The Photoreactions of Aromatic Carbonyl Compounds with Amines. Part II.[1b] The Reactions of Triplet Benzophenone and Other Ketones with Primary and Secondary Aromatic Amines

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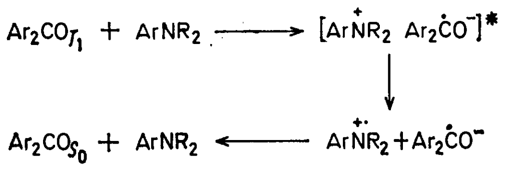
Triplet benzophenone does not react efficiently with aniline, *o*-toluidine, and diphenylamine to give isolable products. However, flash-photolysis studies showed that the ketone quite efficiently abstracts hydrogen from the amines. From a consideration of the kinetics of decay of the α-hydroxydiphenylmethyl radical, pathways were suggested whereby the radicals may react so as to produce the starting compounds. These results lead to a questioning of the assumption that primary and secondary aromatic amines act purely as physical quenchers for triplet ketones and the conclusion is reached that deactivation may be a result of either or both electron transfer and hydrogen-atom transfer. 9,10-Dihydroacridine reacts with excited benzophenone, benzylideneacetophenone, and benzylideneacetone to give isolable reduction products.

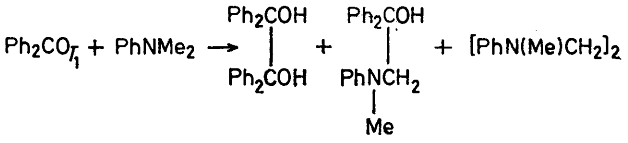
AN intriguing aspect of the photoreactions of aromatic carbonyl compounds with aromatic tertiary amines [1a,b] is that they take place by an electron-transfer mechanism. The nature of the intermediates produced by the electron transfer process, *i.e.*, an exciplex or radical ions (see Scheme 1), depends upon the polarity of the solvent. Kinetic measurements have shown that deactivation of the triplet ketone by the electron-transfer process is very efficient [1b,2] and flash-photolysis experiments have verified that radical-ion formation takes place in polar solvents.[1a,b]

Bäckström and Sandros have reported [3] upon the quenching of biacetyl phosphorescence by primary and secondary aromatic amines and have shown that the rate constants for quenching approach the diffusion-controlled limit. In contrast, triphenylamine was found to be a less efficient quencher. Turro and Engel confirmed these results [4] and interpreted the quenching as occurring by electron transfer from the amine to the triplet ketone. If this mechanism is correct the efficiency of quenching should be related to the ionisation potential of the amine and consequently triphenylamine should be as good a quencher as aniline. In a related study, Cohen and Davis have reported that aniline and diphenylamine quench excited fluorenone much more readily than triphenylamine.[5a] However these workers did find that the quenching ability of a series of anilines was related to their ionisation potentials.[5b]



SCHEME 1

Another curious difference between the reactivity of primary, secondary, and tertiary alkylarylamines is that the last efficiently reduce the excited carbonyl compounds (Scheme 2) [6] whereas reduction with the primary and secondary amines is much less efficient.[7] Prolonged irradiation of benzophenone in the presence of aniline eventually leads to reduction. Similarly benzophenone has been shown to be reduced in low quantum yield by diphenylamine.[8]



SCHEME 2

The reactions of some primary and secondary amines with triplet benzophenone have been investigated with a view to unravelling the reason for these amines being poor reductants for the ketone.

RESULTS

Primary Aromatic Amines.—Ramakrishnan and Santhanam reported that irradiation of oxygenated propan-2-ol solutions containing benzophenone and aniline leads to oxidation of the aniline.[9] A possible explanation [10] is that the benzophenone and aniline react to give radicals which react with oxygen to give the observed products. In the absence of oxygen the initially produced radicals react together to give the starting compounds (Scheme 3). The initial interaction of excited ketone with aniline could take place by an electron-transfer mechanism and the radical ions so produced react efficiently go give α-hydroxydiphenylmethyl and anilino-radicals (Scheme 4). The reactions of benzophenone with aniline and *o*-toluidine were examined by

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[1] (*a*) R. S. Davidson, P. F. Lambeth, J. F. McKellar, P. H. Turner, and R. Wilson, *Chem. Comm.*, 1969, 732; (*b*) R. F. Bartholomew, R. S. Davidson, P. F. Lambeth, J. F. McKellar, and P. H. Turner, *J.C.S. Perkin II*, 1972, 577 is regarded as Part I.

