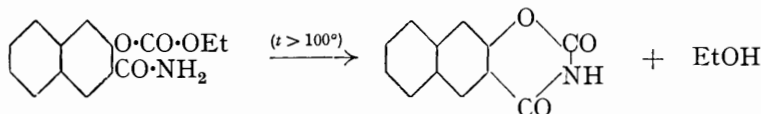


245. *Studies in Pyrolysis. Part III. The Pyrolysis of Carbonic and Sulphurous Esters*

By PATRICK D. RITCHIE.

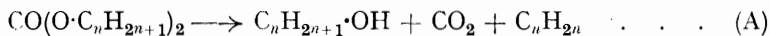
IN Parts I and II (Burns, Jones, and Ritchie, this vol., pp. 400, 714) it has been shown that a derivative of an α -hydroxy-acid, $\text{CH}_3\cdot\text{CR}(\text{OH})\cdot\text{CO}_2\text{H}$, can be converted into the corresponding derivative of the Δ^α -unsaturated acid, $\text{CH}_2\text{:CR}\cdot\text{CO}_2\text{H}$, by acetylation, benzoylation, etc., and pyrolysis of the resulting ester at $400\text{--}600^\circ$. It is now shown that the same unsaturated product is obtained on pyrolysis of the carbonate formed by esterification of the α -hydroxy-compound with carbonyl chloride or a chloroformic ester, and of the sulphite formed by esterification with thionyl chloride. The pyrolysis of the lower alkyl carbonates, both simple and mixed, and of aromatic carbonates, has also been examined, and its nature determined.

(1) *Carbonates*.—Previous references to the action of heat on organic carbonates are few. Gomberg (*Ber.*, 1913, **46**, 226) found that bis(triphenylmethyl) carbonate yielded carbon dioxide and bis(triphenylmethyl) ether when heated at 140° with a copper catalyst. Fries (*Ber.*, 1925, **58**, 2845) has recorded a second case, in which, however, the course of the decomposition is obviously determined by the presence of a second functional group (CO·NH₂) in the ester molecule :



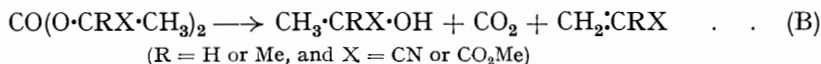
The results now obtained are summarised below.

Simple (Symmetrical) Alkyl Carbonates.—The pyrolysis of simple alkyl carbonates takes place according to the scheme :



Methyl carbonate ($n = 1$), like most methyl esters, has a much higher degree of thermostability than its higher homologues. Under the conditions of pyrolysis employed (see Part I, *loc. cit.*), only 36% undergoes pyrolytic decomposition at 600°, and only 28% at 500°; whereas, in the case of ethyl carbonate ($n = 2$), 66% is "cracked" at 500°. The latter ester yields ethylene directly: the former also yields ethylene, presumably indirectly *via* the methylene radical. In both cases, the carbinol formed as a primary product undergoes slight secondary pyrolysis into hydrogen and the corresponding aldehyde; and, in addition, the formaldehyde thus formed from methyl carbonate, *via* methyl alcohol, suffers further pyrolysis into hydrogen and carbon monoxide.

When the alkyl groups in such symmetrical carbonates both contain in the α -position a negative acidic radical, such as CN or CO₂Me, the same mode of primary pyrolysis is observed :

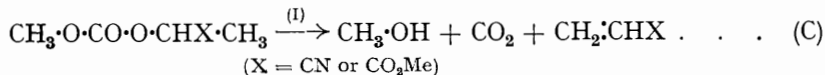


Since methyl carbonate is more thermostable than ethyl carbonate, it might be expected that a substituted ethyl carbonate (*i.e.*, R = H, above) would be more thermostable than the corresponding substituted *isopropyl* carbonate (*i.e.*, R = CH₃, above): this is the case. Various secondary decompositions are liable to occur here, however: *e.g.*, where X = CN, the hydroxylic product, being a cyanohydrin, undergoes complete fission into hydrogen cyanide and an aldehyde or ketone. The substituted olefin CH₂·CRX is itself, in general, fairly thermostable, apart from its tendency to polymerisation.

