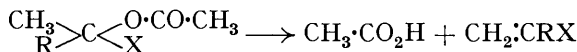


### 88. Studies in Pyrolysis. Part I. The Pyrolysis of Derivatives of $\alpha$ -Acetoxypropionic Acid, and Related Substances.

By ROBERT BURNS, D. TREVOR JONES, and PATRICK D. RITCHIE.

A NEW pyrolytic process has been devised, of very general application, whereby derivatives of  $\alpha$ -hydroxy-acids may be converted smoothly into the corresponding  $\Delta^{\alpha}$ -unsaturated acid derivatives. The difficulty of effecting such a synthesis by *direct* dehydration of  $\alpha$ -hydroxy-acid derivatives is well known, though a derivative of a  $\beta$ -hydroxy-acid very readily yields the desired unsaturated compound on dehydration by any of the usual methods. It has now been found, however, that the elements of water may readily be removed *indirectly* from the  $\alpha$ -hydroxy-compounds, by acetylating the hydroxy-group and submitting the acetoxy-compound to pyrolysis at 400–600°: acetic acid is eliminated smoothly, leaving the desired olefinic compound :

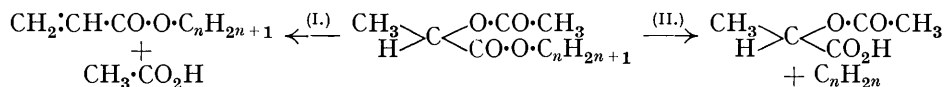


(R = H or alkyl; X = a negative acidic radical, such as CO·O·CH<sub>3</sub> or CN)

The same result may be achieved by esterifying the  $\alpha$ -hydroxy-group with agents other than acetylating agents—*e.g.*, benzoyl chloride, carbonyl chloride, or methyl hydrogen phthalate—and pyrolysing the product.

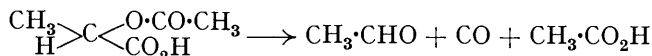
The results obtained where R = hydrogen are now described; others will be described in subsequent papers.

*Pyrolysis of Acetylated  $\alpha$ -Hydroxy-esters.*—Two different mechanisms are involved in the pyrolysis of an acetylated  $\alpha$ -hydroxy-ester. For example, the alkyl  $\alpha$ -acetoxypropionates undergo pyrolytic fission thus :



Decomposition of methyl  $\alpha$ -acetoxypropionate ( $n = 1$ ) follows route (I) exclusively up to about 500°. The well-known thermostability of methyl esters in general prevents fission of olefin from the alkyl group, and methyl acrylate can be obtained in yields of 90%, calculated on the methyl  $\alpha$ -acetoxypropionate actually "cracked." For ethyl  $\alpha$ -acetoxypropionate ( $n = 2$ ), both routes are followed simultaneously. At about 450°, only 20% of the total ester is "cracked" per run, and ethyl acrylate is obtained *via* route (I) in yields of 76%. Route (II) becomes important, however, above 450°; the yield of ethyl acrylate falls off rapidly, ethylene is eliminated from the alkyl group, and acetaldehyde is obtained

in quantity, probably owing to secondary pyrolysis of the resulting  $\alpha$ -acetoxypropionic acid, thus :

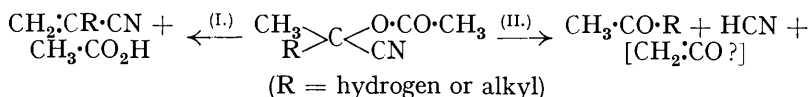


(cf. Hurd, "The Pyrolysis of Carbon Compounds," New York, 1929, p. 535).

With *n*-butyl  $\alpha$ -acetoxypropionate ( $n = 4$ ) the effective limit for the synthesis of alkyl acrylates by this method has been passed. Route (II) predominates markedly, a large amount of acetaldehyde is produced, the waste gases consist largely of butylene and carbon monoxide, and only 15—25% yields of *n*-butyl acrylate are obtained.

