroxyfluorene (1.07 g.) m.p. and mixed m.p. 151–152° [from light petroleum (b.p. 60–80°)].

Photolysis of Fluorenone in Isopropyl Alcohol-Sodium Isopropoxide at -196°.—Fluorenone (0.9 g.) was added to isopropyl alcohol (75 ml.) containing sodium (0.23 g.). An aliquot (3 ml.) of this solution was photolysed in a Pyrex tube at -196° for 4 hr. The u.v. spectrum exhibited no absorption at 452 nm. When the same solution was heated at 35–40° in the dark for 20 hr., the radical-anion was formed.

Photoreduction of Benzophenone by Triethylamine in Ethanol.—Benzophenone (1.8 g.) was dissolved in triethylamine (100 ml.) and water (100 ml.) was added to the solution. The mixture was then photolysed for 2 hr. after which the solvents were evaporated off under reduced pressure. The residue crystallised from ethanol to give 1,1,2,2-tetraphenylethane-1,2-diol (61%), m.p. and mixed m.p. 185–186° (from ethanol). In a similar manner, benzophenone (1.8 g.) was photolysed in a mixture of n-

¹³ J. H. Stocker and D. H. Kern, *J. Org. Chem.*, 1968, **33**, 291.

¹⁴ G. O. Schenck, G. Matthias, M. Pape, M. Czieola, G. von Büнау, E. S. Roselius, and G. Koltzenburg, *Annalen*, 1968, **719**, 80.

¹⁵ S. G. Cohen, N. Stein, and H. M. Chao, *J. Amer. Chem. Soc.*, 1968, **90**, 521.

¹⁶ L. Long and H. Henze, *J. Amer. Chem. Soc.*, 1941, **63**, 1939.

¹⁷ H. V. Carter, B. J. McClelland, and E. Warhurst, *Trans. Faraday Soc.*, 1960, **56**, 455.

butylamine (100 ml.) and water (100 ml.) for 3 hr. to give 1,1,2,2-tetraphenylethane-1,2-diol (5%), m.p. and mixed m.p. 185—186° (from ethanol).

Photoreduction of Benzophenone by Aqueous s-Butylamine.—Benzophenone (3.65 g.) was dissolved in s-butylamine (80 ml.) and water (120 ml.) was added. The mixture was photolysed for 8 hr. A white precipitate was formed which was filtered off and recrystallised from ethanol to give 1,1,2,2-tetraphenylethane-1,2-diol (2.3 g.), m.p. and mixed m.p. 185—186°. The mother liquors were evaporated under reduced pressure and the residue was crystallised from ethanol to give a further quantity of 1,1,2,2-tetraphenylethane-1,2-diol (1.02 g., total yield 73%), m.p. and mixed m.p. 185—186° (from ethanol). Further crystallisation of the mother liquors gave diphenylmethanol (8%), m.p. and mixed m.p. 68—69° [from light petroleum (b.p. 60—80°)].

Photoreduction of 4-Phenylbenzophenone by Triethylamine in Ethanol.—The ketone (2.6 g.) was dissolved in triethylamine (100 ml.) and ethanol (100 ml.) was added to the solution. The mixture was photolysed for 2 hr. The solvents were distilled off under reduced pressure and the

residue was crystallised from chloroform–acetone to give the diol (80%) m.p. 197—199° (from chloroform–acetone).⁹

In a similar way the ketone (1.3 g.) was photolysed in a mixture of triethylamine (100 ml.) and water (100 ml.) for 9 hr. to give the diol (31%) m.p. 197—199° (from chloroform–acetone).⁹

Photoreduction of 2-Acetylnaphthalene by Triethylamine in Ethanol.—The ketone (1.3 g.) was dissolved in triethylamine (75 ml.) and water (75 ml.) was added to the solution. The mixture was photolysed for 24 hr. The solvents were evaporated off under reduced pressure and the residue was chromatographed on alumina (150 g. Spence Type 'H'). Elution with benzene–ether (3:1) gave a mixture of *meso*- and (\pm)-diol (38%) m.p. 165—171° (benzene–light petroleum).¹⁸

We gratefully acknowledge the award of grants from Ipswich County Borough Council (to P. F. L.) and from Eastman Kodak Ltd. (to F. A. Y.).

[9/737 Received, May 6th, 1969]

¹⁸ M. S. Newman, *J. Org. Chem.*, 1961, **26**, 582.