

Novel Photoreaction Between Benzaldehyde and *t*-Butyl Isocyanide

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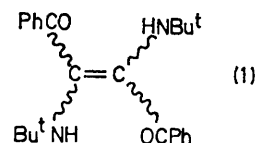
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Summary Irradiation of benzaldehyde and *t*-butyl isocyanide in benzene or acetonitrile at room temperature gives 1,2-dibenzoyl(di-*t*-butylamino)ethylene (1)

The photochemistry of aromatic aldehydes and ketones has been extensively studied and the behaviour of their n, π^* triplet excited states is now fairly well understood.¹ A close parallel exists between the reactivities of triplet ketones and alkoxy radicals, and recent work has shown that alkoxy radicals add efficiently to isonitriles.² In view of the possibility of photochemically excited carbonyl compounds reacting with isonitriles in radical-like fashion and the scarcity of information on the photochemical behaviour of isonitriles,³ we have studied these areas, and report here our preliminary results on the photochemically induced reaction between benzaldehyde and *t*-butyl isocyanide.

A benzene or acetonitrile solution of benzaldehyde (0.5M) and *t*-butyl isocyanide (0.5M), either degassed and sealed in Pyrex tubes or N₂-flushed and sealed in quartz tubes, was irradiated by a Hanovia 450-W medium pressure mercury arc for *ca.* 24 h. Removal of volatile material left a residue which was recrystallized from 95% EtOH to give a

yellow solid (3–7%), m.p. 202–203 °C; i.r. (mull) 3450 and 3220 (free and H-bonded, NH, respectively), 1655, 1600, and 1505 cm⁻¹; δ (CDCl₃) 1.15 (s, 9H), 4.80 br (s, 1H), and 7.13–7.63 (m, 5H); λ_{max} (CHCl₃) 250 and 328 nm (log ϵ 4.30 and 4.02, respectively); m/e 378.† The ¹³C n.m.r. data obtained under proton-noise-decoupled and pulse-Fourier-transform conditions show Bu^t resonances at 27.7 and 54.8 p.p.m., unsaturated resonances at 128.3, 128.6, 132.1, 136.9, and



139.6 p.p.m., and a carbonyl resonance at 194.5 p.p.m. The spectral and physical properties are consistent with the structure (1). Similar results were obtained from irradiation of *p*-chlorobenzaldehyde and *t*-butyl isocyanide.

Structure (1) for the photoproduct was confirmed by independent synthesis (11%) from *trans*-1,2-dibenzoyl-1,2-dibromoethylene and excess of *t*-butylamine in Me₂SO under N₂ at 70 °C for 40 h.† The product formed by this

† Satisfactory combustion analysis obtained.

route was identical with that produced photochemically. The ready isomerization of (1) in solution precluded assignment of the configuration, although a tentative *trans*-configuration may be assigned on the basis of the stereochemical course of nucleophilic vinylic substitutions.

Photolysis of benzaldehyde forms nearly equal amounts of benzoin, deoxybenzoin, and 1,2-diphenylethane-1,2-diol,⁶ all of which as well as benzil⁷ and PhCOCH=NBut[†] were tested photochemically or under free-radical conditions as possible intermediates leading to (1). According to t.l.c. and ¹H n.m.r. analysis, significant amounts of (1) are formed only from the irradiation of benzoin in the presence of *t*-butyl isocyanide, may be as a result of the reversible behaviour of benzaldehyde and benzoin under photoconditions.⁸

Careful t.l.c. monitoring of the photoreaction between benzaldehyde and *t*-butyl isocyanide reveals that (1)

apparently begins forming well before any of the benzaldehyde photoproducts⁶ are detected in significant amounts. While (1) is detected immediately after irradiation, the other products are not detected until after 1–2 h or longer irradiation. We therefore suspect that the isocyanide reacts directly with the excited state of benzaldehyde to form a reactive species, perhaps an imino-oxiran, which rapidly dimerizes. An increase in the quantum yield of (1) from 0.04 to 0.13 upon increasing the concentration of benzaldehyde from 0.1M to 0.5M at constant isocyanide concentration agrees with the dimerization mechanism.‡

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‡ The low chemical yields (3–7%), in spite of the moderate quantum yields measured at low conversion, are probably due to internal quenching of the reaction as (1) increases in concentration. At a 3–4% conversion into (1), exothermic triplet energy transfer from benzaldehyde to (1) would occur with >90% efficiency using our observed lifetime of 200 ns for benzaldehyde triplet in benzene.

[†] P. J. Wagner and G. S. Hammond, *Adv. Photochem.*, 1968, 5, 21; A. A. Lamola and N. J. Turro, 'Energy Transfer and Organic Photochemistry,' Wiley-Interscience, New York, 1969, ch. 3.

[‡] L. A. Singer and S. S. Kim, *Tetrahedron Letters*, 1974, 861.

⁶ V. T. Ramakrishnan and J. H. Boyer, *J.C.S. Chem. Comm.*, 1972, 429; B. K. Dunning, D. H. Shaw, and H. O. Pritchard, *J. Phys. Chem.*, 1971, 75, 580.

⁴ R. E. Lutz, *J. Amer. Chem. Soc.*, 1930, 52, 3405; the Friedel-Crafts acylation of dibromofumaryl chloride was most satisfactory in giving high yields of stereochemically pure (2).

⁵ Z. Rappoport, *Adv. Phys. Org. Chem.*, 1969, 7, 1.

⁶ J. S. Bradshaw, R. D. Knudsen, and W. W. Parish, *J.C.S. Chem. Comm.*, 1972, 1321.

⁷ S. P. Pappas and A. Chattopadhyay, *J. Amer. Chem. Soc.*, 1973, 95, 6484.

⁸ M. Cocivera and A. M. Trozzolo, *J. Amer. Chem. Soc.* 1970, 92, 1772; G. L. Closs and D. R. Paulson, *ibid.*, p. 7229.