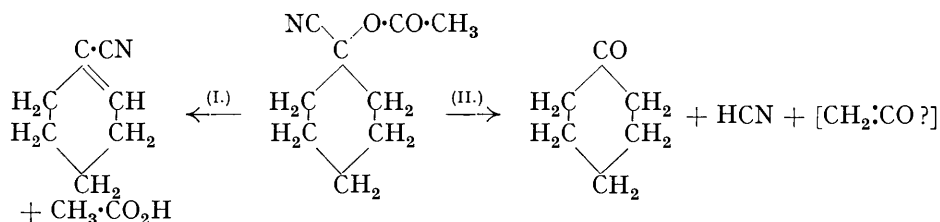
*Benzyl*  $\alpha$ -acetoxypropionate apparently pyrolysed exclusively according to route (I), as was to be expected in view of the known thermostability of the benzyl radical, and *benzyl acrylate* was obtained in yields of about 75%.

*Pyrolysis of Acetylated  $\alpha$ -Hydroxy-nitriles.*—The pyrolytic decomposition of acetylated cyanohydrins ( $\alpha$ -hydroxy-nitriles) involves two different mechanisms :

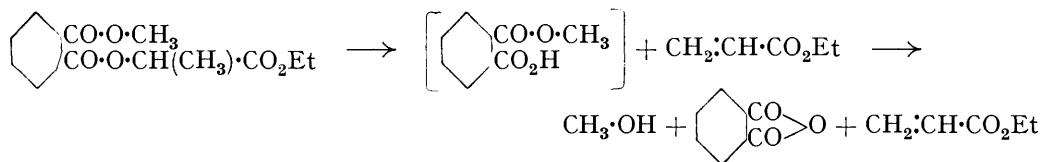


Route (I) predominates up to about 450°, but small amounts of hydrogen cyanide and  $\text{CH}_3 \cdot \text{CO} \cdot \text{R}$  always accompany the nitrile  $\text{CH}_2 \cdot \text{CR} \cdot \text{CN}$ . Keten itself was not identified; presumably it at once united with the free acetic acid, from route (I), forming small quantities of acetic anhydride.

Exactly parallel phenomena were observed on pyrolysis of *1-cyanocyclohexyl acetate* :



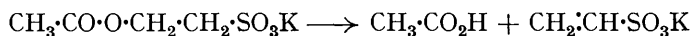
*Scope of the Reaction.*—The above type of pyrolysis into an acid and the olefinic compound  $\text{CH}_2 \cdot \text{CRX}$  is general in application, and holds for  $\alpha$ -hydroxy-compounds esterified with monobasic acids other than acetic, such as benzoic acid. When, for example, ethyl lactate is esterified with methyl hydrogen phthalate, *methyl  $\alpha$ -carbethoxyethyl phthalate* is obtained, which breaks down at 550° into methyl alcohol, phthalic anhydride, and ethyl acrylate. Since Nagel and Abelsdorff (*Wiss. Veröff. Siemens-Konz.*, 1926, 5, 193) have shown that an alkyl hydrogen phthalate is formed as an intermediate stage in the analogous pyrolysis of various dialkyl phthalates, it is probable that pyrolysis occurs here in two successive stages :



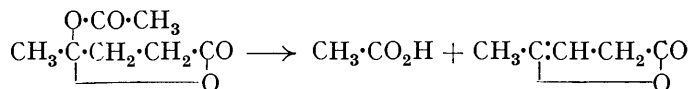
In this case, the yields of ethyl acrylate are poor (about 40%), owing to secondary fission of ethylene from the  $\alpha$ -carbethoxy-group, as described previously.

