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THE REACTION OF 1,3,2-DIOXASTANNOLANS WITH DIACYL CHLORIDES: DECARBONYLATION IN THE REACTION WITH OXALYL CHLORIDE

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Summary

2,2-Dibutyl-1,3,2-dioxastannolans react with carbonyl chloride to give the corresponding ethylene carbonates, and with malonyl chloride or succinyl chloride to give the oligomeric malonates or succinates. The reaction of oxalyl chloride, however, depends of the number of methyl substituents carried by the carbon atoms of the ring; with none, ethylene oxalate is essentially the only product, but increasing methylation induces the evolution of carbon monoxide and the formation of the ethylene carbonate until, with four methyl substituents, only the carbonate of pinacol, and no oxalate is formed, providing a striking example of the Thorpe–Ingold effect. The mechanism of this decarbonylation is discussed.

Introduction

The nucleophilic reactivity of alcohols is enhanced by trialkylstannylation [1], and the dialkylstannylation of unsymmetrical 1,2-diols, particularly in carbohydrates, provides a means of regiospecific activation [2].

Shanzer has investigated the reactions of simple dioxastannolans (I) with diacyl chlorides $ClCO(CH_2)_nCOCl$, ($n = 3$–8), and has shown that they lead to the formation of tetralactones (II) rather than dilactones (III) [3].

The key to this behaviour in reacting regioselectively and in forming dimeric products probably lies in the fact that the dioxastannolans exist in solution not as the monomers (I) but as the dimers (IV) [4].

We report here the results of some parallel studies which we have been carrying out on the reaction of dioxastannolans with the lower acyl dichlorides, viz. carbonyl chloride, oxalyl chloride, malonyl chloride, and succinyl chloride. Whereas the behaviour of the other acid dichlorides was straightforward in that they led to the

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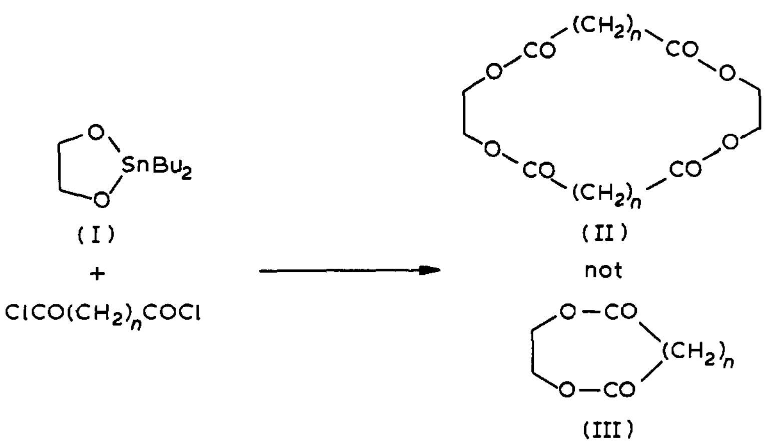
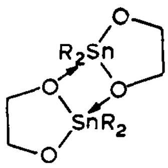


(1)

formation of the corresponding monomeric or polymeric diesters, that of oxalyl chloride is anomalous: alongside the oxalylation, a parallel reaction gives carbon monoxide and the cyclic carbonate, and this may become the principal reaction when the dioxastannolan is suitably substituted.



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Results and discussion

The dioxastannolans derived from dibutyltin oxide and ethane-1,2-diol (Va), propane-1,2-diol (Vb), butane-2,3-diol (Vc), and 2,3-dimethylbutane-2,3-diol (Vd), reacted exothermically with carbonyl chloride to give the monomeric cyclic carbonates in good yield (eq. 2 and Table 1). These carbonates have been prepared previously from the reaction of the diols with carbonyl chloride [5,6], or with diethyl carbonate in the presence of a base [5,7]. This new route to carbonates may be useful particularly in carbohydrate chemistry.