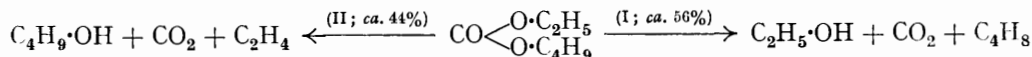
Mixed (Unsymmetrical) Alkyl Carbonates.—The pyrolysis of such carbonates follows a more complex course, two modes of primary fission being involved :



If the simpler of the two alkyl radicals is methyl ($m = 1$), the reaction appears to follow route (I) almost exclusively up to about 500°, and a negative substituent radical attached to the α -carbon atom of the higher alkyl group does not alter the course of primary pyrolysis :

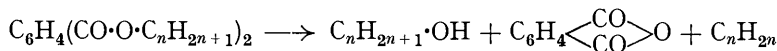


If, however, both alkyl radicals are higher than methyl, and $m < n$, both modes of fission occur simultaneously, route (I) predominating over route (II); *e.g.*, ethyl *n*-butyl carbonate ($m = 2$, $n = 4$) decomposes at 500° in the following way :

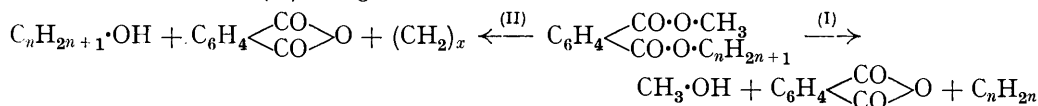


Some acetaldehyde is also formed, presumably by slight secondary pyrolysis of ethyl alcohol.

The above results are strictly analogous to the pyrolysis of methyl α -carbethoxyethyl phthalate (this vol., p. 401), and also to the results recorded by Nagel and Abelsdorff (*Wiss. Veröff. Siemens-Konz.*, 1926, 5, 193), who found that simple (symmetrical) alkyl phthalates undergo thermal decomposition, on prolonged refluxing at about 300°, on the lines :

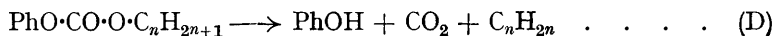


Methyl phthalate ($n = 1$) is much more thermostable than its higher homologues, and undergoes very little pyrolysis at this temperature : and mixed (unsymmetrical) alkyl phthalates, where one of the alkyl radicals is methyl, decompose according to route (I), no evidence for route (II) being obtained :



Nagel and Abelsdorff have identified ethyl hydrogen phthalate as an intermediate product in the pyrolysis of ethyl phthalate, and have demonstrated the secondary pyrolysis of methyl hydrogen phthalate to methyl alcohol and phthalic anhydride at 125° : they therefore postulate a reaction mechanism whereby a molecule of olefin is eliminated primarily, followed by pyrolysis of the resulting alkyl hydrogen ester to carbinol and phthalic anhydride. It is probable that the pyrolysis of alkyl carbonates occurs through a similar mechanism, which would be in accordance with the observed thermostability of methyl carbonate, and the well-known instability of the alkyl hydrogen carbonates, which can exist only at low temperatures (Hempel and Seidel, *Ber.*, 1898, 31, 3001). The only obvious alternative mechanism—a primary elimination of carbon dioxide, followed by slow pyrolysis of the dialkyl ether thus formed, into carbinol and olefin—receives some support from the observations of Gomberg (*loc. cit.*). Nef, however, has shown (*Annalen*, 1901, 318, 198) that diethyl ether is fairly thermostable up to 500°, and we would not, therefore, expect it to undergo appreciable secondary pyrolysis, under the present experimental conditions, into the products actually found. Further, Nef showed that aliphatic ethers, on pyrolysis, yield the aldehyde and paraffin : fission into carbinol and olefin, the products observed in the present work, occurs only in the case of a few rather complex ethers (Kleber, *Annalen*, 1888, 246, 103 ; Merling and Welde, *ibid.*, 1909, 366, 135 ; Biltz and Strufe, *ibid.*, 1917, 413, 164). The second alternative mechanism is therefore extremely improbable, in the cases so far described.

