Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

THIOLYSIS OF ALKYLTIN ALKOXIDES AND OXIDES

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(Received April 23rd, 1966)

The alkoxide derivatives of a number of elements have been shown to possess a marked tendency to react with other alcohols[1]. It has been reported by Bradley[2] that titanium and zirconium alkoxides do not undergo analogous reactions with thiols; this has been ascribed to the weak coordination of sulphur atom with these transition metals.

During the present investigations, it has been confirmed that the alkoxides of aluminium, titanium and zirconium do not react with thiols in the medium of refluxing benzene. However, when dibutyltin diethoxide was treated with thiols in the molar ratio 1 : 2 in benzene, it was found to interchange its ethoxy groups very readily; ethanol in the azeotrope collected by fractionation could be estimated quantitatively. The products were isolated after the excess of benzene was stripped off under reduced pressure:

$$\mathrm{Bu_2Sn(OEt)_2 + 2\,RSH \rightarrow Bu_2Sn(SR)_2 + 2\,EtOH}$$
$$\mathrm{R = n\text{-}C_3H_7,\ n\text{-}C_4H_9,\ tert\text{-}C_4H_9,\ iso\text{-}C_4H_9,\ C_6H_5,\ n\text{-}C_{12}H_{25}\ and\ C_6H_5CH_2}$$

All the products are highly soluble in benzene and can be distilled under reduced pressure except the derivative of dodecanethiol which exhibits a tendency of decomposition. Molecular weight determinations in boiling benzene showed them to be monomeric.

Most of the thiol derivatives of tin have been isolated by the treatment of either dialkyltin oxide with thiols in toluene followed by the removal of water azeotropically[3] or by the reaction of dibutyltin halides with thiols in the presence of bases[3,4]. It has been confirmed during the course of the present investigations that water does not hydrolyse the Sn–S bond and hence dialkylthiodibutylstannanes can be synthesized by refluxing of dibutyltin oxide with thiol in the presence of benzene, and removal of water azeotropically is not essential for the success of this synthesis:

$$\mathrm{Bu_2SnO + 2\,RSH \rightarrow Bu_2Sn(SR)_2 + H_2O}$$
$$\mathrm{R = C_2H_5,\ n\text{-}C_3H_7,\ n\text{-}C_4H_9,\ iso\text{-}C_4H_9,\ tert\text{-}C_4H_9,\ n\text{-}C_{12}H_{25},\ C_6H_5\ and\ C_6H_5CH_2}$$

An attempt was made to isolate products containing both Sn–O and Sn–S linkages. The treatment of diethoxide with butanethiols in the molar ratio 1 : 1 in benzene caused the formation of a material (colourless viscous liquid), the analysis of which corresponded to $\mathrm{Bu_2Sn(OEt)(SR)}$. But these products appeared to disproportionate upon distillation *in vacuo* yielding diethoxide and the corresponding dithiolate. In view of the preferential hydrolytic stability of Sn–S–C bond, the above mixed derivative was treated with cold water in the hope of obtaining the derivative $Bu_2Sn(SR)–O–Sn(SR)Bu_2$, but it gave an insoluble white precipitate of of the crude Bu_2SnO, and the filtrate contained the volatile dithiolate. It seems that these mixed derivatives are equimolecular mixtures of $Bu_2Sn(OEt)_2$ and $Bu_2Sn(SR)_2$; the former suffers hydrolysis to give the crude Bu_2SnO.

Alcoholysis reactions have been extensively employed during the last fifteen years for the synthesis of alkoxides of elements like Ge[5], Sn[6], Ti[7], Zr[8], etc. In view of this it was considered worthwhile to study thiolysis reactions of dialkylthiodibutylstannanes. The reactions of dipropanethiodibutylstannane with dodecane- and α-toluenethiol in the molar ratio 1 : 2 in cyclohexane could be successfully carried out:

$$Bu_2Sn(SC_3H_7)_2 + 2\ RSH \rightarrow Bu_2Sn(SR_2)_2 + 2\ C_3H_7SH$$

where R = dodecane- and α-toluenethiol

and the liberated propanethiol could be fractionated out azeotropically with cyclohexane. The removal of ethanethiol formed from the reaction of $Bu_2Sn(SC_2H_5)_2$ with butanethiol in hexane yielded the higher dialkylthio derivative in quantitative yield. These thiolysis reactions are found to be slower than the corresponding alcoholysis reactions and have to be catalysed by *p*-toluenesulfonic acid.

