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MODE OF DECOMPOSITION OF CHLORO- AND FLUORO-FORMATES OF SOME CARBOHYDRATES AND RELATED COMPOUNDS[1]

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INTRODUCTION

Chloroformates and fluoroformates of simple aliphatic, primary and secondary alcohols may be readily decarboxylated to yield alkyl chlorides[2] and fluorides[3]. However, Welch and Kent[4] reported that they were unable to effect thermal or catalytic decarboxylation of the fluoroformates of 1,2:3,4-di-*O*-isopropylidene-α-D-galactose and 1,2-*O*-isopropylideneglycerol. No experimental details were given. We have found that 6-*O*-fluoroformyl-1,2:3,4-di-*O*-isopropylidene-α-D-galactose and related fluoroformates do react under the thermal and catalytic conditions employed for the decarboxylation of alkyl fluoroformates, to yield dialkyl carbonates, but not fluorides.

RESULTS AND DISCUSSION

Chloroformates are readily prepared by reaction of the appropriate alcohols with an excess of phosgene, and may be converted into the analogous fluoroformates by treatment with thallous fluoride[3]. We have confirmed the observation[4] that high yields are obtained in the latter reaction when methyl cyanide is employed as the reaction solvent, and the extent of reaction may be conveniently followed by means of infrared spectroscopy, since the $C{=}O$ absorptions for chloroformates and fluoroformates occur at *ca.* 1780 and *ca.* 1830 cm^{-1}, respectively.

When a pyridine solution of 6-*O*-fluoroformyl-1,2:3,4-di-*O*-isopropylidene-α-D-galactose (**1**) was stored at 110–120° until reaction was complete, the apparent decarboxylation (see Experimental) was only *ca.* 50%. The predominant, if not the exclusive, reaction product was bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactose) 6,6′-carbonate (**2**); no trace of 6-deoxy-6-fluoro-1,2:3,4-di-*O*-isopropylidene-α-D-galactose[4] could be detected. Authentic bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactose) 6,6′-carbonate was obtained by reaction of phosgene with 2 mol. of 1,2:3,4-di-*O*-isopropylidene-α-D-galactose in the presence of pyridine. Authentic samples of the other dialkyl

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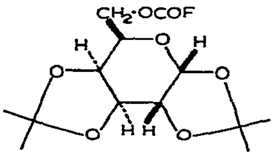
carbonates mentioned below were prepared by similar means. Decomposition of 6-*O*-fluoroformyl-1,2:3,4-di-*O*-isopropylidene-α-D-galactose in the presence of an excess of pyridine, or in *N*,*N*-dimethylformamide containing potassium fluoride and pyridine, also gave the dialkyl carbonate as the sole product. The dialkyl carbonate was also the only product detected when 6-*O*-fluoroformyl-1,2:3,4-di-*O*-isopropylidene-DL-xylitol was decomposed in pyridine.



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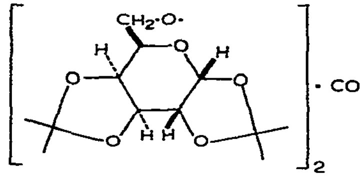
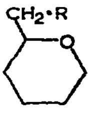
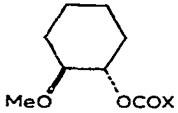


(2)

