The Photoreactions of Aromatic Carbonyl Compounds with Amines. Part III.† The Photoreactions of Fluorenone with Tertiary Amines

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Flash-photolysis experiments have shown that electronically excited fluorenone reacts with *NN*-dimethylaniline in polar solvents, to give the radical cation of the amine and the radical anion of the ketone. In benzene solution, the only radicals detected were the 9-hydroxyfluorenyl radical and the fluorenone radical anion. By the same technique, excited fluorenone was shown to react with triethylamine in both polar and non-polar solvents to give the fluorenone radical anion and the 9-hydroxyfluorenyl radical. The former radical is probably produced by dissociation of the latter radical. The photoreactions of fluorenone with amines are interpreted in terms of exciplex and radical ion intermediates.

IT has been shown that fluorenone has a low-lying triplet state (probably $\pi\pi^*$) [1] which is relatively unreactive, *e.g.*, it does not abstract hydrogen from alkanes, [2a,b] arylalkanes,[2c] alcohols,[2a-c] or ethers.[2c] It is reduced by the much more reactive tri-n-butyltin hydride [3] and by *N*-alkylarylamines [4,5] and tertiary alkylamines.[2b,3] Primary and secondary aliphatic amines are relatively unreactive.[2b,3] The formation and identification of radical

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† Part II, R. S. Davidson, P. F. Lambeth, and M. Santhanam, preceding paper.

[1] K. Yoshihara and D. R. Kearns, *J. Chem. Phys.*, 1966, **45**, 1991.

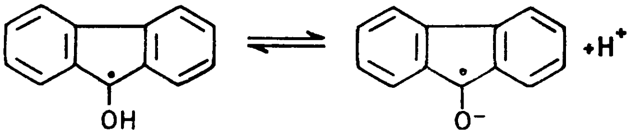
[2] (*a*) W. E. Bachmann, *J. Amer. Chem. Soc.*, 1933, **55**, 391; (*b*) S. G. Cohen and J. B. Guttenplan, *Tetrahedron Letters*, 1968, 5353; (*c*) R. S. Davidson and R. Wilson, *J. Chem. Soc.* (*B*), 1970, 71.

[3] G. A. Davis, P. A. Carapellucci, K. Szoi, and J. D. Gresser, *J. Amer. Chem. Soc.*, 1969, **91**, 2264.

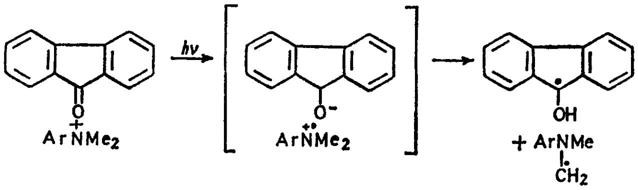
[4] R. S. Davidson and P. F. Lambeth, *Chem. Comm.*, 1967, 1265.

[5] S. G. Cohen and G. Parsons, *J. Amer. Chem. Soc.*, 1970, **92**, 7603.

