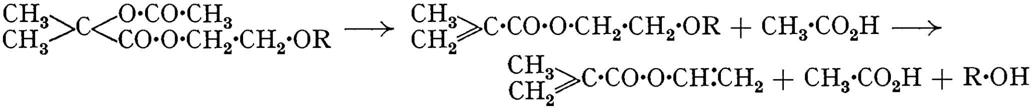
158. *Studies in Pyrolysis. Part II. The Pyrolysis of Derivatives of α-Acetoxy*iso*butyric Acid, and Related Substances.*

By Robert Burns, D. Trevor Jones, and Patrick D. Ritchie.

The new pyrolytic process, applied in Part I (this vol., p. 400) to the synthesis of derivatives of acrylic acid, has now been extended to the synthesis of higher α-substituted homologues of such derivatives.

*Methyl α-acetoxy*iso*butyrate* splits up at 490° into acetic acid and methyl α-methylacrylate, the latter being isolated in yields of over 90%, calculated on the acetoxy-ester " cracked."

Aliphatic ethers, in general, pyrolyse into aldehyde and paraffin, though they are fairly thermostable, whereas certain more complex ethers pyrolyse readily into carbinol and olefin (cf. Hurd, " The Pyrolysis of Carbon Compounds," New York, 1929, pp. 198, 228—230). It seemed not impossible, therefore, that under suitable conditions of pyrolysis *β-methoxyethyl α-acetoxy*iso*butyrate* and *β-phenoxyethyl α-acetoxy*iso*butyrate*, owing to the introduction of an ether group, might give rise to vinyl α-methylacrylate, probably in two stages, thus :



$$\begin{matrix}\mathrm{CH_3}\\\mathrm{CH_3}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{O{\cdot}CO{\cdot}CH_3}\\\mathrm{CO{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}OR}\end{matrix} \longrightarrow \begin{matrix}\mathrm{CH_3}\\\mathrm{CH_2}\end{matrix}\!\geqslant\!\mathrm{C{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}OR} + \mathrm{CH_3{\cdot}CO_2H} \longrightarrow$$

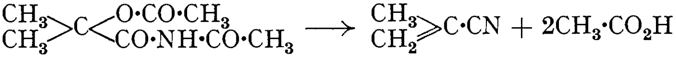
$$\begin{matrix}\mathrm{CH_3}\\\mathrm{CH_2}\end{matrix}\!\geqslant\!\mathrm{C{\cdot}CO{\cdot}O{\cdot}CH{:}CH_2} + \mathrm{CH_3{\cdot}CO_2H} + \mathrm{R{\cdot}OH}$$

$$(\mathrm{R} = \mathrm{CH_3} \text{ or } \mathrm{C_6H_5})$$

Only the first stage occurred, however, *β-methoxyethyl* and *β-phenoxyethyl α-methylacrylate* respectively being obtained, both in good yield.

The pyrolysis of acetylated α-hydroxy-nitriles was considered in Part I (*loc. cit.*). In agreement with the general scheme indicated there, it has now been found that acetylated acetone cyanohydrin (α-acetoxy*iso*butyronitrile) undergoes pyrolysis at 420° in two different ways, the first giving acetic acid and α-methylacrylonitrile in over 90% yield, and the second, which increases in importance as the temperature is raised, yielding small amounts of acetone, hydrogen cyanide, and, presumably, keten.

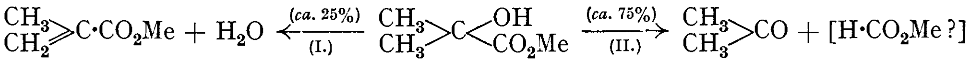
Acetylation of acetone cyanohydrin by means of acetic anhydride in presence of a little perchloric acid yields approximately equivalent amounts of α-acetoxy*iso*butyronitrile and *N-acetyl-α-acetoxy*iso*butyramide* (m. p. 81—82°). The latter compound breaks down as follows, when pyrolysed at 515—530° :



$$\begin{matrix}\mathrm{CH_3}\\\mathrm{CH_3}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{O{\cdot}CO{\cdot}CH_3}\\\mathrm{CO{\cdot}NH{\cdot}CO{\cdot}CH_3}\end{matrix} \longrightarrow \begin{matrix}\mathrm{CH_3}\\\mathrm{CH_2}\end{matrix}\!\geqslant\!\mathrm{C{\cdot}CN} + 2\mathrm{CH_3{\cdot}CO_2H}$$

