910. *Studies in Pyrolysis. Part XIII.* Competitive Alkyl–Oxygen and Acyl–Oxygen Scission in the Pyrolysis of Esters; αα-Disubstituted Cyanomethyl Carboxylates.*

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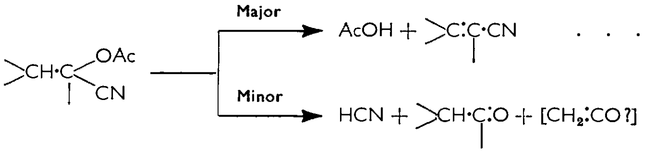
New evidence, coupled with a survey of the literature, shows that the well-known alkyl–oxygen scission of carboxylic esters to carboxylic acid plus alkene (vapour phase, *ca.* 400—500°) occurs in competition with a less familiar acyl–oxygen scission by what is essentially **a** retro-Tishchenko reaction. The molar ratio of these two primary routes can vary over a wide range, with alkyl–oxygen and acyl–oxygen scission as the extreme limiting cases. Factors governing the balance between them are discussed, and the occurrence of further competitive reactions is briefly noted.

Burns, Jones, and Ritchie[1] showed that pyrolysis of 1-cyanoethyl, 1-cyano-1-methylethyl, and 1-cyano*cyclo*hexyl acetate (vapour phase, *ca.* 450—550°) leads chiefly to acetic acid plus olefinic nitrile, by alkyl–oxygen scission (A^1). Although the yields are high (*ca.* 90%), these major products are accompanied by minor by-products (hydrogen cyanide and a carbonyl compound—acetaldehyde, acetone, or *cyclo*hexanone respectively). To account for this, the following pair of competitive breakdown routes was suggested by Burns *et al.*,[1] although the formally possible third component from the minor route (keten) was not actually identified:



. . . . A^1

At the time, the mechanism of the minor competitive route was not further considered. More recently, however, Bennett, Jones, and Ritchie[2] have shown that the dicyano-substituted esters (I; R = Me or Ph), which are dimers of the corresponding acyl cyanides (II) and one of which lacks the β-hydrogen atom necessary for A^1 scission, break down pyrolytically by several competitive routes, including the following minor reversion (B^2) to monomer:

$$\text{(I) } R{\cdot}CO_2{\cdot}CR(CN)_2 \longrightarrow 2R{\cdot}CO{\cdot}CN \text{ (II)} \quad . \; . \; . \; . \; . \; . \; . \; . \; B^2$$

In addition, the monomer (II) breaks down further to carbon monoxide and the corresponding nitrile; where R = Me, there is also a minor competitive scission to keten and hydrogen cyanide.

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* Part XII, *J.*, 1957, 4700.

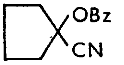
[1] Burns, Jones, and Ritchie, *J.*, 1935, 400, 714.

[2] Bennett, Jones, and Ritchie, *J.*, 1956, 2628.

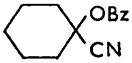
Clearly, these facts suggest a fuller and more precise interpretation of the earlier results,[1] namely, that there is here a primary competition between alkyl–oxygen and acyl–oxygen scission (the former predominating), with subsequent secondary breakdown of some of the primary products. To test the general validity of this concept, six further 1-cyanoalkyl and 1-cyano*cyclo*alkyl esters (III—VIII) have now been studied:

(III) BzO·CMe$_2$·CN (IV) BzO·CMeEt·CN (V) AcO·CMeEt·CN

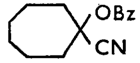
(VI)



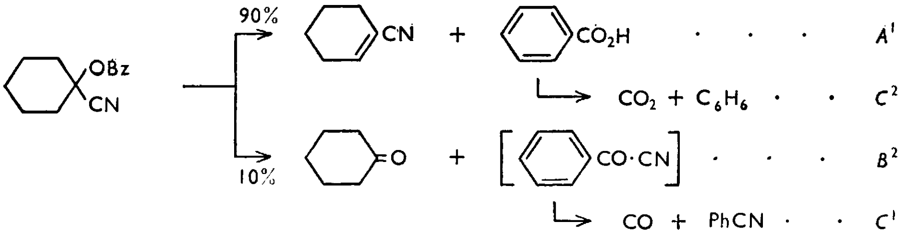
(VII)



(VIII)



The results fully confirm the idea of competition between A^1 and B^2 scissions where both are structurally permissible. All six esters, which each contain at least one β-hydrogen atom, undergo a major A^1 scission (*ca.* 90%) with a competing minor B^2 scission (up to *ca.* 10%). At the high temperatures used (*ca.* 500°), acyl cyanide from the B^2 reaction is too unstable to survive in the pyrolysate, but in each case its known breakdown products[2] are observed, sometimes together with further minor secondary products. The following example is typical of the overall results observed at 500°; the yields are only approximate, allowance being made for losses (cf. Table 1).