A more-detailed study of the reaction was then undertaken by using the haloformates of the model compound, 2-(hydroxymethyl)tetrahydropyran. Addition of pyridine to the chloroformate (3) resulted in an immediate exothermic reaction and, ultimately, 78% decarboxylation on completion of the reaction at 110–120°. 2-(Chloromethyl)tetrahydropyran (4) was formed, and the i.r. absorption at *ca.* 1750 cm^{-1} in the crude product, together with chromatographic data, indicated that bis(tetrahydropyran-2-methyl) carbonate was also formed. On the other hand, the fluoroformate (5) was unaffected by pyridine at room temperature, but decomposition appeared to be complete (53% decarboxylation) after 14 h at 110–120°; bis(tetrahydropyran-2-methyl) carbonate was the sole, detected product. In pyridine at 110–120°, the formation of a pyridinium complex from 2-(fluoroformyloxymethyl)-tetrahydropyran must occur slowly, since, after 2.5 h, a considerable proportion of undecomposed fluoroformate, but no 2-(fluoromethyl)tetrahydropyran (6), could be detected by g.l.c. [the authentic compound is readily obtained by treatment of 2-(toluene-*p*-sulphonyloxymethyl)tetrahydropyran with potassium fluoride in ethane-1,2-diol]; bis(tetrahydropyran-2-methyl) carbonate was also present in the product mixture. Pyridine was not essential for the formation of dialkyl carbonate, since thermal decomposition of 2-(fluoroformyloxymethyl)tetrahydropyran, although slow, gave bis(tetrahydropyran-2-methyl) carbonate.



3 R = OCOCl
4 R = Cl
5 R = OCOF
6 R = F



7 X = Cl
8 X = F

In all of the above cases where decomposition of fluoroformates in pyridine yielded a dialkyl carbonate, but no alkyl fluoride, the grouping F·CO·O·C–C·O is present and, in order to assess the role of the vicinal oxygen atom in the reaction, the decomposition of the chloroformate and fluoroformate of cyclohexanemethanol was examined. As with the other chloroformates, cyclohexanemethyl chloroformate reacted immediately on contact with pyridine at room temperature, although elevation of temperature to 110–120° was necessary to complete the decomposition (89% decarboxylation). Chloromethylcyclohexane was subsequently isolated, and evidence was obtained for the formation of bis(cyclohexanemethyl) carbonate. The fluoroformate of cyclohexanemethanol did not react with pyridine at room temperature, and, after 17 h at 110–120°, only 38% apparent decarboxylation had occurred; the reaction was incomplete, since the product had absorption at *ca.* 1820 cm^{-1} (O·CO·F). The absorption at *ca.* 1750 cm^{-1} indicated the presence of bis(cyclohexanemethyl)-carbonate, and g.l.c. revealed the presence of cyclohexanemethyl fluoride. Thus, the oxygen atom which is vicinal to the fluoroformate group in 2-(fluoroformyloxymethyl)-tetrahydropyran is not solely responsible for the formation of carbonate when the compound is decomposed in pyridine.

In extending the investigation to secondary haloformates, *trans*-2-methoxycyclohexanol was selected as a model compound. In pyridine at *ca.* 100°, the chloroformate (7) had undergone 83% decarboxylation after 22 h. The principal reaction product was *cis,trans*-2-methoxycyclohexyl chloride, in which the *cis,trans*-ratio was 34:1 as established by g.l.c.; t.l.c. and i.r. spectroscopy indicated that bis(2-methoxycyclohexyl) carbonate was also formed. The occurrence of decarboxylation in pyridine with preponderant inversion of configuration parallels the results of other workers[5], as did thermal decomposition (140°; *cis,trans*-ratio, 1:28), and decarboxylation in the presence of boron trifluoride-etherate in boiling hexane (*cis,trans*-ratio, 1:9).

When *trans*-2-methoxycyclohexyl fluoroformate (8) was treated with pyridine at 90°, apparent decarboxylation was slow (21% after 24 h). Fractional distillation of the product mixture at this stage gave starting material and bis(*trans*-2-methoxycyclohexyl) carbonate.

The formation of carbonates in the decomposition of haloformates in pyridine, which, apparently, has not hitherto been recognised, is likely to occur generally, although the proportion will vary and may be very small in some cases, for example, ethyl chloro- and fluoro-formates and cyclohexyl chloroformate, which underwent *ca.* 100% decarboxylation. Cyclohexyl fluoroformate in pyridine at 110–120° underwent 52% decarboxylation during 27 h, and in a parallel experiment, where quinoline was used, the i.r. spectrum of the product had absorption at *ca.* 1750 cm^{-1} typical of dialkyl carbonate.

