Synthesis and Characterisation of Heterobimetallic Organotin(IV) Glycolates Containing Aluminium

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ABSTRACT

Interactions of $\text{Al}(\text{OPr}^i)_3$ with two equivalents of a variety of glycols (HOGOH) yield homometallic glycolates $\text{Al}(\text{OGO})(\text{OGO})$ ($\text{G} = \text{CMe}_2\text{CH}_2\text{CHMe}$ (1), CMe_2CMe_2 (2), or $\text{CMe}_2\text{CH}_2\text{CH}_2\text{CMe}_2$ (3)) having one residual hydroxy group, which on reactions with $\text{Bu}_2\text{Sn}(\text{OPr}^i)_2$ or $\text{Bu}_3\text{Sn}(\text{OPr}^i)$ in 1:1 molar ratio afford heterobimetallic compounds of the general formulae $\text{Al}(\text{OGO})_2\text{Bu}_2\text{Sn}(\text{OPr}^i)$ ($\text{G} = \text{CMe}_2\text{CH}_2\text{CHMe}$ (4), CMe_2CMe_2 (5), $\text{CMe}_2\text{CH}_2\text{CH}_2\text{CMe}_2$ (6)) and $\text{Al}(\text{OGO})_2\text{Bu}_3\text{Sn}$ ($\text{G} = \text{CMe}_2\text{CH}_2\text{CHMe}$ (7), CMe_2CMe_2 (8)), respectively. All these derivatives have been characterised by elemental analyses, molecular weight measurements and spectroscopic (IR; NMR, ^1H , ^{27}Al , and ^{119}Sn) studies.

INTRODUCTION

In spite of some developments in the chemistry of homometallic glycolate derivatives of di- and tetra-valent tin /1-2/, the heterobimetallic glycolates based on organotin(IV) moieties appear not to have been investigated /3/ so far. We, therefore, report in this paper, for the first time, the synthesis and characterisation of heterobimetallic glycolate derivatives of organotin(IV) containing aluminium. The present study assumes additional significance because a heterobimetallic organotin(IV) derivative containing both a reactivity modifier /4/ glycolate group and a reactive alkoxide group(s) may prove a better precursor for the synthesis via sol-gel process of heterometal systems /1-3/ containing an organotin oxide and / or hydroxide moiety.

MATERIALS AND METHODS

Special precautions were taken to exclude moisture from the reaction apparatus, solvents, and reactants. Solvents such as benzene, isopropyl alcohol, *n*-hexane, and dichloromethane were purified and dried by

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standard procedures /5/. $\text{Bu}_2\text{Sn}(\text{OPr}^i)_2$ /6/ and $\text{Bu}_3\text{Sn}(\text{OPr}^i)$ /2/ were prepared by the literature methods. Aluminium isopropoxide was prepared /7/ by the reaction of aluminium foils with isopropyl alcohol in the presence of a catalyst, HgCl_2 or I_2 . Glycols: 2-methylpentane-2,4-diol (b.p. $198^\circ\text{C}/750\text{ mm}$); 2,3-dimethylbutane-2,3-diol (b.p. $171^\circ\text{C}/750\text{ mm}$); and 2,5-dimethylhexane-2,5-diol (sublimation temp. $80^\circ\text{C}/0.1\text{ mm}$) were dried and purified by refluxing over $\text{Al}(\text{OPr}^i)_3$, followed by distillation prior to use. Isopropyl alcohol in the azeotrope was determined /8-10/ oxidimetrically. Aluminium was determined /11/ as oxinate, while tin was determined /11/ as its oxide. Molecular weights were determined cryoscopically in benzene solution. ^1H (89.55 MHz), ^{27}Al (23.29 MHz), and ^{119}Sn (33.35 MHz) NMR were recorded in CDCl_3 and C_6H_6 solutions on a JEOL FX 90Q spectrometer. IR spectra ($4000\text{-}200\text{ cm}^{-1}$) were recorded as Nujol mulls on a Nicolet Magna 550 spectrophotometer. Carbon and hydrogen analyses were performed on a Perkin Elmer-2400 II CHNS/O analyser.