Aromatic Carbonates.—In an unsymmetrical carbonate, where one of the hydrocarbon radicals is an alkyl group and the other is phenyl, olefin can be eliminated in one way only : and primary pyrolysis would therefore be expected to occur according to the scheme :



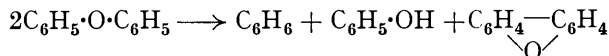
This has been confirmed, phenyl ethyl carbonate ($n = 2$) breaking down in this way to the extent of 85% at 500°. It is not easy to decide which of the two possible reaction mechanisms obtains in this case. Olefin may be eliminated first, as before, followed by pyrolysis of phenyl hydrogen carbonate to phenol and carbon dioxide : but primary elimination of carbon dioxide seems equally possible here, since this would yield phenetole, which has been shown by Bamberger (*Ber.*, 1896, 19, 1820 ; see also Meyer and Hofmann, *Monatsh.*, 1917, 38, 343) to yield phenol and ethylene on pyrolysis at 380—400°.

The elimination of an olefin cannot possibly, however, be the first stage in the pyrolysis of a symmetrical aryl carbonate : and it has, in fact, been found that phenyl carbonate is very much more thermostable than the other carbonates so far considered. Phenyl carbonate has b.p. 301—302° ; and about 82% of the product of pyrolysis at 640—670° boiled above 230°. Carbon dioxide, benzene, and phenol were identified as products of

the decomposition. It is practically certain, therefore, that primary pyrolysis occurred thus :



Secondary pyrolysis of diphenyl ether then presumably occurred, for Graebe and Ullmann (*Ber.*, 1896, **29**, 1877; see also Meyer and Hofmann, *Monatsh.*, 1916, **37**, 681) have observed that this compound splits up in the following way, in a red-hot glass tube :



The high-boiling fraction from the present product of pyrolysis was obviously a mixture, presumably of diphenylene oxide (b.p. 287—288°) and unchanged phenyl carbonate, though it could not be purified sufficiently to identify the former compound definitely.

The foregoing results may be summarised thus :

(1) When the structure of an organic carbonate permits of the elimination of a molecule of olefin, primary pyrolysis appears to follow this course, followed by secondary decarboxylation of the resulting intermediate acid carbonate.

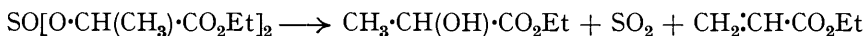
(2) When the molecule is such in structure that no olefin can be eliminated, it tends to lose carbon dioxide primarily, with formation of an ether, which may then undergo secondary pyrolysis.

(3) When the structure of the molecule is such that two different olefins may be eliminated, pyrolysis may follow two independent primary courses, simultaneously.

The action of carbonyl chloride on a mixture of equivalent amounts of pyridine and an α -hydroxy-ester or nitrile, $\text{Me}\cdot\text{CRX}\cdot\text{OH}$ (where $\text{R} = \text{H}$ or Me and $\text{X} = \text{CN}$ or CO_2Me), gave the desired symmetrical carbonate in yields of about 50%, about 20% of the α -hydroxy-compound being lost. The α -chloro-compound $\text{Me}\cdot\text{CRXCl}$ was produced as a by-product in all four cases examined. Where $\text{R} = \text{Me}$, the chloro-compound was obtained in 20—30% yield; but, where $\text{R} = \text{H}$, the yield fell to 10—20%, and a third product, whose nature has not yet been determined, made its appearance. In each case ($\text{X} = \text{CN}$, and $\text{X} = \text{CO}_2\text{Me}$) it was free from halogen, was insoluble in water, and had a sharp b. p. intermediate between that of the other two products.

None of these by-products was observed when esterification was carried out with methyl chloroformate instead of carbonyl chloride. Further, though carbonyl chloride reacted readily with the compound $\text{Me}\cdot\text{CRX}\cdot\text{OH}$ in presence of pyridine, where $\text{R} =$ either H or Me , methyl chloroformate only reacted smoothly where $\text{R} = \text{H}$. Where $\text{R} = \text{Me}$, esterification of the tertiary hydroxyl group proceeded only to a very slight extent—a difficulty previously encountered (this vol., p. 716).