The above examples of formation of dialkyl carbonates must involve intermolecular reactions. An apparently analogous, intramolecular reaction was observed when *trans*-1,2-bis(fluoroformyloxy)cyclohexane was decomposed in quinoline for 22 h at 160°. The preponderant product was the cyclic carbonate of cyclohexane-*trans*-1,2-diol, and this was identified by comparison with the authentic compound[6].

Cyclohexa-1,3-diene (subsequently isolated and characterised as the tetracyanoethylene adduct) and a second, volatile compound (*X*) were also formed in small proportions in the decomposition of *trans*-1,2-bis(fluoroformyloxy)cyclohexane. Compound *X*, which could not be isolated in the pure state, decomposed on storage, evolving hydrogen fluoride and affording cyclohexa-1,3-diene. A comparison may be made with the decomposition of *trans*-1,2-bis(chloroformyloxy)cyclohexane[2] in pyridine at 110–130° which afforded *trans*-1,2-dichlorocyclohexane (18%) and 1-chlorocyclohexene (17%). Cyclohexa-1,3-diene was not detected, and, in view of the above results, the significant proportion of unidentified, high-boiling material could be, at least in part, the cyclic carbonate of cyclohexane-*trans*-1,2-diol.

A study of the mechanism of dialkyl carbonate formation is in hand.

EXPERIMENTAL

Thin-layer chromatography (t.l.c.) was performed on Kieselgel, and detection effected with vanillin–sulphuric acid[7] or iodine vapour. Gas–liquid chromatography (g.l.c.) was performed on (*a*) a Pye-Argon instrument (β-ionization detection) with a column packing of poly(ethylene glycol adipate), and a gas pressure of 8 lb/sq.in; (*b*) a Perkin–Elmer instrument (Katharometer detection) with a column packing of silicone gum–Celite.

Preparation of chloroformates. — (*a*) A solution of 1,2:3,4-di-*O*-isopropylidene-DL-xylitol[8] (48 g) in quinoline (40 ml, 1.5 mol.) and ether (180 ml) was added dropwise to a stirred, ice-cold, 20% solution of phosgene (25 g) in ether. After the solution had been stirred overnight at room temperature, the excess of phosgene was removed at ~12 mm, and the remaining ether solution was poured into water (250 ml). The ethereal layer was washed successively with ice-cold, 10% hydrochloric acid (150 ml), 5% aqueous potassium carbonate, and water. Concentration of the dried ($MgSO_4$) extract, with distillation of the residue, gave 5-*O*-chloroformyl-1,2:3,4-di-*O*-isopropylidene-DL-xylitol (28 g, 50%), b.p. 120°/0.9 mm, ν_{max} 1780 (C=O) and 686 cm^{-1} (C–Cl) (Found: C, 48.6; H, 6.2; Cl, 12.0. $C_{13}H_{19}ClO_7$ calc.: C, 48.9; H, 6.5; Cl, 12.1%).