[2] S. G. Cohen and A. D. Litt, *Tetrahedron Letters*, 1970, 837.

[3] H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, 1958, **12**, 823.

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

[5] (*a*) G. A. Davis and S. G. Cohen, *Chem. Comm.*, 1970, 622; (*b*) S. G. Cohen and G. A. Parsons, *J. Amer. Chem. Soc.*, 1970, **92**, 7603.

[6] R. S. Davidson, *Chem. Comm.*, 1966, 575; R. S. Davidson and P. F. Lambeth, *ibid.*, 1967, 1265.

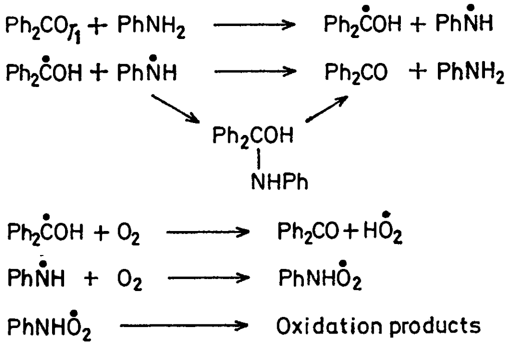
[7] M. Santhanam and V. Ramakrishnan, *Indian J. Chem.*, 1968, **6**, 88.

[8] C. Pac, H. Sakurai, and T. Tosa, *Chem. Comm.*, 1970, 1311.

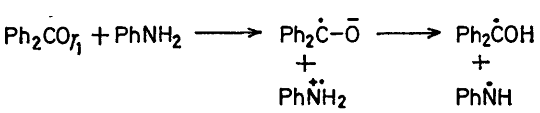
[9] M. Santhanam and V. Ramakrishnan, *Chem. Comm.*, 1970, 344.

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

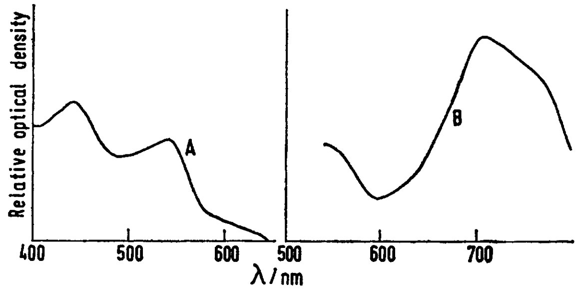
flash photolysis in the hope of detecting radical-ion and radical intermediates. When benzene, acetonitrile, and t-butyl alcohol solutions of benzophenone containing aniline were flashed, no radical-ion formation could be detected. However absorptions due to the α-hydroxydiphenylmethyl radical ($\lambda_{max.}$ 545 nm [11]) and the anilino-radical ($\lambda_{max.}$ 400 and 440 nm [12]) were detected (see Figure). The order of reaction and rates of decay of the radicals were determined and these are shown in Tables 1 and 2. In order to gain some idea of the concentration of radicals produced, optical densities of the ketyl radical at zero time (obtained by extrapolation) were also determined. Similar experiments were carried out with *o*-toluidine. With this amine it is possible that hydrogen abstraction from the methyl group could occur. However from the knowledge that toluene reacts inefficiently with triplet benzophenone [13] compared with aniline [2] it seems reasonable to assume that most of the reaction will be confined to the amino-group.



