

Photochemical Formation of Amides from t-Butylamine and Aromatic Aldehydes and Ketones

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Irradiation of benzaldehyde, substituted benzaldehydes, benzoin, benzil, and t-butyl phenyl ketone in the presence of t-butylamine leads to *N*-t-butylarene-carboxamides. In the case of the aldehydes, imine formation also occurs. The imine is reduced by reaction with α -hydroxybenzyl radicals, which are also generated in the photochemical reaction. Benzyl phenyl ketone does not give products *via* an α -scission reaction, but instead is reduced by the amine. The formation of the amides is rationalised as occurring by attack of benzoyl radicals on the amine.

BENZOYL radicals have been shown to be formed in photochemical reactions of benzaldehyde¹ and in the α -scission reactions of alkyl phenyl ketones.² Thus, irradiation of benzaldehyde in solvents having unreactive

C-H bonds leads to products derived from a radical pair (a benzoyl and an α -hydroxybenzyl radical) formed by attack of an excited aldehyde molecule upon a ground-

¹ (a) M. Cocivera and A. M. Trozzolo, *J. Amer. Chem. Soc.*, 1970, **92**, 1772; (b) G. L. Closs and D. R. Paulson, *ibid.*, p. 7229; (c) P. W. Atkins, J. M. Frimston, P. G. Frith, R. C. Gurd, and K. A. McLauchlan, *J.C.S. Faraday II*, 1973, 1542.

² (a) F. D. Lewis and J. G. Magyar, *J. Org. Chem.*, 1972, **37**, 2102; (b) H.-G. Heine, W. Hartmann, D. R. Kory, J. G. Magyar, C. E. Hoyle, J. K. McVey, and F. D. Lewis, *ibid.*, 1974, **39**, 691; (c) F. D. Lewis, C. H. Hoyle, J. G. Magyar, H.-G. Heine, and W. Hartmann, *ibid.*, 1975, **40**, 488; H.-G. Heine, *Annalen*, 1970, **732**, 165.

state aldehyde molecule.^{1a,b,3} Isolated products include benzoin and 1,2-diphenylethane-1,2-diol. CIDNP studies^{1a,b} have provided elegant proof of the intermediacy of the radical pair. This technique has also shown that the same radical pair is produced on photolysis of benzoin.^{1a,b,4} Irradiation of *t*-alkyl phenyl ketones also leads to benzoyl radicals *via* an α -scission reaction.^{2a}

We now report that irradiation of many precursors of benzoyl radicals in the presence of *t*-butylamine leads to amides.

RESULTS

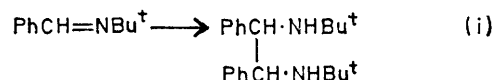
Irradiation of benzaldehyde, 4-chlorobenzaldehyde, 2,4-dichlorobenzaldehyde, and 4-fluorobenzaldehyde in benzene solution containing *t*-butylamine did not lead to reduction products but instead, to *N*-*t*-butylarene-carboxamides. These could be readily separated and their yields, determined by g.l.c. analysis, are shown in the Table. Other products included imines derived by con-

Yields ^a of amides formed on irradiation of carbonyl compounds in the presence of *t*-butylamine

Carbonyl compounds	Irradiation time (h)	Product (% yield)
Benzaldehyde	15	<i>N</i> - <i>t</i> -Butylbenzamide (32)
	4	<i>N</i> - <i>t</i> -Butylbenzamide (18)
4-Chlorobenzaldehyde	4	4-Chloro- <i>N</i> - <i>t</i> -butyl benzamide (29)
2,4-Dichlorobenzaldehyde	4	2,4-Dichloro- <i>N</i> - <i>t</i> -butyl benzamide (17)
4-Fluorobenzaldehyde	4	4-Fluoro- <i>N</i> - <i>t</i> -butyl benzamide (28)
Benzoin	4	<i>N</i> - <i>t</i> -butylbenzamide (52)
Benzil	4	<i>N</i> - <i>t</i> -Butylbenzamide (12)
Dimethyl acetal of benzil ^b	4	<i>N</i> - <i>t</i> -Butylbenzamide (19)
<i>t</i> -Butyl phenyl ketone	15	<i>N</i> - <i>t</i> -Butylbenzamide (95)

^a As determined by g.l.c. analyses and calculated on the assumption that 1 mol of carbonyl compound gives 1 mol of amide. ^b This ketone has been shown^{15a} to undergo the α -cleavage reaction on irradiation.

densation of the amine with the aldehyde. In the case of benzaldehyde, some of the imine was reduced [reaction (i)].