(*plus a trace of* HCN)

Discussion

Early work on pyrolysis of carboxylic esters (well summarised to about 1928 by Hurd[3]) was rather unsystematic, and the results were too varied and apparently inconsistent for any broad generalisations owing to the use of widely varying techniques and to the tendency to concentrate on major products, without seeking (or at least recording) by-products. For example, part of the work of Burns *et al.*[1] was later repeated by Dvořák,[4] who was apparently unaware of the previous studies; but, although he too noted the major A^1 scissions, he recorded no by-product.

Significant by-products from ester pyrolyses have now been so frequently recorded (see, *inter al.*, Hurd and Blunck,[5] Ritchie *et al.*[2,6,7]) that it has gradually become apparent that in general carboxylic esters tend to break down thermally by two or more competitive primary routes. Though much remains to be done, it is becoming possible to sketch the framework of a comprehensive generalisation; an important part of this is the competition between alkyl–oxygen and acyl–oxygen scission.

Alkyl–Oxygen Scission (A^1).—Where the alkyl group contains at least one β-hydrogen atom, the well-known scission to carboxylic acid plus alkene often predominates overwhelmingly. Hurd and Blunck[5] suggested a cyclic hydrogen-bonded transition state (six-membered), a concept also applied later[8] to the analogous Tschugaeff scission of alkyl xanthates; it now seems quite widely accepted that A^1 scission proceeds *via* a concerted

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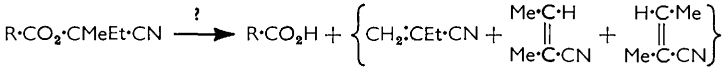
[3] Hurd, " The Pyrolysis of Carbon Compounds," Chemical Catalog Co., New York, 1929, Chap. 17.
[4] Dvořák, *Coll. Trav. chim. Tchécosl.*, 1950, **15**, 907.
[5] Hurd and Blunck, *J. Amer. Chem. Soc.*, 1938, **60**, 2419.
[6] Allan, Forman, and Ritchie, *J.*, 1955, 2717.
[7] Mackinnon and Ritchie, *J.*, 1957, 2564; Allan, McGee, and Ritchie, *J.*, 1957, 4700.
[8] Stevens and Richmond, *J. Amer. Chem. Soc.*, 1941, **63**, 3132.

version of the Hurd and Blunck intermediate, that is to say, by a reaction " in which only one transition state separates reactants and products, all bond-making and -breaking processes occurring simultaneously." [9] At about 300° the vapour-phase reaction appears to be unimolecular and homogeneous, provided that the reaction vessel has been " seasoned " by previous runs [*e.g.*, for *tert.*-butyl formate,[10] acetate,[11] and propionate,[12] and for (—)-menthyl benzoate [13]]. The last-named ester has been shown, in one of the most careful quantitative studies in this field,[13] to follow the A^1 route exclusively, at least up to *ca.* 320°. Here, the olefinic product is a mixture of two isomeric (+)-menthenes (Δ^2 and Δ^3), a reflection of the fact that elimination may occur in two different directions. This dual condition also holds for the two 1-cyano-1-methylpropyl esters (IV, V); here the work of Bailey *et al.*[14] suggests that if the reaction vessel is clean the favoured (perhaps exclusive) olefinic product should be α-ethylacrylonitrile (IX), whereas formation of tiglonitrile (X) and/or angelonitrile (XI) should be favoured by carbonisation on the vessel wall.