SCHEME 3



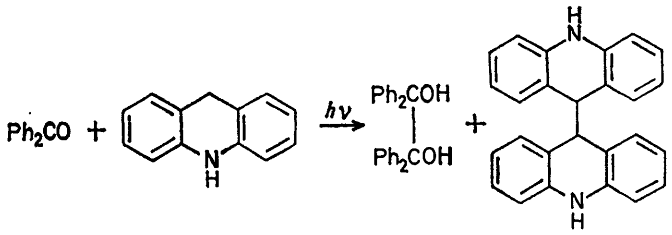
SCHEME 4



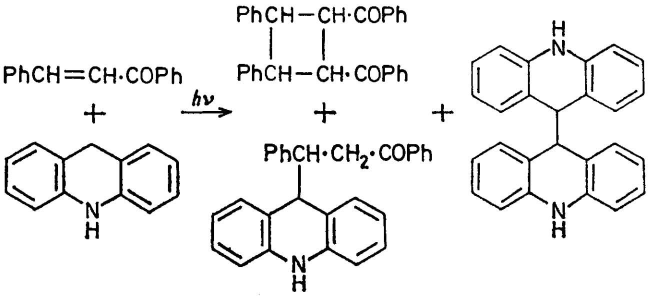
Absorption spectrum of intermediates present after flash photolysis of nitrogen-flushed acetonitrile solutions; A, of benzophenone containing aniline; 5 μs after flash; B, of benzophenone containing diphenylamine, 25 μs after flash

Secondary Aromatic Amines.—The reaction of excited benzophenone with diphenylamine was examined by flash photolysis. Intermediates detected included the α-hydroxydiphenylmethyl ($\lambda_{max.}$ 545 nm) and the diphenylamino-radical and/or the diphenylamine radical cation (see Figure). The kinetics of decay of the α-hydroxydiphenylmethyl radical were examined and are shown in Table 1.

Under the irradiation conditions we normally employ for photoreductions, we found that benzophenone was not photoreduced by diphenylamine in benzene or acetonitrile solution. However the ketone is reduced by 9,10-dihydroacridine, the principal products being 1,1,2,2-tetraphenylethylene glycol and bi-9,10-dihydroacridin-9-yl (Scheme 5).



SCHEME 5



SCHEME 6

Benzylideneacetophenone and benzylideneacetone were also found to be photoreduced by 9,10-dihydroacridine and in each case 1 : 1 adducts were isolated (Scheme 6).

DISCUSSION

Reactions of Primary Aromatic Amines.—In both the reactions of benzophenone with aniline and *o*-toluidine, α-hydroxydiphenylmethyl radicals were observed. Further, in many cases the concentration of radicals produced was quite high. Thus in the reaction of benzophenone with aniline (0·1M) in acetonitrile solution, the optical density of the radicals at zero time was 0·63. This compares with a value of 0·93 for the optical density of the radicals produced in the reaction of benzophenone with propan-2-ol (0·1M) in benzene. This reaction is known to occur with high quantum efficiency.[14] It appears therefore that in reactions of benzophenone with primary aromatic amines, radicals are efficiently produced. It is to be noted that radicals and not radical cations were detected. This does not mean that the latter species are not intermediates since, as previously

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

[12] E. J. Land and G. Porter, *Trans. Faraday Soc.*, 1963, **59**, 2027.

[13] G. S. Hammond, W. P. Baker, and W. M. Moore, *J. Amer. Chem. Soc.*, 1961, **83**, 2795.

[14] A. Beckett and G. Porter, *Trans. Faraday Soc.*, 1963, **59**, 2038.

discussed, it is possible that their transformation into neutral radicals is a particularly efficient process. Besides α-hydroxydiphenylmethyl radicals, anilino-radicals were detected.

