

517. *Studies in Pyrolysis. Part VI.* Competitive Routes in the Pyrolysis of Acyl Cyanides and their Dimeric Forms.*

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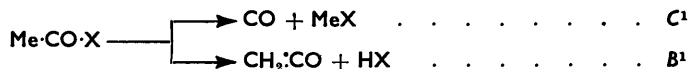
Pyrolysis of acetyl and benzoyl cyanide, and of the esters $R \cdot CO_2 \cdot CR(CN)_2$ derived by their "dimerisation," occurs in the vapour phase by competitive routes, yielding a variety of products. Reaction mechanisms are briefly discussed.

ACETYL and benzoyl cyanide readily undergo a reaction of the Tishchenko type, yielding "dimers" which have been shown¹ to be dicyano-substituted carboxylic esters :



To assist in interpreting the pyrolysis of cyano-alkyl esters, it became necessary to study the pyrolysis of these acyl cyanides and their respective "dimers" 1 : 1-dicyanoethyl acetate and $\alpha\alpha$ -dicyanobenzyl benzoate ; the breakdown of the former only has previously been reported.²

Szwarc and Murawski³ have shown that acetyl bromide ($X = Br$) breaks down at *ca.* 600° by two competitive routes, the first predominating markedly :



The symbols, C^1 , B^1 , etc., are taken from an earlier paper.⁴ Parallel results have now been obtained for acetyl cyanide ($X = CN$). This is thermostable at *ca.* 350°, at which temperature it is synthesised catalytically from keten and hydrogen cyanide ;⁵ but at *ca.* 470° it breaks down as shown above. Decarbonylation (C^1) again predominates ; the competitive

* Part V, *J.*, 1955, 4407.

¹ Marvel, Brace, Miller, and Johnson, *J. Amer. Chem. Soc.*, 1949, **71**, 34.

² Ardis, Averill, Gilbert, Miller, Schmidt, Stewart, and Trumbull, *ibid.*, 1950, **72**, 1305.

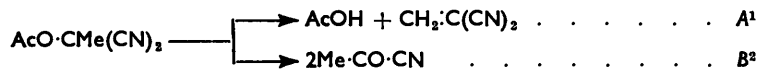
³ Szwarc and Murawski, *Trans. Faraday Soc.*, 1951, **47**, 269.

⁴ Allan, Forman, and Ritchie, *J.*, 1955, 2717.

scission to keten and hydrogen cyanide (a thermal reversal of the synthesis) is analogous to the B^1 type of acyl-oxygen scission of esters discussed recently by Allan, Forman, and Ritchie.⁴

Benzoyl cyanide, on the other hand, cannot eliminate keten in this way; and at *ca.* 500° decarbonylation (C^1) to carbon monoxide and benzonitrile is the only simple breakdown route followed, though this is accompanied by a complex reaction producing tars.

One purpose of the present study was to determine whether the Tishchenko-type addition can be reversed thermally. Ardis *et al.*² have recorded thermal scission of 1:1-dicyanoethyl acetate at 600–650°, yielding only (65%) acetic acid and vinylidene cyanide; but the present authors are indebted to Dr. A. E. Ardis for additional information⁶ that *ca.* 3% of acetyl cyanide was observed in the pyrolysate, and that mass spectrometry showed mass numbers corresponding to the four secondary products which are now predictable, namely, carbon monoxide, acetonitrile, keten, and hydrogen cyanide. It is clear, therefore, that competitive primary scissions occur, the following being a probable reaction scheme, with alkyl-oxygen scission (A^1) predominating:

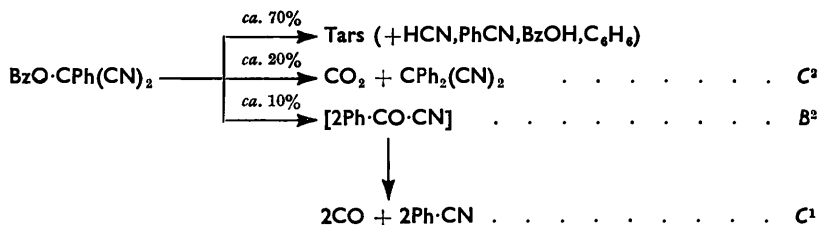


The acetyl cyanide and secondary products observed might arise by acyl-oxygen scissions either of the B^2 type, with migration of a cyano-group from alkyl to acyl, or of the B^1 type previously observed by Allan, Forman, and Ritchie⁴ for vinyl carboxylates, with migration of a hydrogen atom from acyl to alkoxy:



The resulting transient 1:1-dicyanoethanol, being in effect the cyanohydrin of acetyl cyanide, should break down readily to hydrogen cyanide and acetyl cyanide, with subsequent competitive C^1 and B^1 scissions of the latter. Results described below support the B^2 route.