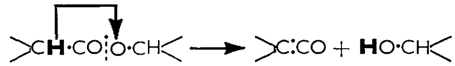


$$\mathrm{R{\cdot}CO_2{\cdot}CMeEt{\cdot}CN} \xrightarrow{?} \mathrm{R{\cdot}CO_2H} + \left\{ \mathrm{CH_2{:}CEt{\cdot}CN} + \begin{matrix}\mathrm{Me{\cdot}C{\cdot}H}\\ \| \\ \mathrm{Me{\cdot}C{\cdot}CN}\end{matrix} + \begin{matrix}\mathrm{H{\cdot}C{\cdot}Me}\\ \| \\ \mathrm{Me{\cdot}C{\cdot}CN}\end{matrix} \right\} \quad . \; . \; . \quad A^1$$

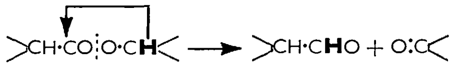
(IV, V) (IX) (X) (XI)

In a related study, Bruylants *et al.*[15] have shown that a mixture of the three isomeric nitriles (IX—XI) is obtained, with (XI) predominating, when ethyl methyl ketone cyanohydrin is dehydrated *directly* (*e.g.*, by heating with phosphoric oxide). In the present work on *indirect* (pyrolytic) dehydration, the main object was simply to seek evidence for B^2 scission, and the major A^1 products were not examined in great detail, but there is some evidence that nitriles (IX) and (X) are both formed, though no evidence for angelonitrile (XI). This may mean that (XI) is not a primary scission product; alternatively, it may indicate secondary thermal isomerisation of (XI) to (X), in agreement with the known [16] geometrical inversion of angelic acid to the more stable tiglic acid on heating.

Acyl–Oxygen Scission (*B^1 and B^2*).—Because it is so often masked by a greatly preponderating A^1 reaction, acyl–oxygen scission has hitherto been almost overlooked as a minor competitive route, though it has been recorded as the sole (or at least major) route in a few cases when the A^1 reaction is precluded by the absence of a β-hydrogen atom. There are two variations [6] of acyl–oxygen scission, which may be designated the *acyl* ⟶ *alkoxyl* (B^1) and *alkoxyl* ⟶ *acyl* (B^2) types, to indicate the direction of migration of an α-hydrogen atom, thus:



$$\mathrm{{>}C\mathbf{H}{\cdot}CO\vdots O{\cdot}CH{<}} \longrightarrow \mathrm{{>}C{:}CO + \mathbf{H}O{\cdot}CH{<}} \quad . \; . \; . \; . \; . \; . \; . \; . \quad B^1$$



$$\mathrm{{>}CH{\cdot}CO\vdots O{\cdot}C\mathbf{H}{<}} \longrightarrow \mathrm{{>}CH{\cdot}C\mathbf{H}O + O{:}C{<}} \quad . \; . \; . \; . \; . \; . \; . \; . \quad B^2$$

Reaction B^1 has been observed for certain very thermostable esters such as phenyl,[5] *iso*propenyl,[7] and *cyclo*hex-1-enyl [7] acetate, where the only mobile α-hydrogen atom available for migration occurs in the acyl group, and the hydroxy-product may be either stable or a labile enol. Reaction B^2 has been recorded for certain methyl esters (*e.g.*, formate,[17] acetate,[18] and phenylacetate [5]) and for benzyl benzoate,[19] in the first three

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[9] Cram, " Steric Effects in Organic Chemistry " (Ed. Newman), Wiley, New York, 1956, Chap. 6.

[10] Gordon, Price, and Trotman-Dickenson, *J.*, 1957, 2813.

[11] Rudy and Fugassi, *J. Phys. Colloid Chem.*, 1948, **52**, 357.

[12] Warrick and Fugassi, *ibid.*, 1948, **52**, 1314.

[13] Barton, Head, and Williams, *J.*, 1953, 1715; cf. also *idem*, *J.*, 1952, 453.

[14] Bailey *et al.*, *J. Amer. Chem. Soc.*, 1955, **77**, 73, 75, 357.

[15] Bruylants, Ernould, and Dekoker, *Bull. Soc. chim. Belg.*, 1925, **37**, 562.

[16] Blaise, *Ann. Chim. Phys.*, 1907, **11**, 111.

[17] Muller and Peytral, *Compt. rend.*, 1924, **179**, 831; Peytral, *Bull. Soc. chim. France*, 1925, **37**, 562.

[18] *Idem*, *ibid.*, 1922, **31**, 118.

