Photoinduced Reactions of Aroyl Cyanides[1]

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In the presence of a sensitizer and a hydrogen-donating organic solvent, an aroyl cyanide is converted photochemically to the corresponding benzil and benzildicyanohydrin. The relative amount of each product can be controlled by choice of the reaction conditions. Some new reactions of benzildicyanohydrin are reported.

Little is known about the photochemistry of aroyl cyanides, although Schönberg and co-workers[2] found that the structurally similar benzoylformic acid is photochemically reduced in the presence of isopropyl alcohol to give diphenyltartaric acid. More recently Leermakers and Vesley[3] reported that pyruvic acid is photochemically reduced to dimethyltartaric acid in the presence of hydrogen-donating organic solvents.

The study described here of the photochemical reactions of a series of aroyl cyanides was undertaken to determine whether these compounds form simple dimers or couple to produce substituted benzils with concurrent elimination of cyanogen.

In ether solution the sterically unhindered aroyl cyanides were photochemically reduced to yield substituted benzils and varying amounts of the corresponding benzildicyanohydrins. Each dicyanohydrin was converted by heat to the corresponding benzil and hydrogen cyanide; benzildicyanohydrin, in the presence of benzophenone, undergoes slow and irreversible photolysis to benzil and hydrogen cyanide. At first benzildicyanohydrin was not considered to be one of the possible products of the irradiation of benzoyl cyanide. One reason was the irradiation product's high melting point, which was as much as 40 to 80° higher than that previously reported for benzildicyanohydrin. Another reason was the nearly total disappearance of the $C\equiv N$ absorption in the infrared spectrum. During initial attempts to establish the structure, benzildicyanohydrin was subjected to several degradation and derivative-forming reactions, some not previously reported for benzildicyanohydrin.

Experimental Section

Apparatus.—A Hanovia 450-w lamp, contained in a double-walled, water-cooled, quartz reaction vessel, was used for all irradiations. The outer 500-ml Pyrex section was equipped with a nitrogen inlet tube and a water-cooled condenser. Except where it is indicated, the irradiations were made without a filter.

A Perkin-Elmer Model 137 Infracord spectrophotometer was used to determine the infrared spectra. The nmr spectra were recorded with a Varian A-60 spectrometer. The ultraviolet spectra were determined with a Cary Model 14 recording spectrophotometer. Melting points were determined with a Kofler hot bench and correspond to "corrected melting points."

Preparation of Aroyl Cyanides.—Benzoyl cyanide, *o*-, *m*-, and *p*-toluyl cyanide, anisoyl cyanide, *p*-chlorobenzoyl cyanide, and α-naphthoyl cyanide were all prepared in good yield by heating the corresponding aroyl chlorides with a slight excess of cuprous cyanide.[4] Furoyl cyanide was prepared by treating dry hydrogen cyanide with furoyl chloride dissolved in an ether–pyridine mixture.[5] *p*-Nitrobenzoyl cyanide was obtained in poor yield by the phosphorous tribromide catalyzed reaction of *p*-nitrobenzoyl chloride with cuprous cyanide.[6] Attempts to treat large amounts (100 g or more) of *p*-nitrobenzoyl chloride with cuprous cyanide resulted in a vigorous and uncontrollable exothermic reaction that destroyed the desired product. Attempts to prepare pure phthaloyl cyanide were unsuccessful.

The aroyl cyanides were purified by repeated fractional distillation and crystallization. Unreacted aroyl chlorides were the most persistent impurities—usually they were successfully removed by adding a little cuprous cyanide to the distillation flask before redistillations of the aroyl cyanides.

