

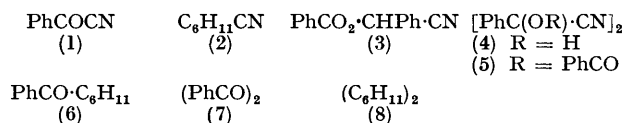
Photolysis of Benzoyl Cyanide in Solution

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Cyano- and benzoyl radicals, photolytically generated from benzoyl cyanide, afford hydrogen cyanide, cyclohexyl cyanide, and nine minor products in cyclohexane; benzonitrile, benzophenone, and biphenyl in benzene; and benzonitrile and chlorobenzene in carbon tetrachloride.

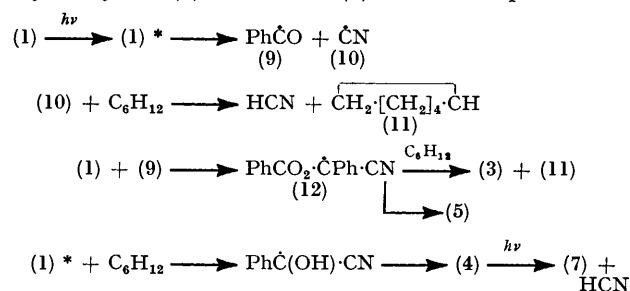
THE cyano-radical, rarely encountered in a liquid-phase organic system,¹⁻³ has been photolytically generated from benzoyl cyanide (1).

Irradiation (300 nm) of benzoyl cyanide (1) in cyclohexane under nitrogen for 8 h gave 92% conversion. Over 80% of the cyano-content of the cyanide (1) consumed was accounted for by the formation of hydrogen cyanide (44%), cyclohexyl cyanide (2) (27%), the benzoate (3) (14%) of benzaldehyde cyanohydrin, benzil biscyanohydrin (4) (<1%), and the dibenzoate (5) (2%). Other products included cyclohexyl phenyl ketone (6) (5%), benzil (7) (3%), bicyclohexyl (8), and traces of benzene, carbon monoxide, and paracyanogen.⁴ Several additional unidentified products in small amounts were detected by g.l.c.



The formation of the products, except for the biscyanohydrin (4), depends on the intermediacy of benzoyl (9), cyano- (10), and cyclohexyl (11) radicals. The absence of benzaldehyde in the product mixture confirms the ineffectiveness of the benzoyl radical in abstracting hydrocarbon hydrogen atoms.⁵ After an equimolar mixture of benzaldehyde and the cyanide (1) in cyclohexane was irradiated (300 nm) for 10 h, benzaldehyde was recovered and there was no significant change in the yield (5%) of the ketone (6) from the cyanide (1) over that obtained in the absence of added aldehyde. Apparently

the ketone (6) is formed by the combination of radicals (9) and (11) rather than by the thermodynamically unfavourable radical transfer reaction $(11) + (1) \rightarrow (6) + (10)$; on the other hand the yield (46%) of the cyanide (2) from cyclohexane and cyanogen chloride in the presence of a peroxide ($C_6H_{11}SO_3OAc$) at 50–60 °C for 2 h⁶ tends to support formation of (2) by the radical transfer reaction $(11) + (1) \rightarrow (2) + (9)$, but it has not been differentiated from the coupling of radicals (10) and (11). Addition of benzoyl radical (9) to (1) at the carbonyl oxygen⁷ can account for (12), the radical precursor of the ester (3) by abstraction of hydrogen and of the diester (5) by dimerisation. Products (7) and (8), dimers of (9) and (11), and (4) can be attributed to abstraction of hydrogen by excited (1) followed by dimerisation. The photochemical transformation of benzil biscyanohydrin (4) into benzil (7) has been reported.⁸



⁴ L. L. Bircumshaw, F. M. Tayler, and D. H. Whiffen (*J. Chem. Soc.*, 1954, 931) describe a paracyanogen with broad i.r. absorption around 1 570 cm^{-1} ($>C=N-$); J. Peška, M. J. Beneš, and O. Wichterle (*Coll. Czech. Chem. Comm.*, 1966, **31**, 243) report i.r. absorption at 1 600 ($>C=N-$) and 2 200 cm^{-1} ($-C\equiv N$) for a related polymer from cyanogen.

⁵ D. Mackay, U. F. Marx, and W. A. Waters, *J. Chem. Soc.*, 1964, 4793.

⁶ R. Graf, *Annalen*, 1952, **578**, 50.

⁷ F. F. Rust, F. H. Seubold, and W. E. Vaughan (*J. Amer. Chem. Soc.*, 1948, **70**, 3258) describe the addition of a benzoyl radical to oxygen of benzaldehyde.

