

ORGANIC DERIVATIVES OF TIN

I. GLYCOLATES OF MONO-n-BUTYLTIN(IV)

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SUMMARY

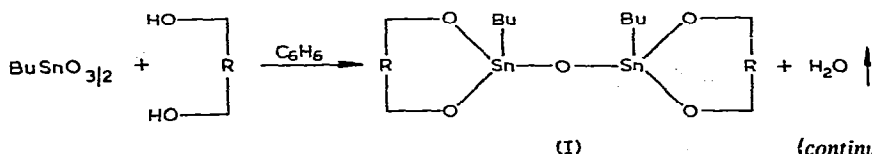
The reactions of mono-n-butyltin oxide and isopropoxide with various glycols in 1/1 and 2/3 molar ratios have given compounds of the types bis(n-butyltin glycolate)-oxide, alkylenedioxybis(n-butyltin glycolate) and n-butyltin glycolate isopropoxide. The molecular complexity of these glycol derivatives in boiling benzene has been determined. Tentative assignments of the IR bands of these compounds have been made.

INTRODUCTION

Spiro tin(IV) diglycolates have been synthesised by the alcohol interchange technique¹. Dibutyltin glycolates have been synthesised by the reactions of chloride^{2,3}, oxide^{4,5} and ethoxide^{6,7} with glycols. The product obtained by the reaction of oxide with ethane-1,2-diol was assigned a ten-membered ring structure, $\text{Bu}_2\text{Sn}(\text{OCH}_2\text{-CH}_2\text{O})_2\text{SnBu}_2$ ⁴.

RESULTS AND DISCUSSION

No work appears to have been carried out on the glycol derivatives of mono-alkyltin(IV). In the present communication we describe the preparation of some mono-n-butyltin derivatives of glycols (*viz.* ethane-1,2-diol, 2-mercaptoethanol, propane-1,2-diol, propane-1,3-diol, butane-1,3-diol, butane-2,3-diol, 2-methylpentane-2,4-diol and 2,3-dimethylbutane-2,3-diol) by the reactions of mono-n-butyltin oxide and isopropoxide with glycols in 1/1 and 2/3 molar ratios in benzene, with continuous azeotropic removal of the water or isopropanol formed:



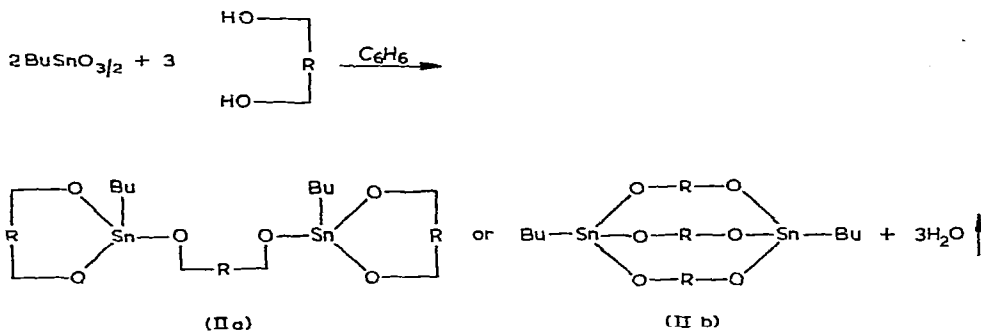
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TABLE I
GLYCOLATES OF MONO-n-BUTYL TIN