Irradiation of Benzoyl Cyanide.—In a typical experiment benzoyl cyanide (30.0 g, 0.229 mole) in 500 ml of dry ether that contained 5.0 g (0.027 mole) of benzophenone was added to the 500-ml irradiation vessel. The vessel was swept with nitrogen, and the solution was stirred with a magnetic stirring bar. Following the irradiation (usually 6 hr) the ether was fractionally distilled. The portion that distilled from 20–30° was redistilled; about 1 ml of acetaldehyde, bp 19–21°, was collected. The acetaldehyde was identified by determining its nmr spectrum (characterized by δ values of 2.20 for the doublet and 9.80 for the quartet) and by converting part of it to the 2,4-dinitrophenylhydrazone, mp 168°. The residue that remained after removal of most of the ether was treated with 300 ml of hexane and was allowed to stand overnight. The crystalline benzildicyanohydrin was washed with hexane and was then recrystallized from acetone–hexane (1:2) to which a few drops of acetic acid was added. The filtrate left after removal of the dicyanohydrin was fractionally distilled. The fraction collected below 130° (2 mm) contained solvent, unreacted benzoyl cyanide, and benzophenone. Benzil was collected over the range 145–155° (2 mm). In this range any benzildicyanohydrin present was converted to benzil and hydrogen cyanide. If an irradiation was followed by distillation only, then it was possible to obtain nearly pure benzil, mp 90–94°, in 90% yield. The use of a Pyrex filter had no affect on the amount of benzil produced.

In one experiment benzoyl cyanide (13.11 g, 0.100 mole) in 500 ml of ether that contained 18.2 g (0.100 mole) of benzophenone was irradiated for only 2 hr. Benzoin (2.0 g) and benzil (4.2 g) were isolated from the reaction products. Benzoin was never identified in the products of reaction mixtures that were irradiated for 6 hr or more.

Benzoyl cyanide (2.62 g, 0.020 mole), benzoin-^{14}C (0.50 g, 0.24 mmole, 6.42 mcuries/mole), and benzophenone (0.50 g, 0.27 mmole) were dissolved in 50 ml of ether; the solution was irradiated for 15 hr. Benzil (1.05 g) was recovered from the products and was recrystallized from benzene–hexane and from methanol–water. The molar radioactivity of the pure benzil was 0.01 mcuries/mole.

Benzoyl cyanide (20.0 g, 0.153 mole), hydrogen cyanide-^{14}C (2.7 g, 0.10 mole, 3 mcuries/mole), and benzophenone (4 g, 0.022 mole) were dissolved in 500 ml of ether; the solution was irradiated for 5 hr. Benzildicyanohydrin was isolated and then was recrystallized from acetone–hexane. The dicyanohydrin was not radioactive.

Benzoyl cyanide (50.0 g, 0.382 mole), benzoyl chloride (21 g, 0.150 mole), and benzophenone (5.0 g, 0.028 mole) were dissolved in 500 ml of ether; the solution was irradiated for 6 hr. Most of the ether was removed by distillation. Hexane (300 ml) was added to precipitate benzildicyanohydrin. The light yellow

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[1] Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

[2] A. Schönberg, N. Latif, R. Monbasher, and A. Sima, *J. Chem. Soc.*, 1364 (1951).

[3] P. A. Leermakers and G. F. Vesley, *J. Am. Chem. Soc.*, **85**, 3776 (1963).

[4] T. S. Oakwood and C. A. Weisgerber in "Organic Syntheses," Coll. Vol. III, E. C. Horning, *et al.*, Ed., John Wiley and Sons, Inc., New York, N. Y., 1955, p 112.

[5] E. Fischer and F. Brauns, *Chem. Ber.*, **46**, 892 (1913).

[6] A. Dornow and H. Grabhöfer, *ibid.*, **91**, 1824 (1958).

solid was washed with hexane and was dried; the yield of benzildicyanohydrin was 25 g (50%). Benzil could not be isolated by distilling the filtrate; therefore, probably less than 10% of the total product was benzil. In a similar experiment, substitution of benzoyl (carbonyl-^{14}C) chloride for benzoyl chloride produced nonlabeled benzildicyanohydrin.