Since dehydration of a hydroxy-acid derivative is rendered easier when the hydroxy-group is transferred from the  $\alpha$ - to the  $\beta$ -position (with reference to the negative acidic group), it became of interest to determine whether pyrolytic deacetylations of the type now described were subject to analogous conditions—that is, whether they occurred more readily when the acetoxy-group was transferred from the  $\alpha$ - to the  $\beta$ -position. This at first sight seemed probable, for, although no such comparable pair of reactions appears in

the literature, several cases have been recorded in which the indirect dehydration of a  $\beta$ - or a  $\gamma$ -hydroxy-acid derivative has been effected by pyrolytic deacetylation of its acetate, either at the boiling point of the latter, or at a temperature much lower than those found necessary in the present work. For example, Kohler (*Amer. Chem. J.*, 1898, **20**, 683) has observed the following pyrolysis at only 185° :

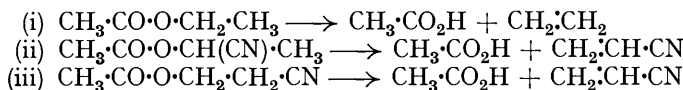


Similarly, the so-called "acetyl lævulinic acid" breaks down on distillation, even at 200—230 mm., in the following way (Thiele, Tischbein, and Lossow, *Annalen*, 1901, **319**, 184; Bredt, *ibid.*, 1890, **256**, 314) :



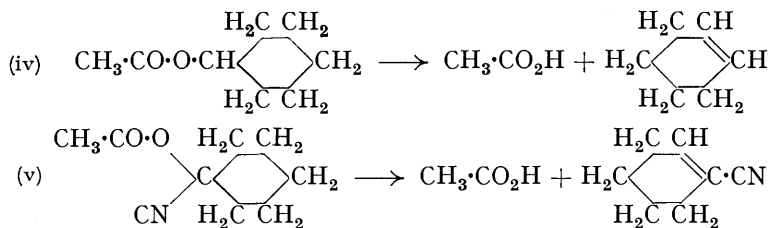
In interpreting such results, however, it should not be overlooked that ease of pyrolysis may here be expected to be affected by two independent factors, (1) the relative positions of the negative acidic group and the carbon atom to which the acetoxy-group is attached, and (2) the degree of substitution at this carbon atom. Just as tertiary carbinols undergo pyrolytic dehydration more readily, in general, than primary and secondary, so it has been found that their acetates undergo pyrolysis at relatively low temperatures (Menschutkin, *Ber.*, 1882, **15**, 2512). It is, therefore, probable that the ready pyrolysis of "acetyl lævulinic acid" is due more to the tertiary condition of the  $\gamma$ -carbon atom which bears the acetoxy-group than to the remoteness of the latter from the  $\text{CO}\cdot\text{O}^-$  group.

This reservation should be borne in mind in considering the following three pyrolyses, which were carried out under strictly comparable conditions, ethyl acetate being included for comparison with the  $\alpha$ - and the  $\beta$ -cyanoethyl acetate :



Reaction (iii) proceeded more readily than (ii), and (ii) slightly more readily than (i). Here, therefore, the ease of pyrolysis increases when the acetoxy-group is transferred from the  $\alpha$ - to the  $\beta$ - position—a not unexpected result when the analogous dehydration of the parent  $\alpha$ - and  $\beta$ -hydroxy-compounds is remembered. The concurrent transformation of the carbon atom which carries the acetoxy-group from the secondary to the primary state is here probably of subordinate importance.

The introduction of a cyano-group into the alkyl radical of ethyl acetate appears to increase the ease of pyrolysis slightly : and in this connection it is interesting to note that reaction (v) proceeds slightly more readily than (iv) :



The table summarises these results.

The apparatus used entirely obviated the objectionable charring and strong discoloration produced in most modes of organic pyrolysis. By keeping the temperature and the time of contact well below the optima for complete "cracking," secondary reactions were largely, and in some cases entirely, suppressed; after recovery of the "uncracked" material, yields of the desired unsaturated compound approaching the theoretical (calculated in all cases on the material destroyed) could often be obtained by working up the crude product suitably.