(2)

(Va; $R_2 = R'_2 = H_2$;
Vb; $R_2 =$ Me,H; $R'_2 = H_2$;
Vc; $R_2 =$ Me,H; $R'_2 =$ Me,H (*erythro*/*threo* = 1/2);
Vd; $R_2 = R'_2 = Me_2$)

The reaction of the dioxastannolans with malonyl chloride or succinyl chloride in carbon tetrachloride was similarly exothermic. The solvent was removed and the

(Continued on p. 255)

TABLE 1

PROPERTIES OF CARBONATES OF 1,2-DIOLS

Parent diol	Carbonate yield (%)	M.p. (°C) b.p.(°C/mmHg)	ν(C=O) (cm^{-1})	NMR τ($CDCl_3$) (Hz)	Mass spectrum m/z (int-%)
$HOCH_2CH_2OH$	78	33–34	1780, 1810	5.45 (s, CH_2O)	88 (40, M^+), 58 (5, M-CH_2O), 44 (24, $M-CO_2$) 43 (56, CH_3CO), 42 (6, CH_2CO), 30 (14, CHO), 29 (100, CHO).
$HOCHMeCH_2OH$	79	70(0.02)[a]	1800	8.49 (3H, d, CH_3) J 6, 5.88 (1H, t, CHH′), 5.40 (1H, t, CHH') J 7, 5.16 (1H, sextet, CHMe) J 7,	102 (4, M^+), 87 (16, $M-CH_3$), 58 (17, $M-CO_2$), 57 (100, $CHCO_2$), 43 (78, CH_3CO) 30 (67, CH_2O), 29 (86, CHO).
HOCHMeCHMeOH	93	85(0.06)[b]	1800	8.54 (6H, d, CH_3) J 6, 5.42–5.77 (2H, m, CH)	116 (2, M), 101 (2, $M-CH_3$), 57 (6, $CHCO_2$) 43 (100, CH_3CO), 29 (43, CHO).
$HOCMe_2CMe_2OH$	79	179–180[c]	1780	8.57 (s, Me).	145 (2, M-H), 85 (46, $M-CH_3CO_2$), 59 (100, CH_3CO_2); 58 (55, CH_2CO_2), 57 (54, $CHCO_2$), 43 (90, CH_3CO), 42 (70, CH_2CO), 41 (78, CHCO), 40 (11; C_3H_4) 39 (27, C_3H_3), 31 (10, CH_3O), 29 (30, CHO).

[a] Lit. [14] b.p. 79–80°C/0.08 mmHg. [b] Lit. [14] b.p. 83°C/0.06 mmHg. [c] Lit. [7] b.p. 180–181°C.

TABLE 2

PROPERTIES OF MALONATES OF 1,2-DIOLS

Parent diol	Malonate yield (%)	M.p. (°C)	M(obs. (calcd.))	M(obs.)/ M(calc.)	ν(C=O) (cm^{-1})	NMR $\tau(CDCl_3)$, J (Hz)
$HOCH_2CH_2OH$	77	–	–	polymer	–	6.53 (2H, s, CH_2CO), 5.55 (4H, s, CH_2O).
	19	157–158 [a]	265 [b,c] (130)	2.04	1746	
$HOCHMeCH_2OH$	62	viscous semi-solid	644 [d] (144)	4.47	1745	8.73 (3H, d, Me) J 7, 6.56 (2H, s, CH_2CO), 5.74(2H, d, CH_2O), 4.57–5.01 (1H, m, CHO)
HOCHMeCHMeOH	78	viscous oil	1282 [d] (158)	8.11	1740	8.75 (6H, d, Me), 6.58 (2H, s, CH_2CO), 4.95 (2H, q, CHO).
$HOCMe_2CMe_2OH$	87	120 (dec.)	751 [d] (186)	4.04	1730	8.75 (12H, s, Me), 6.70 (2H, s, CH_2CO)

[a] Sublimed from the polymers at 170–180°C/0.02 mmHg. [b] m/z 230 (1.3%, $M-CH_2O$), 217 (5%, $M-C_2H_3O$), 172 (6%, $M-CO_2C_2H_4O$), 144 (12%, $M-CO_2C_2H_5O_2C$), 131 (44%, $OCCH_2CO_2C_2H_4OH$), 113 (100%, $OCCH_2CO_2C_2H_3$), 86 (50%, $OCCH_2CO_2$), 69 (23%, HC_3O_2), 43 (41%, CH_3CO), 42 (88%, CH_2CO). This is the same as the spectrum reported in ref. 8. [c] In acetone. [d] In chloroform.