The following compounds were prepared in an essentially similar manner from the appropriate alcohols. 2-(Chloroformyloxymethyl)tetrahydropyran (87%, b.p. 100–101°/17 mm, ν_{max} 1778 and 685 cm^{-1} (Found: C, 47.3; H, 6.2; Cl, 19.6. $C_7H_{11}ClO_3$ calc.: C, 47.1; H, 6.2; Cl, 19.9%); reaction of the chloroformate with aniline, or of 2-(tetrahydropyran)methanol with phenyl isocyanate, gave the carbanilate, m.p. 86–87° (Found: C, 66.4; H, 7.2; N, 5.9. $C_{13}H_{17}NO_3$ calc.: C, 66.4; H, 7.3; N, 5.6%). (Chloroformyloxymethyl)cyclohexane (84%), b.p. 76–77°/10 mm (Found: Cl, 20.1. $C_8H_{13}ClO_2$ calc.: Cl, 20.1%); reaction with aniline gave the carbanilate, m.p. 81.5–82.5° [from light petroleum (b.p. 60–80°)], as did the reaction of cyclohexanemethanol with phenyl isocyanate (Found: C, 72.2; H, 8.3; N, 5.9. $C_{14}H_{19}NO_2$ calc.: C, 72.1; H, 8.2; N, 6.0%). *trans*-2-Methoxycyclohexyl chloroformate (44%), b.p. 106°/~20 mm. (Found: C, 50.0; H, 6.7; Cl, 18.6. $C_8H_{13}ClO_3$ calc.: C, 49.9; H, 6.8; Cl, 18.4%); reaction of the chloroformate with aniline, or of *trans*-2-methoxycyclohexanol with phenyl isocyanate, gave the carbanilate, m.p. 67–69° (Found: C, 67.3; H, 7.5; $C_{14}H_{19}NO_3$ calc.: C, 67.4; H, 7.7%).

Preparation of fluoroformates. — (*a*) A mixture of 5-*O*-chloroformyl-1,2:3,4-di-*O*-isopropylidene-DL-xylitol (22.5 g) and methyl cyanide (32 ml) was stirred and boiled under reflux in the presence of thallous fluoride (37 g) for 62 h (in subsequent experiments, the course of reaction was followed by i.r. spectroscopy and shown to be essentially complete in 3 h). The filtered solution was concentrated, and the residue distilled to yield 5-*O*-fluoroformyl-1,2:3,4-di-*O*-isopropylidene-DL-xylitol (15 g, 70%), b.p. 95°/0.9 mm, which crystallized on storage, m.p. 41–42° (from acetone) and ν_{max} 1830 cm^{-1} (C=O) (Found: C, 52.1; H, 6.8; F, 7.1. $C_{13}H_{19}FO_7$ calc.: C, 51.8; H, 6.8; F, 6.8%).

By essentially the above method (but with reaction times of 2–3 h), the relevant chloroformates were converted into the following compounds: 6-*O*-fluoroformyl-1,2:5,6-di-*O*-isopropylidene-α-D-galactose (80%), m.p. 72° (from acetone), $[\alpha]_D^{30}$ $-51°$ (*c* 1.0, chloroform), ν_{max} 1825 cm^{-1}; lit.[4], m.p. 74° and $[\alpha]_D^{21}$ $-50°$ (chloroform); 2-(fluoroformyloxymethyl)tetrahydropyran (70%), b.p. 73–74°/17 mm, ν_{max} 1828 cm^{-1} (Found: C, 51.8; H, 6.8; F, 12.3. $C_7H_{11}FO_3$ calc.: C, 51.9; H, 6.8; F, 11.7%), characterised as the carbanilate, m.p. 86–87°; *trans*-2-methoxycyclohexyl fluoroformate (92%), b.p. 86–88°/~20 mm, ν_{max} 1825 cm^{-1} (Found: C, 54.45; H, 7.3. $C_8H_{13}FO_3$ calc.: C, 54.55; H, 7.4%) (carbanilate, m.p. 67–69°); (fluoroformyloxymethyl)cyclohexane (84%), b.p. 82–84°/30 mm, ν_{max} 1826 cm^{-1} (Found: C, 59.9; H, 8.2; F, 11.4. $C_8H_{13}FO_2$ calc.: C, 60.0; H, 8.2; F, 11.9%).