Benzildicyanohydrin decomposes at 208–210° when it is heated rapidly on a metal hot stage. The decomposition is catalyzed by glass. An intimate mixture of benzildicyanohydrin with powdered glass decomposes rapidly at 70°. The dicyanohydrin prepared by Dakin and Harington[7] was reported by them to melt at 180°; its crystalline form was probably the same as that of the compound prepared by irradiation of benzoyl cyanide. Jacoby[8] described a synthesis of benzildicyanohydrin in which he added a strong acid to a mixture of the carbonyl compound and sodium cyanide so that hydrogen cyanide was generated *in situ*. The synthesis was repeated; it gave benzildicyanohydrin whose decomposition temperature (208–210°) was much higher than the melting point (132°) reported by Jacoby. The products of both preparations have the same infrared spectrum, which includes a very weak absorption band at 2200 cm^{-1}.[9] Both products decompose thermally to give quantitative yields of benzil and hydrogen cyanide.

Irradiation of Benzildicyanohydrin.—Benzildicyanohydrin (8.7 g, 0.033 mole) and benzophenone (4.0 g, 0.022 mole) were dissolved in 500 ml of ether, and the solution was irradiated for 6 hr. Ether was distilled from the light yellow solution until the volume had been reduced to about 25 ml. Benzene–hexane (150 ml, 1:1) was then added to precipitate benzildicyanohydrin which, when collected on a filter and dried, weighed 3.3 g (38% recovery). The filtrate was distilled to remove the solvent; about 6 g of benzophenone and benzil was collected below 150° (2 mm). The yellow oil was chromatographed on Florisil; the eluent was benzene–hexane (1:1). Most of the benzophenone was eluted before the benzil appeared. The effluent that contained the benzil was reduced in volume and was treated with hexane to give 1.6 g of pure benzil, mp 94–95°.

Irradiation of α-Naphthoyl Cyanide.—The irradiation of α-naphthoyl cyanide under the same conditions as for benzoyl cyanide (except for the longer period of 14 hr) was ineffective. However, when α-naphthoyl cyanide (3.04 g, 0.015 mole), 1 g of acetophenone, and 50 ml of ether were irradiated for 24 hr, a photoinduced reaction occurred. At the end of the irradiation period the ether was removed by distillation. The residue was dissolved in benzene and was chromatographed on Florisil. Elution with benzene left a dark band at the top of the column. Part (2.2 g) of the unreacted α-naphthoyl cyanide was removed from the column effluent by reducing the volume of solvent and adding hexane. The remaining α-naphthoyl cyanide was removed by stirring the benzene–hexane solution with a warm saturated solution of sodium bicarbonate, which converted the nitrile to water-soluble sodium naphthoate and hydrogen cyanide. The organic layer was separated from the aqueous layer, dried, reduced in volume by distillation, and then cooled; 0.25 g (11%) of bi-1-naphthoyl (α-naphthil), mp 185–190°, was precipitated. Recrystallization from methanol gave the pure compound, mp 189–190°.

Action of Hydrocyanic Acid on Benzil and Related Compounds.—By a procedure similar to that of Lachman,[10] benzil (20.0 g, 0.095 mole) was allowed to react with excess hydrogen cyanide (20 ml). The reactants were placed in a heavy walled tube (55 cm long × 12 mm i.d.) prepared from a length of Pyrex pipe that had been sealed at one end. The open end was closed with a Neoprene gasket clamped down with a pipe flange. After the tube was filled, it was placed in a protective copper jacket (1-in. pipe) and was heated on a steam bath (in a fume hood) at ~95° for 5 hr. The tube was then cooled to 20° and was opened to permit the excess hydrogen cyanide to distil slowly. The white, crystalline benzildicyanohydrin was dislodged mechanically and was washed out with benzene, which dissolved the small amount of unreacted benzil. The benzildicyanohydrin was recovered in nearly quantitative yield.

The dicyanohydrins of *p*-tolil and of phenyl *p*-tolyl diketone were prepared similarly. Anisildicyanohydrin could not be prepared according to Lachman's procedure. In two experiments, anisil was recovered unchanged; in a third, the tube exploded. Furil was unaffected by heating with hydrogen cyanide.