Preparation of glycolate derivatives

Due to similarity in the synthetic procedures for the new homo- and heterobimetallic derivatives, only one typical synthesis of each class is described in detail for the sake of brevity, while preparative and analytical details of all the derivatives are summarized in Table I.

Preparation of $\text{Al}(\text{OCMe}_2\text{CH}_2\text{CHMeO})(\text{OCMe}_2\text{CH}_2\text{CHMeOH})$ (1)

A benzene (~50 ml) solution containing $\text{Al}(\text{OPr}^i)_3$ (2.42 g, 11.84 mmol) and $\text{HOCMe}_2\text{CH}_2\text{CHMeOH}$ (2.80 g, 23.69 mmol) was refluxed under a fractionating column for ~6 h with continuous removal of the liberated isopropyl alcohol as an azeotrope with benzene and estimated periodically to monitor the progress and completion of the reaction. When the distillate showed negligible presence of isopropyl alcohol, refluxing was stopped and the excess solvent was removed under reduced pressure to obtain a white sticky solid (3.06 g, 99%) (1). The recrystallization from 2:1 mixture of *n*-hexane and dichloromethane at -20°C yielded a white powdery solid. Yield 2.78 g (91%).

Adopting a similar procedure compounds (2) and (3) were also prepared respectively by the reactions of $\text{Al}(\text{OPr}^i)_3$ with $\text{HOCMe}_2\text{CMe}_2\text{OH}$ and $\text{HOCMe}_2\text{CH}_2\text{CH}_2\text{CMe}_2\text{OH}$.

Preparation of $\text{Al}(\text{OCMe}_2\text{CH}_2\text{CHMeO})_2\text{Bu}_2\text{Sn}(\text{OPr}^i)$ (4)

The reaction mixture consisting of $\text{Al}(\text{OCMe}_2\text{CH}_2\text{CHMeO})(\text{OCMe}_2\text{CH}_2\text{CHMeOH})$ (1.77 g, 6.79 mmol) and $\text{Bu}_2\text{Sn}(\text{OPr}^i)_2$ (2.39 g, 6.80 mmol) in benzene (~30 ml) was refluxed for ~4 h. The liberated isopropyl alcohol (0.40 g) was fractionated out during the above-mentioned time and determined. After completion of the reaction, the volatile components from the solution were removed under reduced pressure to yield a white waxy solid (3.63 g) (4), which was distilled at $193^\circ\text{C}/0.3\text{ mm}$ as an analytically pure product in quantitative yield (3.23 g, 89 %).

Derivatives (5), (6), (7), and (8) were also prepared in a manner similar to (4). Preparative, analytical, and