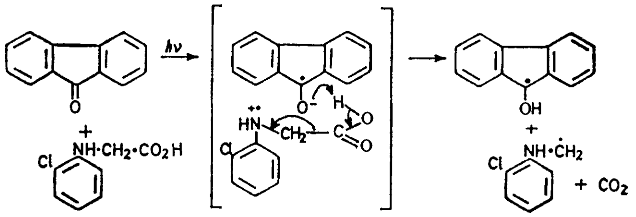
intermediates in reactions of tertiary amines with fluorenone has been accomplished by means of e.s.r. spectroscopy.[2c,6] Thus irradiation of the ketone in the presence of triethylamine or *NN*-dimethylaniline in solvents such as tetrahydrofuran, 1,2-dimethoxyethane, or toluene produces the 9-hydroxyfluorenyl radical. The use of ethanolic solutions of triethylamine resulted in the formation of the fluorenone radical anion.[6] This is thought to be produced by dissociation (Scheme 1) of the initially produced 9-hydroxyfluorenyl radical. Whilst the products of the reductions have been well characterised,[2b,3-6] there is much less known about the processes which lead to radical production. It has been shown that the efficiency of intersystem crossing in fluorenone is solvent-dependent and decreases as solvent polarity is increased.[7a,b] However, it is hard to assess quantitatively the effect of solvent upon the yield of fluorenone triplets. Studies on the quenching of the fluorescence of of fluorenone by tertiary amines have shown that reaction with the first excited singlet state of the ketone occurs efficiently.[3,7a,8] From the observation that reduction of fluorenone in neat triethylamine is relatively inefficient compared with reaction of a cyclohexane solution of triethylamine,[2b] it has been concluded [7a] that reaction of the first excited singlet state of fluorenone with amines leads to quenching. Reaction of triplet fluorenone with tertiary amines is also efficient,[5] as judged by rate-constant data, and also leads to reduction. The reactions are often sufficiently efficient to occur in the presence of relatively high concentrations of oxygen.[9] A particularly interesting finding is that the efficiency of quenching of the fluorenone triplet state by a series of substituted anilines is directly related to the electron-donor ability of the amine.[5] This observation lends credence to the suggestion that triplet fluorenone reacts with aromatic amines (Scheme 2) by an electron-transfer mechanism.[2b,c] Recently we have shown [10] that fluorenone can sensitise the decarboxylation of carboxylic acids, *e.g.*, (phenylthio)acetic acid, (*n*-butylthio)acetic acid, and *N*-(*o*-chlorophenyl)glycine, and these reactions can be readily understood in terms of an electron-transfer mechanism (Scheme 3).



SCHEME 1

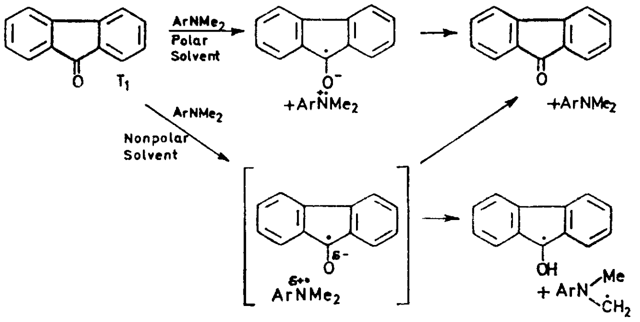


SCHEME 2



SCHEME 3

One of the unexplained facts about the photoreduction of fluorenone by amines is the effect of solvent upon the reactions. Thus, reduction by triethylamine occurs readily in benzene or cyclohexane solution but is suppressed in acetonitrile or propan-2-ol solution.[2a] It is conceivable that intersystem crossing is so poor in the polar solvents that the triplet yield is so low that little reaction occurs. An alternative suggestion is that as the solvent polarity increases, radical-ion formation is favoured and that these species react to regenerate starting ketone and amine. In solvents of low polarity, the electron-transfer process does not go to completion, *i.e.*, an exciplex is formed and this may either react to give products or lead to quenching (Scheme 4). In order to test this hypothesis we have studied the photoreactions of fluorenone with *NN*-dimethylaniline and triethylamine in solvents of varying polarity by means of the flash-photolysis technique.[11]



SCHEME 4

RESULTS

Solutions of fluorenone in acetonitrile, ethanol, and benzene solutions containing either *NN*-dimethylaniline or tri-

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[6] R. S. Davidson, P. F. Lambeth, F. A. Younis, and R. Wilson, *J. Chem. Soc.* (*C*), 1969, 2203.

[7] (*a*) R. A. Caldwell, *Tetrahedron Letters*, 1969, 2121; (*b*) S. G. Cohen and J. B. Guttenplan, *Tetrahedron Letters*, 1969, 2125.

[8] R. S. Davidson and P. F. Lambeth, *Chem. Comm.*, 1969, 1098.

[9] R. F. Bartholomew, R. S. Davidson, and M. J. Howell, *J. Chem. Soc.* (*C*), 1971, 2804.

[10] R. S. Davidson, K. Harrison, and P. R. Steiner, *J. Chem. Soc.* (*C*), 1971, 3480.