Just as with lactic acid derivatives, the pyrolysis method of indirect dehydration can here be applied in several ways. For instance, in addition to its acetate, the *benzoate* and the chloride of methyl α-hydroxy*iso*butyrate yield methyl α-methylacrylate at about 500°, by elimination of the appropriate acid, though in the latter case the liberation of hydrogen chloride appears to lead to complications and the yield of methyl methylacrylate is poor.

We have also examined the pyrolysis of acetone cyanohydrin and methyl α-hydroxy*iso*butyrate in order to determine to what extent, if any, *direct* dehydration occurs at temperatures of 400—600°. The former, as expected, decomposed completely into acetone and hydrogen cyanide, no preferential fission into water and methylacrylonitrile occurring at 510°. Methyl α-hydroxy*iso*butyrate, on the other hand, appeared to split up in two ways at 470—480° :



$$\begin{matrix}\mathrm{CH_3}\\\mathrm{CH_2}\end{matrix}\!\geqslant\!\mathrm{C{\cdot}CO_2Me} + \mathrm{H_2O} \xleftarrow[\text{(I.)}]{(ca.\ 25\%)} \begin{matrix}\mathrm{CH_3}\\\mathrm{CH_3}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{OH}\\\mathrm{CO_2Me}\end{matrix} \xrightarrow[\text{(II.)}]{(ca.\ 75\%)} \begin{matrix}\mathrm{CH_3}\\\mathrm{CH_3}\end{matrix}\!>\!\mathrm{CO} + [\mathrm{H{\cdot}CO_2Me}\,?]$$

About 63% of the hydroxy-ester was recovered unchanged, the remainder undergoing pyrolysis by routes I and II in approximately the ratio shown. Though acetone was identified in the product, the methyl formate (b. p. 32·5°) which would be expected to accompany it was not observed. It may, perhaps, have undergone secondary pyrolysis into gaseous products (Peytral, *Bull. Soc. chim.*, 1925, **37**, 562); and it is at least significant that the total loss of weight in each of three pyrolyses was approximately that calculated for methyl formate from the amount of acetone isolated. Further, no pyrolysis into methyl alcohol and the corresponding cyclic " lactide " was observed.

EXPERIMENTAL.

The apparatus and methods employed were those described in Part I (*loc. cit.*). Where pyrolysis of a solid had to be carried out, the substance was dissolved in acetone (which does not undergo appreciable pyrolysis below 700°), and the solution run into the heated tube as usual.

*Methyl α-Acetoxy*iso*butyrate.*—This *ester* was obtained in 84—90% yield by acetylating methyl α-hydroxy*iso*butyrate with acetyl chloride, or acetic anhydride in presence of a little concentrated sulphuric acid, and fractionating the product. It is a colourless mobile liquid with a pleasant sweetish odour; b. p. 76—77°/18 mm., 78—79°/20 mm., and 169—171°/750 mm., $n_D^{20^\circ}$ 1·413, and $d_{4^\circ}^{20^\circ}$ 1·058 (Found : C, 52·2; H, 7·4. $C_7H_{12}O_4$ requires C, 52·5; H, 7·5%). It is insoluble in water and brine, and soluble in acetone, ether, ethyl alcohol, benzene, and ligroin.

Pyrolysis. 437 G. of the pure ester were run (5·5 c.c./min.) into the vertical pyrolysis tube, maintained at 480—500°, and 428 g. of liquid were collected. Owing to the proximity of their boiling points (100° and 118°, respectively) methyl α-methylacrylate and acetic acid could not be rigorously separated by distillation alone; but 272 g. of crude methyl α-methylacrylate, b. p. 85—106°, were obtained, and a further 10 g. by extraction of the succeeding (acetic acid) fraction with brine. After washing with brine to remove acetic acid, and refractionation, 253 g. of almost pure methyl methylacrylate were obtained, b. p. 96—106° (92% yield, calc. on acetoxy-ester actually destroyed). 21 G. of unchanged acetoxy-ester were recovered, partly by distillation and partly by brine-extraction of the acetic acid fractions.