A variety of other compounds which yield aroyl radicals on irradiation were irradiated in the presence of *t*-butylamine; the results are shown in the Table. In the case of benzoin,^{*} there was the possibility that amide formation occurred *via* benzaldehyde generated during photolysis of the benzoin.^{1b} That this was not the case was shown by the fact that amide production occurs faster in the reaction of benzoin than in that of benzaldehyde; also careful monitoring of the reaction of benzoin by g.l.c. did not reveal the presence of benzaldehyde. These observations indicate that reaction of the radical pair composed of a benzoyl and an α -hydroxybenzyl radical to give benzaldehyde is relatively in-

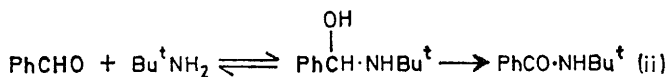
^{*} Benzoin has been shown to be photoreduced by amines having reactive α -C-H bonds.⁵

³ J. S. Bradshaw, R. D. Knudsen, and W. W. Parish, *J.C.S. Chem. Comm.*, 1972, 1321.

efficient, and that the *t*-butylamine is an efficient scavenger of benzoyl radicals. The reaction of benzyl phenyl ketone differs from the others in that reduction occurs. No trace of products derived by an α -cleavage reaction of the ketone was detected.

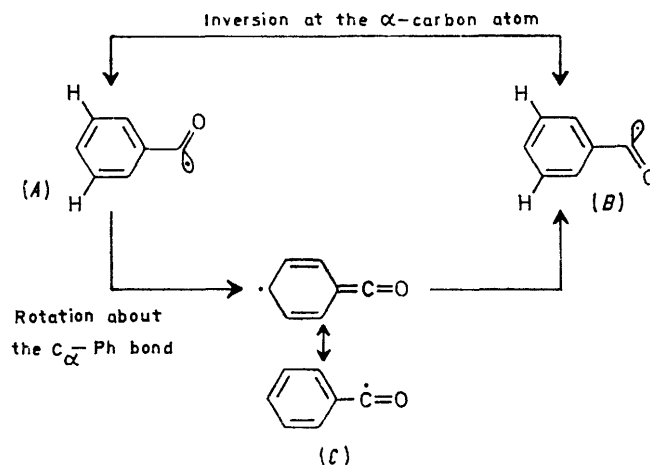
DISCUSSION

The formation of amides on irradiation of benzaldehydes in the presence of *t*-butylamine is unprecedented, and the mechanism of their formation needs to be elucidated. One possible route involves a carbinolamine [reaction (ii)]. However, examination of the reaction



mixture by n.m.r. spectroscopy before, during, and after the irradiation, failed to reveal the presence of any carbinolamine. Thus it is unlikely that it is formed in any substantial quantity and therefore even less likely that it is oxidised in a bimolecular photochemical reaction involving the triplet aldehyde. This reactive species is far more likely to react with either the amine or ground state aldehyde, both of which are present at relatively high concentration.

The fact that aromatic aldehydes and the other compounds shown in the Table give amides on irradiation in the presence of the amine suggests that aroyl radicals are precursors of the amides. In the case of ketones shown in the Table, amide formation *via* a carbinolamine is impossible. E.s.r. studies⁶ on the benzoyl radical have established that it is a σ -radical. Since hyperfine coupling occurs to both *meta*-protons, the radicals (A) and (B) must be rapidly interconverting on the e.s.r.



time-scale. This may occur either by inversion at the α -carbon atom or by rotation about the $\text{C}_\alpha\text{-Ph}$ bond. If the latter process occurs, the intermediate radical (C) can

⁴ A. Ledwith, P. J. Russell, and L. H. Sutcliffe, *J.C.S. Perkin II*, 1972, 1925.

⁵ D. L. Bunbury and T. M. Chan, *Canad. J. Chem.*, 1972, **50**, 2499.

⁶ (a) P. J. Krusic and T. A. Rettig, *J. Amer. Chem. Soc.*, 1970, **92**, 722; (b) L. Salem, *ibid.*, 1974, **96**, 3486.

efficient trap for benzoyl radicals and that it should prove useful as a probe for the mechanism of α -scission reactions.

EXPERIMENTAL

Benzene, *t*-butylamine, and benzaldehyde were redistilled under nitrogen prior to use. Apart from benzaldehyde, the aldehydes were used as received. *t*-Butyl phenyl ketone¹⁴ and *t*-butyl 4-*t*-butylphenyl ketone¹⁴ and the dimethyl acetal of benzoin^{15a,b} were prepared according to literature methods.¹⁴ Petroleum refers to the fraction of b.p. 60–80°.

¹H N.m.r. spectra were recorded for solutions in deuteriochloroform (with tetramethylsilane as internal standard), with a Varian T-60 instrument. I.r. spectra for samples in Nujol were obtained with a Perkin-Elmer 257 spectrophotometer.