TABLE 3

PROPERTIES OF SUCCINATES OF 1,2-DIOLS

Parent diol	Succinate yield (%)	M.p. (°C)	M (obsd. (calcd.)	M(obs.)/ M(calcd.)	ν(C=O) (cm^{-1})	NMR ($CDCl_3$), J (Hz)
$HOCH_2CH_2OH$	89	99–100	288 [a] (144)	–	1728	7.34 (4H, s, CH_2CO), 5.69 (4H, s, CH_2O).
$HOCHMeCH_2OH$	65	–	875 [b] (158)	5.54	1739	8.72 (3H, d, Me) J 7, 7.32 (4H, s, CH_2CO), 5.80 (2H, d, CH_2O) J 6, 4.45–5.12 (1H, m, CH)
HOCHMeCHMeOH	68	–	703 [b] (172)	4.08	1738	8.77 (6H, d, Me) J 6, 7.32 (4H, s, CH_2CO), 4.70–5.30 (2H, m, CHO)
$HOCMe_2CMe_2OH$	70	139–141	599 [b] (200)	3.00	1728	8.47 (12H, s, Me), 7.42 (4H, s, CH_2CO)

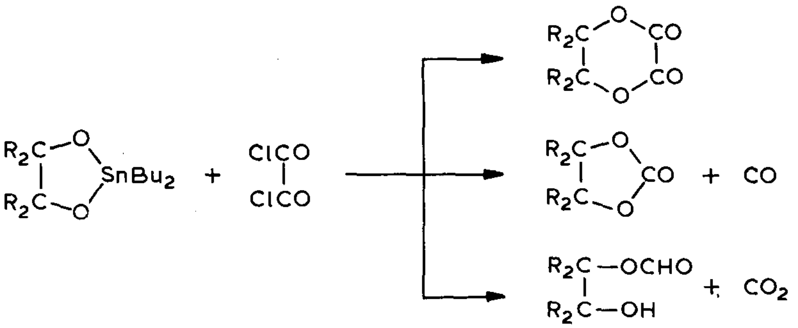
[a] By mass spectrometry. [b] By vapour pressure osmometry, in $CHCl_3$.

residue was thoroughly washed with pentane to remove dibutyltin dichloride. The properties of the products are given in Tables 2 and 3.

Under these conditions, the dioxastannolan (Va) with malonyl chloride gives a polymer which, by distillation from solid potassium carbonate, gave some dimer, identical (m.p., IR, NMR, and mass spectra) with material reported in the literature [8]. A polymer of molecular weight 2000–3000 has also been described [9]. The dioxastannolans Vb, Vc, and Vd gave oligomers with the average degree of polymerisation ca. 4.5, 8, and 4, respectively. The reaction of pinacol with malonyl chloride has been reported to give an oligomeric ester, m.p. 95°C, *M* 1420 [10].

Similarly, succinyl chloride reacted with Va to give an oligomer, m.p. 99–100°C, which showed a fragment ion for M_2^+ in the mass spectrum. The dimer has been reported to have m.p. 176–180°C. Under the same conditions, Vb, Vc, and Vd, gave oligomers with degree of polymerisation ca. 5.5, 4, and 3, respectively.

The nature of the reaction of the dioxastannolans with oxalyl chloride, however, depended on the degree of methylation of the diol moiety.



(3a)

(3b)

(3c)

The dioxastannolan from ethane-1,2-diol reacted exothermically with oxalyl chloride at 0°C with the evolution of a small amount of gas, and the ethylene oxalate was isolated in 85% yield (eq. 3a).

With progressive methylation of the diol, the amount of gas which was evolved in the reaction of the dibutyltin derivative with oxalyl chloride increased. The gas was collected and analysed by infrared and mass spectroscopy, and by absorption by potassium hydroxide, and was found to be largely carbon monoxide together with a small amount of carbon dioxide (see Table 4). The products were isolated by

TABLE 4

REACTIONS OF DIOXASTANNOLANS WITH OXALYL CHLORIDE

Dioxastannolan	Yields (%)			
	CO	CO_2	Carbonate	Oxalate
Va	6.5	0.35	–	85
Vb	19.0	1.2	19	66
Vc	55.1	2.9	51 [a]	36
Vd	76.0	2.0	72 [b]	–

[a] Found: C, 51.5; H, 6.66. $C_5H_8O_3$ calcd.: C, 51.7; H, 6.94%. [b] Found: C, 58.3; H, 8.43. $C_7H_{12}O_3$ calcd.: C, 58.3; H, 8.39%.