S. No.	Mono-n-butyltin oxide (θ)	Glycols added (θ)	Molar ratio	Product formed (state)	Yield (%)	M.p. ($^{\circ}$ C)	Analysis found (calcd.) (%) Sn	Mol. wt. found (calcd.)
1	3.01	HOCH ₂ CH ₂ OH (0.93)	1/1	(BuSnOCH ₂ CH ₂ O) ₂ O (White solid)	92	190-93	48.5 (48.7)	2305 (488)
2	1.84	HOCH ₂ CH ₂ OH (0.86)	2/3	(BuSnOCH ₂ CH ₂ O) ₂ (OCH ₂ CH ₂ O) (White solid)	86	98-100	45.0 (44.6)	1585 (532)
3	3.20	HOCH ₂ CH ₂ SH (1.27)	1/1	(BuSnOCH ₂ CH ₂ S) ₂ O ^e (Viscous liquid crystallises out as white solid on cooling)	89	107-109	46.0 (45.6)	916 (520)
4	3.43	HOCH ₂ CH ₂ SH (2.01)	2/3	(BuSnOCH ₂ CH ₂ S) ₂ (OCH ₂ CH ₂ S) ^b (Viscous liquid crystallises out as white solid on cooling)	91	103-105	40.7 (40.9)	665 (580)
5	3.53	HOCHMeCH ₂ OH (1.34)	1/1	(BuSnOCH ₂ CHMeO) ₂ O (White solid)	96	115-120	46.4 (46.0)	1046 (516)
6	3.56	HOCHMeCH ₂ OH (2.04)	2/3	(BuSnOCH ₂ CHMeO) ₂ (OCH ₂ CHMeO) (White solid)	97	78-80	41.8 (41.4)	751 (574)
7	4.21	HOCH ₂ CH ₂ CH ₂ OH (1.58)	1/1	(BuSnOCH ₂ CH ₂ CH ₂ O) ₂ O (White solid)	92	95-100	45.8 (46.0)	1035 (516)
8	4.18	HOCH ₂ CH ₂ CH ₂ OH (2.42)	2/3	(BuSnOCH ₂ CH ₂ CH ₂ O) ₂ (OCH ₂ CH ₂ CH ₂ O) (Low melting white solid)	85		41.7 (41.4)	623 (574)
9	3.70	HOCHMeCH ₂ CH ₂ OH (1.69)	1/1	(BuSnOCHMeCH ₂ CH ₂ O) ₂ O (Viscous liquid)	87		43.9 (43.6)	1025 (544)
10	3.70	HOCHMeCH ₂ CH ₂ OH (2.51)	2/3	(BuSnOCHMeCH ₂ CH ₂ O) ₂ (OCHMeCH ₂ CH ₂ O) (Viscous liquid)	92		38.3 (38.5)	594 (616)
11	4.18	HOCHMeCHMeOH (1.88)	1/1	(BuSnOCHMeCHMeO) ₂ O (White solid)	88	75-77	43.9 (43.6)	1060 (544)

12	3.74	HOCHMeCHMeOH (2.54)	2/3	(BuSnOCHMeCHMeO) ₂ (OCHMeCHMeO) (White solid)	86	42-44	38.7 (38.5)	635 (616)
13	4.12	HOCHMeCH ₂ CMe ₂ OH (2.43)	1/1	(BuSnOCHMeCH ₂ CMe ₂ O) ₂ O (Viscous liquid)	70		39.3 (39.6)	582 (600)
14	3.80	HOCHMeCH ₂ CMe ₂ OH (3.33)	2/3	(BuSnOCHMeCH ₂ CMe ₂ O) ₂ (OCHMeCH ₂ CMe ₂ O) (Viscous liquid)	85		34.1 (33.9)	669 (700)
15	3.84	HOCMe ₂ CMe ₂ OH (2.28)	1/1	(BuSnOCMe ₂ CMe ₂ O) ₂ O ^f (Viscous liquid crystallizes out as low melting white solid on cooling)	87		39.2 (39.6)	565 (600)
16	3.45	HOCMe ₂ CMe ₂ OH (3.07)	2/3	(BuSnOCMe ₂ CMe ₂ O) ₂ (OCMe ₂ CMe ₂ O) ^d (Viscous liquid)	86		34.1 (33.9)	675 (700)

^a % (-OCH₂CH₂S-); found: 29.2; calcd. 29.3%^b % (-OCH₂CH₂S-); found: 39.2; calcd. 39.4%^c % (-OCMe₂CMe₂O-); found: 38.4; calcd. 38.7%^d % (-OCMe₂CMe₂O-); found: 49.5; calcd. 49.8%.