(2) *Sulphites*.—Carré and Libermann (*Compt. rend.*, 1934, **198**, 274; *Bull. Soc. chim.*, 1934, **1**, 1248) have pyrolysed benzyl, β -phenylethyl, and γ -phenyl-*n*-propyl sulphites. The first two eliminate sulphur dioxide, with formation of the corresponding ether—a result parallel to that recorded by Prinz for ethyl sulphite (*Annalen*, 1884, **223**, 374). The third ester splits up on pyrolysis into a carbinol, sulphur dioxide, and olefin, and a similar result is obtained with a long-chain alkyl sulphite, such as $\text{SO}(\text{O}\cdot\text{C}_{10}\text{H}_{21})_2$. The latter mode of decomposition is parallel to that described above for the carbonic esters, and it is of interest that α -carbethoxyethyl sulphite undergoes primary pyrolysis at 400—500° in the same way :



The yields of the two ethyl esters were, however, poor. Various secondary pyrolyses occurred, such as the fission of ethylene from the carbethoxy-groups, just as was observed in the pyrolysis of the higher alkyl α -acetoxypionates, and of methyl α -carbethoxyethyl phthalate (Part I).

EXPERIMENTAL.

The apparatus and methods are described in Part I (this vol., p. 403), and the manipulation of solids in Part II (p. 715). In the case of the α -substituted esters, carbon dioxide was

passed through a bubbler (25 bubbles per min.) and then through the pyrolysis tube to facilitate passage of the vapours.

Unless otherwise stated, the carbinols, aldehydes, and olefins mentioned hereafter were identified as their 3:5-dinitrobenzoates, 2:4-dinitrophenylhydrazones, and dibromides, respectively. The first two were tested by the mixed m. p. method, and the last-named by estimation of bromine in a purified sample.

All the yields are calculated on the original ester destroyed on pyrolysis.

Pyrolysis of Methyl Carbonate.—The pure ester, b. p. 89.5—90°/760 mm., was run (2.1 c.c./min.) into the pyrolysis tube at 500° and at 600° in two experiments:

	I.	II.
Temperature	500–510°	590–600°
Ester used, g.	129	101
Liquid recovered, g.	103.5	74
Loss of weight on pyrolysis, %	20	27
"Uncracked" ester recovered, g.	92 (72%)	65 (64%)

The recovered liquid was a mixture of methyl alcohol and unchanged carbonate, from which the former was isolated by fractionation. The carbonate content of the residue was estimated by removing the last of the alcohol by brine. The gaseous products of pyrolysis were passed into bromine, whereby ethylene dibromide was obtained, b. p. 131—132°. The exit gases (from Experiment II), after removal of olefin, consisted of about 90% of carbon dioxide, 3% of carbon monoxide, and 6% of hydrogen.

Pyrolysis of Ethyl Carbonate.—146 G. of ethyl carbonate, b. p. 127—127.5°/760 mm., were run into the pyrolysis tube (2 c.c./min.; 495—505°). 75 G. of liquid were recovered, which yielded (i) 11 g., b. p. 70—82°; (ii) 22.5 g., b. p. 82—90°; (iii) 6 g., b. p. 90—123°; (iv) 34 g., b. p. 123—126°; (v) 3 g. of residue. Fractions (i) and (ii) were mainly ethyl alcohol. Fraction (iv) and the residue were "uncracked" carbonate, of which a further 13 g. were recovered by washing fractions (i), (ii), and (iii) with brine. The gaseous products of pyrolysis gave 84 g. of ethylene dibromide, b. p. 130—130.5°.

Pyrolysis of Ethyl n-Butyl Carbonate.—The pure ester had b. p. 168°/763 mm., n_D^{24} 1.3990, d_4^{20} 0.9426. From 192 g. of the carbonate (2.1 c.c./min.; 500—510°), 82.5 g. of liquid were recovered, which yielded six fractions: (i) 3 g., b. p. 40—70°, mainly acetaldehyde; (ii) 14 g., b. p. 70—85° (mostly ca. 80°), crude ethyl alcohol; (iii) 8 g., b. p. 85—110°, ethyl and n-butyl alcohols; (iv) 17.5 g., b.p. 110—122° (mostly 114—116°), crude n-butyl alcohol; (v) 14 g., b. p. 122—160°, butyl alcohol and unchanged ester; (vi) 28 g., b. p. 160—163° (mostly 162.5—163°/755 mm.), and residue, about 1 g., both consisting of unchanged ester.

The gaseous products of pyrolysis gave a mixture of olefin dibromides, which yielded (i) 42 g., b. p. 138—145°; (ii) 19 g., b. p. 145—155°; (iii) 56 g., b. p. 155—168° (mostly 165—166°); (iv) 7 g. of black residual liquid. Fractions (i) and (iii) on refractionation yielded ethylene dibromide, b. p. 131.5—132.5°, and $\alpha\beta$ -dibromobutane, b. p. 163—164°, respectively. Fraction (ii) was a mixture of both.

