[Contribution from the Noyes Chemical Laboratory, University of Illinois]

Benzoyl Cyanide Dimer and the Addition of Benzoyl Cyanide to Aromatic Aldehydes[1]

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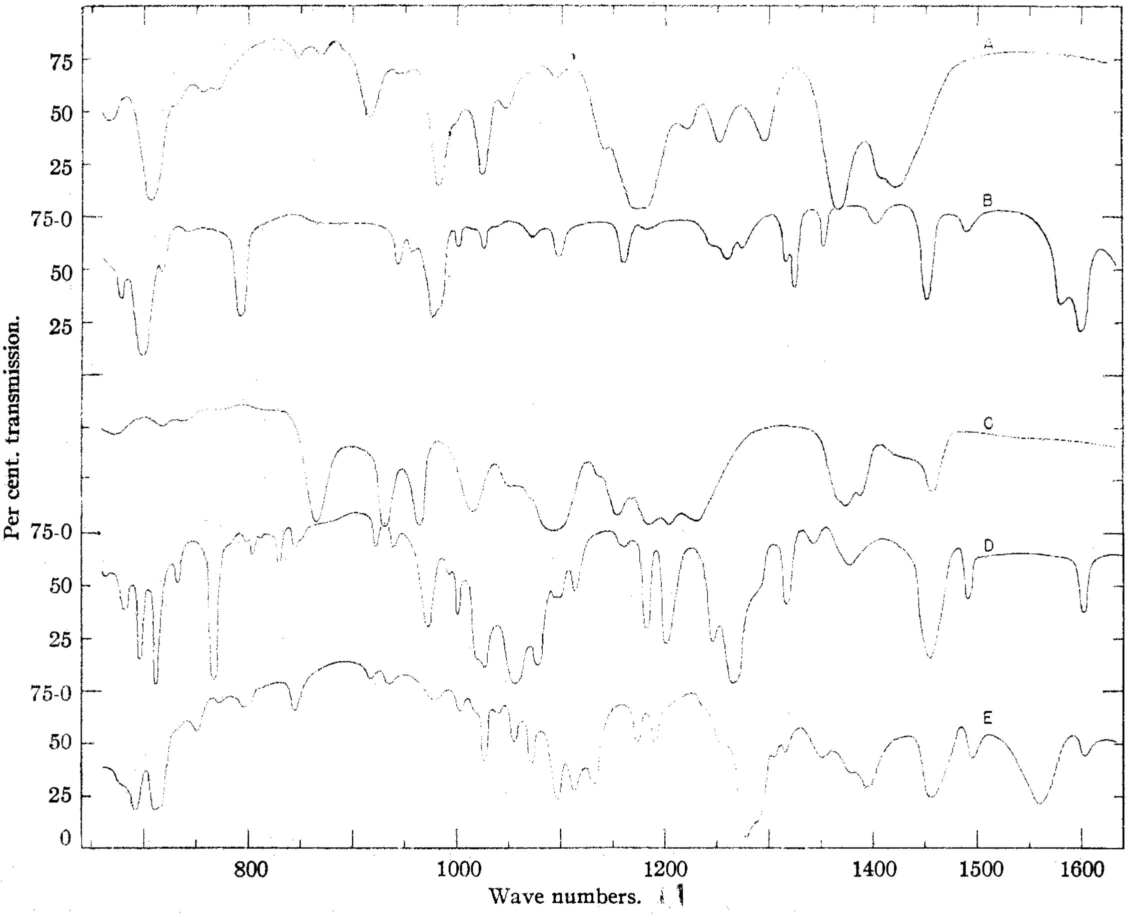
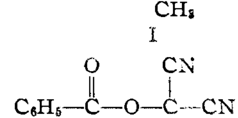
While acetyl cyanide and benzoyl cyanide dimers are well characterized compounds, the structure of the latter has not been definitely determined. Brunner[2] assigned Formula I to acetyl cyanide dimer and this structure has been accepted by later workers.[3,4] Diels and Pillow[5] have suggested quite a different type of structure for benzoyl cyanide dimer (Formula II).