[19] Hurd and Bennett, *J. Amer. Chem. Soc.*, 1929, **51**, 1197.

cases competing at rather high temperatures (*ca.* 600° and upwards) with other primary routes. It is, furthermore, the *sole* recorded breakdown-route, at only *ca.* 200—300°, of certain trichloroacetates [20] (*e.g.*, benzyl and phenethyl), in which the highly electronegative trichloromethyl group markedly weakens the acyl–oxygen bond, even to the extent of excluding completely the A^1 scission expected of the phenethyl ester. An allied acyl–oxygen scission is the reversion [21] of dimeric carbonyl chloride (trichloromethyl chloroformate) to its monomer, at only *ca.* 300°. This demonstrates an interesting migration of α-chlorine, where no α-hydrogen is available.

It is possible, though as yet unproven, that routes B^1 and B^2 may be followed competitively by a single ester. For example, ethyl acetate at *ca.* 550° yields [5] a complex pyrolysate the composition of which is compatible with this idea, though A^1 scission is of course the main breakdown-route.

B^2 Scission considered as a Retro-Tishchenko Reaction.—Several of the observed routes by which esters break down thermally are equivalent to reversal of well-known addition reactions (usually catalytic) by which the pyrolysand may be produced otherwise than by normal esterification. Thus, alkyl–oxygen (A^1) and alkenyl–oxygen (A^2) scission [6, 7] constitute thermal reversal of the catalysed addition of carboxylic acid to alkene and alkyne respectively; B^1 scission is a reversal of the addition of a keten to a hydroxy-compound (which may be an enol); and, similarly, B^2 scission is a reversal of the catalysed self-addition (dimerisation) of carbonyl compounds exemplified by the Tishchenko variation of the Cannizzaro reaction.[22] Hence, since all alkyl carboxylates can formally be regarded as products of this carbonyl–carbonyl addition reaction, either simple or crossed (whether or not they can actually be synthesised thus in practice), it is reasonable to enquire whether its reversal always occurs in their pyrolysis. This idea was examined by Bilger and Hibbert [23] but rejected because they could not detect aldehydes or ketones in the pyrolysates from a series of alkyl esters; nevertheless, the evidence now summarised makes it clear that B^2 scission is one of the main competing routes in ester pyrolysis. Thus, the B^2 scission of benzyl benzoate [19] is a reversal of the simple Tishchenko reaction by which this ester can be prepared from benzaldehyde; [24] the B^2 scission of benzyl trichloroacetate [20] is, on the other hand, the reversal of a crossed Tishchenko reaction between chloral and benzoaldehyde, not apparently realised in practice.

As might be expected, there is no observable tendency for an α-alkyl group to migrate rather than the α-cyano-group during a retro-Tishchenko reaction. No alkyl phenyl ketone was observed in the pyrolysis of esters (III—V), and no opening of the ring for esters (VI—VIII), though all yielded small amounts of the appropriate purely aliphatic ketone.

Summarising, then, we say that a carboxylic ester may in principle follow at least two distinct thermal breakdown-routes, A^1 and B^2, the balance being dictated (sometimes to the effective exclusion of one route) by the presence or absence of some critical structural feature, such as a mobile hydrogen atom or a highly polar group. It is clear, for example, from the wide variety of temperatures required to bring about the B^2 scissions listed above,[17–21] that the number and type of α-substituents in a methyl ester have a critical bearing on the result. Presumably, too, the reaction temperature itself influences the $A^1 : B^2$ ratio.

Formation of Hydrogen Cyanide from Esters (VI—VIII).—Although the various benzoates now studied cannot yield hydrogen cyanide by the same route as does the acetate (V) (*i.e.*, *via* an acyl cyanide), the esters (VI—VIII) produce a slight trace of it on pyrolysis. Its origin is uncertain. It may be due to a very minor thermal reversal of

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[20] Hibbert and Greig, *Canad. J. Res.*, 1931, **4**, 254.

[21] Ramsperger and Waddington, *J. Amer. Chem. Soc.*, 1933, **55**, 214.

[22] Geissman, " Organic Reactions," Wiley, New York, 1944, Vol. II, Chap. 3; Wagner and Zook, " Synthetic Organic Chemistry," Wiley, New York, 1953, p. 494.

[23] Bilger and Hibbert, *J. Amer. Chem. Soc.*, 1936, **58**, 823.