The exit gases, after removal of olefins, consisted of about 93% of carbon dioxide and 7% of hydrogen.

Hence 17% of the carbonate remained "uncracked" and about 14% of the ethyl alcohol primarily formed underwent secondary pyrolysis into hydrogen and acetaldehyde.

Pyrolysis of Phenyl Ethyl Carbonate.—The ester was freed from traces of phenol, and had b. p. 107—108°/13 mm. 91 G. (2 c.c./min.; 500—520°) gave 52 g. of liquid, which yielded 35 g. of almost pure phenol, b. p. 180—181°/765 mm., identified by formation of 2:4:6-tri-bromophenol. The residue (16 g.) was washed with caustic soda solution to remove phenol, and then yielded 14 g. of unchanged carbonate. The gaseous products of pyrolysis consisted of equal volumes of carbon dioxide and ethylene.

Pyrolysis of Phenyl Carbonate.—The ester had b. p. 309°/761 mm., and m. p. 79° after six crystallisations from ligroin (Kempf, *J. pr. Chem.*, 1870, 1, 404, gives m. p. 78°, and Richter, *ibid.*, 1883, 27, 41, m. p. 88°). A solution of 125 g. of the ester in 125 g. of acetone was run (2 c.c./min.) into the pyrolysis tube at 640—670°; 206 g. of liquid were recovered, which yielded: (i) 100 g., b. p. 55—230°; (ii) 14 g., b. p. 230—275°; (iii) 15 g., b. p. 275—300°; (iv) 74 g., b. p. 300—305°. Fraction (i) was redistilled, and after removal of acetone a small water-insoluble fraction was obtained, b. p. 70—80°, which smelt of benzene and gave the odour of nitrobenzene on nitration. A small fraction was then obtained, b. p. 160—190°,

which yielded 2 : 4 : 6-tribromophenol on bromination. Fraction (iv) was unchanged phenyl carbonate. Fractions (ii) and (iii) partly solidified on cooling, the latter yielding a solid, m. p. 70—85°, but nothing definite was isolated.

Preparation of α -Carbomethoxyethyl Carbonate.—Carbonyl chloride was blown into a vigorously stirred mixture of 208 g. (2 mols.) of methyl lactate and 160 g. (2 mols.) of pyridine until 140 g. (1.4 mols.) had been absorbed (with only 1 mol., the yields obtained were poor). The mass was heated at 100° for 2 hours, poured into water, and extracted with ether, and the residue from the dried extract distilled in a vacuum. Three fractions were isolated. (i) The first (48 g.), b. p. 48°/20 mm., was crude methyl α -chloropropionate (20% yield, calc. on hydroxy-ester): refractionation gave an impure sample, b. p. 130—132°/767 mm. (Kahlbaum, *Ber.*, 1879, 12, 343, records b. p. 132.5°) (Found: Cl, 26.4. Calc.: Cl, 28.9%). (ii) The second (32 g.) was a colourless liquid, b. p. ca. 110°/22 mm. When united with the corresponding fraction (59 g.) from a second preparation and refractionated, it gave a liquid, b. p. 197—200°/767 mm., n_D^{20} 1.4115 (Found: C, 44.3; H, 5.8%; M , cryoscopic in benzene, 156), which awaits further investigation. (iii) The third fraction was the desired carbonate (94 g.; 40% yield, calc. on hydroxy-ester). It was a fairly viscous, colourless liquid, miscible with acetone, ether, and ethyl alcohol; b. p. 172°/32 mm., n_D^{20} 1.428, d_4^{20} 1.193 (Found: C, 46.4; H, 5.9; M , cryoscopic in benzene, 234. $C_6H_{14}O_7$ requires C, 46.2; H, 6.2%; M , 234).