Acetate.	Temp.	Rate, c.c. per min.	Weight, g., used.	Weight, g., recovered.	Ester recovered, %.	Olefin, %, calc. on ester destroyed.
Ethyl † .....	340—360°	4.5	118	117	99—100	Not measured
	440—460	4.5	136	130	95	" "
	550—560	4.5	143	126	70	" "
$\alpha$ -Cyanoethyl.....	350—370	5	111	109.5	96—97	Not measured.
	440—460	5	132	128	92	" "
	540—550	4.5	113	108	64 *	" ca. 95
$\beta$ -Cyanoethyl.....	350—370	4	116	113	80 *	Not measured
	450—460	6	199	194	70 *	" "
	540—560	4.5	220	211	12	" "
<i>cyclo</i> Hexyl .....	350—360	4	66	65	98—99	" Negligible
	460—470	4	117	116	66	> 90
	550—560	4.5	115	111	1	94
1-Cyanocyclohexyl	340—350	8	86	83	89	ca. 80
	440—450	8	122	113	54	81
	540—550	5	134	128	< 1	80

\* Figures only approximate : error of about  $\pm 3\%$ .

† The pyrolysis of ethyl acetate was described by Oppenheimer and Precht (*Ber.*, 1876, **9**, 325), but no temperatures were recorded.

#### EXPERIMENTAL.

The apparatus was essentially as follows : A 40" iron tube, 1½" in diameter, was lined with Pyrex glass, and supported inside a vertical cylindrical electric furnace. The lower (exit) end was drawn out into a 6" nozzle, ½" in diameter : a similar nozzle was fitted to the upper (entrance) end by a gas-tight threaded joint. The liquid was dropped vertically into the tube from a 300-c.c. tap-funnel, connected to the nozzle by a glass adapter and stout rubber tubing and fitted with the usual device for equalising the pressures above and below the liquid. The adapter carried an inlet tube by which a gentle current of an inert gas (carbon dioxide or nitrogen) could be passed through the whole system. A sulphuric acid bubbler, and a T-piece safety valve dipping below a 12" head of water, were provided for the entering gas stream, and also a trap, just before the entrance nozzle, to catch any volatile product of pyrolysis which might tend to distil back. The temperature of the gas stream was registered by a platinum-iridium thermocouple, placed in the centre of the pyrolysis tube, and connected to a direct-reading galvanometer by wires passing out of the exit nozzle through slits in the stopper connecting it to the receiver. This was a well-cooled flask ; any uncondensed vapour was led through a condenser to a second receiver. The exit gases were passed, where necessary, through wash-bottles of bromine, etc.

The pyrolysis tube was loosely packed with quartz chips, the free space being about 200 c.c. This packing offered a very large heated contact-surface to the vapour, and was used in all the experiments described in this series, unless otherwise stated. (A 30" helix of strip aluminium proved almost equally efficient : pyrolysis also occurred, though to a markedly less extent, without any packing.)

Except where described in detail, the crude product was worked up by collecting three fairly sharply boiling fractions—the unsaturated compound, acetic acid, and uncracked material. The intermediate fractions were washed with brine till free from acetic acid, and the insoluble portion added to the appropriate main fraction, which was then further fractionated. In all cases where a polymerisable liquid was being distilled, a little quinol or sulphur was added to minimise the risk of heat-polymerisation.

*Methyl  $\alpha$ -Acetoxypropionate.*—*Preparation.* Methyl lactate was treated with acetic anhydride and a little concentrated sulphuric acid. The mixture was distilled in a vacuum : pure methyl  $\alpha$ -acetoxypropionate was obtained in 79—82% yield, and a further quantity of slightly crude product (ca. 13%) by extracting the intermediate fractions with brine. Freudenberg and Rhino (*Ber.*, 1924, **57**, 1552) give b. p. 168—170° for the pure ester. We have found b. p. 171.5—172°/760 mm., 76—77°/12 mm.,  $n_D^{20}$  1.4111, and  $d_4^{20}$  1.088.