Methyl α-methylacrylate readily polymerised to a clear hard colourless resin when warmed to 60° with 1% of benzoyl peroxide. The indefinite b. p. recorded above was due to slow partial polymerisation on distillation; but cautious fractionation of a small sample gave a sharper fraction, b. p. 98—102°. The characteristic odour of this ester is unmistakable (1·5840 g. required 32·32 c.c. of *N*/2-sodium hydroxide. Found : saponification equiv., 98. Calc. for $C_5H_8O_2$: equiv., 100).

The amounts of methyl α-acetoxy*iso*butyrate " cracked " were approximately 67% at 400°, 95% at 480—500°, and 100% at 560°; at the last temperature there was 16% loss in total weight due to secondary decompositions.

*β-Methoxyethyl α-Acetoxy*iso*butyrate.*—Equimolecular amounts of acetone cyanohydrin, water, concentrated sulphuric acid, and " methyl cellosolve " (ethylene glycol monomethyl ether) were refluxed at 80—100°, the ammonium hydrogen sulphate which separated was filtered off, the filtrate distilled in a vacuum, and the β-methoxyethyl α-hydroxy*iso*butyrate, b. p. 80—100°/20 mm., acetylated with a slight excess of acetic anhydride. Fractionation gave *β-methoxyethyl α-acetoxy*iso*butyrate* as a colourless mobile liquid, with a pleasant ethereal odour, b. p. 105°/12 mm., $n_D^{24^\circ}$ 1·4210 (Found : C, 52·8; H, 7·8. $C_9H_{16}O_5$ requires C, 52·9; H, 7·8%). Yield, 42%.

Pyrolysis. 200 G. (2 c.c./min.; 450°) gave 192 g. of liquid, which, washed with brine and distilled in a vacuum, yielded 107 g. of pure *β-methoxyethyl α-methylacrylate* (yield, 76%; no unchanged acetoxy-ester was recovered) as a colourless mobile liquid with the characteristic pleasant odour of the α-methylacrylates; b. p. 88—89°/20 mm., $n_D^{24^\circ}$ 1·4283, $d_{4^\circ}^{20^\circ}$ 0·9933 (Found : C, 58·2; H, 8·3. $C_7H_{12}O_3$ requires C, 58·3; H, 8·3%). When heated with 0·5% of benzoyl peroxide, it polymerised to a transparent solid colourless resin.

*β-Phenoxyethyl α-Acetoxy*iso*butyrate.*—Equimolecular amounts of acetone cyanohydrin, water, concentrated sulphuric acid, and β-phenoxyethyl alcohol, treated as above, gave a 45% yield of *β-phenoxyethyl α-hydroxy*iso*butyrate* as a colourless mobile liquid, b. p. 156—157°/5 mm., $n_D^{21^\circ}$ 1·5040, $d_{4^\circ}^{20^\circ}$ 1·1142 (Found : C, 64·5; H, 7·1. $C_{12}H_{16}O_4$ requires C, 64·3; H, 7·1%). This ester after acetylation gave a 91% yield of *β-phenoxyethyl α-acetoxy*iso*butyrate* as a colourless, slightly viscous liquid, b. p. 166°/4 mm., $n_D^{21^\circ}$ 1·4910, $d_{4^\circ}^{20^\circ}$ 1·1216 (Found : C, 63·3; H, 6·6. $C_{14}H_{18}O_5$ requires C, 63·2; H, 6·8%).