[11] G. Porter, in 'Technique of Organic Chemistry,' eds. S. L. Friess, E. S. Lewis, and A. Weissberger, Fulerscience, New York, 1963, vol. VIII, part II, pp. 1055—1106.

ethylamine were flash photolysed and the absorption spectra of the short-lived intermediate species recorded. These are shown in Figures 1—6. In many cases these absorption spectra were checked by analysis of the kinetics of the appropriate decay curves. The order of reaction for decay of the intermediate species was determined at wavelengths for which absorption maximum were recorded. The results are shown in the Table. In order to be able unequivocally to assign absorption bands due to the 9-hydroxyfluorenyl radicals, the radical was generated by flash photolysis of a solution of bi-9-hydroxyfluoren-9-yl[12] (Figure 7). Irradiation of this compound has been shown, by e.s.r. spectroscopy, to produce these radicals. The absorption spectra of the fluorenyl radical anion[13] and the *NN*-dimethylaniline radical cation[14] have been previously recorded.

Kinetics of decay of intermediates produced in the reaction of fluorenone (1×10^{-4}M) with amines

Amine	Solvent	$\lambda_{max.}$/nm of intermediate	Order of decay reaction	Rate constant / l mol^{-1} s^{-1}	Identity of intermediate[a]
NN-Dimethylaniline	Acetonitrile	438	2nd	$4{\cdot}7 \times 10^5$	
		458	2nd	$5{\cdot}4 \times 10^5$	Ketone$^{-\cdot}$
		470	2nd	$9{\cdot}3 \times 10^5$	Amine$^{+\cdot}$
NN-Dimethylaniline	Ethanol	448	2nd	$3{\cdot}9 \times 10^5$	Ketone$^{-\cdot}$
		470	2nd	$1{\cdot}8 \times 10^6$	Amine$^{+\cdot}$
NN-Dimethylaniline	Benzene	450	Mixed		Ketone$^{-\cdot}$
		500	Mixed		Ketone radical
Triethylamine	Acetonitrile	448	2nd	5×10^5	Ketone?
		500(sh)	2nd	$9{\cdot}7 \times 10^5$	Ketone radical?
		530	2nd	$7{\cdot}4 \times 10^5$	
Triethylamine	Ethanol	460	2nd	$4{\cdot}0 \times 10^5$	Ketone$^{-\cdot}$
		490	2nd	$1{\cdot}1 \times 10^5$	Ketone radical
Triethylamine	Benzene	450	Mixed		Ketone$^{-\cdot}$
		500	2nd	$1{\cdot}4 \times 10^6$	Ketone radical

[a] Ketone$^{-\cdot}$ = fluorenone radical anion. Ketone radical = 9-hydroxyfluorenyl radical. Amine$^{+\cdot}$ = *NN*-dimethylaniline radical cation.

In a number of examples, an intermediate having an absorption band around 360 nm was observed. This has been tentatively identified as the fluorenone triplet.[3]

DISCUSSION

The most striking observation in the reaction of fluorenone with *NN*-dimethylaniline in polar solvents, *e.g.*, ethanol and acetonitrile, was that an intermediate having an absorption maximum in the 460—470 nm range was produced (Figures 1 and 2). This intermediate was not formed when a non-polar solvent, *e.g.*, benzene was used for the reaction. The absorption band is ascribed to the *NN*-dimethylaniline radical cation following the work of Porter and Tsubomura.[14] In both polar and non-polar solvents an intermediate having an absorption band at 450 nm was observed and this was ascribed to the fluorenone radical anion. In benzene solution another intermediate having an absorption maxima at 500 nm was observed (Figure 3). This absorption was ascribed to the 9-hydroxyfluorenyl radical on the grounds that flash photolysis of benzene solutions of bi-9-hydroxyfluoren-9-yl gave an intermediate having a similar absorption spectrum (Figure 7). Thus, excited fluorenone appears to react with *NN*-dimethylaniline in