Table 1

Optical density (at zero time) and rate constants for decay of the α-hydroxydiphenylmethyl radical produced by flash photolysis of solutions of benzophenone (5×10^{-3}M) containing amines and propan-2-ol

Amine	Concn. M	Solvent	O.D.[a]	Order[b]	k[c]
Aniline	5×10^{-3}	Bu^{t}OH	0·45	First	$2{\cdot}5 \times 10^{1}$ s^{-1}
Aniline	1×10^{-2}	Bu^{t}OH		Mixed	
Aniline	1×10^{-1}	Bu^{t}OH	0·67	Second	$9{\cdot}7 \times 10^{7}$ l mol^{-1} s^{-1}
Aniline	5×10^{-3}	Benzene	*d*		
Aniline	1×10^{-1}	Benzene	0·40	Second	$3{\cdot}3 \times 10^{9}$ l mol^{-1} s^{-1}
Aniline	5×10^{-3}	MeCN	*d*		
Aniline	1×10^{-2}	MeCN	0·47	Second	$1{\cdot}0 \times 10^{9}$ l mol^{-1} s^{-1}
Aniline	1×10^{-1}	MeCN	0·63	Second	$9{\cdot}6 \times 10^{8}$ l mol^{-1} s^{-1}
o-Toluidine	5×10^{-3}	Bu^{t}OH	0·33	First	$1{\cdot}8 \times 10^{-1}$ s^{-1}
o-Toluidine	1×10^{-2}	Bu^{t}OH		Second	$1{\cdot}7 \times 10^{8}$ l mol^{-1} s^{-1}
o-Toluidine	1×10^{-1}	Bu^{t}OH	0·6	Second	$1{\cdot}2 \times 10^{8}$ l mol^{-1} s^{-1}
o-Toluidine	5×10^{-3}	Benzene	*d*	*d*	
o-Toluidine	1×10^{-2}	Benzene	0·4	First	$2{\cdot}7 \times 10^{3}$ s^{-1}
o-Toluidine	1×10^{-1}	Benzene	0·47	First	$3{\cdot}1 \times 10^{3}$ s^{-1}
o-Toluidine	5×10^{-3}	MeCN	*d*		
o-Toluidine	1×10^{-2}	MeCN	0·60	Second	$8{\cdot}0 \times 10^{8}$ l mol^{-1} s^{-1}
o-Toluidine	1×10^{-1}	MeCN	0·60	Second	$1{\cdot}4 \times 10^{9}$ l mol^{-1} s^{-1}
Diphenylamine	5×10^{-3}	Bu^{t}OH	0·45	First	$2{\cdot}5 \times 10^{2}$ s^{-1}
Diphenylamine	1×10^{-1}	Bu^{t}OH	0·80	Second	$1{\cdot}0 \times 10^{9}$ l mol^{-1} s^{-1}
Diphenylamine	5×10^{-3}	Benzene	*d*		
Diphenylamine	1×10^{-1}	Benzene	0·25	Mixed	
Diphenylamine	1×10^{-2}	MeCN		First	1×10^{3} s^{-1}
Diphenylamine	1×10^{-1}	MeCN	0·46	First	$2{\cdot}1 \times 10^{3}$ s^{-1}
	None	Propan-2-ol (0·1M) in benzene	0·93	Second	

[a] Optical density of radical at 545 nm at zero time. [b] Order of reaction for decay of radical. [c] Rate constant for decay of radical. [d] No transient absorption at 545 nm. observed.

The finding that radicals are produced relatively efficiently in the reaction of benzophenone with primary aromatic amines begs the question as to why the ketone is reduced so inefficiently to isolable products. It appears that the radicals can react in such a way that only the starting compounds are produced. The kinetics of decay of the α-hydroxydiphenylmethyl radical indicate that the reactions of this species are dependent on more than one factor. Usually it was observed that the order of reaction for decay of the radical changed from first through mixed kinetics to second as the concentration of the amine was increased. Further, if the concentration of benzophenone is increased, and the concentration of amine is kept constant, the order of decay of the radical changes from first to second (Table 3). These results may be rationalised by postulating that at low amine and benzophenone concentrations, the radical reacts with the ground-state amine. At higher amine or benzophenone concentrations the radical disappears by reaction with another radical, *e.g.*, the anilino-radical. One instinctively feels that the greater the amine concentration, the more likely the reaction of α-hydroxydiphenylmethyl radicals with amine should become. However the greater the amine concentration or benzophenone concentration, the higher the concentration of the radicals generated by the photolysis flash will be and consequently radical–radical reactions will become more favoured.