In one experiment excess hydrogen cyanide from 30 g of sodium cyanide was added to a mixture of 1.50 g of powdered glass (Harshaw Chemical Co., soft glass), 5.00 g of benzil, and 20 ml of benzene. The mixture was stirred with a magnetic stirring bar for 45 min after which time most of the yellow color (benzil) had disappeared. The reaction was then quenched by adding a solution of 0.5 ml of glacial acetic acid in 20 ml of hexane. The benzildicyanohydrin (5.02 g, 80%) was collected on a filter, extracted with chloroform, and recrystallized twice from acetone–hexane to give a finely divided, crystalline product that decomposed at 208–210°.

Because many of the dicyanohydrins are unstable, even at room temperature, the results of elementary analyses do not always agree with calculated values.

Anal.[11] Calcd for $C_{16}H_{12}N_2O_2$ (benzildicyanohydrin, 208–210° dec): C, 72.72; H, 4.58; N, 10.60. Found: C, 72.59; H, 4.48; N, 10.39. Calcd for $C_{18}H_{16}N_2O_2$ (*p*-tolildicyanohydrin, 246–248° dec): C, 73.96; H, 5.52; N, 9.58. Found: C, 73.71; H, 5.67; N, 9.50. Calcd for $C_{18}H_{16}N_2O_2$ (*m*-tolildicyanohydrin, 200–210° dec): C, 73.96; H, 5.52; N, 9.58. Found: C, 73.58; H, 5.62; N, 9.21. Calcd for $C_{18}H_{16}N_2O_4$ (anisildicyanohydrin, 216–218° dec): C, 66.67; H, 4.97; N, 8.63. Found: C, 65.53; H, 4.99; N, 8.48. Calcd for $C_{16}H_{10}Cl_2N_2O_2$ (4,4′-dichlorobenzildicyanohydrin, 226–230° dec): C, 57.69; H, 3.03; N, 8.40. Found: C, 58.00; H, 3.42; N, 7.85.

Benzoyl cyanide has a strong ultraviolet absorption maximum[12] at 268, *p*-chlorobenzoyl cyanide absorbs strongly at 280, and α-naphthoyl cyanide[13] shows three very strong absorptions, one at 213, together with broad absorptions at 250 and 347 mμ. Benzildicyanohydrin has a strong absorption maximum at 218 mμ; that of 4,4′-dichlorobenzildicyanohydrin occurs at 229 mμ.

Acetylation of Benzildicyanohydrin.—Benzildicyanohydrin (3.00 g, 0.011 mole) was added to 12 ml of isopropenyl acetate and 0.3 g of *p*-toluenesulfonic acid contained in a 50-ml flask. The flask was equipped with a 25-cm Vigreux column; the mixture was heated at such a rate that acetone and some isopropenyl acetate distilled during 5 hr. The benzildicyanohydrin diacetate (3.50 g, 81% yield) was recrystallized twice from acetone–hexane. The stable, high-melting compound (268–269°, sublimes) showed a weak $C\equiv N$ absorption at 2220 cm^{-1}.

The diacetate was also prepared (<10% yield) by the dropwise addition of pyridine to a hot (steam bath) mixture of benzil dicyanohydrin and acetic anhydride.

Anal. Calcd for $C_{20}H_{16}N_2O_4$: C, 68.96; H, 4.63; N, 8.04. Found: C, 68.82; H, 4.77; N, 7.90.

Oxidation of Benzildicyanohydrin.—The dicyanohydrin (2.00 g, 0.0076 mole) was added to 20 ml of glacial acetic acid and 0.7 g of chromium trioxide. The mixture was heated at 92° for 10 min and then was poured onto ice. The precipitated benzoyl cyanide was collected on a filter. The slightly moist product (mp 20–32°) weighed 2.02 g.

Ammonolysis of Benzildicyanohydrin.—A 20-g (0.076-mole) sample of benzildicyanohydrin was dissolved in 40 ml of liquid ammonia. The solution was maintained at −33° for 1 hr. The ammonia was then distilled off, and benzamide (9.0 g, 49%) was isolated by washing the ammonolysis residue with hexane. The hexane washings contained 6.5 g (40%) of benzaldehyde (isolated as the 2,4-dinitrophenylhydrazone).[14]

Results and Discussion

In Table I are listed the major products and the yields obtained in the photochemical reactions of a number of

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[7] H. D. Dakin and C. R. Harington, *J. Biol. Chem.*, **55**, 487 (1923).