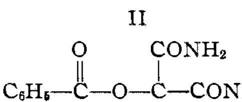
Figs. 1a and b.—Infrared absorption spectra: A, acetyl cyanide [0.025 mm. liquid cell]; B, benzoyl cyanide [crystalline melt between rocksalt plates]; C, acetyl cyanide dimer; D, benzoyl cyanide dimer; E, diamide from benzoyl cyanide dimer. [These samples were prepared by grinding the crystalline compounds with paraffin oil to reduce light scattering. Absorptions due to the C–H frequencies of the paraffin oil occur at 2920, 2855, 1459 and 1378 cm.$^{-1}$ and partially mask the C–H frequencies of the compounds.]

We isolated these two dimers as by-products in a reaction we were studying and became interested in their structures and the way in which they were formed. Since the formula for benzoyl cyanide dimer seemed to be less satisfactory than that of the acetyl cyanide dimer, we have re-examined this material and find that it is better described by Formula III.

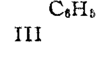


$\mathrm{CH_3{-}\overset{\overset{O}{\|}}{C}{-}O{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CN}{|}}{C}}{-}CN}$

I

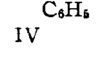


II



$\mathrm{C_6H_5{-}\overset{\overset{O}{\|}}{C}{-}O{-}\underset{\underset{C_6H_5}{|}}{\overset{\overset{CN}{|}}{C}}{-}CN}$

III



$\mathrm{C_6H_5{-}\overset{\overset{O}{\|}}{C}{-}O{-}\underset{\underset{C_6H_5}{|}}{\overset{\overset{CONH_2}{|}}{C}}{-}CONH_2}$

IV

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[1] This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation in connection with the Government Synthetic Rubber Program.

[2] Brunner, *Monatsh.*, **15**, 747 (1894).

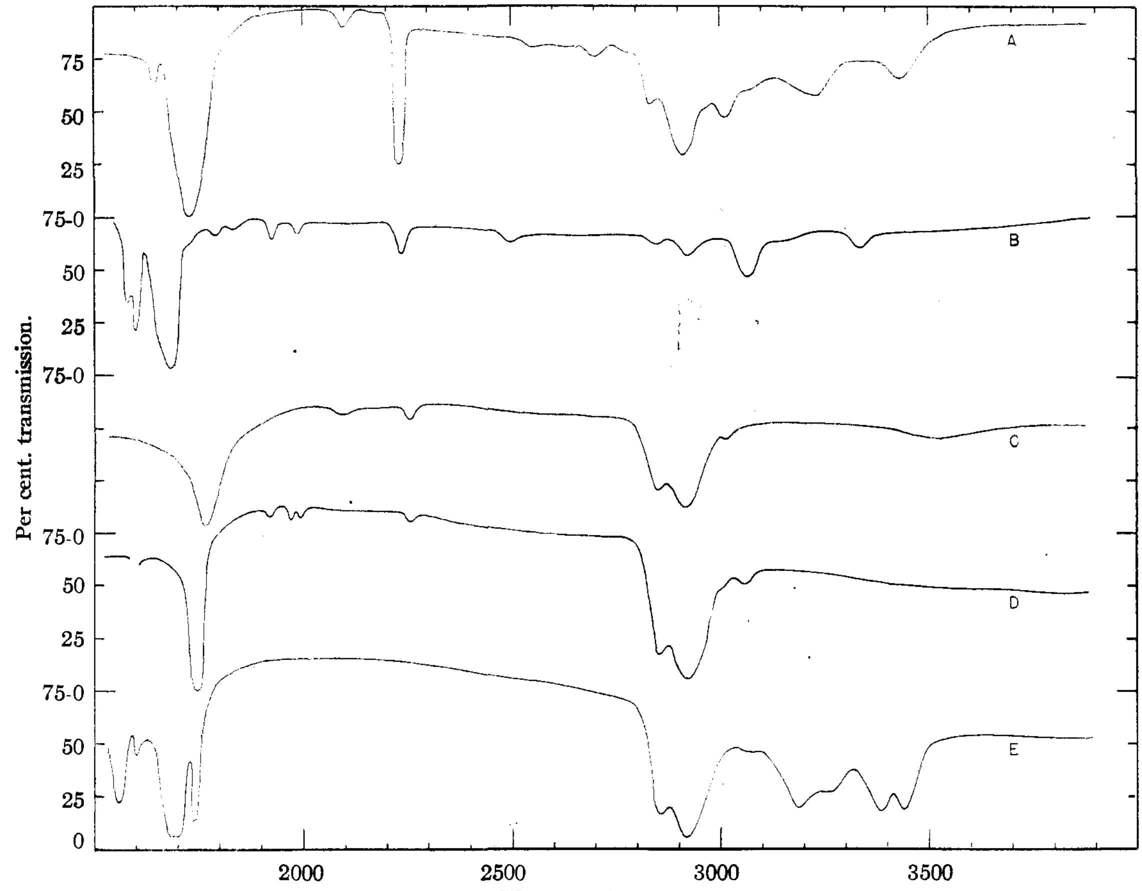
[3] Bardroff, *ibid.*, **33**, 859 (1912).