(*b*) A stirred mixture of *trans*-1,2-bis(chloroformyloxy)cyclohexane (30 g) and methyl cyanide (150 ml) was boiled under reflux for 27 h in the presence of thallous fluoride (87.5 g, 3 mol.). The product was extracted with ether, the extract was concentrated, and the residue was distilled to yield, as the minor fraction, *trans*-1,2-bis(fluoroformyloxy)cyclohexane (3 g), b.p. 71°/4 mm (Found: C, 46.6; H, 4.6; F, 18.7. $C_8H_{10}F_2O_4$ calc.: C, 46.2; H, 4.8; F, 18.3%). Reaction with aniline gave the dicarbanilate[2], m.p. 214°. The major (unidentified) fraction, b.p. 120°/4 mm, crystallized on storage, and had m.p. 74–74.5° (from aqueous methanol) and ν_{max} 1750 cm^{-1} (C=O) (Found: C, 59.1; H, 6.8. $C_{14}H_{20}O_6$ calc.: C, 59.2; H, 7.0%). The molecular weight determined by micro-osmometry was 233, and saponification gave cyclohexane-*trans*-1,2-diol, m.p. 103–104°.

When a mixture of *trans*-1,2-bis(chloroformyloxy)cyclohexane (37 g), thallous fluoride (140 g), and methyl cyanide (50 ml) was boiled under reflux for 72 h, the difluoroformate (27.4 g, 86%), b.p. 48.5°/0.2 mm, was isolated. In subsequent experiments, the reaction course was followed by i.r. spectroscopy and shown to be complete in 3 h.

Preparation of alkyl fluorides. —A mixture of 2-(toluene-*p*-sulphonyloxymethyl)-tetrahydropyran (10 g), anhydrous potassium fluoride (10 g), and ethane-1,2-diol (60 ml) was stirred for 2 h at 130°. The cooled mixture was diluted with water (150 ml), and extracted with ether (2 × 100 ml). The combined extracts were washed with water (200 ml), dried ($MgSO_4$), and concentrated, and the residue was distilled to give 2-(fluoromethyl)tetrahydropyran (1.8 g, 40%), b.p. 121–123° (Found: C, 61.3; H, 9.2; F, 16.7. $C_6H_{11}FO$ calc.: C, 61.0; H, 9.3; F, 16.1%). Similarly, cyclohexanemethyl toluene-*p*-sulphonate (m.p. 82–82.5°) was converted into cyclohexanemethyl fluoride (56%), b.p. 116–118°, which was freed from olefinic material by preparative g.l.c.

(Wilkens Autoprep, silicone gum–Celite, 120°) (Found: C, 72.2; H, 11.3; F, 16.7. $C_7H_{13}F$ calc.: C, 72.4; H, 11.2; F, 16.4%).

Preparation of dialkyl carbonates. — A solution of 1,2:3,4-di-*O*-isopropylidene-α-D-galactose (5 g) in dry pyridine (30 ml) was added dropwise to a solution of phosgene (1.5 g, 1.1 mol.) in dry hexane (100 ml). After being stirred for 3.5 h at room temperature, the mixture was poured into ice-water (700 ml) and extracted with benzene (3 × 100 ml). The combined extracts were washed quickly, and successively, with ice-cold, N hydrochloric acid (400 ml), 10% aqueous cadmium chloride, 5% aqueous sodium hydrogen carbonate, and water. The dried ($MgSO_4$) extract was decolourised with charcoal, and concentrated, and the residue was recrystallised from methanol to yield bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose) 6,6′-carbonate (3 g, 37%), m.p. 134–135°, $[\alpha]_D^{30}$ $-73°$ (*c* 1.0, chloroform), ν_{max} 1738 cm^{-1} (C=O) (Found: C, 55.2; H, 7.2. $C_{25}H_{38}O_3$ calc.: C, 54.9; H, 7.0%).