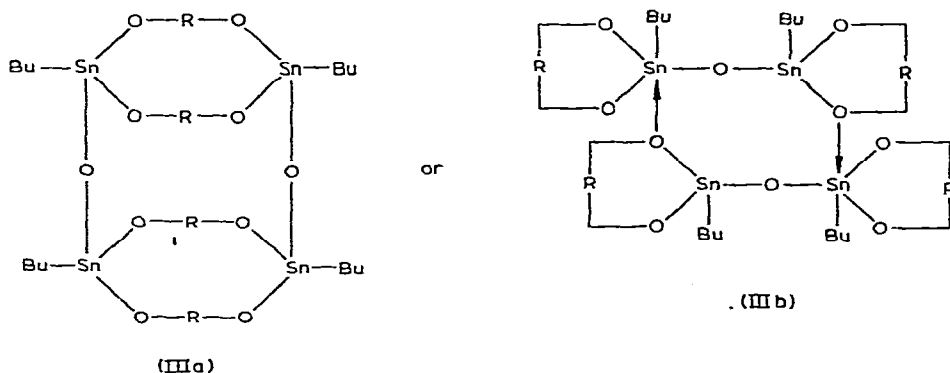


(R = $-\text{CH}_2\text{CH}_2-$, $-\text{CHMeCH}_2-$, $-\text{CH}_2\text{CH}_2\text{CH}_2-$, $-\text{CHMeCH}_2\text{CH}_2-$, $-\text{CHMeCHMe}-$, $-\text{CHMeCH}_2\text{CMe}_2-$ and $-\text{CMe}_2\text{CMe}_2-$)

The reactions proceed readily, and require 4–5 h for completion in refluxing benzene, except with the bulkier glycols (2-methylpentane-2,4-diol and 2,3-dimethylbutane-2,3-diol); in these cases, the reactions appear to be slowed down by steric effects.

The products are white solids or viscous liquids. Compounds of type (I) are dimeric in refluxing benzene, except for those derived from ethane-1,2-diol, 2-methylpentane-2,4-diol, or 2,3-dimethylbutane-2,3-diol; the product from ethane-1,2-diol has an average molecular association of 5 whereas those from the other two diols are monomeric. The 2/3 molar products, which can be represented as in (IIa) or (IIb), are all monomeric, except for the ethane-1,2-diol derivative, which is trimeric.

The association behaviour of these glycolates almost parallels those of the corresponding dibutyl products⁶, for which the ethane-1,2-diol derivative again shows the highest association. The dibutyltin derivatives of 2-methylpentane-2,4-diol and 2,3-dimethylbutane-2,3-diol are, however, dimeric⁶. In agreement with structures suggested by earlier workers for dialkyltin glycolates⁶, the dimeric compounds of the type (I) can be represented as the alternative structures (IIIa) or (IIIb).

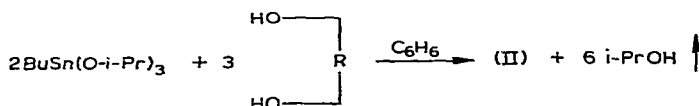
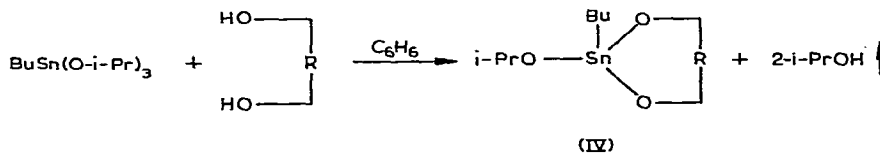


The molecular complexities of the products obtained from 2-mercaptoethanol are much lower than those of products derived from ethane-1,2-diol. The tendency towards reduction of the molecular complexity on replacement of an oxygen by a sulphur atom can be explained on the basis of the lower electronegativity of sulphur

compared with that of oxygen.

The marked lowering of molecular association in 2-methylpentane-2,4-diol and 2,3-dimethylbutane-2,3-diol derivatives appears to favour formula (IIIa) for the dimeric species.

Glycol derivatives of mono-*n*-butyltin have also been prepared by the reaction of mono-*n*-butyltin triisopropoxide with glycols in 1/1 and 2/3 molar ratios:



(R = $-\text{CH}_2\text{CH}_2-$ and $-\text{CHMeCH}_2\text{CMe}_2-$)

The 2/3 molar products obtained from these reactions are identical with those prepared from the oxide.

Thermograms of $\text{BuSnO}_{3/2}$ and of compounds 1,2 and 5 (see Table 1) were examined. The rate of decomposition was slow initially in each case, indicating a slow decomposition of the tin-carbon bonds, but this was followed by a rapid decrease in weight at about 250° (maxima observed for $\text{BuSnO}_{3/2}$ and compounds 1,2 and 5 were at 250 , 270 , 290 and 270°), and SnO_2 was finally produced.

IR spectra

The IR spectra (see Table 2) of mono-butyltin trichloride⁸ shows two $\nu(\text{Sn-C})$ bands at 596 and 518 cm^{-1} which are thought to arise from the conformational isomers. In all the mono-butyltin glycolate derivatives, two bands have been observed at $610 \pm 5\text{ cm}^{-1}$ and $520 \pm 20\text{ cm}^{-1}$ which may be due to $\nu(\text{Sn-C})$. Another common feature of the spectra of these compounds is the presence of a band of strong to medium intensity at $665\text{--}670\text{ cm}^{-1}$. This band is probably due to $\nu(\text{OSnO})$. A band has been observed at $\sim 650\text{ cm}^{-1}$ in alkyltin trialkoxides also and has been assigned to $\nu(\text{Sn-O})$ ⁹.