⁸ V. F. Raaen (*J. Org. Chem.*, 1966, **31**, 3310) reported benzoyl cyanide in carbon tetrachloride to be stable to irradiation.

¹ H. D. Hartzler in 'The Chemistry of the Cyano Group,' ed. Z. Rappoport, Wiley, New York, 1970, pp. 709–710.

² P. Spagnolo, L. Testaferri, and M. Tiecco, *J. Chem. Soc. (B)*, 1971, 2006.

³ T. Tominaga, Y. Odaira, and S. Tsutsumi (*Bull. Chem. Soc. Japan*, 1964, **37**, 596) obtained low yields of hydrogen and cyclohexyl cyanides by irradiation of ethyl cyanofornate in cyclohexane.

Under similar conditions the irradiation (96 h) of benzoyl cyanide (1) in benzene (0.25M and 0.007M) gave 7% conversion, and in carbon tetrachloride (0.2M) gave 3% conversion. In benzene, phenyl cyanide (21%), benzophenone (15%), and biphenyl (22%) and in carbon tetrachloride, phenyl cyanide (27%), and chlorobenzene (2%) were produced along with traces of an unidentified substance detected by g.l.c. The polymer thought to be paracyanogen was also found.⁴

The formation of phenyl cyanide in approximately the same yield from (1) in benzene (at two concentrations) and from (1) in carbon tetrachloride can be accounted for by the decarbonylation of (1) with simultaneous or subsequent combination of phenyl and cyano-radicals before a productive interaction between the cyano-radical and benzene. An absence of aromatic substitution by the cyano-radical generated from benzoyl cyanide (1) in benzene is not in disagreement with the suggestion¹ that the formation of an aryl cyanide depends on oxidation of an arene-cyano-adduct by an iodine atom when a mixture of cyanogen iodide (but not cyanogen chloride⁹ nor bromide¹⁰) and an arene is photolysed^{2,11} ($\text{ArHCN} + \text{I} \rightarrow \text{ArCN} + \text{HI}$).

Although both a cyanide and an isocyanide have been formed by the combination of the cyano- (isocyano-) and another radical,¹² there is no evidence that an isocyanide is produced by the photolysis of benzoyl cyanide (1).¹³

EXPERIMENTAL

Instruments included a Perkin-Elmer 237B grating i.r. spectrophotometer, Varian A60 and T60 n.m.r. spectrometers, and an A.E.I. MS 30 double-beam mass spectrometer.

Irradiations were carried out in a Rayonet RPR 100 photochemical chamber reactor (Southern New England Ultraviolet Co.) equipped with 16 low-pressure lamps having a principal emission at 300 nm. Before irradiation under nitrogen, solutions were flushed with a stream of nitrogen (prepurified grade). Spectroscopic grade cyclohexane was distilled from lithium aluminium hydride directly into the quartz reactor tube. Spectroscopic grade benzene and carbon tetrachloride were used without further purification. All solvents were degassed with a stream of prepurified nitrogen for 1 h prior to irradiation.

G.l.c. analyses were carried out with a Varian 1800 gas chromatograph equipped with flame ionisation detector, and a Varian 20 recorder with disc integrator. Preparative g.l.c. was carried out with a Varian Autoprep 700 gas chromatograph with a column of 30% SE-30 on Chromosorb W (45–60 mesh) in an aluminium tube (6.1 × 0.94 m) at a helium flow rate of 75 ml min⁻¹ (column at 199 °C, injection port at 225 °C, and detector at 250 °C). For analytical g.l.c. a 1.8 m 10% SE-30 on Chromosorb W AW (80–100 mesh) column was used at 99, 173, or 198 °C (injection port at 225 °C and detector at 245 °C).

⁹ D. D. Tanner and N. J. Bunce, *J. Amer. Chem. Soc.*, 1969, **91**, 3028.

¹⁰ D. D. Tanner, G. Lycan, and N. J. Bunce, *Canad. J. Chem.*, 1970, **48**, 1492.

¹¹ Ref. 1, p. 710; L. Ebersson and S. Nilsson, *Discuss. Faraday Soc.*, 1968, **45**, 242.

All yields are based on starting material consumed. Compounds (2)–(8), phenyl cyanide, benzophenone, biphenyl, and chlorobenzene were identified by comparison with data from authentic materials.