[24] Kamm and Kamm, *Org. Synth.*, 1922, **2**, 5.

the known catalysed addition of hydrogen cyanide to alk-1-enyl carboxylates (*e.g.*, the conversion of vinyl benzoate into 1-cyanoethyl benzoate [25]). Alternatively, it may be due to a minor breakdown of the olefinic nitrile in the primary pyrolysate, by thermal reversal of the known catalysed addition of hydrogen cyanide to alkynes (*e.g.*, the conversion of acetylene into acrylonitrile [25]). A control experiment showed that acrylonitrile does, in fact, break down thus on pyrolysis, but the nitrile is very thermostable, the yield of hydrogen cyanide being only *ca.* 0·2% even at *ca.* 650°.

Other Competitive Routes.—In all the examples now described (III—VIII), the α-carbon atom of the alkyl group is fully substituted. Where, however, this is not so, and the α-carbon atom bears at least one hydrogen atom, simple competition between A^1 and B^2 scissions may be complicated by the appearance of at least two other concurrent competitive reactions. One of these (the formation of α-diketones) is of considerable novelty; the results will be described elsewhere.

EXPERIMENTAL

Apparatus and Procedure.—The reaction vessel, receiver, and traps, together with the mode of operation, cleaning, and flushing with nitrogen, have been described.[6] Three different flow-vessels were used, P.1 and P.2 (of Pyrex glass) and S (of stainless steel). All were packed with Pyrex tubing, the free unpacked space being 125, 50, and 80 ml. respectively.

Results.—*Analytical methods.* Tables 1 and 2 summarise the general conditions and results for 14 runs. Apparent overall losses in weight are due to carbonisation and/or hold-up in the packed vessel. Contact times are calculated as before.[26]

The examination of typical pyrolysates is detailed below. Hydrogen cyanide was removed from the exit gases by a cold trap, and keten (Runs 3—9) by an aniline–ether trap. Aldehydes and ketones were characterised as their 2 : 4-dinitrophenylhydrazones, benzene as *m*-dinitrobenzene, and benzonitrile by conversion [27] into benzamide by alkaline hydrogen peroxide; all solid derivatives or pyrolysis products were identified by mixed m. p.

1-*Cyano*-1-*methylethyl Benzoate* (III).—*Preparation.* Francis and Davis's [28, 29] method yielded the ester as a colourless oil (42%), b. p. 184—185°/70 mm., solidifying to crystals, m. p. 36° (lit.,[29] b. p. 185—190°/70—80 mm., m. p. 35—36°).

Pyrolysis: *Run* 1. No hydrogen cyanide could be detected in (*b*). Distillation of (*a*) yielded (i) a trace of acetone, b. p. *ca.* 60°, (ii) 44 g., b. p. 70—95°, and (iii) a solid residue which frothed on attempted distillation. Fraction (ii), strongly cooled, deposited crystalline benzene; the liquid portion, decanted and fractionally distilled, yielded α-methylacrylonitrile, b. p. 91—91·5° (Found: N, 20·8. Calc. for C_4H_5N: N, 20·9%). Residue (iii), washed with aqueous sodium hydrogen carbonate, yielded 30 g. of benzoic acid; the final residue, distilled, yielded 2·0 g., b. p. 68—72°/10 mm., containing benzonitrile.

1-*Cyano*-1-*methylpropyl Benzoate* (IV).—*Preparation* (i). Equimolar quantities of ethyl methyl ketone, benzoyl chloride, and potassium cyanide (aqueous) were treated as for the ester (III). The final reaction mixture was extracted with ether; the extract was washed with sodium carbonate, dried, and distilled under reduced pressure, giving the ester (40%) as a colourless liquid, b. p. 175—180°/15 mm. (ii). Equimolar quantities of redistilled ethyl methyl ketone cyanohydrin, benzoyl chloride, and technical pyridine were heated at 100° (1 hr.) and allowed to cool; after deposition of solid (pyridine hydrochloride) the liquid was decanted off, washed in succession with brine, sodium carbonate, and hydrochloric acid, and distilled under reduced pressure. The *ester* (35%) had b. p. 175°/18 mm (Found: C, 71·0; H, 6·4. $C_{12}H_{13}O_2N$ requires C, 71·1; H, 6·4%).

Pyrolysis: *Run* 2. The pyrolysis of ester (IV) was not studied in full detail, but sufficient evidence was obtained to demonstrate qualitatively the competition between A^1 and B^2 scissions. Distillation of (*a*) yielded a trace of ethyl methyl ketone, a main liquid fraction,

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[25] Kurtz, *Annalen*, 1951, **572**, 23.
[26] Allan, Jones, and Ritchie, *J.*, 1957, 524.
[27] Radziszewski, *Ber.*, 1885, **18**, 355.
[28] Francis and Davis, *J.*, 1909, **95**, 1403.
[29] Davis, *J.*, 1910, **97**, 949.