Pyrolysis. 149 G. of the acetoxy-ester (3 c.c./min.; 500°) gave 134 g. of liquid, which, washed with brine and sodium carbonate and fractionated in a vacuum, yielded 60 g. of pure *β-phenoxyethyl α-methylacrylate* (51% yield; no unchanged acetoxy-ester was recovered) as a colourless mobile pleasant-smelling liquid, b. p. 138°/7 mm., 268°/760 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·5160, $d_{4^\circ}^{20^\circ}$ 1·0858 (Found: C, 70·0; H, 6·9. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%). When maintained for some time just below its b. p., it polymerises to a clear gummy mass.

*α-Acetoxy*iso*butyronitrile and* N-*Acetyl-α-acetoxy*iso*butyramide*.—When acetone cyanohydrin is run gradually into acetic anhydride containing acetyl chloride or sulphuric acid as catalyst, the heat of reaction keeps the mixture refluxing gently; by distillation as soon as it has cooled, α-acetoxy*iso*butyronitrile is obtained in 81—86% yield. With perchloric acid as catalyst, the mixture being maintained at 100° for about 5 hours, α-acetoxy*iso*butyronitrile and N-*acetyl-α-acetoxy*iso*butyramide* are formed each in about 50% yield. The latter is readily isolated, either by distillation in a vacuum, coming over as a rapidly solidifying syrup, b. p. 120—130°/13 mm., or by distillation of the acetoxy-nitrile and crystallisation of the residue from ligroin; it then forms slender colourless prisms and needles (m. p. 81—82°), frequently arranged in rosettes, showing high polarisation colours, no pleochroism, and parallel or symmetrical extinction. It is readily soluble in cold acetone, ether, ethyl alcohol, benzene, chloroform, and carbon tetrachloride and in hot ligroin and water (Found: C, 51·6; H, 7·2; N, 7·4. $C_8H_{13}O_4N$ requires C, 51·3; H, 7·0; N, 7·5%). The molecular weight, determined cryoscopically, was 250, 254, 260 in benzene, 150 in camphor by Rast's method, and 198 in acetic acid (calc., 187).

No appreciable acetylation of acetone cyanohydrin could be effected by glacial acetic acid, with or without catalysts, even on prolonged refluxing with benzene to bring about the azeotropic removal of any water formed (contrast Part I, p. 405).

*Pyrolysis of α-Acetoxy*iso*butyronitrile*.—287 G. (7 c.c./min.; 425—435°) gave 284 g. of liquid, which on fractionation yielded: (i) 3 g., b. p. < 88°; (ii) 132 g., b. p. 88—98°; (iii) 140 g., b. p. 98—185°; (iv) a small residue. Fraction (i) contained acetone and hydrogen cyanide, identified as the 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 125—127°, and silver cyanide respectively. Fraction (ii) was slightly crude α-methylacrylonitrile. From fraction (iii), by further fractionation, the higher fractions being washed with brine, 27 g. of α-acetoxy*iso*butyronitrile were recovered. Fractions (i) and (ii), united and redistilled, gave 132 g. of almost pure α-methylacrylonitrile, b. p. 90—96° (yield, 96%, calc. on the acetoxy-nitrile destroyed); by washing with sodium carbonate solution, drying over phosphoric oxide, and refractionation, a sample was obtained, b. p. 90—90·5°, having an extremely characteristic, unpleasant, fresh, bitter odour (Found: C, 71·5; H, 7·9; N, 20·5. Calc. for C_4H_5N: C, 71·6; H, 7·5; N, 20·9%). This sample polymerised spontaneously to a hard colourless resin after 3 months. A similar sample polymerised and become yellow when heated at 100° for some hours with 1% of benzoyl peroxide.

The secondary formation of acetone and hydrogen cyanide becomes marked at temperatures higher than the above; *e.g.*, 17% of the product of pyrolysis at 550—560° boiled below 78° and contained very little methylacrylonitrile.

Pyrolysis of N-*Acetyl-α-acetoxy*iso*butyramide*.—51 G. of the amide, dissolved in 130 g. of acetone, were run (5 c.c./min.) into the pyrolysis tube at 515—530°; 161 g. of liquid were collected, from which 123 g. of acetone were recovered by distillation. The remaining 38 g. of liquid, on fractionation, yielded 14 g. of crude methylacrylonitrile and 24 g. of almost pure acetic acid; from the former, on refractionation, 12·5 g. of almost pure material were obtained (65% yield), which readily polymerised (molecular ratio of methylacrylonitrile and acetic acid = 1 : 2).