[4] Johnson and Newton, U. S. Patent 2,395,930 (1946); *C. A.*, **40**, 4078 (1946).

[5] Diels and Pillow, *Ber.*, **41**, 1893 (1908).

Diels and Pillow[5] suggested the nitrile–isonitrile structure (II) because they obtained only a monoamide on hydrolysis. We have found that a diamide (IV) can be obtained, and it is a sharper melting compound than the monoamide previously described.[5] Bardroff[3] had similarly prepared the diamide of acetyl cyanide dimer and proved its structure. He recognized that the structure postulated by Diels and Pillow[5] for benzoyl cyanide dimer was not satisfactory, but he did not attempt to relate the structure of this compound to that of acetyl cyanide dimer.

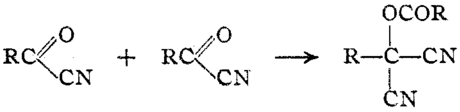
Infrared spectroscopic examination of acetyl cyanide dimer and benzoyl cyanide dimer show they are much alike in structure, and there is no evidence for a four-membered ring containing two oxygen atoms in the latter. Comparison of the spectra (Figs. 1a and b, curves C and D) of the two dimers indicates that they have analogous structures. Both show weak C≡N absorption (2256 cm.$^{-1}$) and strong C═O stretching frequencies (1746 and 1767 cm.$^{-1}$). The fact that the C═O band of the benzoyl cyanide dimer is 20 cm.$^{-1}$ lower than that of the acetyl cyanide dimer indicates that it is conjugated with the phenyl group. In the spectrum of the diamide of the benzoyl cyanide dimer (Figs. 1a and b, curve E) the C≡N absorption is absent and strong amide C═O absorption (1675–1700 cm.$^{-1}$) appears in addition to the C═O frequency found in the original compound. A complex series of N–H stretching frequencies also appear between 3190 and 3450 cm.$^{-1}$. Both these spectra (Figs. 1a and b, curves D and E) show the characteristic carbon-carbon stretching frequencies of the phenyl group, at 1493 and 1602 cm.$^{-1}$. The presence of two strong bands around 700 cm.$^{-1}$, where the mono-substituted phenyl group absorbs, indicates two types of mono-substitution, *e. g.* $C_6H_5C\overset{O}{/\!\!/}$ and $C_6H_5{-}\overset{|}{\underset{|}{C}}{-}$. The remainder of the strong absorption bands in the spectra (from 800–1400 cm.$^{-1}$) are due to vibrations of C—O, C—C, C—N linkages and extensive parts of the molecules. These frequencies are too greatly affected by slight changes in structure to be of any value in interpretation.