Similarly, the following compounds were prepared from the respective alcohols: bis(1,2:3,4-di-*O*-isopropylidene-DL-xylitol) 5,5′-carbonate, b.p. 204–206°/0.5 mm, ν_{max} 1760 cm^{-1} (Found: C, 56.2; H, 7.8. $C_{23}H_{38}O_{11}$ calc.: C, 56.3; H, 7.8%); bis-(tetrahydropyran-2-methyl) carbonate, b.p. 132°/0.3 mm, ν_{max} 1747 cm^{-1} (Found: C, 60.3; H, 8.6. $C_{13}H_{22}O_5$ calc.: C, 60.4; H, 8.6%); bis(cyclohexanemethyl) carbonate (54%), b.p. 112°/0.25 mm, ν_{max} 1750 cm^{-1} (Found: C, 71.3; H, 10.3. $C_{15}H_{26}O_3$ calc.: C, 71.0; H, 10.3%; bis(*trans*-2-methoxycyclohexyl) carbonate (56%), b.p. 144°/0.5 mm, ν_{max} 1750 cm^{-1} (Found, C, 63.1; H, 9.2. $C_{15}H_{26}O_5$ calc.: C, 62.9; H, 9.15%).

Decomposition of haloformates. — Each haloformate was decomposed in a stream of nitrogen that was subsequently passed through Drechsel bottles containing aqueous barium hydroxide. The barium carbonate formed was collected, washed, dried, and weighed, and the amount was used to calculate the percentage of apparent decarboxylation. It must be emphasised that carbon dioxide is not necessarily the sole, gaseous product evolved.

(*a*) *6-*O*-Fluoroformyl-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactose.* A mixture of the fluoroformate (1.77 g) and pyridine (5 ml, 1.5 mol.) was heated for 15 h at 110–120° (50% decarboxylation). A solution of the reaction products in ether (100 ml) was washed successively with water, 10% aqueous cadmium chloride, 5% aqueous sodium hydrogen carbonate, and water. Evaporation of the dried ($MgSO_4$) ethereal solution, with recrystallisation of the residue from methanol, gave bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactose) 6,6′-carbonate, m.p. and mixed m.p. 134–135°. Examination of the mother liquors by t.l.c. (benzene–ether, 3:1) revealed a single component having mobility indistinguishable from that of the above dialkyl carbonate; no 6-deoxy-6-fluoro-1,2:3,4-di-*O*-isopropylidene-α-D-galactose[4] could be detected.

When the fluoroformate (3 g) was decomposed in pyridine (150 ml) for 15 h at 110–120°, the only detectable materials in the product mixture were the dialkyl carbonate and unchanged fluoroformate. A similar result was obtained when the fluoroformate was decomposed by boiling a solution in *N*,*N*-dimethylformamide containing pyridine and anhydrous potassium fluoride.

(*b*) *5-*O*-Fluoroformyl-1,2:3,4-di-*O*-isopropylidene-*DL*-xylitol.* A mixture of the fluoroformate (1.23 g) and pyridine (4 ml) was heated for 18 h at 110–120° (52% decarboxylation). The product mixture was processed essentially as in (*a*) to give a crude product (ν_{max} 1760 cm^{-1}) that contained a single component having a mobility in t.l.c. identical to that of bis(1,2:3,4-di-*O*-isopropylidene-DL-xylitol) 5,5′-carbonate. A portion (*ca.* 300 mg) of the product was saponified by treatment with a mixture of N sodium hydroxide (10 ml) and ethanol (10 ml) for 2 h at 60°. The mixture was extracted with chloroform (60 ml), and the extract was dried ($MgSO_4$) and concentrated to yield a product having a mobility in t.l.c. identical to that of 1,2:3,4-di-*O*-isopropylidene-DL-xylitol; the product gave[9] a *p*-phenylazobenzoate, m.p. 110–111° alone or in admixture with the ester prepared from 1,2:3,4-di-*O*-isopropylidene-DL-xylitol (Found: C, 65.2; H, 6.2; N, 6.3. $C_{24}H_{28}N_2O_6$ calc.: C, 65.5; H, 6.4; N, 6.4%).