A solution of benzoyl cyanide (301 mg, 2.27 mmol), freshly distilled (b.p. 209 °C) from copper(I) cyanide, in anhydrous cyclohexane (12 ml) was irradiated (300 nm) for 8 h. A light yellow solid accumulated as a suspension during the first 3 h and then disappeared. When this was separated by filtration and washed with benzene, it afforded benzil bis-cyanohydrin (4) (2 mg, <1%), m.p. 183–186°, ν_{max} (KBr) 3 340 cm⁻¹ (OH). Carbon monoxide, as it was produced, was swept by a stream of nitrogen from the reaction flask and was detected by the formation of a characteristic black solid complex on contact with a solution of palladium chloride.

After removal of most of the cyclohexane, g.l.c. of the residue showed the presence of a trace of benzene, and gave cyclohexyl cyanide (2), (64 mg, 27%), t_R 13 min.

In another run methylene chloride (15 ml) was added after irradiation and before concentration. Distillation then removed a solution in methylene chloride, b.p. 40 °C, of hydrogen cyanide, ν_{max} (CH₂Cl₂) 3 240, 2 091, 1 455, and 772 cm⁻¹. The yield was determined in a separate run by collecting silver cyanide (126 mg, 44%), as a stream of nitrogen flushed the hydrogen cyanide through a solution of silver nitrate.

The residue left after irradiation and concentration in another run was chromatographically separated on a silica gel column. Bicyclohexyl (8) (1 mg) was eluted by n-hexane–benzene (4 : 1). Mixtures richer in benzene eluted cyclohexyl cyanide (2) and benzoyl cyanide (1). Benzene–chloroform (4 : 1) eluted cyclohexyl phenyl ketone (6) (18 mg, 5%). Continued elution with benzene–chloroform (4 : 1) separated *O*-benzoylmandelonitrile (33 mg, 14%), m.p. 52–54° (lit.,¹⁴ 63–64°) (Found: C, 76.15; H, 4.95; N, 5.85. Calc. for C₁₅H₁₁NO₂: C, 75.95; H, 4.65; N, 5.9%); M^+ 237; followed by benzil (6 mg, 3%); ν_{max} (CHCl₃) 1 675 cm⁻¹ (CO).

Crystalline 2,3-bisbenzoyloxy-2,3-diphenylsuccinonitrile (6 mg, 2%), m.p. 271–272° (lit.,¹⁵ 260–261°), separated from the fraction eluted with benzene–chloroform (1 : 3) and diluted with ether (Found: C, 76.0; H, 4.45; N, 6.0. Calc. C₃₀H₂₀N₂O₄: C, 76.25; H, 4.25; N, 5.95%).

A solution of benzoyl cyanide (302 mg, 2.3 mmol; 0.7 × 10⁻² M) in benzene (350 ml) was irradiated (300 nm) for 5 days under nitrogen. G.l.c. analysis determined that 94% of benzoyl cyanide was present and that biphenyl (5.3 mg, 50%), benzophenone (3.4 mg, 27%), benzonitrile (1.9 mg, 13%), and a brown amorphous solid [ν_{max} (KBr) 1 600–1 700 and 110 cm⁻¹, insoluble in organic solvents and slightly soluble in concentrated sulphuric acid], thought to be

¹² B. C. McKusick, W. E. Mochel, and F. W. Stacey, *J. Amer. Chem. Soc.*, 1960, **82**, 723; D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, 1967, **47**, 278; S. Yamada, M. Shibasaki, and S. Tereshima, *Chem. Comm.*, 1971, 1008; K. Taki, P. H. Kim, and S. Namba, *Bull. Chem. Soc. Japan*, 1972, **45**, 2052; S. Terashima, K. Takashima, T. Sato, and S. Yamada, *Chem. and Pharm. Bull. (Japan)*, 1973, **21**, 1135; K. Yoshida and S. Tsutsumi, *J. Org. Chem.*, 1966, **31**, 3635.

¹³ H. Douchis (*J. Org. Chem.*, 1972, **37**, 2583) suggested the formation of both benzoyl cyanide and benzoyl isocyanide by the combination of benzoyl and cyano-radicals.

¹⁴ F. Francis and O. C. M. Davis, *J. Chem. Soc.*, 1909, **95**, 1403.

¹⁵ F. Michel, R. Austrup, and A. Striebeck, *Chem. Ber.*, 1961, **94**, 132.

paracyanogen, were formed. A more concentrated solution of benzoyl cyanide (0.25M) gave benzonitrile (21%), benzophenone (15%), and biphenyl (22%).

Similar treatment of benzoyl cyanide (300 mg, 2.3 mmol) in carbon tetrachloride (12 ml) (irradiation for 4 days) gave benzonitrile (2.1 mg, 27%), chlorobenzene (0.2 mg), and an

unidentified product; 10 mg (3%) of benzoyl cyanide were consumed.

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