In compounds of the type (I), a band of rather low intensity occurs at $765 \pm 5\text{ cm}^{-1}$. This may be tentatively assigned to $\nu(\text{SnOSn})$. In bis(trialkyltin)oxides¹⁰, this band is generally found at $\sim 770\text{ cm}^{-1}$.

EXPERIMENTAL

Special precautions were taken to exclude moisture. Benzene (B.D.H.) was stored over sodium wire, and finally dried azeotropically with ethanol. All glycols were distilled before use. $\text{BuSnO}_{3/2}$ (Nitto Kasei Co. Ltd., Japan) was used as supplied. $\text{BuSn(O-}i\text{-Pr)}_3$ was prepared by the sodium method¹¹.

Molecular weight determinations were carried out in boiling benzene in a Galienkamp semi-micro ebullimeter. IR spectra were recorded on a Perkin-Elmer

TABLE 2

IR^a SPECTRA OF MONO-*n*-BUTYL TIN GLYCOLATES

$(\text{BuSnOCH}_2\text{CH}_2\text{O})_2\text{O}^b$: 2950 vs(br), 2850 vs(br), 1450 vs. 1400(sh), 1360 s, 1325(sh), 1290 vw, 1260–1240 w(br), 1180(sh), 1160 w, 1115 and 1105 m(d), 1070 vs, 1060 (sh), 1030(sh), 1010 vw, 900 vs(br), 850(sh), 800 vw, 770 vw, 720(sh), 670 s, 615 s(br), 505 m, 455 m.

$(\text{BuSnOCH}_2\text{CH}_2\text{O})_2(\text{OCH}_2\text{CH}_2\text{O})^b$: 2950 vs(br), 2850 vs(br), 1450 vs, 1400(sh), 1360 s, 1325(sh), 1200(sh), 1145 w, 1115(sh), 1070 vs, 1020(sh), 890 m(br), 715 vw, 665 w, 610 m(br), 510 w(br), 440 w(br).

$(\text{BuSnOCH}_2\text{CH}_2\text{S})_2\text{O}^b$: 2950(sh), 2920 vs, 2850 vs, 1600 vw(br), 1440 m, 1360 m, 1278 m, 1245(sh), 1210 w, 1178 w, 1145 w, 1080 w, 1050(sh), 1040 vs, 1015 s, 1005 vs, 950(sh), 938 s, 875 vw, 855 w, 840 m, 715 vw(br), 665 and 655 w(d), 605 m, 585 s, 540(sh), 415 w(br).

$(\text{BuSnOCH}_2\text{CH}_2\text{S})_2(\text{OCH}_2\text{CH}_2\text{S})^b$: 2965–2945 vs(br), 1600 vw(br), 1440 vs. 1400(sh), 1355 s, 1280 vs, 1245 w, 1215 m, 1180 m, 1150 m, 1080(sh), 1060(sh), 1045 vs, 1015(sh), 1010 vs, 940 vs, 875(sh), 855(sh), 845 s, 760 vw, 735 vw, 710 vw, 692 w, 680(sh), 660 m, 610(sh), 600(sh), 585 vs, 505 vw, 430 m(br).

$(\text{BuSnOCH}_2\text{CHMeO})_2\text{O}^b$: 2950(sh), 2905 vs, 2850 vs, 1600 vw(br), 1440 s, 1400(sh), 1355 m, 1250 vw(br), 1215(sh), 1175(sh), 1135 s(br), 1120 s(br), 1075(sh), 1045 vs(br), 1010(sh), 990(sh), 940 m(br), 845 m, 765 m, 610 s(br), 485 m(br).

$(\text{BuSnOCH}_2\text{CHMeO})_2(\text{OCH}_2\text{CHMeO})^b$: 2950(sh), 2905 vs, 2850 vs, 1600 vw(br), 1440 s, 1400(sh), 1355 m, 1250 vw(br), 1140–1120 s(br), 1095 s(br), 1050 vs(br), 1000 m(br), 930 m(br), 845 m, 715 w(br), 670 m, 610 s(br), 520 w(br).