TABLE 1. *Pyrolysis of cyano-esters* (III, IV, VI, VII, VIII).

Pyrolysand, run no.	(III), 1	(IV), 2	(VI), 10 *	(VII), 11	(VII), 12 *	(VII), 13	(VIII), 14 *
Reaction vessel	S	S	P.2	P.2	P.2	P.2	P.2
Temp.	400°	510°	495°	395°	495°	555°	495°
Feed-rate (g./min.)	1·46	1·25	0·60	0·60	0·80	0·50	0·43
Contact time (sec.)	11	12	17	21	16	20	27
Wt. pyrolysed (g.)	90·7	100·0	69·0	63·0	76·0	49·0	64·0
(*a*) In main receiver (g.)	82·4	—	67·2	61·0	71·0	47·2	63·0
(*b*) Gaseous pyrolysate (l.)	5·6	0·5	1·5	—	4·0	—	1·2
Composition (%) of (*b*) (approx.):							
CO	11	Pres.	25	—	11	—	26
CO_2 †	89	Pres.	75	—	88	—	74
Unsat. hydrocarbons	Nil	—	Nil	—	1	—	Nil
Composition of total pyrolysate (approx.): ‡							
Benzoic acid	Pres.	Pres.	32·0 (84)	17·6 (57)	31·0 (82)	20·3 (81)	17·7 (56)
Olefinic nitrile	Pres.	Pres.	22·5 (78)	14·7 (54)	25·5 (77)	18·2 (83)	18·0 (58)
Ketone	Pres.	Pres.	1·2 (5)	8·7 (35)	2·0 (6)	0·8 (4)	8·6 (29)
Benzonitrile	Pres.	Pres.	1·8 (6)	9·7 (37)	1·8 (6)	0·7 (3)	7·5 (28)
Benzene	Pres.	—	3·0	Nil	0·8	0·4	0·3
Unchanged pyrolysand	—	—	Nil	2·8 (5)	Nil	Nil	Nil
Hydrogen cyanide	—	—	(0·7)	(0·1)	(0·1)	(0·2)	(0·3)
Processing losses, tars, gases, etc.	—	—	8·5	9·5	14·9	8·6	11·9

* Gas analyses done by separate runs (10 min.), at same temperature, in semimicro-reaction vessel;[33] yield of gas, 7 ml. from 0·32 g. of (VI), 10 ml. from 0·30 g. of (VII), 10 ml. from 0·30 g. of (VIII).

† Including traces of hydrogen cyanide (no alkali trap used).

‡ Figures in parentheses represent percentage yields; other figures in g.

— Not examined. Pres. = Present.

TABLE 2. *Pyrolysis of* 1-*cyano*-1-*methylpropyl acetate* (V).

Run No.	3	4	5	6	7	8	9
Reaction vessel	P.1	P.1	P.1	P.1	P.1	P.1	P.1
Temp.	425°	425°	425°	475°	475°	475°	525°
Feed-rate (g./min.)	2·0	3·3	9·7	2·5	4·4	10·9	4·4
Contact time (sec.)	9	6	2	7	4	2	4
Wt. pyrolysed (g.)	100·0	100·0	100·0	100·0	100·0	100·0	100·0
(*a*) In main receiver (g.)	99·9	99·7	99·6	88·5	95·2	98·5	91·6
(*b*) Gaseous pyrolysate (l.)	2·9	2·2	2·0	—	1·4	2·6	2·7
Composition (%) of (*b*) (approx.):							
CO	—	38	31	—	65	52	51
CO_2	—	2	Nil	—	6	1	12
Unsat. hydrocarbons	—	Nil	Nil	—	4	2	7
Sat. hydrocarbons	—	60	69	—	25	45	30
Composition (g.) of total pyrolysate (approx.): *							
Acetic acid: by titration †	40·7	41·2	37·5	—	—	39·0	39·9
by fractionation ‡	38·1	37·9	42·1	40·3	38·5	40·5	39·3
B. p. 112—116°: total	23·0	10·2	16·8	26·2	24·1	16·3	11·6
nitrile (IX)	20·2	8·6	14·4	24·0	20·8	12·3	10·0
B. p. 117—119°: total	6·8	11·9	2·8	Nil	Nil	12·5	2·1
nitriles (IX) + (X)	6·5	11·6	1·7	Nil	Nil	11·7	1·2
B. p. 120—124°: total	11·6	18·3	17·7	8·2	5·7	8·1	15·6
nitrile (X)	10·4	16·5	16·0	7·6	5·5	6·2	15·1
B. p. <92°: mostly Me·CO·Et	4·2	3·1	3·2	0·2	0·2	2·4	3·8
Unchanged pyrolysand	3·0	1·5	9·5	3·0	1·0	4·0	1·0
Hydrogen cyanide	0·01	Trace	Trace	0·02	0·01	0·01	0·01