TABLE 5

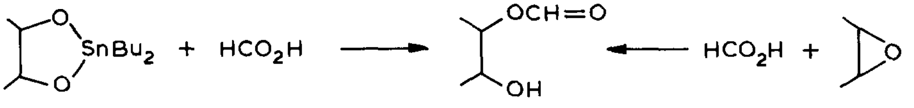
PROPERTIES OF OXALATES OF 1,2-DIOLS

Parent diol	Oxalate yield (%)	M.p. (°C) or b.p. (°C/mmHg)	M (obsd. (calcd.))	M(obsd.)./ M(calcd.)	ν(C=O) (cm^{-1})	NMR (τ), J (Hz)
$HOCH_2CH_2OH$	85	180 (dec.)	Polymer, insoluble [c]		1765	5.42 (s, CH_2) [a]
		147–156	Polymer, soluble [c]		1760	5.45 (s, CH_2) [a]
		138–140	123 (116)	1.06	1760	5.40 (s, CH_2); ($CDCl_3$) 5.30 [a]
HOCHMeCH_2OH	4	101 (dec.)	1392 (130)	10.7		8.57 (3H, d, Me) J 7, 5.40–5.70 (2H, m, CH_2O), 4.33–4.88 (1H, m, CHO) [b]
	62 [d]	128–132/0.07	139 (130)	1.07	1778	8.48 (3H, d, Me) J 7, 5.40–5.55 (2H, m, CHO), 4.71–5.28 (1H, m, CH) [b]
HOCHMeCHMeOH	36 [e]	110–115/0.07	152 (144)	1.05	1780	8.57 (6H, d, Me) J 7, 5.50–5.86 (2H, s, CH) [b]

[a] DMSO. [b] $CDCl_3$. [c] In acetone. [d] Found: C, 45.7; H, 4.81. $C_5H_6O_4$ calcd.: C, 46.2; H, 4.65%. [e] Found: C, 49.9; H, 5.27. $C_6H_8O_4$ calcd.: C, 50.0; H, 5.60%.

distillation and shown to comprise the oxalate (eq. 3a and Table 4) and the carbonate which was equivalent in amount to the carbon monoxide evolved (eq. 3b and Table 4). Properties of the oxalates are given in Table 5. When the diol carried four methyl groups, only the carbonate, and no oxalate, was isolated.

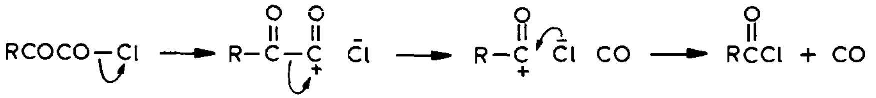
The small amount of organic product resulting from the loss of carbon dioxide was identified from the NMR spectrum as the appropriate 2-hydroxyethyl formate (eq. 3c), and this was confirmed by preparing the authentic material from the reaction of the dioxastannolan or the oxiran with formic acid (e.g. eq. 4).



(4)

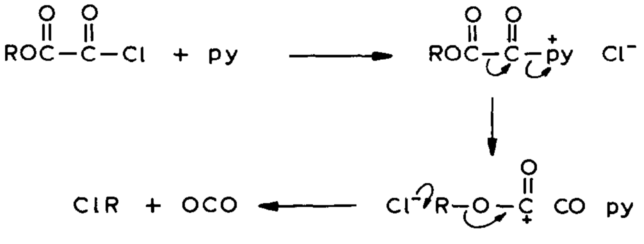
The carbonates from reaction 3b were identical with those obtained from reaction 2. The initial oxalate from 2,2-dibutyl-1,3,2-dioxastannolan itself (eq. 3a, $R_4 = H_4$) was shown to be largely a polymer by its insolubility in acetone; after sublimation from solid potassium carbonate it was obtained in both polymeric and dimeric forms, but the significance of this in relation to Shanzer's work is obscured by the fact that the monomer and polymer are known to be readily interconvertible [11]. Monomeric forms of the oxalates of propane-1,2-diol and 2,3-dimethylbutane-2,3-diol were isolated after distillation.

A number of reactions of oxalyl chloride are known which involve decarbonylation, but these can usually be understood in terms of the capture of an acylium ion by a chloride ion.