Pyrolysis. 99 G. of the carbonate (4 c.c./min.; 420—430°) gave 81 g. of liquid, which yielded (i) 14 g., b. p. mostly ca. 80°/760 mm.; (ii) 12 g., b. p. 143—150°/760 mm.; (iii) 46 g., b. p. 165—171°/30 mm. Fraction (i), washed with water, yielded 10 g. of almost pure methyl acrylate (51% yield, calc. according to equation B). A sample polymerised to a clear, almost colourless, tough, rubbery resin when warmed to 60° with 0.5% of benzoyl peroxide (Found: saponification equiv., 82. Calc., 86). Fraction (ii) (water-soluble) was methyl lactate (51% yield, calc. according to equation B) (Found: saponification equiv., 101. Calc., 104). Fraction (iii) was "uncracked" carbonate.

Preparation of α -Cyanoethyl Carbonate.—Carbonyl chloride was blown into a mixture of 395 g. (2 mols.) of acetaldehyde cyanohydrin and 420 g. (2 mols.) of pyridine; when 250 g. (1 mol.) had been absorbed, the whole was heated at 100° for 4½ hours and kept over-night. The product, worked up as before, gave three fractions. (i) The first, b. p. 30—34°/32 mm., was washed with water, and yielded 32 g. (6% yield, calc. on cyanohydrin taken) of almost pure α -chloropropionitrile, b. p. 122.5—123°/760 mm. (Henry, *Bull. Acad. roy. Belg.*, 1898, 35, 360, gives b. p. 122—123°) (Found: N, 15.8; Cl, 38.5. Calc.: N, 15.6; Cl, 39.7%). (ii) The second (80 g.), b. p. ca. 95°/15 mm., after several fractionations gave a product, b. p. 92—93°/17 mm. (Found: C, 51.5; H, 6.8%; M , cryoscopic in benzene, 96), which awaits further investigation. (iii) The third fraction was the desired carbonate (260 g.; 56% yield, calc. on cyanohydrin). It distilled at 165—168°/16 mm. as a pale yellow, viscous liquid, which rapidly set to a solid, almost colourless, crystalline mass. Recrystallised from xylene or dilute ethyl alcohol, it formed long, flattened, colourless prisms, m. p. 44—44.5°, the acute angle between the long edges and the ends being approx. 71.5°. They exhibit high polarisation colours and no pleochroism, and show oblique extinction, $\theta = 6^\circ$ (approx.). The ester is readily soluble in acetone and ether (Found: C, 50.1; H, 4.5; N, 16.8; M , cryoscopic in benzene, 170. $C_7H_8O_3N_2$ requires C, 50.0; H, 4.8; N, 16.7%; M , 168).

Pyrolysis. A solution of 224 g. of the carbonate in 148 g. of acetone (4 c.c./min.; 460—480°) gave 304 g. of liquid, which yielded three fractions: (i) 158 g., b. p. 30—59°/760 mm.; (ii) 65 g., b. p. 59—70°/760 mm. (mostly ca. 68°); (iii) 56 g., b. p. 160—165°/14 mm. Fraction (i) was mainly acetone, but acetaldehyde and hydrogen cyanide were identified in the first few grams of distillate. Fraction (ii) was mostly acrylonitrile, 40 g. of which were obtained on washing with water (76% yield, calc. according to equation B); when dried and fractionated, this had b. p. 78—79°/770 mm. (Found: N, 26.0. Calc.: N, 26.4%). Fraction (iii) was "uncracked" carbonate.

Preparation of α -Carbomethoxyisopropyl Carbonate.—Prepared from 480 g. (2 mols.) of methyl α -hydroxyisobutyrate, 320 g. (2 mols.) of pyridine, and 245 g. (1.25 mols.) of carbonyl chloride as in the preceding case, the product was distilled in two fractions: (i) 191.5 g., b. p. ca. 48°/15 mm., which yielded on fractionation 105 g. of methyl α -chloroisobutyrate, b. p. 133—135°/760 mm. (Found: Cl, 25.7. $C_5H_9O_2Cl$ requires 26.0%); (ii) α -carbomethoxyisopropyl carbonate (246 g.). The latter, b. p. 152—154°/15 mm., was a pale yellow, viscous liquid, which rapidly set to a crystalline mass. Recrystallised from ligroin, it formed long, narrow, colourless, prismatic needles, m. p. 66—67°. Rapid crystallisation gave typical irregular "corn-sheaf" aggregates. The needles show no pleochroism, and parallel extinction. The ester is readily

soluble in acetone, ether, and ethyl alcohol (Found: C, 50.3; H, 6.6; *M*, cryoscopic in benzene, 252. $C_{11}H_{18}O_7$ requires C, 50.4; H, 6.9%; *M*, 262).