Table I
Preparative, analytical, and some physical data for the new derivatives

Reactants (g, mmol)		Liberated Pr ¹ OH Found (Calcd.)	Product Colour and state (b.p. °C/mm) yield (g, %)	% Analysis Found (Calcd.)				M. Wt ^c Found (Calcd.)
A((OPr ¹) ₃)	HOGOH			SN	AL	C	H	
(2.42, 11.84)	G = OCM ₂ CH ₂ CHMeO (2.80, 23.69)	2.12 (2.13)	Al(OCMe ₂ CH ₂ CHMeO)(OCMe ₂ CH ₂ CHMeOH) (1) White solid, m.p. 66°C, 2.78 ^a , 91	-	10.32 (10.37)	55.55 (55.31)	9.61 (9.68)	289 (260)
(1.73, 8.46)	G = OCM ₂ CH ₂ CHMeO (2.00, 16.92)	1.51 (1.52)	Al(OCMe ₂ CH ₂ CHMeO)(OCMe ₂ CH ₂ CHMeO) (2) White solid, m.p. 72°C, 1.95 ^a , 89	-	10.32 (10.37)	54.89 (55.31)	9.76 (9.68)	275 (260)
(2.97, 14.53)	G = OCM ₂ CH ₂ CH ₂ CHMeO (1.25, 29.06)	2.62 (2.62)	Al(OCMe ₂ CH ₂ CH ₂ CHMeO)(OCMe ₂ CH ₂ CH ₂ CHMeOH) (3) White solid, m.p. 68°C, 4.28 ^a , 93	-	8.51 (8.53)	60.28 (60.67)	10.14 (10.51)	324 (316)
(1) (1.77, 6.79)	Bu ₂ Sn(OPr ¹) ₂ (2.39, 6.80)	0.39 (0.40)	Al(OCMe ₂ CH ₂ CHMeO) ₂ Bu ₂ Sn(OPr ¹) (4) Colourless waxy solid (193/0.3), 3.23 ^b , 89	21.52 (21.58)	4.85 (4.89)	49.88 (50.05)	8.84 (8.89)	573 (551)
(2) (1.78, 6.83)	(2.40, 6.83)	0.41 (0.41)	Al(OCMe ₂ CH ₂ CHMeO) ₂ Bu ₂ Sn(OPr ¹) (5) White waxy solid (190/0.2), 3.24 ^b , 85	21.50 (21.58)	4.85 (4.89)	50.56 (50.06)	9.04 (8.89)	564 (551)
(3) (1.17, 3.69)	(1.30, 3.70)	0.22 (0.22)	Al(OCMe ₂ CH ₂ CH ₂ CHMeO) ₂ Bu ₂ Sn(OPr ¹) (6) White waxy solid (193/0.3), 3.23 ^b , 89	19.26 (19.53)	4.46 (4.44)	53.32 (53.34)	9.80 (9.45)	628 (607)
(1) (2.14, 8.22)	Bu ₃ Sn(OPr ¹) (2.87, 8.22)	0.48 (0.49)	Al(OCMe ₂ CH ₂ CHMeO) ₂ Bu ₃ Sn (7) White waxy solid (130/0.2), 3.82 ^b , 85	21.58 (21.60)	4.90 (4.91)	52.50 (52.42)	9.48 (9.35)	561 (549)
(2) (1.68, 6.45)	(2.25, 6.44)	0.37 (0.38)	Al(OCMe ₂ CH ₂ CHMeO) ₂ Bu ₃ Sn (8) White waxy solid (134/0.2), 3.11 ^b , 88	21.54 (21.60)	4.89 (4.91)	52.40 (52.42)	9.41 (9.35)	567 (549)

^a Refers to recrystallized compound. ^b Refers to distilled compound. ^c For freshly prepared compound.

some physical data are listed in Table 1.

RESULTS AND DISCUSSION

Reactions of $\text{Al}(\text{OPr}^i)_3$ with different glycols in 1:2 molar ratio in benzene afford soluble homometallic derivatives (eq (1)):

$\text{G} = \text{CMe}_2\text{CH}_2\text{CHMe}$ (**1**), CMe_2CMe_2 (**2**), $\text{CMe}_2\text{CH}_2\text{CH}_2\text{CMe}_2$ (**3**)

Reactions of (**1**), (**2**), or (**3**) with $\text{Bu}_2\text{Sn}(\text{OPr}^i)_2$ or $\text{Bu}_3\text{Sn}(\text{OPr}^i)$ in 1:1 molar ratio in benzene under refluxing condition yield heterobimetallic derivatives (**4**), (**5**), (**6**) (eq. (2)), (**7**), and (**8**) (eq (3)):

$\text{G} = \text{CMe}_2\text{CH}_2\text{CHMe}$ (**4**), CMe_2CMe_2 (**5**), $\text{CMe}_2\text{CH}_2\text{CH}_2\text{CMe}_2$ (**6**)

$\text{G} = \text{CMe}_2\text{CH}_2\text{CHMe}$ (**7**), CMe_2CMe_2 (**8**)

All these new derivatives (**1**)-(**8**) are white solids, soluble in common organic solvents. The freshly prepared complexes (**1**)-(**8**) depict monomeric behaviour, but on aging homometallic derivatives (**1**)-(**3**) exhibit a tendency to association.

