A STUDY OF THE TETRA-ALKYLTHIOSTANNANES, Sn(SR)₄

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Abstract—The synthesis of tetra-alkylthiostannanes, $Sn(SR)_4$, (where $R = C_2H_6$, $n-C_3H_7$, iso- C_4H_7 , iso- C_4H_9 , iso- C_4H_9 , tert- C_4H_9 , $n-C_{12}H_{25}$, C_6H_5 and C_6H_5 CH₂) through an alternative convenient route employing ammonia as a proton acceptor is described. Stannic isopropoxide also exchanges its isopropoxy groups with thiols. Thiolysis reactions of $Sn(SEt)_4$ and $Sn(SPr)_4$ with higher thiols have been investigated for the first time.

A STUDY of the M-S bonded derivatives of the Group IV elements has been extended⁽¹⁾ to tin. BACKER and KRAMER⁽²⁾ reported the preparation of tetrathiostannanes, $Sn(SR)_4$, by the reaction of sodium mercaptides with tin tetrachloride. However, the yields were poor. In the present investigation, the derivatives, $Sn(SR)_4$, (where $R = C_2H_5$, $n-C_3H_7$, $iso-C_3H_7$, $n-C_4H_9$, $iso-C_4H_9$, $tert-C_4H_9$, $n-C_{12}H_{25}$, C_6H_5 and C_6H_5 ·CH₂) have been synthesised in greater than 80% yield by passing ammonia into a mixture of tin tetrachloride and the thiol in benzene:

 $SnCl_4 + 4RSH + 4NH_3 \rightarrow Sn(SR)_4 + 4NH_4Cl_1$

EXPERIMENTAL

Tin was determined by decomposing the compound with concentrated nitric acid in a silica crucible and ignition to the dioxide. Other experimental details have been described by $us^{(1,3)}$ previously.

Preparation of tetra-alkylthiostannanes

The calculated amount of thiol (approx. 4-5 mole) was added to a benzene solution of tin tetrachloride, the reaction being exothermic. Dry ammonia was then slowly passed into the solution when an exothermic reaction developed with the formation of ammonium chloride. The passage of ammonia was discontinued when the reaction mixture attained room temperature. Ammonium chloride was filtered and the filtrate evaporated to remove excess of ammonia. The product was finally distilled under reduced pressure after removing the excess solvent. The results are compiled in Table 1.

Reaction of stannic isopropoxide with n-butane thiol

n-Butane thiol (1.82 g) was added to a n-hexane (60 g) solution of stannic isopropoxide (1.921 g) and the mixture was refluxed (90-100°C). The isopropanol produced was distilled off slowly as a binary azeotrope and estimated. Completion of the reaction required 5 hr. Excess of the solvent was removed under reduced pressure and the product was finally distilled at 200°C/1.0 mm. Yield: 2.05 g. Found: Pr'OH in the azeotrope 1.35 g (5 mole require 1.38 g;) Sn, 24.48; -SR, 74.41%. $C_{16}H_{38}S_4Sn$ calcd: Sn, 24.99; -SR, 75.01%.

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⁽²⁾ H. J. BACKER and J. KRAMER, Recl. Trav. chim. Pays-Bas Belg. 52, 916 (1933); ibid. 53, 1101 (1934).

⁽³⁾ R. C. MEHROTRA, V. D. GUPTA and D. SUKHANI, J. Organometal. Chem. 7, 85 (1967).

	Calcd.	363-18	419-30	419-30	475-38	475-38	475-38		555-34	611-42
Mol. wt.	Found	356, 378, 361, 353	456. 471. 476. 420	416, 455, 483, 435	500, 533, 459, 460	462, 425, 457	484, 453, 495, 468	• •	485, 498, 510	622, 636, 598, 617
	Total wt. of sub- stance added (g/15 ml)	0-2359	0-3677	0-2719	0-2640	0-2158	0-3075		0-4387	0-3718
Analysis (%)	-SR	67-30	71-69	71-69	75-02	75-02	75-02	87-16	78-62	80-58
	Cal Metal	32-70	28-31	28-31	24-98	24-98	24-98	12.84	21-38	19-42
	nd —SR	66-22	70-36	71-12	74-50	73-30	75-50	87-00	17-60	<u> 79-69</u>
	Fou Metal	32-75	28-10	28.17	23-73	24-01	26-34	12·12	20-35	19-67
	Distillation (°C/mm) or Sublimation	152/0-8	160/0.1	145/0-1	182-184/0-1	166-167/0-1	180-190/0-8	Decomposition	120-140/0.5	Decomposition
	Properties	Colourless, viscous liquid	Colourless, viscous liguid	Colourless, viscous liquid	Colourless, viscous liquid	Colourless, viscous figuid	White crystalline solid	Colourless, low melting solid	Pale yellow crystalline solid	Colourless viscous liquid
	Yield (%)	87	80	76	80	95	6	66	94	66
	Thiol (g)	Ethane thiol 8-00	n-Propane thiol 12-00	iso-Propane thiol 6.58	n-Butane thiol 6.80	iso-Butane thiol 4.00	ter-Butane thiol	n-Dodecane thiol 5-00	Thiophenol 5.80	Toluene-α-thiol 4·50
	SnCl ₄ taken (g)	3.55	6.76	3.04	3.19	2.88	5.04 1	1-48	3-41	2-32
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A study of the tetra-alkylthiostannanes, Sn(SR)₄