$(\text{BuSnOCH}_2\text{CH}_2\text{CH}_2\text{O})_2(\text{OCH}_2\text{CH}_2\text{CH}_2\text{O})^b$: 2950(sh), 2905 vs, 2850 vs, 1600 vw(br), 1440 s, 1400(sh), 1355 m, 1250 vw(br), 1180 w(br), 1060 vs(br), 980 m, 935–915 m(br), 865 vw, 840(sh), 815 vw, 765(sh), 665 s(br), 615 vs(br), 530 vs(br).

$(\text{BuSnOCHMeCHMeO})_2\text{O}^b$: 2960(sh), 2915 vs, 2850 vs, 1525 w, 1430 s, 1400(sh), 1350 s, 1280 w(br), 1160 m, 1125 m, 1090(sh), 1080(sh), 1070 vs(br), 1010 s, 990(sh), 960 w, 920 s, 880 m, 815 vw, 770 vw(br), 700(sh), 665 m(br), 610 s(br), 540 s, 460 w(br).

$(\text{BuSnOCMe}_2\text{CMe}_2\text{O})_2\text{O}^b$: 2950 vs, 2925 vs, 2855 vs, 1600 vw(br), 1450 m, 1360 m, 1325(sh), 1245 vw, 1180(sh), 1155 vs, 1105(sh), 1020–1000 w(br), 945 s, 880 m, 820 w, 765(sh), 665 s, 615 vs(br), 540 vs(br), 490(sh).

$(\text{BuSnOCMe}_2\text{CMe}_2\text{O})_2(\text{OCMe}_2\text{CMe}_2\text{O})^b$: 2960–2925 vs(br), 2860 vs, 1600 vw(br), 1450 s, 1415 s, 1250 vw, 1180(sh), 1160–1145 vs(br), 1110(sh), 1085(sh), 1020–1005 w(br), 950 vs, 920(sh), 880 s, 825 w, 685(sh), 670 s(br), 615 vs(br), 540 s(br).

$(\text{BuSnOCHMeCH}_2\text{CMe}_2\text{O})_2\text{O}^c$: 2960 vs, 2930 vs, 2860 vs, 1600 vw(br), 1450 and 1400 m(d), 1360 s, 1310 w, 1290 vw, 1255 w, 1230(sh), 1155 vs, 1115 m, 1075 m(br), 1040 m(br), 1005(sh), 965 w, 940 vw, 900 s, 875 m, 830 w, 760 w, 665 s(br), 615 vs(br), 540 vs(br).

$(\text{BuSnOCHMeCH}_2\text{CMe}_2\text{O})_2(\text{OCHMeCH}_2\text{CMe}_2\text{O})^c$: 2960 vs, 1935 vs, 2870 vs, 1600 vw(br), 1450 and 1405 s(d), 1360 vs, 1310 m, 1290 vw, 1255 m, 1225(sh), 1155 vs, 1115 m, 1075 m, 1040 m, 1015(sh), 965 w, 940 vw, 900 s, 875 m, 835 m, 760 w, 670 s(br), 615 vs(br), 535 s(br).

$\text{BuSn}(O-i\text{-Pr})(\text{OCH}_2\text{CH}_2\text{O})^c$: 2950–2850 vs(br), 2660 w, 1560 vw, 1445 s, 1400 m, 1355 s, 1330 s, 1290 w, 1250(sh), 1240 w, 1160 s, 1120 vs, 1080–1060 vs(br), 975 and 950 s(d), 890 vs(br), 830 m, 755 vw, 670 vs, 620–595 vs(br), 530 m(br).

$\text{BuSn}(O-i\text{-Pr})(\text{OCHMeCH}_2\text{CMe}_2\text{O})^c$: 2955 vs, 2920 vs, 2850 s, 1450 s, 1410 m, 1355 vs, 1325 s, 1260 m, 1220 m, 1180 s, 1155 vs, 1120 vs, 1075 s, 1035 s, 970–955 s(br), 925 vs, 875–860 w(br), 840–825 m(br), 780 w, 665 w(br), 615(sh), 590–570 vs(br), 500 w(br).

^a IR data are given in cm^{-1} followed by an indication of intensity. The following abbreviations are used: s strong, vs very strong, m medium, w weak, vw very weak, (br) broad, d doublet, (sh) shoulder, ^b IR of solid compounds as nujol mull. ^c IR of neat liquid.

337 Grating Spectrophotometer. Thermogravimetric analyses were carried out on Stanton (Mass-flow type) Automatic Recording Thermogravimetric Balance.