Table 2

Rate constants for decay of anilino-radicals produced by flash photolysis of solutions of benzophenone (5×10^{-3}M) containing aniline (1×10^{-1}M)

	Order of reaction and rate constant	
Solvent	At 400 nm	At 440 nm
Bu^{t}OH	*a*	Second; $1{\cdot}7 \times 10^{8}$ l mol^{-1} s^{-1}
Benzene	Second; $6{\cdot}6 \times 10^{8}$ l mol^{-1} s^{-1}	Second; $6{\cdot}1 \times 10^{8}$ l mol^{-1} s^{-1} [b]

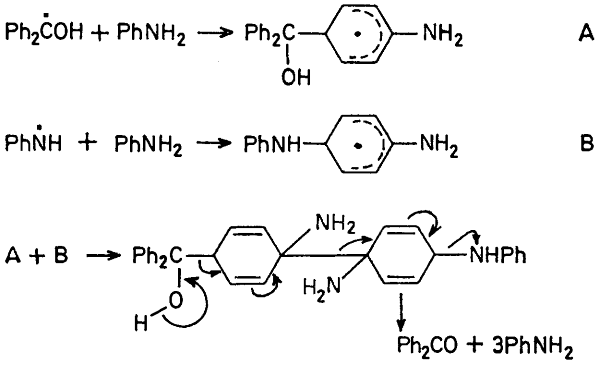
[a] Difficult to tell whether first- or second-order decay owing to the weak absorption of the species. [b] Optical density at zero time found to be 0·12.

Table 3

Effect of changing concentration of benzophenone upon the kinetics of decay of the α-hydroxydiphenylmethyl radical produced in reactions of the ketone with amines

Benzophenone concn./M	Amine	Concn./M	Solvent	Order of reaction for decay of radical	Rate constant for decay of radical
5×10^{-3}	Aniline	5×10^{-3}	Bu^{t}OH	First	$2{\cdot}5 \times 10^{1}$ s^{-1}
1×10^{-2}	Aniline	5×10^{-3}	Bu^{t}OH	Second	$8{\cdot}7 \times 10^{7}$ l mol^{-1} s^{-1}
5×10^{-3}	*o*-Toluidine	1×10^{-2}	Benzene	First	$1{\cdot}1 \times 10^{3}$ s^{-1}
1×10^{-2}	*o*-Toluidine	1×10^{-2}	Benzene	First	$1{\cdot}0 \times 10^{3}$ s^{-1}
1×10^{-1}	*o*-Toluidine	1×10^{-2}	Benzene	Second	$4{\cdot}2 \times 10^{9}$ l mol^{-1} s^{-1}

Whether the decay of the radicals be by first-order or second-order processes, the reactions must ultimately lead to the generation of the starting compounds. We have already speculated as to the nature of the second-order process (see Results section). The finding that the rate constants for decay of anilino-radicals and the α-hydroxydiphenylmethyl radical are very similar supports this suggested mechanism. We feel that, owing to the lack of experimental evidence, extensive speculation as to the reactions involved in the first-order decay process is unwarranted. However, a suggested pathway is shown in Scheme 7.



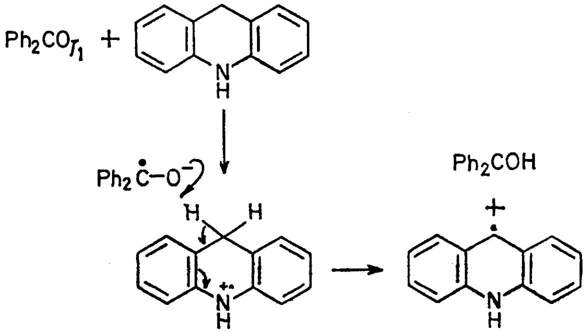
SCHEME 7

The finding that radicals are produced in the reaction of triplet benzophenone with primary aromatic amines calls into question the mechanism by which the amines quench the excited ketone. We cannot assume that the quenching is a purely physical process on the grounds that isolable reactions products are ineffectively produced and therefore the enigma remains as to whether quenching is by an electron-transfer process or by hydrogen-atom transfer.