Pyrolysis. A solution of 227 g. of the carbonate in 150 g. of acetone (6 c.c./min.; 445—455°) gave 291 g. of liquid, which yielded: (i) 126 g., b. p. 55—58° (acetone); (ii) 112 g., b. p. 90—100°; (iii) 42 g., b. p. 132—138°. Fraction (ii), on purification, yielded 73 g. of almost pure methyl methacrylate (84% yield, calc. according to equation B). A sample polymerised to a clear, hard, colourless resin when warmed to 60° with 0.5% of benzoyl peroxide (Found: saponification equiv., 96. Calc., 100). Fraction (iii) (water-soluble) was methyl α -hydroxyisobutyrate (52% yield, calc. according to equation B) (Found: saponification equiv., 116. Calc., 118). No "uncracked" carbonate was recovered.

Preparation of α -Cyanoisopropyl Carbonate.—The quantities were 255 g. (2 mols.) of acetone cyanohydrin, 237 g. (2 mols.) of pyridine, and 185 g. (1.25 mols.) of carbonyl chloride. The product, worked up as before, gave a first fraction (60 g.), b. p. 55°/10 mm., of impure α -chloroisobutyronitrile (Chrzaszczewska and Sobieranski, *Rocz. Chem.*, 1927, 7, 470, give b. p. 51.5—52.5°/6 mm.) (Found: Cl, 32.4. Calc.: Cl, 34.3%). The residue on further set to a mass of pale yellow crystals (147 g.) of slightly impure α -cyanoisopropyl carbonate. This crystallised from dilute ethyl alcohol in thick, flattened, colourless, rhombic prisms, m. p. 76—77°, with an acute angle of about 82°. They exhibited moderately high polarisation colours and no pleochroism, and showed symmetrical extinction. Elongated prismatic needles showing parallel extinction were also occasionally found. The ester is readily soluble in acetone and ether (Found: C, 55.0; H, 5.8; N, 14.4; *M*, cryoscopic in benzene, 200. $C_5H_{12}O_3N_2$ requires C, 55.1; H, 6.1; N, 14.3%; *M*, 196).

Pyrolysis. 98 G. of the carbonate in 146 g. of acetone, pyrolysed (3.5 c.c./min.) at 430—450°, gave 192 g. of liquid which yielded: (i) 145 g., b. p. ca. 60°, mainly acetone; (ii) 20 g., b. p. 65—76°, a mixture of acetone and α -methylacrylonitrile, from which 5 g. of the latter were obtained on shaking with water; and (iii) 25 g., b. p. 77—90°, which yielded a further 13 g. of the nitrile on extraction with water. The total nitrile (54% yield, calc. according to equation B), when dried and fractionated, yielded the pure nitrile, b. p. 88—89°/750 mm. (Found: N, 20.5. Calc. for C_4H_5N : N, 20.9%). The total acetone found in the product exceeded that taken as solvent; and fraction (i) contained hydrogen cyanide.

Preparation of Methyl α -Carbomethoxyethyl Carbonate.—210 G. (1.1 mol.) of methyl chloroformate were added (2 hours) to a cooled and stirred mixture of 208 g. (1 mol.) of methyl lactate and 160 g. (1 mol.) of pyridine, which was then heated at 100° under reflux for 4 hours, kept over-night, and shaken with water and ether; the ethereal extract was washed with dilute hydrochloric acid, dried, and evaporated. The residual oil, on distillation in a vacuum, yielded 238 g. (73% yield, calc. on lactate) of methyl α -carbomethoxyethyl carbonate as a colourless liquid with a faint smell, b. p. 91.5—92°/12 mm., 97—98°/18 mm., and 198—200° (slight decomp.)/759 mm., n_D^{20} 1.4102, d_4^{20} 1.157 (Found: C, 44.3; H, 5.9; *M*, cryoscopic in benzene, 158. $C_6H_{10}O_5$ requires C, 44.4; H, 6.2%; *M*, 162).

Pyrolysis. This was carried out at three different temperatures (see under A in the table).