Spectroscopic Studies

Infrared spectra

Homometallic glycolates (**1**)-(**3**) (Figure 1, Table II), exhibit broad absorption bands in the 3333-3233 cm^{-1} region due to the presence of intramolecular hydrogen-bonded OH group. Other structurally important infrared absorptions appear at 1048-1008 cm^{-1} ($\nu(\text{C-O})$) and 653-647 cm^{-1} ($\nu(\text{Al-O})$). As expected, the heterobimetallic derivatives (**4**)-(**8**) show absence of band due to OH group and presence of absorption bands due to $\nu(\text{C-O})$ and $\nu(\text{Al-O})$ without considerable shifting. The derivatives (**4**)-(**6**) exhibit additional absorptions characteristic of the Bu_2SnO_2 moiety /12/ in the regions 729-680 (Sn-CH_2 *gauche*), 666-640 (Sn-CH_2 *trans*), 598-582 cm^{-1} ($\nu(\text{Sn-O}) + \nu(\text{Sn-C})$), 526-516 cm^{-1} ($\nu(\text{Sn-C})$) and 484-451 cm^{-1} ($\nu(\text{Sn-O})$). The band appearing at $\sim 465 \pm 15 \text{ cm}^{-1}$ may be attributed to $\nu(\text{O} \rightarrow \text{Sn})$ /13/. The presence of tributyltin moiety in derivatives (**7**) and

Table II
IR (cm⁻¹) and NMR (¹H, ¹¹⁹Sn, and ²⁷Al) (δ, ppm) spectral data for homo and heterometallic glycolates

Compd. No.	ν(OH)	ν(OPr ⁱ)	ν(C-O)	ν(Al-O)	ν(Sn-C)	ν(Sn-O)	¹ H	²⁷ Al	¹¹⁹ Sn
(1)	3278	-	1041 1008	647	-	-	1.17 (d, 6H, CHMe); 1.27 (s, 6 H, CMe), 1.33 (s, 6H CMe) 1.51 (d, 4H, CH ₂); 3.38 (br, 1H, OH); 4.34 (br, 2H, CHMe)	55	-
(2)	3233	-	1048 1016	648	-	-	1.20 (s, 24H, CMe ₂); 2.01 (s, 1H, OH)	63	-
(3)	3333	-	1033 1022	653	-	-	1.24 (s, 24H, CMe ₂); 1.59 (s, 8H, (CH ₂) ₂); 1.74 (s, 1H, OH)	61	-
(4)	-	1180 1147	1041 1010	648	516 582	451 582	0.97 (t, 6H, Sn(CH ₂) ₃ Me); 1.17-1.34 (m, 24H, CHMe + CMe ₂ + CHMe ₂); 1.45-1.59 (m, 16H, Sn(CH ₂) ₃ Me + CH ₂ (G)); 4.27 (br, 3H, CHMe + CHMe ₂)	62	-179
(5)	-	1180 1164	1032 1022	631	526 598	484 593	0.95 (t, 6H, Sn(CH ₂) ₃ Me); 1.22 (d, 30H, CMe ₂ + CHMe ₂); 1.37-1.71 (m, 12H, Sn(CH ₂) ₃ Me); 4.12 (m, 1H, CHMe ₂)	74	-138
(6)	-	1174 1140	1023 1011	664	516 582	466 580	0.99 (t, 6H, Sn(CH ₂) ₃ Me); 1.21 (d, 30H, CMe ₂ + CHMe ₂); 1.39-1.59 (m, 20H, (CH ₂) ₂ (G) + Sn(CH ₂) ₃ Me); 3.58 (br, 1H, CHMe ₂)	60	-142
(7)	-	-	1033 1016	631	500 533	482 583	0.90 (t, 9H, Sn(CH ₂) ₃ Me); 1.14-1.38 (m, 18H, CHMe + CMe ₂); 1.57-1.61 (m, 22H, Sn(CH ₂) ₃ Me + CH ₂ (G)); 4.23 (br, 2H, CHMe)	50	-12
(8)	-	-	1037 1016	614	500 546	484 581	0.91 (t, 9H, Sn(CH ₂) ₃ Me); 1.22 (s, 24H, CMe ₂); 1.32-1.59 (m, 18H, Sn(CH ₂) ₃ Me)	53	-14