Alcohols are reported to attack Si–S bond[9,10] readily yielding Si–OR derivatives. In view of this and the hydrolytically stable nature of the Sn–S bond in these alkylthio derivatives, a study was made of the reaction of excess anhydrous ethanol over $Bu_2Sn(SC_3H_7)_2$, this compound being chosen because the product propanethiol, forms a convenient azeotrope with ethanol:

$$Bu_2Sn(SC_3H_7)_2 + \underset{\text{large excess}}{2\ EtOH} \rightarrow Bu_2Sn(OEt)_2 + 2\ C_3H_7SH$$

The reaction was very slow, but could be catalysed to some extent by *p*-toluenesulfonic acid, and then required about 200 hours of refluxing for completion. The progress of the reaction could be followed by the estimation of propanethiol in the fractionated azeotrope, and the product $Bu_2Sn(OEt)_2$ could then be distilled *in vacuo*. It is apparent that the filled *d* orbitals of tin alter its properties from silicon which obviously cannot form dative π-bonding in analogous Si–S compounds.

EXPERIMENTAL

Apparatus and chemicals

Special precautions were taken to exclude moisture. Apparatus and analytical methods have already been described[11]. Gibutyltin diethoxide was synthesized as earlier[11]. Dibutyltin oxide (Pure Chemicals) was used as such. Thiols (B.D.H.) were kept over anhydrous $CaCl_2$ and fractionated twice. Benzene and ethanol were dried as reported[11]. Cyclohexane and hexane were made anhydrous by storage over sodium wire and distillation.

Carbon and hydrogen were analysed by Chemical Laboratories, Aligarh Muslim University, and thiol content was estimated by standard iodine solution[12]. Molecular weights were determined by a semi-micro ebulliometer (Gallenkamp) with thermistor sensing.

(1) Reaction of dibutyltin diethoxide with thiols in the molar ratio 1 : 2 in benzene

To a benzene solution of ethoxide was added the calculated amount of thiol. The reaction mixture was refluxed at 120–130° and ethanol produced was immediately fractionated as binary azeotrope and estimated. Excess of solvent was removed under reduced pressure at room temperature (30–35°/1.0 mm). The products were distilled under reduced pressure. The results of these experiments are given in Table 1 and 2.

TABLE 1

PROPERTIES OF DIBUTYLTIN DITHIOLATES[a]

Thiol	*Distillation*[b] *temp. (°C/mm)*		*Molecular weight*[c]		
			Weight[d]	*Found*	*Calcd.*
Ethanethiol	97–100/0.4	(o)	0.284	364, 347, 355, 347	355
Propanethiol	121–123/0.15 140–142/0.5	(o) (e)	0.292	372, 376, 383, 378	383
Butanethiol	157–160/0.7 170/1.5	(o) (e)	0.363	380, 427, 405, 403, 419	411
Isobutanethiol	148/0.6 147–148/0.6	(o) (e)	0.335	410, 393, 412, 384, 397	411
tert-Butanethiol	118/0.1 113–119(0.1)	(o) (e)	0.750	410, 422, 401, 411, 399	411
Dodecanethiol	Decomposes		0.388	572, 545, 607, 572	635
Thiophenol	179/0.1 200/0.6	(o) (e)	0.404	454, 440, 460, 443, 444	451
α-Toluenethiol	210/0.5 220/1.0	(o) (e)	0.313	463, 490, 458, 455,	479

[a] Colourless viscous liquids; $Bu_2Sn(SC_{12}H_{25})_2$ is turbid; $Bu_2Sn(SC_6H_5)_2$ is pale yellow. [b] From dibutyltin oxide (o) or ethoxide (e). [c] Mol. wt. ebulliometrically in benzene. [d] Total weight (g) of substance added to 15 ml of benzene.

(2) Reaction of dibutyltin oxide with thiols in the molar ratio 1 : 2 in benzene

To a benzene suspension of dibutyltin oxide was added calculated amount of the thiol and the mixture refluxed at about 110° for 3 to 4 h. Benzene was removed under reduced pressure at room temperature and the product distilled under reduced pressure. The results are given in Table 1 and 2.