(*c*) *2-(Chloroformyloxymethyl)tetrahydropyran.* On addition of pyridine (3 ml) to the chloroformate (1.46 g) at room temperature, smooth decomposition occurred and was complete after storage for 18 h at 110–120° (78% decarboxylation). The reaction mixture was processed as in (*a*), after the ether extract had been washed with dilute hydrochloric acid, to give a product, having ν_{max} 1750 (C=O) and 740 cm^{-1} (C-Cl), which contained components having mobilities identical to those of bis(tetrahydropyran-2-methyl) carbonate (t.l.c.) and 2-(chloromethyl)tetrahydropyran [g.l.c., (*b*)]. In a larger-scale experiment, fractional distillation of the product mixture gave 2-(chloromethyl)tetrahydropyran (70%), b.p. 165° (Found: C, 53.2; H, 7.4; Cl, 26.1. $C_6H_{11}ClO$ calc.: C, 53.5; H, 8.2; Cl, 26.4%).

(*d*) *2-(Fluoroformyloxymethyl)tetrahydropyran.* No evolution of gas occurred when a mixture of the fluoroformate (1.52 g) and pyridine (3 ml) was stored at room temperature, and decomposition was complete (53% decarboxylation) after 14 h at 110–120°. The product, isolated essentially as described in (*c*), had ν_{max} at 1750 cm^{-1}, and contained a single component having a mobility (t.l.c.) identical to that of bis(tetrahydropyran-2-methyl) carbonate. No 2-(fluoromethyl)tetrahydropyran could be detected by g.l.c. (*b*). In a subsequent experiment, distillation of the product gave bis(tetrahydropyran-2-methyl) carbonate (58%), b.p. 116°/0.05 mm.

(*e*) trans-*2-Methoxycyclohexyl chloroformate.* A mixture of the chloroformate (2.19 g) and pyridine (6.8 ml) was heated at *ca.* 100°, and the extent of decomposition, expressed as percentage of decarboxylation, was as follows: 45 min, 66%; 5.5 h, 81%; 22 h, 83%. The product was isolated as in (*c*) and distilled to give *cis,trans*-2-methoxycyclohexyl chloride (0.685 g, 40%), b.p. 80–90°/~20 mm. (Found: C, 56.8; H, 9.0; Cl, 23.6. $C_7H_{13}ClO$ calc.: C, 56.6; H, 8.8; Cl, 23.85%); examination by g.l.c. [(*a*), 126°] revealed two peaks in the ratio of 34:1, with the faster component preponderating. The slower component had a retention distance identical to that of *trans*-2-methoxycyclohexyl chloride (for preparation, see below).

A higher-boiling fraction (b.p. 90–200°/20 mm) from the above mixture had ν_{max} 1750 cm^{-1} (C=O) and a mobility (t.l.c., benzene–methanol, 9:1) identical to that of bis(*trans*-2-methoxycyclohexyl) carbonate.

(*f*) trans-*2-Methoxycyclohexyl fluoroformate.* When a mixture of the fluoroformate (1.0 g) and pyridine (4.0 ml) was heated at 90°, the decomposition, expressed as percentage of decarboxylation, was as follows: 4 h, 4%; 21 h, 18%; 24 h, 21%. The product was isolated as in (*c*) and distilled to yield starting material (0.24 g), b.p. 86°/~20 mm, and bis(*trans*-2-methoxycyclohexyl) carbonate.

(*g*) (*Chloroformyloxymethyl*)*cyclohexane*. When the chloroformate (7 g) was treated with pyridine (11 ml), an exothermic reaction occurred which was completed by elevation of the temperature to 110–120° for 24 h (89% decarboxylation). The cooled reaction mixture was extracted with ether (150 ml) as in (*c*), and the product was distilled to give (chloromethyl)cyclohexane (4 g, 74%), b.p. 168–170° (Found: C, 63.4; H, 9.8; Cl, 26.8. $C_6H_{11}Cl$ calc.: C, 63.4; H, 9.6; Cl, 26.8%).