[8] O. Jacoby, *Chem. Ber.*, **19**, 1514 (1886).

[9] An apparent absence of a $C\equiv N$ absorption was at first thought to be sufficient reason for considering that the dicyanohydrin was not a possible product. The author is grateful to Dr. J. H. Stocker for the explanation that the triple-bond character of the $C\equiv N$ group can be greatly modified by interaction of that group with neighboring hydroxyl groups.

[10] A. Lachman, *J. Am. Chem. Soc.*, **45**, 1522 (1923).

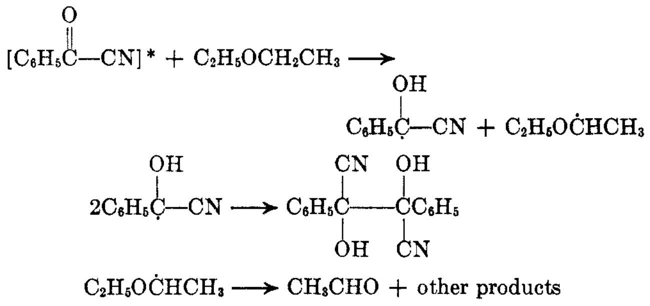
[11] Elemental analyses were performed by Huffman Laboratories, Inc., Wheatridge, Colo. 80033.

[12] All compounds determined as a solution in dioxane.

[13] α-Naphthoyl cyanide is a bright yellow, crystalline solid whose solutions in organic solvents are colorless.

[14] Benzil was not produced in the ammonolysis reaction. In this respect the ammonolysis reaction resembles the reaction with methanolic potassium hydroxide. With the latter reagent benzil dicyanohydrin is rapidly converted to a mixture of benzaldehyde, potassium benzoate, and potassium cyanide. However, benzil (>50% yield), benzaldehyde, and benzoic acid are obtained when benzildicyanohydrin is hydrolyzed at 25° in 15% sodium hydroxide solution.

aroyl cyanides. The choice of solvents was limited, because aroyl cyanides are reactive toward hydroxylic compounds. A hydrogen-donating organic solvent is essential; no reaction occurs in carbon tetrachloride. In ether, triplet benzoyl cyanide reacts with hydrogen from diethyl ether in a manner that is perhaps comparable with that proposed[3] for the photoreduction of pyruvic acid in methanol; the reactions are as shown below.



$$[C_6H_5\overset{\overset{O}{\|}}{C}{-}CN]^* + C_2H_5OCH_2CH_3 \longrightarrow C_6H_5\overset{\overset{OH}{|}}{\underset{\cdot}{C}}{-}CN + C_2H_5O\dot{C}HCH_3$$

$$2C_6H_5\overset{\overset{OH}{|}}{\underset{\cdot}{C}}{-}CN \longrightarrow C_6H_5\overset{\overset{CN}{|}}{\underset{\underset{OH}{|}}{C}}{-}\overset{\overset{OH}{|}}{\underset{\underset{CN}{|}}{C}}C_6H_5$$

$$C_2H_5O\dot{C}HCH_3 \longrightarrow CH_3CHO + \text{other products}$$

It has not been determined whether the benzildicyanohydrin isolated from the irradiation products of benzoyl cyanide is racemic, *meso*, or a mixture of both. Notwithstanding the difference among the "melting points" previously reported for benzildicyanohydrin, the same modification is obtained regardless of the method of preparation.

All the dicyanohydrins obtained from the irradiation of aroyl cyanides decompose on heating or prolonged irradiation to benzil (or substituted benzils) and hydrogen cyanide. It has not been possible to account for the formation of benzoin. It is apparent, as a result of the tracer studies, that benzoin is not an intermediate in the formation of benzil, and, in this sense, the reaction differs from that for the photochemically induced oxidation of acetoin to biacetyl.[3]

The photochemical decomposition of benzildicyanohydrin is not reversible. However, equilibrium between benzil, hydrogen cyanide, and benzildicyanohydrin is readily attained at 95° in a sealed glass tube or at 25° in the presence of powdered glass. In both instances reaction is catalyzed by the glass surface. The synthesis in which powdered glass is used as the catalyst is certainly the most satisfactory method for preparing benzildicyanohydrin.