(3) Reaction of dibutyltin ethoxide with butanethiol in the molar ratio 1 : 1 in benzene

To a benzene (60 g) solution of dibutyltin ethoxide (3.459 g) was added butanethiol (0.975 g). The reaction mixture was refluxed and ethanol liberated was fractionated immediately. The excess of solvent was distilled off and the product dried under reduced pressure. It gave a colourless viscous liquid (3.76 g, yield, 96%). Found: ethanol in the azeotrope 0.45 g (one mole requires 0.49 g). (Found: Sn, 32.8. $C_{14}H_{32}OSSn$ calcd.: Sn, 32.35%.) Distillation gave two fractions: (*i*) at 125°/0.5 mm (Found: Sn, 36.70. $C_{12}H_{28}O_2Sn$ calcd.: Sn, 36.76%.); (*ii*) at 160°/0.6 mm (Found: Sn, 28.6. $C_{16}H_{36}S_2Sn$ calcd.: Sn, 28.96%.)

A benzene solution of the product (2.7 g) obtained above was treated with water (about 0.4 g), shaken for 10 min, kept for half an hour and filtered. (*i*) Insoluble solid (0.86 g, yield 94%) (Found: Sn, 47.06. $C_8H_{18}OSn$ calcd.: Sn, 47.73%.). (*ii*) Liquid (1.50 g, yield, 97%) (Found: Sn, 29.17. $C_{16}H_{36}S_2Sn$ calcd.: 28.96%.).

TABLE 2

PREPARATION AND ANALYSIS OF DIALKYLTHIODIBUTYLSTANNANES

$Bu_2Sn(OEt)_2$ (e) or Bu_2SnO (o) (g)	*Mercaptan (g)*	*Yield (%)*	*EtOH (g) (calcd.) found*	*C (%) (calcd.) found*	*H (%) (calcd.) found*	*Sn (%) (calcd.) found*	*SR (%) (calcd.) found*
	EtSH					(33.49)	(34.06)
1.681 (o)	2.0	98				34.02	34.62
	PrSH		(0.655)	(43.8)	(8.3)	(30.97)	(39.24)
2.371 (o)	1.50	99		43.81	8.94	31.5	37.98
2.30 (e)	1.261	99	0.62			31.9	37.77
	BuSH		(0.89)	(46.79)	(8.76)	(28.96)	(43.36)
2.183 (o)	1.58	98		46.44	8.63	29.02	41.97
3.148 (e)	1.761	99	0.804			28.93	42.55
	iso-BuSH		(1.03)	(46.79)	(8.76)	(28.96)	(43.36)
1.168 (o)	0.90	98				29.18	42.71
3.616 (e)	2.018	99	0.91	47.0	8.76	28.75	43.62
	tert-BuSH		(1.10)			(28.96)	(43.36)
2.543 (o)	1.90	90				28.99	43.47
3.883 (e)	2.189	92	1.00			28.94	43.29
	$C_{12}H_{25}SH$		(0.918)			(18.69)	
1.137 (o)	1.85	99				18.5	
3.223 (e)	4.062	99	0.804			17.72	
	C_6H_5SH		(0.978)			(26.31)	(48.32)
2.24 (o)	2.00	96				26.25	47.83
3.428 (e)	2.396	98	0.904			26.74	47.61
	$C_6H_5CH_2SH$		(0.852)	(55.1)	(6.7)	(24.78)	(51.36)
1.743 (o)	1.80	98		53.01	6.4	24.03	49.3
2.993 (e)	2.31	97	0.756			24.68	52.20

(4) Reaction of dibutyltin ethoxide with tert-butanethiol in the molar ratio 1:1 in benzene

To a benzene (65 g) solution of ethoxide (4.029 g) was added tert-butanethiol (1.130 g). The contents were refluxed, ethanol fractionated and dried as before. It gave a colourless viscous liquid (4.54 g, yield, 99%). Found: ethanol in the azeotrope 0.50 g (one mole requires 0.57 g). (Found: Sn, 32.85. $C_{14}H_{32}OSSn$ calcd.: Sn, 32.35%.) Attempted distillation of the products gave two fractions: (*i*) at 120°/0.5 mm (Found: Sn, 36.00. $C_{12}H_{28}O_2Sn$ calcd.: 36.76%). (*ii*) at 135°/0.6 mm (Found: Sn, 29.01. $C_{16}H_{36}S_2Sn$ calcd.: 28.96%.)