Reactions of Secondary Aromatic Amines.—Examination of the absorption spectra of the intermediates produced in flash photolysis of a solution containing benzophenone and diphenylamine reveals the presence of species absorbing in the region 600—800 nm besides one at 545 nm (identified as the α-hydroxydiphenylmethyl radical [11]). Since the diphenylamine radical cation has an absorption maximum at 690 nm [15a,b] and that of the diphenylamino-radical has one at 740 nm,[15a] it is difficult unequivocally to assign the absorption at 600—800 nm to any particular species. There is the possibility that both species are present. In nearly all the examined cases it was found that the α-hydroxydiphenylmethyl radical decayed by a first-order process and we suggest that the radical is reacting with diphenylamine. This fits nicely with the observation of Pac *et al.* that benzophenone reacts with diphenylamine to give 4-(*N*-phenylamino)phenyldiphenylmethanol.[8]

Although reaction of triplet benzophenone with diphenylamine to give isolable products occurs in poor yield (as judged by the long irradiation times required to effect reaction) the reaction with 9,10-dihydroacridine occurs efficiently. Further, unsaturated ketones react with this amine is preference to undergoing dimerisations. The feature of interest in these reactions is that hydrogen abstraction apparently occurs from the methylene and not the amino-group of the amine. It is tempting to suggest that the ketone reacts with the amine by an electron-transfer reaction and that this is followed by proton transfer from the methylene group. An alternative suggestion is that hydrogen abstraction from the N-H bond does occur and that the amino-radical so formed abstracts hydrogen from the methylene group of a dihydroacridine molecule (Scheme 8). There is evidence that the ' carbon radical ' is more stable than the nitrogen radical.[16] Whichever process is taking place, it is strange that a similar process does not occur in the reaction of benzophenone with *o*-toluidine.

In conclusion the results show that triplet benzophenone reacts with primary and secondary aromatic amines to give radicals. The results do not indicate whether the radicals are formed by hydrogen-atom abstraction or by electron transfer from the amine to the excited ketone followed by proton transfer.



SCHEME 8

EXPERIMENTAL

Instrumentation.—I.r. spectra were recorded on Perkin-Elmer 237 and 257 grating spectrophotometers; ^1H n.m.r. spectra were recorded for solutions in deuteriochloroform (with tetramethylsilane as internal standard) with a Varian T-60 spectrometer; m.p.s (uncorrected) were determined with a Kofler hot-stage apparatus. Flash photolyses were carried out with a Northern Precision FPI instrument. The Pyrex sample cell had dimensions 20 cm × 1 cm. For photographic recording of spectra a Garton flash tube (Chelsea Instruments Ltd.) was used as a spectral lamp. Spectra were obtained with a Hilger medium quartz spectrograph and recorded on Ilford HP3 plates (for spectra in the range 300—650 nm) and Kodak IR ER plates (for spectra in the range 300—1000 nm). For kinetic measurements, a quartz–iodine lamp, operated from a stabilised power supply, was used as the monitoring light. Changes in light absorption were recorded with an E.M.I. 9660 B photo-

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[15] (*a*) G. N. Lewis and D. Lipkin, *J. Amer. Chem. Soc.*, 1947, **64**, 2801; (*b*) T. Shida and W. H. Hamill, *J. Chem. Phys.*, 1966, **44**, 2369.

[16] A. Kira and M. Koizumi, *Bull. Chem. Soc. Japan*, 1969, **42**, 625.

multiplier whose output was fed into a Dynamco 7110 storage oscilloscope.

Preparative-scale reactions were carried out with a Hanovia 100 W medium-pressure mercury lamp which was housed in a water-cooled Pyrex jacket. This jacket fitted into a vessel containing the solution to be irradiated. The solutions were purged with oxygen-free nitrogen throughout the irradiation period and for 30 min before it.