(8) is indicated by the appearance of bands at 540 ± 6 and 500 assignable to $\nu(\text{Sn-C})$ stretching vibration and at 580 ± 2 and $483 \pm 1 \text{ cm}^{-1}$ due to $\nu(\text{Sn-O})$. These observations regarding derivatives (7) and (8) can be rationalized in terms of the *trans*- Bu_3SnO_2 structure [14] as depicted in Figure 2. Derivatives (4), (5), and (6) also exhibit characteristic absorptions for isopropoxy group(s) at 1175 ± 5 and $1135 \pm 10 \text{ cm}^{-1}$.

¹H NMR spectra

Homometallic derivatives (1)-(3) (Table II) exhibit a broad peak in the δ 1.74-3.38 region due to the residual OH group in addition to the signals characteristic of the glycolate moieties : δ 1.17 - 1.33 (CMe_2), 1.51-1.59 (CH_2), 4.34 (CHMe). The heterobimetallic derivatives (4)-(6) show a doublet and a multiplet for methyl and methine protons of the isopropoxy groups at δ 1.17 - 1.34 and 3.58 - 4.27, respectively along with signals due to glycolate moieties at δ 1.17-1.34 (CMe_2), 1.39-1.59 (CH_2), 4.27 (CHMe). A triplet due to $\text{Me}(\text{CH}_2)_3\text{Sn}$ protons in (4)-(8) appears at δ 0.97 ± 0.02 .

²⁷Al NMR spectra

The presence of tetracoordinated aluminium/15/ (Figures 1 and 2) in derivatives(1), (2), (3), (4), (5), (6), (7), and (8) is supported by the appearance of broad ($\omega_{1/2} = \sim 157.32 \text{ Hz}$) ²⁷Al NMR signals at δ 55, 63, 61, 62, 74, 60, 50, and 53, respectively.

- (1) ($\text{G} = \text{CMe}_2\text{CH}_2\text{CHMe}$), (2) ($\text{G} = \text{CMe}_2\text{CMe}_2$), and
(3) ($\text{G} = \text{CMe}_2\text{CH}_2\text{CH}_2\text{CMe}_2$).

Fig. 1: Suggested structure for homometallic derivatives

¹¹⁹Sn NMR spectra

The appearance of sharp ¹¹⁹Sn NMR signals at δ -179, -138, -142, -12, and -14, respectively for the derivatives (4), (5) (6), (7), and (8) is consistent with five-coordinate/16-17/ organotin (IV) derivatives (Figure 2).

- (4) ($\text{R} = \text{OPr}^i$, $\text{G} = \text{CMe}_2\text{CH}_2\text{CHMe}$), (5) ($\text{R} = \text{OPr}^i$, $\text{G} = \text{CMe}_2\text{CMe}_2$), (6) ($\text{R} = \text{OPr}^i$, $\text{G} = \text{CMe}_2\text{CH}_2\text{CH}_2\text{CMe}_2$), (7) ($\text{R} = \text{Bu}$, $\text{G} = \text{CMe}_2\text{CH}_2\text{CHMe}$), and (8) ($\text{R} = \text{Bu}$, $\text{G} = \text{CMe}_2\text{CMe}_2$).

Fig. 2 : Suggested structure for heterobimetallic derivatives

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