TABLE I

PRODUCTS OBTAINED IN THE IRRADIATION OF AROYL CYANIDES[a]

Compd irradiated	Major products	Overall yield, %
C_6H_5COCN[b]	$C_6H_5COCOC_6H_5$	40
	$C_6H_5COCHOHC_6H_5$	19
C_6H_5COCN	$C_6H_5COCOC_6H_5$	90
C_6H_5COCN[c]	No reaction	...
C_6H_5COCN[d]	$C_6H_5COH(CN)COH(CN)C_6H_5$	50
p-$CH_3C_6H_4COCN$	*p*-$CH_3C_6H_4COCOC_6H_4$-*p*-CH_3	60
m-$CH_3C_6H_4COCN$	*m*-$CH_3C_6H_4COCOC_6H_4$-*m*-CH_3	23
o-$CH_3C_6H_4COCN$	*o*-$CH_3C_6H_4COH(CN)COH$-$(CN)C_6H_4$-*o*-CH_3	<5
	(Recovered *o*-$CH_3C_6H_4COCN$)	>70
p-$CH_3OC_6H_4COCN$	*p*-$CH_3OC_6H_4COCOC_6H_4$-*p*-OCH_3	27
	p-$CH_3OC_6H_4COH(CN)COH$-$(CN)C_6H_4$-*p*-OCH_3	18
p-ClC_6H_4COCN	*p*-$ClC_6H_4COCOC_6H_4$-*p*-Cl	13
	p-$ClC_6H_4COH(CN)COH(CN)$-C_6H_4-*p*-Cl	17
p-$NO_2C_6H_4COCN$[e]	No identifiable products	...
α-Naphthoyl[f] cyanide	No reaction	...
α-Naphthoyl[g] cyanide	α-$C_{10}H_7COCO$-α-$C_{10}H_7$	11
Furoyl cyanide	No reaction	...

[a] Sensitizer, benzophenone; solvent, diethyl ether except as noted; irradiation time, 6 hr except as noted. [b] Irradiation time, 2 hr. [c] Solvent, carbon tetrachloride. [d] Benzoyl chloride present. [e] Tetrahydrofuran added to increase solubility of *p*-nitrobenzoyl cyanide. [f] Irradiation time, 14 hr. [g] Sensitizer, acetophenone; irradiation time, 24 hr.

The photochemical reactions described in this paper do not have completely general applicability for the preparation of substituted benzils. However, they are useful for the preparation of unhindered benzils that are not readily obtained by way of the benzoin condensation–oxidation sequence.

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The Kinetics and Mechanism of the Hydrolysis of Benzohydroxamic Acid[1]

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The rate of hydrolysis of benzohydroxamic acid has been determined as a function of hydronium and hydroxide ion concentrations at high concentrations of these catalytic agents. First-order dependence on hydronium ion is observed in the acid-catalyzed reaction. Both first- and second-order dependence on hydroxide ion is inferred in the base-catalyzed reaction. Mechanisms consistent with the rate data are proposed.

The alkaline hydrolysis of an amide, trifluoroacetanilide, which contains a weakly acidic hydrogen attached to nitrogen has recently been investigated.[2] We now wish to report an investigation of the acidic and alkaline hydrolysis of benzohydroxamic acid. This substance contains two weakly acidic hydrogen—its conjugate base is a tautomeric mixture.[3]

Results and Discussion

All kinetic measurements were carried out with excess hydronium or hydroxide ion thus ensuring that all rates were pseudo first order. The results for the acid- and base-catalyzed hydrolyses in aqueous solution are listed in Tables I and II, respectively. The

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[1] From the M.A. Thesis of R. L. Fuller, Western Michigan University, 1966.

[2] P. M. Mader, *J. Am. Chem. Soc.*, **87**, 3191 (1965).

[3] G. M. Steinberg and R. Swidler, *J. Org. Chem.*, **30**, 2362 (1965).