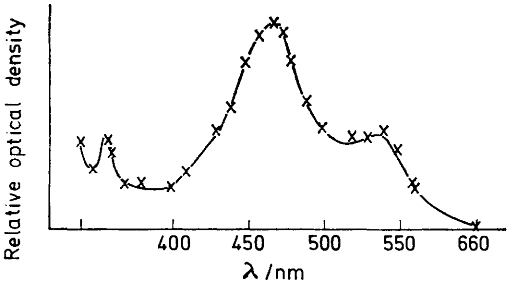

FIGURE 1 Absorption spectrum of intermediates present 25 μs after flash photolysis of a nitrogen-flushed acetonitrile solution of fluorene (1×10^{-4}M) containing *NN*-dimethylaniline (8×10^{-4}M)

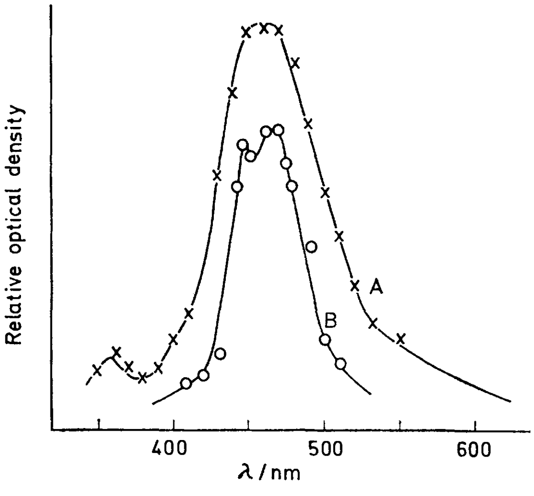

FIGURE 2 Absorption spectrum of intermediates produced by flash photolysis of a nitrogen-flushed ethanolic solution of fluorene (2×10^{-4}M) containing *NN*-dimethylaniline (2×10^{-3}M); A, 25 μs after flash; B, obtained by analysis of decay curves of intermediates

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[12] R. S. Davidson, F. A. Younis, and R. Wilson, *Chem. Comm.*, 1969, 826.

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

[14] E. J. Land and G. Porter, *Trans. Faraday Soc.*, 1963, **59**, 2027; S. Arimitsu, K. Kimura, and H. Tsubomura, *Bull. Chem. Soc. Japan*, 1969, **42**, 1858.

benzene solution to give the 9-hydroxyfluorenyl radical and the fluorenone radical anion. The latter is probably produced by dissociation of the former radical.[15] Dissociation of the 9-hydroxyfluorenyl radical should be particularly favourable because of the stability of the fluorenone radical anion. If the anion had been produced by electron transfer from the amine, the amine radical cation should have been observed.

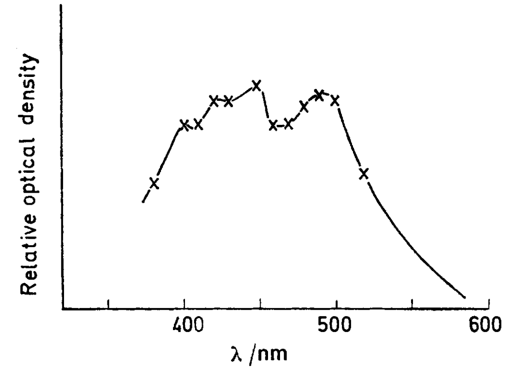

FIGURE 3 Absorption spectrum of intermediates present 100 μs after flash photolysis of a nitrogen-flushed benzene solution of fluorenone ($2{\cdot}5 \times 10^{-4}$M) containing *NN*-dimethylaniline ($2{\cdot}5 \times 10^{-3}$M)

The apparent lack of evidence for the formation of the 9-hydroxyfluorenyl radical in reactions of excited fluorenone with *NN*-dimethylaniline in ethanol or acetonitrile solutions and observation of the amine radical cation and ketone radical anion as intermediates is in accord with the suggestion that in polar solvents the amine reacts with the ketone by an electron-transfer mechanism. Further, since in the experiments the amine and ketone concentrations were low, reaction must be emanating from the triplet state and not the singlet state of the ketone.