*Methyl α-Benzoyloxy*iso*butyrate*.—Benzoyl chloride (286 g.) was added ($\frac{3}{4}$ hour) to methyl α-hydroxy*iso*butyrate (236 g.) and pyridine (160 g.) and after 1 hour the mixture was heated at 100° for 1 hour and poured into cold water. Ether extracted an oil, which, distilled in a vacuum, gave 43 g. of the hydroxy-ester and 324 g. (89% yield) of the desired *benzoyl* derivative. The latter was freed from a small amount of benzoic acid by shaking in ether with dilute sodium carbonate solution, refractionated, and obtained as a colourless, somewhat viscous oil with an aromatic odour; b. p. 124°/4 mm., 156°/19 mm., 205—210°/760 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·4992, $d_{4^\circ}^{20^\circ}$ 1·120 (Found: C, 64·6; H, 6·1; *M*, cryoscopic in benzene, 227. $C_{12}H_{14}O_4$ requires C, 64·9; H, 6·3%; *M*, 222).

Pyrolysis. 108 G. of the ester (4 c.c./min.; 410—420°) gave 100 g. of a pasty yellowish product, which was shaken in ether with sodium carbonate solution; this removed 42 g. of benzoic acid. The ethereal layer was dried and the oil obtained therefrom was distilled, giving (i) 5 g., b. p. < 85°; (ii) 28 g., b. p. 85—101° (mostly 98—100°); (iii) 27 g., b. p. *ca.* 120°/4 mm. Fraction (i) was discarded. From fraction (ii), on refractionation, pure methyl α-methylacrylate, b. p. 99—100°, was obtained (Found: saponification equiv., 98. Calc., 100), characterised by its odour and polymerisation. The yields of benzoic acid and methyl methylacrylate were 94% and 77% respectively, calculated on the benzoyloxy-ester destroyed.

*Methyl α-Chloro*iso*butyrate.*—This was a by-product in the reaction of carbonyl chloride and methyl α-hydroxy*iso*butyrate (to be described in Part III). It had b. p. 133—135°/760 mm.

Pyrolysis. 45 G. (2 g./min.; 500—510°) gave hydrogen chloride and 31 g. of a fuming yellowish liquid. This was mostly " uncracked " α-chloro-ester, but distillation gave 5 g. of a liquid, b. p. *ca.* 90—110°, which, washed with aqueous potassium carbonate, had the extremely characteristic odour of methyl methylacrylate and polymerised when warmed for a few hours with 1% of benzoyl peroxide.

Pyrolysis of Acetone Cyanohydrin.—100 G., pyrolysed as above at 510°, yielded 97·5 g. of a mixture of acetone and hydrogen cyanide, b. p. 49—56°.

*Pyrolysis of Methyl α-Hydroxy*iso*butyrate.*—250 G. (2·5 c.c./min.; 470—480°) gave 214 g. of liquid, which on fractionation yielded: (i) 27 g., b. p. 50—61°; (ii) 11 g., b. p. 62—94°; (iii) 15 g., b. p. 95—107°; (iv) 11 g., b. p. 107—135°; (v) 144 g., b. p. 136—138°; (vi) a minute residue. Fraction (i) was mainly acetone (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 124—126°), and fraction (v) was unchanged hydroxy-ester. Fraction (iii) was crude methyl α-methylacrylate; this together with the crude ester remaining after water-washing of fractions (ii) and (iv), was dried and refractionated, yielding almost pure methyl methylacrylate, b. p. 96—101°.

The total loss of weight on pyrolysis was 14% at 470—480°, 19% at 480—500°, and 26% at 570°.

The authors thank the Directors of Imperial Chemical Industries Limited for permission to publish this work.

RESEARCH DEPARTMENT, I.C.I. (EXPLOSIVES GROUP), LTD.,
STEVENSTON, AYRSHIRE.

[*Received, February 28th,* 1935.]