The still residue was shown by g.l.c. (*b*) and i.r. spectroscopy to be a mixture of (chloromethyl)cyclohexane and bis(cyclohexylmethyl) carbonate.

(*h*) (*Fluoroformyloxy*)*cyclohexane*. No reaction occurred when the fluoroformate (1.4 g) was treated with pyridine (3.5 ml) at room temperature. Gas evolution began at 85–90° and was complete after 24 h at 110–120° (38% decarboxylation). The products were extracted with ether as in (*c*), and examination by g.l.c. (*b*) and i.r. spectroscopy revealed the presence of starting material, bis(cyclohexylmethyl) carbonate, and (fluoromethyl)cyclohexane.

(*i*) trans-*1,2-Bis*(*fluoroformyloxy*)*cyclohexane*. A mixture of the difluoroformate (6.5 g) and quinoline (2.6 g) was stored for 22 h at 160° in a stream of nitrogen. The material (1.5 ml) in the effluent gas stream was trapped at liquid air temperature and shown by g.l.c. (silicon gum–Celite) to contain cyclohexa-1,3-diene [characterised as the tetracyanoethylene adduct, m.p. 268° (from ethanol)] and a component (*X*) of higher retention time. On storage, hydrogen fluoride was evolved from the mixture, and the proportion of component *X* diminished.

The residual, non-volatile material was extracted with ether (100 ml), and the extract was washed with 3.5N hydrochloric acid (2 × 40 ml), dried ($MgSO_4$), and evaporated. Recrystallisation of the residue (1.3 g, 30%) from aqueous methanol gave the cyclic carbonate of cyclohexane-*trans*-1,2-diol, m.p. 54–55° alone or in admixture with the authentic compound[6], ν_{max} 1810 cm^{-1} (C=O) [Found: C, 59.1; H, 7.0: mol.wt. (micro-osometry), 143. $C_7H_{10}O_3$ calc.: C, 59.2; H, 7.0%; mol.wt., 142]. Saponification of the cyclic carbonate gave cyclohexane-*trans*-1,2-diol (63%), m.p. 102–103°.

trans-*2-Methoxycyclohexyl chloride*. *trans*-2-Chlorocyclohexanol[10] (10 g), on methylation with methyl iodide (40 g) and silver oxide (30 g) in the conventional manner, gave the title compound (5.27 g) (isolated by fractional distillation through a 10-cm Vigreux column), b.p. 106°/~15 mm (Found: C, 56.2; H, 8.5; Cl, 23.2. $C_7H_{13}ClO$ calc.: C, 56.6; H, 8.8; Cl, 23.8%). Examination of the product by g.l.c. (*a*) revealed *ca.* 2% of unidentified impurities.

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SUMMARY

It has been established that thermal and catalytic decomposition of certain alkyl haloformates affords dialkyl carbonates in addition to alkyl halides. Pyridine(or quinoline)-catalysed decomposition of ethyl and cyclohexyl chloroformate and ethyl fluoroformate affords high yields of alkyl halides, but cyclohexyl fluoroformate yields a significant proportion of dialkyl carbonate. In compounds containing the structural unit O·C-C·O·CO·Hal, chloroformates yield alkyl chlorides and dialkyl carbonates, whereas with fluoroformates, dialkyl carbonates are the sole products. The haloformates of the following compounds have been examined: cyclohexanemethanol, 2-(hydroxymethyl)tetrahydropyran, 1,2:3,4-di-*O*-isopropylidene-α-D-galactose, 1,2:3,4-di-*O*-isopropylidene-DL-xylitol, and *trans*-2-methoxycyclohexanol.

Quinoline-catalysed decomposition of *trans*-1,2-bis(fluoroformyloxy)cyclohexane affords mainly the cyclic carbonate of cyclohexane-*trans*-1,2-diol, together with small proportions of cyclohexa-1,3-diene and an unidentified, volatile product.

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