	A.			B.	
	I.	II.	III.	I.	II.
Temp.	470°	500—520°	550—570°	480—490°	550—570°
Rate of addition of ester (c.c./min.)	7	4	4	6	5
Ester used (g.)	52	334	128	51	42
Liquid recovered (g.)	41	260	86	41.5	25
Ester "uncracked" (g.)	31 (60%)	120 (36%)	13 (10%)	29 (57%)	9 (21%)
Crude methyl acrylate (A) or acrylonitrile (B) isolated (g.)	6 (54%)	69 (61%)	40.5 (67%)	6 (66%)	9 (66%)

In each case the mixture of methyl alcohol and methyl acrylate was distilled from the high-boiling "uncracked" carbonate. The first few drops of distillate, b. p. 66—68°, were methyl alcohol (characterised as methyl hydrogen phthalate). The remainder of the alcohol was removed from the mixture by brine; the insoluble layer was readily polymerisable methyl acrylate. (The yields recorded above are calculated according to equation C.) The crude ester from experiment III yielded 32 g. of methyl acrylate, b. p. 80—81°/761 mm. (Found: C, 55.4; H, 7.1. Calc.: C, 55.8; H, 7.0%).

Preparation of Methyl α -Cyanoethyl Carbonate.—By the process described in the preceding preparation, 184 g. (1.1 mols.) of methyl chloroformate, 128 g. (1 mol.) of acetaldehyde cyanohydrin, and 145 g. (1 mol.) of pyridine gave 142 g. of methyl α -cyanoethyl carbonate as a colourless

liquid with a faint pleasant odour, b. p. 80.5°/10 mm., 82—83°/13 mm., 92°/22 mm., n_D^{20} 1.4046, d_4^{20} 1.110 (Found: C, 46.4; N, 5.4; *M*, cryoscopic in benzene, 130. $C_8H_7O_3N$ requires C, 46.5; H, 5.4%; *M*, 129).

Pyrolysis. This was carried out at two different temperatures (see under B in the preceding table). The product was treated exactly as described in the preceding case (with the substitution of "acrylonitrile" for "methyl acrylate"). From the total crude acrylonitrile (15 g.) obtained, a sample of the pure nitrile was isolated, b. p. 77—78°/762 mm. (Found: N, 26.2. Calc.: N, 26.4%).

Preparation of α -Carbethoxyethyl Sulphite.—The method of Frankland and Garner (J., 1914, 105, 1112), who described the small-scale preparation of the dextrorotatory form of this ester (b. p. 167°/13 mm.), which they termed "ethyl thionyl-lactate," gave in our hands somewhat uncertain results on a larger scale. The optically inactive ester has now been prepared by the gradual addition of thionyl chloride (1 mol.) to a cooled and stirred mixture of ethyl lactate (2 mols.) and pyridine (2 mols.), the product being heated at 100° for 2 hours and shaken with water. *α -Carbethoxyethyl sulphite*, isolated by extraction with ether, and distilled in a vacuum, was obtained in poor yield (ca. 25%), b. p. 158—160°/4 mm. (Found: S, 12.0. $C_{10}H_{18}O_7S$ requires S, 11.4%).

Pyrolysis. 162 G. of the sulphite (4 g./min.; 390—420°) gave 130 g. of liquid, which yielded: (i) 9 g., b. p. < 110°; (ii) 16 g., b. p. 110—150°; (iii) 17 g., b. p. 150—155° (ethyl lactate: saponification equiv. found, 116; calc., 118); (iv) 64 g., b. p. 120°/70 mm.—186°/43 mm. (unchanged sulphite); a residue (18 g.) of viscous high-boiling liquid, apparently lactide. Fraction (i) contained acetaldehyde: it was united with fraction (ii) and washed with aqueous sodium carbonate; the residual 14 g. of ethyl acrylate, dried and fractionated, gave 10 g. of almost pure ester, b. p. 95—100°. The exit gases from the pyrolysis tube contained ethylene and sulphur dioxide.

In a second pyrolysis, carried out at 485—495° with 83 g. of the sulphite (5 g./min.), extensive decomposition occurred. Only 33 g. of liquid were collected, from which 10 g. of crude ethyl acrylate, 10 g. of crude ethyl lactate, and 12 g. of mixed "uncracked" sulphite and lactide were obtained.

The author thanks Mr. D. Trevor Jones, M.Sc., and Dr. Robert Burns for many helpful suggestions, and the Directors of Imperial Chemical Industries Limited for permission to publish the work.

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[Received, March 5th, 1935.]