Alkyl-oxygen scission (A^1) is precluded for $\alpha\alpha$ -dicyanobenzyl benzoate by the absence of a β (or α)-hydrogen atom in the alkyl group, and B^1 scission by the absence of an α -hydrogen atom in the acyl group. The only predictable route, therefore, is reversion to benzoyl cyanide by a B^2 scission, followed by decarbonylation of this product without competitive elimination of hydrogen cyanide. Nevertheless, pyrolysis of this ester at *ca.* 500° proceeded by at least three routes. The products, and their relative abundance, are best accounted for by the scheme:



The yield of benzonitrile (*ca.* 20% of theoretical) is about twice that of carbon monoxide, so that the former cannot all arise by the B^2 - C^1 route: part of it must originate in the tar-forming reaction or reactions, which almost certainly include high-temperature radical reactions, since there is no obvious simple molecular mechanism for the formation of hydrogen cyanide (*ca.* 12% of theoretical) and benzoic acid (trace). It is possible that routes B^2 , C^1 , and C^2 also include radical mechanisms.

The unexpected decarboxylation (C^2) to diphenylmalononitrile adds an interesting example to the few known ester-decarboxylations.^{4,7} This nitrile is difficult to hydrolyse

⁵ Ray, U.S.P. 2,396,201/1946: cf. Gresham, B.P. 583,646/1946.

⁶ Ardis, personal communication, 1953.

⁷ Anschütz, *Ber.*, 1885, 18, 1945; Anschütz and Wirtz, *ibid.*, p. 1947; Roberts and Bowden, *Rec. Trav. chim.*, 1930, 49, 665.

by acid or alkali; but prolonged acid hydrolysis leads, not to the readily decarboxylated diphenylmalonic acid,⁸ but to its breakdown product, diphenylacetic acid.

The occurrence here of the B^2 reaction confirms, though it does not prove, that the pyrolytic by-products from the analogous 1:1-dicyanoethyl acetate⁶ arise by a B^2 rather than a B^1 acyl-oxygen scission. This is supported by the pyrolysis of other cyano-substituted carboxylic esters, which will be described later.

EXPERIMENTAL

Apparatus.—The substances were pyrolysed in flow reaction vessels of the type described previously⁴ (a stainless-steel reaction vessel, *S*; and a Pyrex-glass reaction vessel, *P*), temperatures being controlled ($\pm 5^\circ$) by a Variac transformer. Before each run the system was several times evacuated and filled with nitrogen, to avoid oxidation of the heated vapours.

Analytical Methods.—Chemical examination of pyrolysate fractions was in some cases supplemented by infrared spectrometry. Benzonitrile was characterised by conversion⁹ into benzamide by alkaline hydrogen peroxide, and hydrogen cyanide by the copper acetate-benzidine acetate test. Hydrogen cyanide was determined quantitatively by the standard titration method.¹⁰ All solid products were identified by mixed m. p.s.

Acetyl Cyanide.—*Preparation.* The cyanide, prepared from acetyl bromide and cuprous cyanide as described by Migrdichian¹¹ (yield *ca.* 55%), was a colourless liquid, b. p. 93—93.5° (lit.,¹¹ 93°).

Pyrolysis. The cyanide (50 g.), fed into vessel *P* (0.71 g./min.) at *ca.* 470°, yielded a liquid pyrolysate (27.9 g.). Keten was removed from the exit gases by conversion into acetanilide (m. p. and mixed m. p. 114°) in an aniline-ether trap; the exit gases from this trap (after removal of hydrogen cyanide and any trace of carbon dioxide by aqueous alkali) consisted of carbon monoxide (60.3%), unsaturated hydrocarbons (1.3%), and displaced nitrogen (38.4%). The liquid pyrolysate yielded hydrogen cyanide (3.2 g.), b. p. 30—32°, impure acetonitrile (11.2 g.), b. p. 80—93°, and acetyl cyanide (12.3 g.), b. p. 93° (loss: 1.2 g.). The acetonitrile, on redistillation, yielded 8.9 g., b. p. 81—83° (Found: C, 58.0; H, 7.2. Calc. for C_2H_3N : C, 58.5; H, 7.3%), which on hydrolysis gave acetic acid (*p*-bromophenacyl ester, m. p. and mixed m. p. 110—111°).