*Pyrolysis.* 327 G. of the ester were run into the pyrolysis tube at 470—485°, at the rate of 5 c.c./min. 313 G. of liquid were collected, which yielded 68 g. of almost pure, recovered acetoxy-ester and 122 g. of slightly crude methyl acrylate, b. p. mostly 80—83° (88% yield, calculated on the methyl  $\alpha$ -acetoxy-propionate destroyed). The latter on refractionation yielded pure methyl acrylate, b. p. 79—80°/740 mm. (Found : C, 55.7 ; H, 6.9. Calc. : C, 55.8 ; H, 7.0%). When this was heated at 100° in presence of 1% of benzoyl peroxide, it polymerised with vigorous

frothing, giving a pale yellow, tough, rubbery mass, which did not harden after 20 hours' heating.

*Ethyl  $\alpha$ -Acetoxypropionate.*—*Preparation.* This was prepared from ethyl lactate, acetic anhydride, and concentrated sulphuric acid in yields of 87—91%.

*Pyrolysis.* 126 G. of the pure ester (b. p. 177—178°) were run at the rate of 5 g./min. into the pyrolysis tube at 450°. 119 G. of liquid were collected, which yielded 100 g. of unchanged acetoxy-ester and 10.5 g. of crude ethyl acrylate (76% yield). The latter was washed, dried, and refractionated, yielding ethyl acrylate, b. p. 96—98°/744 mm. (Found: C, 59.6; H, 7.7. Calc.: C, 60.0; H, 8.0%). Heating at 100° with 1% of benzoyl peroxide produced a soft, pale yellow polymeride, which remained elastic and "tacky" after 20 hours' heating.

Pyrolysis at higher temperatures caused considerable loss in weight (25% at 500°; 44% at 600°), large quantities of ethylene were formed, and the yield of ethyl acrylate fell to about 40%. The amount of ethyl  $\alpha$ -acetoxypropionate recovered was 31% at 500° and 10% at 600°. In all three pyrolyses, acetaldehyde was formed, and identified by its 2:4-dinitrophenylhydrazone, m. p. and mixed m. p. 156—159°; the amount was small at 450°, but much larger at 500° and 600°.

A fourth pyrolysis was carried out, at 450°, in which silica gel was substituted for half the packing in the tube. There was a 53% loss of weight; the recovered ethyl  $\alpha$ -acetoxypropionate amounted to only 13% of the total, and the yield of ethyl acrylate fell to 36%. The silica gel was thickly coated with glistening graphite, but the quartz chips were practically unaltered.

*n-Butyl  $\alpha$ -Acetoxypropionate.*—*Preparation.* *n*-Butyl lactate (b. p. 86—87°/10 mm.) (438 g.) was gradually added to a mixture of 330 g. (8% excess) of acetic anhydride and 1 c.c. of concentrated sulphuric acid kept at 40—45°. After standing over-night, the whole was fractionated; 520 g. of almost pure *n*-butyl  $\alpha$ -acetoxypropionate were obtained (92% yield), and 29 g. (8% yield) of *n*-butyl acetate. *n-Butyl  $\alpha$ -acetoxypropionate* is a colourless mobile liquid, with a pleasant fruity odour. It is soluble in acetone, alcohol, and ether, and boils at 105°/15 mm., 111°/19 mm., 126°/41 mm., and 213—214°/767 mm. It has  $n_D^{24}$  1.4147 and  $d_4^{20}$  1.0001 (Found: C, 57.3; H, 8.5.  $C_9H_{16}O_4$  requires C, 57.4; H, 8.5%).

A preliminary preparation, in which the reaction mixture was kept for a week, and heated (intermittently) at 100° for 50 hours, gave only a 27% yield of the desired ester, but a 61% yield of *n*-butyl acetate.

*Pyrolysis.* The pure ester was run at the rate of 4.5 g./min. into the pyrolysis tube. At 450—460°, 61% was recovered unchanged; at 510—530°, 46%; and at 560—580°, 11%.