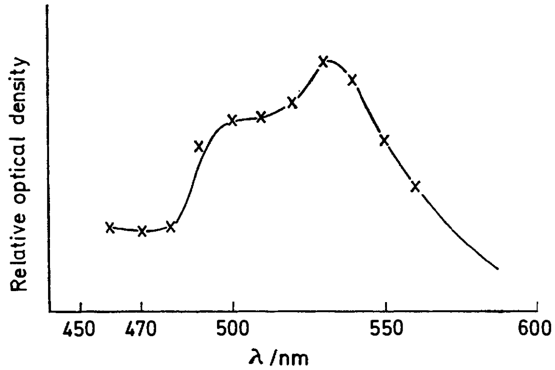

FIGURE 4 Absorption spectrum of intermediates present 6 ms after flash photolysis of a nitrogen-flushed acetonitrile solution of fluorenone (1×10^{-4}M) containing triethylamine (1×10^{-3}M)

Reaction of excited fluorenone with triethylamine in either ethanolic or benzene solution was found to give both the fluorenone radical anion and the 9-hydroxyfluorenyl radical (Figures 5 and 6). In contrast, it was very difficult to ascertain from the absorption spectra the exact nature of the intermediates produced in acetonitrile solution (Figure 4). The strong basic character of triethylamine undoubtedly favours ionisation of the 9-hydroxyfluorenyl radical and it is not surprising that in ethanolic solution the concentration of the radical anion is much greater than the protonated radical. It is possible that the ready formation of the radical anion in ethanolic solution suppresses the reduction since dimerisation of the radical anion or reaction of the radical anion with the 9-hydroxyfluorenyl radical is likely to be much less efficient than dimerisation of the 9-hydroxy-

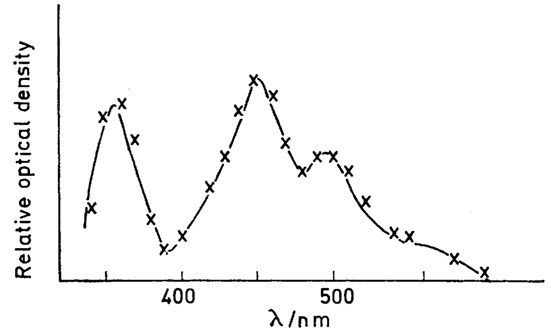

FIGURE 5 Absorption spectrum of intermediates present 50 μs after flash photolysis of a nitrogen-flushed ethanolic solution of fluorenone (2×10^{-4}M) containing triethylamine (2×10^{-3}M)

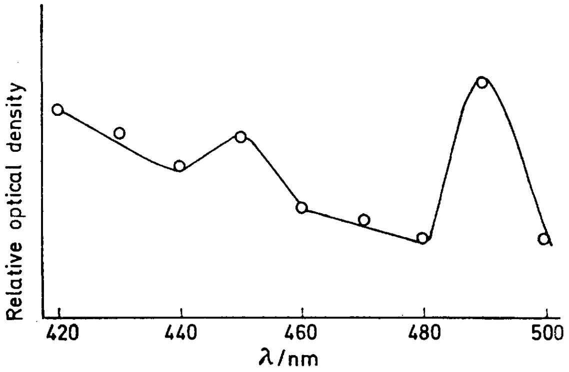

FIGURE 6 Absorption spectrum of intermediates present 6 ms after flash photolysis of a nitrogen-flushed benzene solution of fluorenone (1×10^{-4}M) containing triethylamine (1×10^{-3}M)

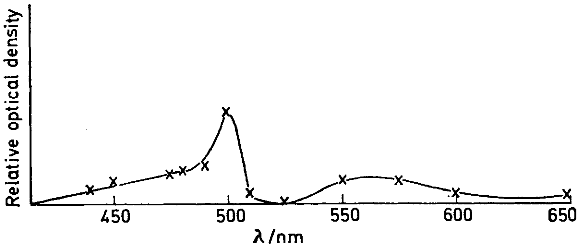

FIGURE 7 Absorption spectrum of intermediates present 50 μs after flash photolysis of a nitrogen-flushed benzene solution of bi-9-hydroxybifluoren-9-yl (1×10^{-2}M)