Tin was estimated as SnO_2 . Pinacol¹², isopropanol (in azeotrope)¹³ and thio groups¹⁴ were estimated by oxidimetric methods.

Reaction of $\text{BuSnO}_{3/2}$ with ethane-1,2-diol in 1/1 molar ratio

To a benzene solution of $\text{BuSnO}_{3/2}$ (3.01 g; 15.1 mmoles) was added ethane-1,2-diol (0.93 g; 15 mmoles). The mixture was shaken well for about 5 min and then refluxed (bath temp. 115–120°) for about 4 h, while the water formed was continuously removed azeotropically with benzene. The excess of solvent was distilled out. On drying the product under reduced pressure, a white crystalline solid (3.4 g; m.p. 190–193°) was obtained. (Found: Sn, 48.9. Mol. wt., 2305. $\text{Sn}_2\text{C}_{12}\text{H}_{26}\text{O}_5$ calcd.: Sn, 48.7%. Mol. wt., 488.)

Reaction of $\text{BuSnO}_{3/2}$ with ethane-1,2-diol in 2/3 molar ratio

By the above procedure, a mixture of $\text{BuSnO}_{3/2}$ (1.84 g; 9.21 mmoles) and ethane-1,2-diol (0.86 g; 13.9 mmoles) gave a white crystalline solid (2.62 g; m.p. 98–100°). (Found: Sn, 45.0. Mol. wt., 1585. $\text{Sn}_2\text{C}_{14}\text{H}_{30}\text{O}_6$ calcd.: Sn, 44.6%. Mol. wt., 532.)

Similar compounds prepared with various glycols are summarised in Table 1.

Reaction between $\text{BuSn}(\text{O-i-Pr})_3$ and ethane-1,2-diol in 1/1 molar ratio

$\text{BuSn}(\text{O-i-Pr})_3$ (1.70 g; 4.82 mmoles) and ethane-1,2-diol (0.30 g; 4.84 mmoles) were mixed in 70 ml benzene. The reaction was exothermic. This mixture was refluxed and the binary azeotrope (benzene/isopropanol) was collected. Removal of the excess of solvent under vacuum gave a yellow coloured viscous liquid (1.40 g). (Isopropanol in azeotrope; found: 0.56 g. Calcd.: 0.57 g.) (Found: Sn, 40.5. $\text{SnC}_9\text{H}_{20}\text{O}_3$ calcd.: Sn, 40.2%.)

Reaction between $\text{BuSn}(\text{O-i-Pr})_3$ and ethane-1,2-diol in 2/3 molar ratio

By the above procedure a mixture of $\text{BuSn}(\text{O-i-Pr})_3$ (2.34 g; 6.63 mmoles) and ethane-1,2-diol (0.62 g; 10 mmoles) yielded a white crystalline solid (1.61 g; m.p. 98–100°). Isopropanol in azeotrope; found: 1.12 g. Calcd.: 1.20 g.) (Found: Sn, 44.9. Mol. wt., 2231. $\text{Sn}_2\text{C}_{14}\text{H}_{30}\text{O}_6$ calcd.: Sn, 44.6%. Mol. wt., 532.)

Reaction between $\text{BuSn}(\text{O-i-Pr})_3$ and 2-methylpentane-2,4-diol in 1/1 molar ratio

$\text{BuSn}(\text{O-i-Pr})_3$ (2.27 g; 6.43 mmoles) and 2-methylpentane-2,4-diol (0.76 g; 6.44 mmoles) gave a yellow coloured viscous liquid (2.24 g). (Isopropanol in azeotrope; found: 0.76 g. Calcd.: 0.77 g.) (Found: Sn, 33.5. $\text{SnC}_{13}\text{H}_{28}\text{O}_3$ calcd.: Sn, 33.8%.)

Reaction between $\text{BuSn}(\text{O-i-Pr})_3$ and 2-methylpentane-2,4-diol in 2/3 molar ratio

A mixture of $\text{BuSn}(\text{O-i-Pr})_3$ (1.67 g; 4.73 mmoles) and 2-methylpentane-2,4-diol (0.84 g; 7.12 mmoles) gave a yellow coloured viscous liquid (1.65 g). (Isopropanol in azeotrope; found: 0.83. Calcd.: 0.85 g.) (Found: Sn, 33.5. Mol. wt., 571. $\text{Sn}_2\text{C}_{26}\text{H}_{54}\text{O}_6$ calcd.: Sn, 33.9%. Mol. wt., 600.)

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