Reaction of stannic isopropoxide with n-dodecane thiol

n-Dodecane thiol (3.520 g) was added to a benzene (60 g) solution of stannic isopropoxide (1.802 g) and the mixture was refluxed (110–120°C). The isopropanol produced was separated and estimated as before. A low melting solid (4.01 g) was isolated after the usual process of drying ($40^{\circ}C/1.0 \text{ mm}$). Found: Pr'OH in the azeotrope, 1.20 g (5 mole require 1.30 g); Sn, 13.04; -SR, 83.95%. C₄₈H₁₀₀S₄Sn calcd: Sn, 12.84; -SR, 87.16%.

Reaction of Sn(SEt)₄ with n-butane thiol

n-Butane thiol (3.49 g, 8 mole) was added to a benzene (70 g) solution of $Sn(SEt)_4$ (1.71 g) and the mixture was refluxed (110–120°C). Benzene, together with ethane thiol, was fractionated off slowly. The product was distilled (198°C/0.6 mm) after removing the excess of solvent. Yield: 2.0 g. Found: Sn, 24.68; -SR, 74.22%. C₁₆H₃₆S₄Sn, calcd: Sn, 24.99; -SR, 75.01%.

Reaction of $Sn(SPr)_4$ with toluene- α -thiol

Toluene- α -thiol (2.728 g) was added to a cyclohexane (60 g) solution of Sn(SPr)₄ (2.301 g) and the mixture was refluxed (110–120°C). Propane thiol was distilled off slowly as a binary azeotrope and estimated. After the usual process of drying, the product was finally dried at 60°C/1.5 mm to yield (3.34 g) a viscous liquid. Found: PrSH in the azeotrope 1.62 g (4 mole require 1.67 g); Sn, 18.90; --SR, 80.17%. C₂₈H₂₈S₄Sn calcd: Sn, 19.63; --SR, 80.37%.

Reaction of Sn(SPr)4 with water in ethanol solution

An ethanolic solution of $Sn(SPr)_4$ (4.436 g) was treated with water, shaken for 15 min and kept overnight. The liquid (4.10 g) obtained after stripping off ethanol and water was analysed. Found: Sn, 28.49; -SR, 71.07%. C₁₂H₂₈S₄Sn calcd: Sn, 28.31; -SR, 71.69%.

RESULTS AND DISCUSSION

Tetra-alkylthiostannanes are mostly viscous liquids (the derivatives of tert- C_4H_9SH , n- $C_{12}H_{25}SH$ and C_6H_5SH are solids), miscible with benzene and they could be purified by distillation *in vacuo* (except the higher ones like toluene- α -thiol and n-dodecane thiol). Molecular weight determination ebullioscopically in benzene showed them to be monomeric. The volatile and monomeric nature of these tetra-alkylthiostannanes presents a sharp contrast with the normal and secondary stannic alkoxides, Sn(OR)₄, which are usually non-volatile and polymeric;⁽⁴⁾ the mercaptide bridge in these products appears to be too weak for polymerisation.

Stannic isopropoxide when treated with thiols exchanges its isopropoxy groups readily; the reaction appears to be faster than in the case of germanium.⁽¹⁾

$$Sn(OPr^i)_4 \cdot Pr^iOH + 4RSH \rightarrow Sn(SR)_4 + 5Pr^iOH^{\uparrow}$$

 $(R = n-C_4H_9 \text{ and } n-C_{12}H_{25}).$

The completion of these reactions was ascertained by estimating isopropanol liberated in the azeotrope. As with germanium, an attempt to isolate mixed derivatives containing Sn–O and Sn–S bonds, by carrying out the reaction in limited molar ratios, was unsuccessful.

The thiolysis reactions of tetrathiopropylstannane were carried out in cyclohexane, which forms a convenient azeotrope with the liberated propane thiol:

$$Sn(SR)_4 + 4R'SH \rightarrow Sn(SR')_4 + 4RSH$$

$$(\mathbf{R} = \mathbf{Et}, \mathbf{n}-\mathbf{Pr}; \mathbf{R}' = \mathbf{n}-\mathbf{C}_{4}\mathbf{H}_{9}, \text{ and } \mathbf{C}_{6}\mathbf{H}_{5}\mathbf{CH}_{2}).$$

(4) J. C. MAIRE, Ann. Chim., Paris 6, 969 (1961).

Like the alcoholysis reactions of ethoxides, isopropoxides⁽⁵⁻⁷⁾ etc. in the presence of benzene, this appears to be a very convenient method for the synthesis of higher derivatives, including mixed products.

These tetra-alkylthiostannanes appear to be resistant to hydrolysis due to the strength of dative π bonding from metal to sulphur atom.

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