260 G., pyrolysed at 510—530°, yielded 208.5 g. of liquid, which on distillation gave (i) 5 g., b. p. < 100°, (ii) 57 g., b. p. 100—175°, (iii) 27 g., b. p. 190—208°, (iv) 90 g., b. p. 208—213°, and (v) 5 g. of residue. The loss in weight was probably due to acetaldehyde, which was identified in fraction (i) as its 2:4-dinitrophenylhydrazone, m. p. and mixed m. p. 157—159°. Fraction (ii) consisted mainly of acetic acid and *n*-butyl acrylate: the latter was obtained in a slightly crude form (27 g.) by extracting the fraction with brine, but though carefully refractionated, it could not be rigorously purified. Fractions (iii), (iv), and (v) were mainly unchanged *n*-butyl  $\alpha$ -acetoxypropionate.

*n-Butyl acrylate* is a colourless mobile liquid, with the characteristic fresh pleasant odour of the acrylates. Heated at 100° with 1% of benzoyl peroxide for some hours, it polymerises to a soft, plastic, almost colourless polymeride, which does not harden on prolonged heating. The monomeride boils at 59°/23 mm. and has  $n_D^{17.5}$  1.420 and  $d_4^{20}$  0.906 (Found: C, 64.6; H, 9.3.  $C_7H_{12}O_2$  requires C, 65.6; H, 9.4%).

The exit gases from the pyrolysis tube were passed through two wash-bottles containing bromine, from which crude  $\alpha\beta$ -dibromobutane was obtained. On refractionation, this had b. p. 166—167°, but was still slightly impure (Found: Br, 73.4. Calc.: Br, 74.1%). The exit gases from the wash-bottles consisted of carbon monoxide, residual ethylene, and the carbon dioxide which was passed slowly through the tube during the pyrolysis.

The yields of crude *n*-butyl acrylate were 15% at 450—460°, 24% at 510—530°, and 18% at 560—580°.

*Benzyl  $\alpha$ -Acetoxypropionate.*—*Preparation.* Ethyl lactate and benzyl alcohol in equimolecular proportion were heated during 20 hours from 150° to 200°, about 90% of the theoretical amount of ethyl alcohol being eliminated; the residue was fractionated. The benzyl lactate, b. p. 134°/4 mm.,  $n_D^{25.5}$  1.5049,  $d_4^{20}$  1.1355 (yield, 75%), and a slight excess of acetic anhydride (trace of sulphuric acid) below 70° gave after a few days a 70% yield of *benzyl  $\alpha$ -acetoxypropionate*, b. p. 145—148°/4 mm.,  $n_D^{21}$  1.4874,  $d_4^{20}$  1.1227 (Found: C, 63.5; H, 6.3.  $C_{12}H_{14}O_4$  requires C, 64.8; H, 6.3%).

*Pyrolysis.* 100 G. of the ester were run at the rate of 3 g./min. into the pyrolysis tube at 530°. 84 G. of liquid were collected, which on fractionation yielded 52 g., b. p. 120°/75 mm.—150°/15 mm., and 18.5 g. of recovered acetoxy-ester, b. p. 150°/5 mm. The former fraction was washed with brine, and aqueous potassium carbonate, until free from acetic acid, yielding 42 g. of crude benzyl acrylate (74% yield). Two further fractionations gave 14 g. of pure *benzyl acrylate*, a pleasant-smelling, colourless, mobile liquid, b. p. 94°/6 mm., 213°/760 mm.,  $n_D^{20}$  1.5143,  $d_4^{20}$  1.0573 (Found : C, 74.0; H, 6.3.  $C_{10}H_{10}O_2$  requires C, 74.1; H, 6.2%).

*Methyl  $\alpha$ -Carbethoxyethyl Phthalate.*—*Preparation.* Ethyl lactate and methyl hydrogen phthalate in equimolecular proportion were refluxed with an equal volume of benzene, containing 0.5% by weight of concentrated sulphuric acid. The water formed was progressively removed from its azeotropic mixture with the benzene, and the residue distilled in a vacuum, giving *methyl  $\alpha$ -carbethoxyethyl phthalate* as a colourless oil, b. p. 140°/3 mm.,  $n_D^{20}$  1.4970,  $d_4^{20}$  1.1632 (Found : C, 59.9; H, 5.8.  $C_{14}H_{16}O_6$  requires C, 60.0; H, 5.7%).