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[15] G. Porter and F. Wilkinson, *Trans. Faraday Soc.*, 1961, **57**, 1686.

fluorenyl radical. Further if the stationary-state concentration of the radical anion is reasonably high, then efficient paramagnetic quenching of the triplet ketone may result.[16]

A detailed analysis of the kinetics of decay of the intermediate species is hampered by a lack of knowledge of the extinction coefficients of the radicals. The similarity in the second-order rate constants for decay of the intermediate with an absorption at 470 nm, produced in the reactions with *NN*-dimethylaniline, is in accord with the assignment that the same intermediate (the amine radical cation) is produced in both acetonitrile and ethanolic solution. The order of the decay reaction is also in accord with the suggestion that it decays by an electron-transfer reaction with the radical anion.

We believe that the results support the conclusion that triplet fluorenone reacts with *NN*-dimethylaniline to give neutral radicals and that this probably occurs *via* an exciplex, whereas in polar solvents an electron-transfer reaction takes place and radical ions are produced. The reactions with triethylamine are thought to occur in a similar way. It may be asked why the *NN*-dimethylaniline radical cation and the fluorenone radical anion do not undergo a proton-transfer reaction to give neutral radicals. One explanation is that stability of the radical anion mitigates against the reaction, *e.g.*, it is known that the anion is stable in propan-2-ol solution.[6] If the amine contained a suitably located acidic proton, reaction should ensue.

In nearly all the previous studies on electron-transfer reactions of carbonyl compounds [17] and aromatic hydrocarbons [18] with amines, there has always been only *one* excited state which participates in the reactions, *i.e.*, either the first excited singlet state or triplet state. Like biacetyl,[8,19] fluorenone appears to be rather exceptional in that both its first excited singlet state and triplet state can react. This raises the question as to whether the exciplexes derived from the singlet and triplet states of the ketone are the same or not and if they are different whether the singlet exciplex can decay to the triplet exciplex. Such questions will only be answered when more direct spectroscopic evidence for the intermediates becomes available.

EXPERIMENTAL

The flash-photolysis equipment for studying the kinetics of decay of intermediates is described in the preceding paper. For the direct observation of the absorption spectra of intermediates with a spectrograph, a Chelsea Instruments flash photolysis unit was used. The xenon-filled flash lamps gave a flash of duration of *ca.* 100 μs with a 2·5 kJ input. The monotoring flash was obtained with a Garton flash tube (Chelsea Instruments Ltd.).

All solutions were thoroughly purged with oxygen-free nitrogen before use. The amines were freshly distilled under nitrogen before use.

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[16] R. A. Caldwell and R. E. Schwerzel, *J. Amer. Chem. Soc.*, 1972, **94**, 1035.

[17] S. G. Cohen and H. M. Chao, *J. Amer. Chem. Soc.*, 1968, **90**, 165; R. S. Davidson and P. F. Lambeth, *Chem. Comm.*, 1968, 511; S. G. Cohen and B. Green, *J. Amer. Chem. Soc.*, 1969, **91**, 6824; S. G. Cohen and N. Stein, *ibid.*, p. 3690; S. G. Cohen and J. I. Cohen, *J. Phys. Chem.*, 1968, **72**, 3782; S. G. Cohen, G. A. Davis, and W. D. K. Clark, *J. Amer. Chem. Soc.*, 1972, **94**, 869.

[18] D. Rehm and A. Weller, *Z. phys. Chem.* (*Frankfurt*), 1970, **89**, 183; *Ber. Bunsengesellschaft Phys. Chem.*, 1969, **73**, 834; *Israel J. Chem.*, 1970, **8**, 259; R. S. Davidson, *Chem. Comm.*, 1969, 1450.

[19] N. J. Turro and R. Engel, *J. Amer. Chem. Soc.*, 1969, **91**, 7113.