* Excluding processing losses, tars, etc.

† By titration of aliquot portion of (*a*).

‡ Acid in brine extract (by titration) plus acid in nitrile fractions (by difference, after Kjeldahl determination of nitrile).

— Not recorded.

b. p. 110—130°, and a semi-solid residue of benzoic acid containing a trace of benzonitrile. The boiling range of the main fraction embraced the b. p.s of nitriles (IX) and (X) (114° and 122° respectively [30]); the liquid had a strong characteristic smell closely similar to that of α-methylacrylonitrile, was unsaturated, and evolved ammonia when heated with alkali, all confirming the presence of olefinic nitriles.

1-*Cyano*-1-*methylpropyl Acetate* (V).—*Preparation.* Ethyl methyl ketone cyanohydrin and acetic anhydride (equimolar) were warmed with a trace of concentrated sulphuric acid; the cooled reaction mixture was shaken with brine, and the non-aqueous layer distilled, giving pure ester (68%), b. p. 92—94°/13 mm., 198—199° (lit.,[30] b. p. 195°).

Pyrolysis: *Runs* 3—9. These runs gave qualitatively similar results (Table 2). In each run, the products were worked up in four stages. (i) Liquid (*a*) was distilled: the first volatile fraction (b. p. $<50°$) was added to any liquid in the cold trap, and the hydrogen cyanide content determined volumetrically. (ii) The presence of keten in the exit gases was shown by the detection of acetanilide in the aniline trap. (iii) The total free acetic acid was determined by titrating a 2 ml. sample of liquid (*a*): a control experiment showed that the presence of olefinic nitriles did not interfere with the titration. (iv) The bulk of the acetic acid was removed from liquid (*a*) by shaking with brine; the insoluble layer was dried and fractionally distilled. The plot of cumulative distillate volume against b. p. showed well-marked plateaux at *ca.* 80° (small: fraction contained ethyl methyl ketone), 112—116° [nitrile (IX) has b. p. 114°], 120—124° ([nitrile (X) has b. p. 122°], and *ca.* 200° (small: fraction mainly unchanged pyrolysand). There was no plateau at 140°, the b. p. of angelonitrile (XI).[30] The nitrile content of the fractions with b. p. 112—116° and 120—124°, and of the intermediate fraction (b. p. 117—119°) containing a mixture of nitriles, was measured *via* the nitrogen content of those fractions (Kjeldahl: concentrated sulphuric acid, with selenium catalyst): see Table 2.

1-*Cyano*cyclo*pentyl Benzoate* (VI).—*Preparation.* Aloy and Rabaut's method [31] yielded colourless prisms from ethanol (65%), m. p. 51—52° (lit.,[31] m. p. 52—53°) (Found: N, 6·9. Calc. for $C_{13}H_{13}O_2N$: N, 6·5%).

Pyrolysis 10. Distillation of (*a*) (pasty solid) yielded (i) 3·3 g., b. p. 70—96°, (ii) 0·8 g., b. p. 130—132°, (iii) 23·0 g., mostly b. p. 164—170°, (iv) 1·6 g., b. p. 170—198°, and (v) 36·0 g. of greyish crystalline residue (overall loss, 2·5 g.). Fraction (i) yielded benzene and *cyclo*pentanone; fraction (ii) yielded *cyclo*pentanone (combined yield of ketone from both fractions, *ca.* 5%); fraction (iii) yielded 1-cyano*cyclo*pentene (78%), b. p. 165—166°, which on alkaline hydrolysis gave *cyclo*pent-1-enecarboxylic acid (86% based on nitrile); fractions (iv) and (v) yielded benzonitrile (*ca.* 6%), b. p. 190—191°, and benzoic acid (84%), b. p. 115—120°/5 mm. There was no unchanged (VI). The alkali trap retained *ca.* 0·7% of hydrogen cyanide.