Materials.—Benzophenone (B.D.H.) was used as received since recrystallisation did not affect its m.p. Benzene (dried over sodium), t-butyl alcohol (dried over calcium hydride), and acetonitrile (Koch–Light) were distilled under a stream of nitrogen before use. Similarly aniline and *o*-toluidine were distilled before use. Diphenylamine (m.p. 53—54 °C) was recrystallised from aqueous ethanol. 9,10-Dihydroacridine was prepared by reduction of acridine with lithium aluminium hydride [17] and had m.p. 170 °C (from methanol) (lit.,[17] m.p. 169 °C).

Photoreduction Reactions.—*Reaction of benzophenone with* 9,10-*dihydroacridine*. A benzene solution (150 ml) of benzophenone (1·5 g) containing 9,10-dihydroacridine (1·5 g) was irradiated for 17 h. The precipitate formed in the reaction was filtered off and recrystallised from pyridine to give bi-9,10-dihydroacridin-9-yl (1·2 g), m.p. and mixed m.p. 236 °C; [18] i.r. spectrum was identical with that of an authentic sample. The filtrate was concentrated to give 1,1,2,2-tetraphenylethane-1,2-diol (1·2 g), m.p. and mixed m.p. 185—186 °C (from ethanol).

Reaction of benzylideneacetophenone with 9,10-*dihydroacridine*. A benzene solution (150 ml) of benzylideneacetophenone (1·5 g) containing 9,10-dihydroacridine (1·8 g) was irradiated for 17 h. The precipitate formed was filtered off and recrystallised from pyridine to give bi-9,10-dihydroacridin-9-yl (0·8 g), m.p. and mixed m.p. 235—239 °C; i.r. spectrum was identical with that of an authentic specimen. The filtrate was concentrated. Addition of light petroleum (b.p. 40—60 °C) gave a solid which recrystallised from ethanol–chloroform to give 3-(9,10-*dihydroacridin*-9-*yl*)-3-*phenylpropiophenone* (0·6 g), m.p. 181·5—182·5 °C (Found: C, 87·0; H, 5·9; N, 3·7. $C_{28}H_{23}NO$ requires C, 86·4; H, 6·0; N, 3·6%), τ 2·83 (18H, m), 5·85br (1H, s), and 6·72br (4H, m), $\nu_{max.}$ 3400, 1680, 1600, 1290, 750, and 700 cm^{-1}. The mother liquors gave on concentration the ‘ head-to-head ’ dimer of benzylideneacetophenone (0·15 g), m.p. 124—125 °C (from ethanol) (lit.,[19] m.p. 125°).

Reactions of benzylideneacetone with 9,10-*dihydroacridine*. A benzene solution (150 ml) of benzylideneacetone (1·1 g) containing 9,10-dihydroacridine (1·8 g) was irradiated for 16 h. The white precipitate formed in the reaction was filtered off and recrystallised from pyridine to give bi-9,10-dihydroacridin-9-yl (0·5 g), m.p. and mixed m.p. 236—239 °C; i.r. spectrum was identical with that of an authentic specimen. Evaporation of the benzene from the filtrate gave a residue which on crystallisation from ethanol yielded unchanged 9,10-dihydroacridine (0·7 g), m.p. and mixed m.p. 169 °C. The mother liquors gave, on cooling to 0 °C, colourless crystals of 4-(9,10-*dihydroacridin*-9-*yl*)-4-*phenylbutan*-2-*one* (0·4 g), m.p. 178—179 °C (from ethanol) (Found: C, 83·6; H, 6·3; N, 4·3. $C_{23}H_{21}NO$ requires C, 84·4; H, 6·5; N, 4·3%); τ 3·05 (13H, m), 4·05br (1H, s), 5·84 (2H, m), 72·5 (2H, d), and 8·1 (3H, s), $\nu_{max.}$ 3350, 1700, 1600, 1290, 760, and 700 cm^{-1}.

We thank Dr. J. F. McKellar for discussions and the S.R.C. for an equipment grant and fellowship (to M. S.).

[2/1382 *Received*, 15*th June*, 1972]

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