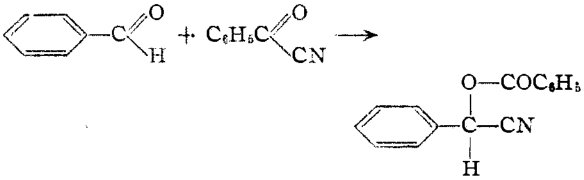
The infrared absorption curves of acetyl (Figs. 1a and b, curve A) and benzoyl (Figs. 1a and b, curve B) cyanide both show a C≡N stretching frequency at 2235 cm.$^{-1}$ and ketone C═O around 1700 cm.$^{-1}$. This is at a lower frequency in the benzoyl where it is more highly conjugated. Characteristic phenyl frequencies appear in curve

B at 1600, 1580, 1490 cm.$^{-1}$ and at 700 cm.$^{-1}$ for the mono-substituted phenyl group. As is typical of methyl ketones, except acetone, the acetyl cyanide absorbs in the CH_3 region (1370 cm.$^{-1}$) and has a strong band around 1170 and one between 700 and 800 cm.$^{-1}$.

The dimers thus have the structure that might be expected if one acyl cyanide molecule adds to the carbonyl group of another molecule. A reaction of this general type for acyl halides and aldehydes was reported by Adams and his students[6]



some years ago. It has now been found that benzoyl cyanide will indeed add to the active carbonyl group of an aromatic aldehyde in the presence of catalytic amounts of aqueous potassium hydroxide. This furnishes a convenient method of converting an aromatic aldehyde to the benzoate of the corresponding cyanohydrin.



The reaction works well with benzaldehyde and anisaldehyde, but thus far we have not extended it to aliphatic aldehydes or to any ketone. It is obvious that for the reaction to go well the carbonyl compound used with an acyl cyanide must have a more active carbonyl group than the acyl cyanide itself.

Experimental

Acetyl Cyanide Dimer and Benzoyl Cyanide Dimer.—α-Acetoxy-α-methylmalononitrile was obtained by high vacuum distillation of the residue of a reaction employing acetic anhydride and aqueous potassium cyanide as clear liquid, b. p. 82° (6 mm.), which on cooling solidified to a white solid, m. p. 69°, having an odor reminiscent of hydrogen cyanide and acetic acid. The solid was crystallized from aqueous alcohol solution. Brunner[3] gives the melting point for acetyl cyanide dimer as 69°.

Anal. Calcd. for $C_6H_6O_2N_2$: C, 52.17; H, 4.38; N, 20.29. Found:[7] C, 52.01; H, 4.18; N, 20.28.

Similarly, α-benzoyloxy-α-phenylmalononitrile was obtained by high vacuum distillation of the residue of a reaction employing benzoyl chloride and aqueous potassium cyanide as a yellow, viscous liquid, b. p. 150° (1 mm.), which solidified on cooling to a white solid, m. p. 95°. The solid was recrystallized from alcohol, m. p. 95°.

Anal. Calcd. for $C_{16}H_{10}O_2N_2$: C, 73.30; H, 3.85; N, 10.64. Found: C, 72.76; H, 3.66; N, 10.48.

α-Phenyl-α-benzoyloxymalonamide.—Two grams of α-benzoyloxy-α-phenylmalononitrile was placed in a 125-ml. erlenmeyer flask and dissolved in 10 ml. of concentrated sulfuric acid. As a few drops of water were added, the temperature rose to 85°. The flask was cooled in an ice-bath, and a white solid separated out as 100 ml. of water was slowly added with stirring. The solid was collected on a Buchner funnel and washed with cold water. The material was recrystallized from 100 ml. of benzene containing a small amount of alcohol. The recrystallized material, after drying at 55°, melted at 185–190°. After further recrystallization from benzene containing a little alcohol and ether, the solid melted at 203.5–204.5° (uncor.).