*Pyrolysis.* 140 G. of the ester were run into the pyrolysis tube, at 550°, at the rate of 2.5 c.c./min. The condensed product (99 g.) was a pasty semi-solid mass; on filtration and washing with small amounts of ether, 35 g. of phthalic anhydride were obtained. The filtrate was fractionated : acetaldehyde was detected in the first (ethereal) fraction, and characterised as its 2 : 4-dinitrophenylhydrazone; 25 g. of liquid were then collected, b. p. 50—140°, followed by 25 g. of the unchanged phthalate. The fraction of b. p. 50—140°, on further fractionation, yielded 5 g. of methyl alcohol (characterised as its 3 : 5-dinitrobenzoate) and 18 g. of crude ethyl acrylate, b. p. 101—105° (yield, 41%). This readily polymerised in the usual way, in presence of 0.5% of benzoyl peroxide.

*$\alpha$ -Acetoxypropionitrile ( $\alpha$ -Cyanoethyl Acetate).*—*Preparation.* Redistilled acetaldehyde cyanohydrin, heated with acetic anhydride (1 mol.)—sulphuric acid for  $\frac{1}{2}$  hour at 100°, gave pure  $\alpha$ -acetoxypropionitrile, b. p. 80—82°/25 mm.,  $n_D^{20}$  1.403, in 90% yield. When heating was carried out for 18 hours (including 5 hours at 170°) in presence of a little perchloric acid, the yield of  $\alpha$ -acetoxypropionitrile fell to 40% and a high-boiling fraction was obtained, which yielded slightly impure *N*-acetyl- $\alpha$ -acetoxypropionamide, m. p. 65—70° (from ethyl alcohol) (Found : C, 48.2; H, 6.4; N, 9.4 to 10; *M*, cryoscopic in benzene, 171. Calc. for  $C_7H_{11}O_4N$  : C, 48.6; H, 6.4; N, 8.1%; *M*, 173). Colson (*Bull. Soc. chim.*, 1897, 17, 55) records m. p. 75°.

When acetaldehyde cyanohydrin was refluxed with excess of glacial acetic acid, along with benzene to bring about azeotropic removal of any water formed, acetylation proceeded to the extent of almost 70% in 48 hours, but could not be carried further.

*Pyrolysis.* 113 G. of pure  $\alpha$ -acetoxypropionitrile were run at the rate of 4.5 g./min. into the pyrolysis tube at 540—550°. 108 G. of liquid were collected, which yielded 72 g. of recovered  $\alpha$ -acetoxypropionitrile (64% of total) and 18 g. of slightly crude acrylonitrile (95% yield). This on fractionation yielded acrylonitrile, b. p. 76—78°/759 mm. (Found : C, 67.7; H, 5.7. Calc. for  $C_3H_3N$  : C, 67.9; H, 5.7%). In addition, acetaldehyde and hydrogen cyanide were detected in the pyrolysis product, the former as its 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 152—156°, the latter as its silver salt. These two substances were also obtained in the pyrolysis at 440—460°.

*$\beta$ -Acetoxypropionitrile ( $\beta$ -Cyanoethyl Acetate).*—*Preparation.* The nitrile was prepared in 78% yield from ethylene cyanohydrin and acetic anhydride in presence of a little concentrated sulphuric acid. It had b. p. 210—212°/773 mm. Henry (*Compt. rend.*, 1886, 102, 771) records b. p. 205—208°.

*Pyrolysis.* This was carried out at three temperatures, as summarised in the table on p. 403. The three products were united and fractionated : the first fraction was washed with brine till free from acetic acid, and gave a 63% yield of crude acrylonitrile (calculated as usual on the acetoxy-nitrile destroyed). This was dried over calcium chloride, then over phosphoric oxide, and fractionated, yielding acrylonitrile, b. p. 76—78°/761 mm. (Found : C, 67.4; H, 5.7%).

*Pyrolysis of Ethyl Acetate.*—Purified commercial ethyl acetate, b. p. 78—79°/760 mm., was pyrolysed at three different temperatures (see table). In each case, the degree of pyrolysis was determined by titration after an aliquot portion of the resulting mixture of acetic acid and unchanged ester had been boiled with a known excess of alkali.