1-*Cyano*cyclo*hexyl Benzoate* (VII).—*Preparation.* Aloy and Rabaut's method [32] yielded colourless prisms from ethanol (70%), m. p. 73—74° (lit.,[32] m. p. 71°) (Found: C, 73·3; H, 6·7. Calc. for $C_{14}H_{15}O_2N$: C, 73·4; H, 6·5%).

Pyrolyses 11—13. These three runs gave similar results; those of Run 12 are given as typical. Distillation of (*a*) (pasty solid) yielded (i) 0·8 g., b. p. *ca.* 80° (benzene), (ii) 27 g., b. p. 84—170°, (iii) 33 g., b. p. 170—220°, (iv) 27 g., b. p. 144—148°/19 mm. (benzoic acid), and (v) 4·5 g. of residual tar (overall loss, 3·0 g.). Fraction (ii), redistilled, yielded 2·0 g., b. p. 156—157° (*cyclo*hexanone: *ca.* 6%). Fraction (iii), redistilled, yielded 1·8 g., b. p. 190—195° (mainly benzonitrile) and 25·5 g., b. p. 195—198° (mainly 1-cyano*cyclo*hexene; *ca.* 77%). The latter sub-fraction was converted by alkaline hydrolysis into *cyclo*hex-1-enecarboxylic acid (dibromo-derivative). Fraction (iii) and residue (v) yielded a further 4 g. of benzoic acid (total yield 82%). There was no unchanged (VII). The alkali trap retained *ca.* 0·1% of hydrogen cyanide.

1-*Cyano*cyclo*heptyl Benzoate* (VIII).—*Preparation.* This *benzoate* was prepared (20%) on the same lines as esters (VI) and (VII), as colourless prisms from methanol, m. p. 72·5°. Several variations in the method failed to give yields comparable with those of (VI) and (VII) (Found: C, 73·9; H, 6·8; N, 5·5. $C_{15}H_{17}O_2N$ requires C, 74·1; H, 7·0; N, 5·8%).

Pyrolysis 14. Distillation of (*a*) (pasty solid) yielded (i) 0·3 g., b. p. *ca.* 80° (benzene), (ii) 41 g., b. p. 176—225°, (iii) 16·5 g., b. p. 118—120°/5 mm. (benzoic acid), and (iv) 3 g. of

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[30] Stull, *Ind. Eng. Chem.*, 1947, **39**, 517.

[31] Aloy and Rabaut, *Bull. Soc. chim. France*, 1918, **23**, 98.

[32] *Idem*, *Compt. rend.*, 1913, **156**, 1547.

residual tar (overall loss, 2·2 g.). Fraction (ii), redistilled, yielded a sub-fraction (20·9 g.), b. p. 178—200°, containing *cyclo*heptanone and benzonitrile. A rigorous separation of these substances proved impossible, but careful fractionation gave 8·6 g., b. p. 180—182° (mostly *cyclo*heptanone: *ca.* 29%), and 7·5 g., b. p. 192—194° (mostly benzonitrile: *ca.* 28%). Fraction (ii) yielded a further sub-fraction consisting of 1-*cyano*cyclo*heptene* (*ca.* 58%), b. p. 213—214° (Found: C, 79·6; H, 8·7. $C_8H_{11}N$ requires C, 79·3; H, 9·2%), converted by alkaline hydrolysis into *cyclo*hept-1-enecarboxylic acid. Fraction (ii) and residue (iv) yielded a further 1·2 g. of benzoic acid (total yield 56%). There was no unchanged (VIII). The alkali trap retained *ca.* 0·3% of hydrogen cyanide.

Acrylonitrile. Freshly redistilled commercial nitrile, from L. Light and Company Ltd., was used, b. p. 78—79°.

Pyrolysis 15. Preliminary runs (vessel P.2) showed that the nitrile was very thermostable at 500—600°. At 650°, 20 g. of nitrile yielded 17·3 g. of unchanged material plus 2·0 g. of high-boiling tars; an alkali trap removed hydrogen cyanide (0·2%) from the exit gases (0·4 l.), the remainder of which consisted of displaced nitrogen plus a little acetylene (infrared).

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