Benzoyl Cyanide.—*Preparation.* The cyanide, prepared from benzoyl chloride (highly purified) and cuprous cyanide as described by Drake¹² (yield *ca.* 45%), had b. p. 208—210° (lit.,¹² 208—209°) and m. p. 30—32° (lit.,¹¹ 32—33°).

Pyrolysis. Molten cyanide (23 g.), fed into vessel *S* (0.94 g./min.) at *ca.* 470°, yielded a liquid pyrolysate (12.1 g.) and 7.1 l. of a gas which consisted of carbon monoxide (44%, *ca.* 4 g.) and displaced nitrogen (56%); there was no hydrogen cyanide, carbon dioxide, or olefin. Tars and carbonised matter retained in the reactor accounted for the overall loss (*ca.* 7 g.). The liquid pyrolysate consisted mainly of benzonitrile and unchanged benzoyl cyanide. These could not be adequately separated by fractional distillation, but, after removal of crude benzoyl cyanide by freezing, the liquid residue was identified as benzonitrile by its infrared spectrum and by conversion⁹ into benzamide.

α -Dicyanobenzyl Benzoate.—*Preparation.* The ester, prepared as described by Nef¹³ (yield *ca.* 20%), was obtained as needles (from ethanol), m. p. 97° (lit.,¹³ 99°) (Found: C, 73.1; H, 3.9; N, 10.9. Calc. for $C_{16}H_{10}O_2N_2$: C, 73.3; H, 3.8; N, 10.7%).

Pyrolysis. Molten ester (30.0 g.) was fed into vessel *P* (0.24 g./min.) at *ca.* 500°. A liquid pyrolysate (19.5 g.) was collected; a solid carbon dioxide trap removed hydrogen cyanide (*ca.* 11%) from the exit gases; the uncondensed exit gases (2.7 l.) consisted of carbon monoxide (8%), carbon dioxide (59%), hydrogen cyanide (trace), and displaced nitrogen (33%). Tars and carbonised matter retained in the reactor accounted for the overall loss (*ca.* 6.5 g.). The liquid pyrolysate yielded (i) hydrogen cyanide (trace), b. p. 23—30°, (ii) benzene (characterised as *m*-dinitrobenzene) (1.25 g.), b. p. 78—80°, (iii) 1.25 g., b. p. 180—200°, (iv) 0.25 g., b. p.

⁸ Morsman, *Helv. Chim. Acta*, 1935, **18**, 1466.

⁹ Radziszewski, *Ber.*, 1885, **18**, 355.

¹⁰ Cumming and Kay, "Quantitative Chemical Analysis," Oliver and Boyd, London, 9th Edn., 1945, p. 178.

¹¹ Migrdichian, "The Chemistry of Organic Cyanogen Compounds," Reinhold, New York, 1947, p. 11.

¹² Drake, *Org. Synth.*, 1944, **24**, 14.

¹³ Nef *Annalen*, 1895, **287**, 305.

70—140°/10 mm., (v) 4.0 g., b. p. 140—170°/10 mm., (vi) 2.0 g., b. p. 180—210°/10 mm., and (vii) 8.25 g. of high-boiling tar (loss : 2.5 g.). Fractions (iii) and (iv) consisted of benzonitrile together with a trace of benzoic acid. Fraction (v) was a mixture of yellowish liquid and colourless solid; the latter was *diphenylmalononitrile*, isolated from aqueous methanol or ethanol as colourless needles, m. p. 87.5°, insoluble in water and soluble in methanol, ethanol, acetone, ether, benzene, or glacial acetic acid [Found : C, 82.5; H, 4.7; N, 12.8%; *M* (Rast : camphor), 217. $C_{15}H_{10}N_2$ requires C, 82.6; H, 4.6; N, 12.8%; *M*, 218]. It shows major infrared absorption bands at 3040 (m), 2220 (w), 1950 (w), 1875 (w), 1795 (w), 1746 (w), 1595 (m), 1490 (s), 1450 (s), 762 (s), 742 (s), 702, 691 (doublet : s) cm^{-1} . The nitrile, when refluxed with glacial acetic acid and concentrated hydrochloric acid for 48 hr., yielded diphenylacetic acid as needles (from aqueous methanol), m. p. and mixed m. p. 147° (Found : C, 79.2; H, 5.8. Calc. for $C_{14}H_{12}O_2$: C, 79.2; H, 5.7%). The yellowish filtrate from fraction (v) contained benzonitrile, benzoic acid, and diphenylmalononitrile (infrared spectrum). Fraction (vi) also contained the nitrile, together with tar; no further specific substances could be identified in the tarry residues.

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