Anal. Calcd. for $C_{16}H_{14}O_4N_2$: C, 64.42; H, 4.73; N, 9.39. Found: C, 64.60; H, 4.90; N, 9.20.

Acetyl Cyanide and Benzoyl Cyanide.—Acetyl cyanide was prepared from cuprous cyanide and acetyl bromide according to the directions given by Migrdichian[8] and benzoyl cyanide by the method given in "Organic Syntheses."[9]

Benzoate of *p*-Methoxybenzaldehyde Cyanohydrin.—Three grams (0.023 mole) of benzoyl cyanide and 3 g. (0.023 mole) of anisaldehyde were mixed in a 50-ml. glass-stoppered bottle, and 6 ml. of 10% aqueous potassium hydroxide solution was added. The bottle was shaken about ten minutes. An emulsion formed first, and later a viscous yellow oil settled out. The aqueous layer was decanted and the residual oil crystallized from alcohol. There was obtained 2.8 g. (46%) of a solid, m. p. 64–65°; the mother liquor contained additional material which did not crystallize. Recrystallization of the solid did not change the melting point.

A mixed melting point determination with an authentic sample of the benzoate of *p*-methoxybenzaldehyde cyanohydrin (m. p. 64–65°) prepared by the method of Francis and Davis[10] showed no depression. These authors gave the value of 66–67° for the melting point of this compound.

Anal. Calcd. for $C_{16}H_{13}O_3N$: C, 71.91; H, 4.86; N, 5.24. Found: C, 72.09; H, 4.78; N, 5.14.

Benzoate of Benzaldehyde Cyanohydrin.—In a 50-ml. glass-stoppered bottle were placed 2 g. (0.015 mole) of benzoyl cyanide, 1.6 g. (0.015 mole) of benzaldehyde and 6 ml. of 5% aqueous potassium hydroxide. The bottle was shaken for about fifteen minutes and a white solid ball formed. The aqueous solution was decanted, and the solid was recrystallized from alcohol. There was obtained 0.45 g. of the benzoate of benzaldehyde cyanohydrin, m. p. 59°, and 0.3 g. of a white solid, m. p. 121° (probably benzoic acid). From the mother liquor there was obtained by further evaporation 1.3 g. of solid, m. p. 54–55°, making a total yield of 49%. Recrystallization of the material melting at 59° did not change its melting point.

Anal. Calcd. for $C_{15}H_{11}NO_2$: C, 75.93; H, 4.67; N, 5.90. Found: C, 76.03; H, 4.73; N, 5.91.

Francis and Davis[10] report the melting point of the benzoate ester of benzaldehyde cyanohydrin as 63–64°.

Summary

Benzoyl cyanide dimer has been shown to be α-benzoyloxy-α-phenylmalononitrile. It is apparently formed by one molecule of benzoyl cyanide adding to the carbonyl group of another. This view is favored by the fact that benzoyl cyanide adds readily to aromatic aldehydes to give the benzoate of the corresponding cyanohydrin.

Urbana, Illinois Received August 19, 1948

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[6] Adams and Vollweiler, This Journal, **40**, 1732 (1918); Adams and French, *ibid.*, **43**, 651 (1921); Adams and Ulich, *ibid.*, **43**, 660 (1921).

[7] We are indebted to Mr. H. S. Clark, Clark Microanalytical Laboratory, for all microanalyses reported in this communication.

[8] Migrdichian, "The Chemistry of Organic Cyanogen Compounds," Reinhold Publishing Corporation, New York, N. Y., 1947, p. 11.

[9] Drake, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., **24**, 14 (1944).

[10] Francis and Davis, *J. Chem. Soc.*, **95**, 1403 (1909).