G.l.c. Analysis.—Analyses were carried out with a Pye Series 104 chromatograph, equipped with a flame ionisation detector. The detector gave a linear response over the whole range of concentrations used. The identities of products were confirmed by comparison of their retention times with those of authentic samples. Quantitative estimations were carried out by using biphenyl as an internal standard. Two determinations were made for each reaction mixture. Analyses were carried out on a 1.5 m × 4 mm i.d. glass column packed with 3% OV17 on silanised 100–120 mesh Diatonite C 'Q' at 130 °C.

Irradiation Procedure.—An immersion apparatus was used in which a 100 W Hanovia medium-pressure mercury lamp was contained in a Pyrex water-cooled well. The reaction mixture (165 ml) surrounded this well and was stirred by a stream of oxygen-free nitrogen, admitted through a sinter at the bottom of the vessel.

*Irradiation of Benzaldehyde in the Presence of *t*-Butylamine.*—A solution in benzene (165 ml) of benzaldehyde (3.5 g) and *t*-butylamine (15 ml) was irradiated for 16 h. Evaporation left an oil which on trituration with petroleum gave a solid (1.84 g). Recrystallisation from benzene-petroleum gave *N*-*t*-butylbenzamide, m.p. and mixed m.p. 135–136°. The residue from the mother liquors was dissolved in ethyl

¹⁴ D. E. Pearson, *J. Amer. Chem. Soc.*, 1950, **72**, 4169.

¹⁵ (a) R. Kuhn and H. Trischmann, *Chem. Ber.*, 1961, **94**, 2258; (b) M. R. Sandner and C. L. Osborn, *Tetrahedron Letters*, 1974, 415.

¹⁶ J. H. Stocker and D. H. Kern, *J. Org. Chem.*, 1968, **33**, 1271.

acetate. At –25 °C this solution afforded a solid (0.35 g). Recrystallisation from ethanol gave 1,2-diphenyl-*NN'*-di-*t*-butylethane-1,2-diamine, m.p. 133–134° (Found: C, 81.2; H, 10.0; N, 8.65. C₂₂H₃₂N₂ requires C, 81.5; H, 9.9; N, 8.65%); *m/e* (no molecular ion) 309 [1%, (*M* – CH₃)], 251 (2%, Ph⁺CH⁺CHPhNHBu^t), 236 (2%, Ph⁺CH⁺CHPhN⁺CMe₂), 196 [5%, Ph⁺CHC⁺(NH)Ph], 162 (100%, Ph⁺CH⁺NHBu^t), 147 (6%, Ph⁺CH⁺NHCHMe₂), 146 (53%, Ph⁺CH⁺NH⁺CMe₂), and 106 (25%, Ph⁺CH⁺NH₂), τ 9.15 (18 H, s), 8.65 (2 H, s, NH), 6.3 (2 H, s, CH), and 2.8 (10 H, m, aromatic). On removal of the solvent from the mother liquors an oil remained. The n.m.r. spectrum showed singlets at τ 1.95 and 8.9, characteristic of the CH and CH₃ groups of *N*-*t*-butylbenzylideneamine. The i.r. spectrum showed an absorption at 1 745 cm⁻¹ (C=N).

*Irradiation of 4-Fluorobenzaldehyde, 4-Chlorobenzaldehyde, *t*-Butyl Phenyl Ketone, and *t*-Butyl 4-*t*-Butylphenyl Ketone in the Presence of *t*-Butylamine.*—A solution in benzene (165 ml) of the carbonyl compound (3.5 g) and *t*-butylamine (15 ml) was irradiated for 16 h. Evaporation left an oil which on trituration with petroleum gave the crude *N*-*t*-butylarenecarboxamide. These were recrystallised and identified by comparison (mixed m.p. and i.r. and n.m.r. spectra) with authentic samples prepared from the appropriate acid chloride and an excess of *t*-butylamine. The yields of isolated pure amides from the aldehydes are: 4-fluoro-*N*-*t*-butylbenzamide (0.8 g), *N*-*t*-butyl-4-chlorobenzamide (0.9 g). *t*-Butyl phenyl ketone gave *N*-*t*-butylbenzamide (1.1 g), and *t*-butyl 4-*t*-butylphenyl ketone gave *N*,4-di-*t*-butylbenzamide (1.0 g).

*Irradiation of Benzyl Phenyl Ketone in the Presence of *t*-Butylamine.*—A solution in benzene (165 ml) of the ketone (3.5 g) and *t*-butylamine (15 ml) was irradiated for 16 h. Evaporation left a residue which on trituration with petroleum gave a solid (0.6 g). This was recrystallised from heptane to give *meso*-1,2-dibenzyl-1,2-diphenylethane-1,2-diol, m.p. 212–214°. The mother liquors yielded a further crop (0.2 g) which crystallised from heptane to give the (\pm)-isomer, m.p. 170–172°. The n.m.r. spectra for the diols agreed with previously reported data.¹⁶ The mother liquors from the crystallisation were shown to contain a large proportion of unchanged ketone by i.r. and n.m.r. spectroscopy.

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