Hydrolysis of the product (3.5 g) obtained by 1 : 1 reaction gave (*i*) an insoluble solid (2.0 g, yield, 89%). (Found: Sn, 48.05. $C_8H_{18}OSn$ calcd.: 47.73%.) (*ii*) A liquid (1.2 g, yield, 99%) (Found: Sn, 29.3. $C_{16}H_{36}S_2Sn$ calcd.: Sn, 28.96%.)

(5) Reaction of dipropanethiodibutyltin with α-toluenethiol in cyclohexane (1:2)

To a cyclohexane (60 g) solution of dibutyltin bis(propanethiolate) (2.33 g) was added α-toluenethiol (1.33 g). The reaction mixture was refluxed (130° bath) and propanethiol liberated was fractionated off slowly as the binary azeotrope (67.7°) with cyclohexane. The excess solvent was removed under reduced pressure and distilled at 208–212°/0.3 mm which gave a colourless viscous liquid (2.1 g, yield 93%). Found: propanethiol in the azeotrope 0.82 g (two moles require 0.92 g). (Found: Sn, 25.4; SR, 51.14. $C_{22}H_{32}S_2Sn$ calcd.: Sn, 24.78; SR, 51.39%.)

(6) Reaction of dipropanethiodibutyltin with dodecanethiol in cyclohexane (1:2)

To a cyclohexane (55 g) solution of dithiolate (2.073 g) was added dodecanethiol (2.191 g). The reaction mixture was refluxed, fractionated and dried as in the preceding reaction which gave a colourless viscous liquid (3.56 g, yield 98%). Found: propanethiol in the azeotrope 0.75 g (two moles require 0.82 g). (Found: Sn, 18.64. $C_{32}H_{68}S_2Sn$ calcd.: Sn, 18.69%.)

(7) Reaction of $Bu_2Sn(SC_2H_5)_2$ with butanethiol in the molar ratio 1:2 in hexane

To a hexane (54 g) solution of $Bu_2Sn(SC_2H_5)_2$ (1.957 g) was added butanethiol (1.0 g). The reaction mixture was refluxed and the ethanethiol produced was fractionated slowly. Solvent was removed under reduced pressure to yield a colourless viscous liquid (1.9 g, yield 85%) at 159°/0.4 mm. (Found: Sn, 28.68; SR, 43.48; $C_{16}H_{36}S_2Sn$ calcd.: Sn, 28.96; SR, 43.36%.)

(8) Reaction of $Bu_2Sn(SC_3H_7)_2$ with excess ethanol

To 2.638 g of dipropanethiodibutylstannane was added ethanol (60 g) and a crystal of *p*-toluenesulfonic acid (0.002 g). The mixture was refluxed at 120–125° and the propanethiol was fractionated off slowly as the binary azeotrope with ethanol. As the reaction proceeds very slowly so it was refluxed for about 200 h with the addition of fresh ethanol and catalyst till no more propanethiol could be found in the azeotrope. The product was distilled at 117°/1.0 mm to yield a colourless liquid (yield 90%). Found: propanethiol in the azeotrope 0.75 g (two moles require 0.78 g). (Found: Sn, 35.94. $C_{12}H_{28}O_2Sn$ calcd.: Sn, 36.76%.)

ACKNOWLEDGEMENT

The financial support of the Council of Scientific and Industrial Research, New Delhi to one of us (D.S.) is gratefully acknowledged. The authors wish to express their grateful thanks to Prof. G. J. M. VAN DER KERK, Director of the Institute for Organic Chemistry, TNO, for a gift of dibutyltin dichloride and Dr. W. A. JOHNSON, Pure Chemicals Limited, for a gift of dibutyltin oxide.

SUMMARY

Dibutyltin diethoxide was found to interchange its ethoxy groups readily with thiols forming $Bu_2Sn(SR)_2$. These thiolates can also be synthesized by refluxing the crude Bu_2SnO with thiols in the presence of benzene. Molecular weight determinations showed them monomeric. Some of these higher homologues can be pre-

pared by displacement reactions with higher thiols. The reaction of dipropanethiodibutylstannane with ethanol is very slow even in the presence of catalyst.

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