(5)

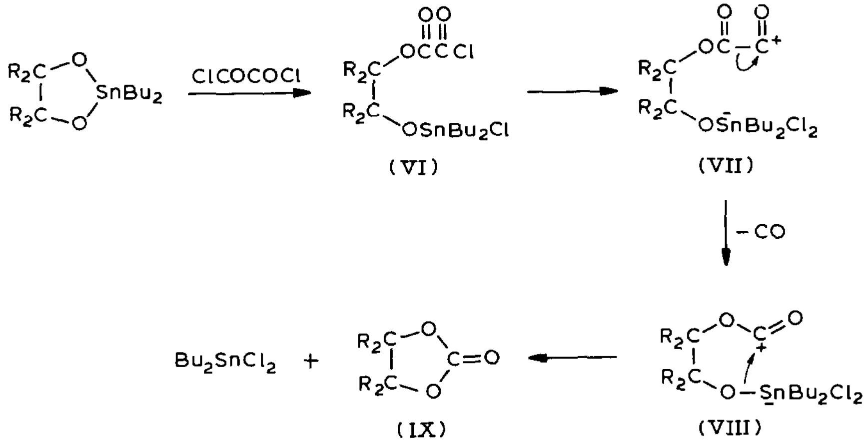
There appears to be no precedent for the formation of carbonate. The nearest analogy to our reaction is the study by Rhoads and Michel [12] of the reaction of the monoesters of oxalyl chloride with pyridine, when both CO and CO_2 are lost to give alkyl chlorides. Optically active 2-octyl- or 1-phenylethyl-oxalyl chlorides reacted with inversion of configuration, and it was concluded that the decarboxylation involved an S_N2 step. The decarbonylation and decarboxylation were written as synchronous processes, but in eq. 6 they are separated for clarity.



(6)

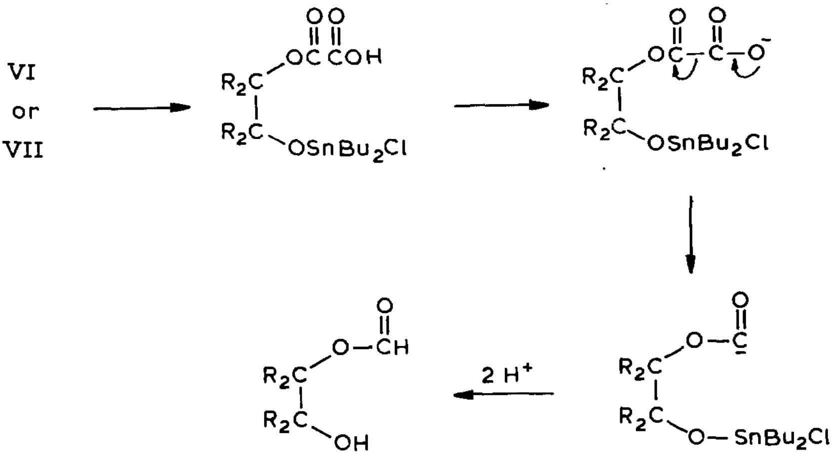
Our reaction 3b can be rationalised along similar lines. The first-formed alkyloxalyl chloride (VI) donates a chloride ion to the organotin moiety acting as an internal Lewis acid; the oxalylium ion (VII) decarbonylates to give the acylium ion

(VIII), which is captured by the β-stannyloxy nucleophile to give the carbonate IX and dibutyltin dichloride.



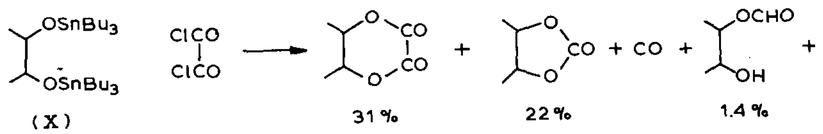
(7)

The side-reaction 3c to give the monoformate might then result from hydrolysis of VI or VII by adventitious water, followed by loss of electrofugal CO_2 rather than nucleofugal CO (eq. 8).



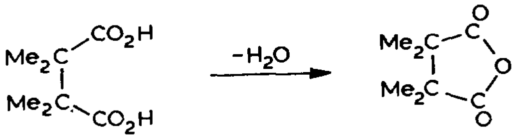
(8)

The decarbonylation and decarboxylation reactions to give carbonates and formates, are not confined to the dialkyltin derivatives of 1,2-diols, and the bis(tributyltin) derivative (X) reacted in the same way, to give the yields of isolated compounds shown in eq. 9.



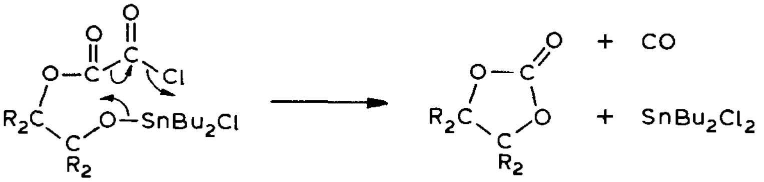
(9)

An interesting aspect of these reactions is the remarkable dependence of their course on the number of methyl substituents on the diol: with none, essentially only oxalate is formed, but with four, only carbonate. This presents a further example of the effect of substituents on the rate of ring-closure reactions to give small cyclic structures (the Thorpe–Ingold effect) [13] for which a number of interpretations have been proposed. An example in the literature, closely parallel to ours, is the facile dehydration of tetramethylsuccinic acid (eq. 10) compared with succinic acid itself [13].