*Pyrolysis of cycloHexyl Acetate.*—Purified commercial cyclohexyl acetate, b. p. 175.5—176°/750 mm., was pyrolysed at three different temperatures, with results summarised in the table. In each case, on distillation of the crude product, the first fraction (b. p. < 90°) separated into two layers, of which the bottom layer, a few c.c., was strongly acid. This separation was due to water produced by pyrolysis of a trace of cyclohexanol present in the ester : for it was found

that, although *cyclohexene* and glacial acetic acid are completely miscible, addition of a mere trace of water causes separation into two layers.

The *cyclohexene* was separated by washing the first fractions (hydrocarbon plus acetic acid) with brine. The *cyclohexene* produced at 550° was given a final wash with aqueous potassium carbonate, and carefully dried ( $d_4^{20}$  0.8211; iodine value 254). It was then fractionated: a portion, b. p. 80—83°, was rejected, and a fraction, b. p. 83—84°/761 mm., collected, having  $d_4^{20}$  0.8117 (Found: C, 87.5; H, 12.1; iodine value, 286. Calc. for  $C_6H_{10}$ : C, 87.8; H, 12.2%; iodine value, 310. Calc. for  $C_6H_6$ : C, 92.3; H, 7.7%; iodine value, 0). It seems likely that the crude *cyclohexene* was originally contaminated by a little benzene, produced at 550° by pyrolytic dehydrogenation, this being largely eliminated on further fractionation.

**1-Cyanocyclohexyl Acetate.**—*Preparation.* *cycloHexanone* cyanohydrin was prepared by running 193 c.c. of hydrogen cyanide into 480 g. of commercial *cyclohexanone* in the presence of a little aqueous caustic potash, the temperature being maintained at 40—50°. After 30 minutes' stirring, 7.5 c.c. of concentrated sulphuric acid were added, slowly followed by 550 g. of acetic anhydride. The product was distilled in a vacuum: the fraction having b. p. 80—130°/5 mm. was refractionated, yielding 375 g. of pure 1-*cyanocyclohexyl acetate*, b. p. 110—115°/5 mm. (nearly all at 112—113°/5 mm.). The product remained liquid unless shaken, or strongly cooled; it then rapidly and completely crystallised: the refractive index of the supercooled liquid was readily obtainable. The acetate crystallised well from ligroin, in fine matted fibrous needles, m. p. 48—49°, b. p. 112—113°/5 mm.,  $n_D^{20}$  1.4585 in the liquid state (Found: C, 65.0; H, 7.7; N, 8.8; *M*, cryoscopic in benzene, 167.  $C_9H_{13}O_2N$  requires C, 64.7; H, 7.8; N, 8.4%; *M*, 167).

*Pyrolysis.* This was carried out at three different temperatures (see table). The solid ester was melted, and heated to 80° before being placed in the dropping-funnel, in order to prevent crystallisation.

The crude product of pyrolysis at 440—450° was distilled in a vacuum to remove the acetic acid and 1-*cyanocyclohexene* from the unchanged acetoxy-compound. The first few grams smelt strongly of hydrogen cyanide and gave a curdy precipitate on addition of silver nitrate. On redistillation of these low-boiling fractions, a few drops were collected at about 140°, which yielded a 2:4-dinitrophenylhydrazone, m. p. 152—155°, alone or mixed with authentic *cyclohexanone-2:4-dinitrophenylhydrazone*. The 1-*cyanocyclohexene* was washed with brine till free from acetic acid, then with aqueous potassium carbonate, dried, and fractionated. A pure sample, b. p. 78—80°/12 mm., was obtained (Found: C, 78.2; H, 8.4. Calc. for  $C_7H_9N$ : C, 78.5; H, 8.4%). Van Coillie records b. p. 73.9—74.2°/11.5 mm. (*Bull. Soc. chim. Belg.*, 1933, 42, 419).

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