(10)

As eq. 7 is written, the yield of carbonate is determined in the decarbonylation step VII → VIII, and it seems rather unlikely that this would be so strongly influenced by the change from a primary to a tertiary alkyl ester. The relative reactivity can however be rationalised if the steps VII → VIII and VIII → IX are combined so that decarbonylation is brought about by nucleophilic attack of the alkoxy group; t-alkoxy would be a better nucleophile than *p*-alkoxy, and would lead to more decarbonylation. Indeed it is possible that the three steps VI → VII, VII → VIII, and VIII → IX are all coupled so that the ring closure takes place through a 5-centre transition state (eq. 11).



(11)

Experimental

The dioxastannolans were prepared by azeotropic dehydration of a mixture of the 1,2-diol and dibutyltin oxide in toluene. Phosgene was obtained as a 20% solution in toluene (Fluka); oxalyl chloride, malonyl chloride, and succinyl chloride were commercial products (Aldrich).

Molecular weights in solution were measured using a Hewlett–Packard Vapour Pressure Osmometer, Model 302, operating at 37°C, using chloroform or acetone as solvent. The values given are averages of two of three measurements at different concentrations within the range 0.01–0.13 *M*.

Reaction of dioxastannolans with diacyl chlorides

The diacyl chloride in carbon tetrachloride or chloroform was added to the dioxastannolan in the same solvent, under nitrogen and with stirring, during 10–20 min, when an exothermic reaction occurred. The mixture was stirred for a further 30 min, then the solvent was removed on a rotary evaporator. The residue was extracted with pentane to remove dibutyltin dichloride, then purified by distillation, sublimation, or recrystallisation. The products were characterised by IR, ^{1}H NMR, and mass spectrometry, by measurement of molecular weights in solution, and by elemental analysis. Details of the carbonates are given in Table 1, malonates in Table 2, succinates in Table 3, and oxalates in Table 5.

Analysis of gases

The reaction between the dioxastannolans and oxalyl chloride was carried out on a 25 mmol scale in a 250 cm^3 flask connected to a gas burette. The evolved gas was analysed by IR spectroscopy using a 10 cm path cell, and by mass spectrometry, and by passing the gas through a trap containing 50% aqueous KOH and measuring the gain in weight of the trap. The results are given in Table 4.

Preparation of 3-hydroxybut-2-yl formate

(i) 2,3-Epoxybutane (3.6 g) and formic acid (2.3 g) were mixed, with cooling, in carbon tetrachloride (30 cm^3). The mixture was stirred at room temperature for 30 min, then distilled, yielding 3-hydroxybut-2-yl formate (2.8 g; 49%), b.p. 178–179°C, ν(C=O) 1725 cm^{-1}, $\tau(CDCl_3)$ 1.79 (1H, s, CHO), 4.72–5.22 (1H, m, C*H*OCHO), 5.73–6.64 (1H, m, C*H*OH), 8.60–9.01 (6H, m, Me). Mass spectrum m/z 117 (0.05%, $M-H$), 74 (51%, $M-$ MeCOH), 57 (11%, $CHCO_2$), 45 (100%, HCO_2). Found: C, 50.2; H, 8.70. $C_5H_{10}O_3$ calcd.: C, 50.8; H, 8.53%.

(ii) 2,2-Dibutyl-4,5-dimethyl-1,3,2-dioxastannolan (0.1 mol) prepared in benzene from butanediol and dibutyltin oxide, was treated with formic acid. Next day, two distillations gave $Bu_4Sn_2(O_2CH)_2O$ (44%), b.p. 114–116°C/0.03–0.04 mmHg, $\tau(CDCl_3)$ 1.67 (2H, s, CHO), 8.03–9.35 (18H, m, Bu), and 3-hydroxy-but-2-yl formate (38%), b.p. 179–180°C.

(iii) From the reaction between the bis(tributyltin) derivative of butane-2,3-diol and oxalyl chloride at room temperature in carbon tetrachloride, 3-hydroxy-but-2-yl formate was isolated in 1.4% yield.

Acknowledgement

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