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SYNTHESIS OF STANNOUS CHELATE COMPOUNDS

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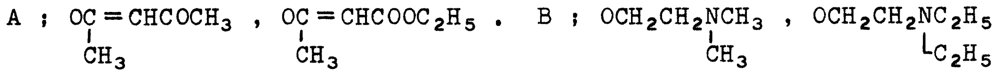
The synthesis of a novel type of stannous compounds was studied. The products are distillable and have high solubilities in organic solvents. The structures of the product were examined by tin analysis, molecular-weight determination, and studies of the IR and NMR spectra.

Stannous ethoxide was first obtained by Meerwein and Geschke[1)] in 1936 as a component of pyrolysis products of tin tetraethoxide. Since Amberger and Kula[2)] prepared stannous methoxide by the reaction of stannous bromide with sodium methoxide in methanol, several stannous compounds[3-5)] have been reported. It is known that the stannous alkoxideslike alkyl and aryl stannous derivatives are less volatile and have low solubilities in organic solvents. This paper presents a preparation of a novel type of monomeric stannous compounds soluble in organic solvents, such as n-hexane, benzene, tetrahydrofuran , ethanol, and methylene chloride. These compounds were prepared in good yields according to the following equation.

$$Sn(OC_2H_5)_2 + 2\ HA\ (or\ 2\ HB) \longrightarrow SnA_2\ (or\ SnB_2) + 2\ C_2H_5OH$$



$$A\ ;\ \underset{CH_3}{OC}=CHCOCH_3\ ,\ \underset{CH_3}{OC}=CHCOOC_2H_5\ .\quad B\ ;\ OCH_2CH_2\underset{CH_3}{N}CH_3\ ,\ OCH_2CH_2\underset{\llcorner C_2H_5}{N}C_2H_5$$

The reagent, HA or HB (0.2 mol), was added to $Sn(OC_2H_5)_2$ (0.1 mol) at room temperature, then the mixture was heated for 10 min. at 90 °C. There was a formation of quantitative amount of ethanol, which was distilled of under reduced pressure. The residue was distilled in vacuo to give a pall yellow, transparent liquid which is extremely sensitive to atomospheric moisture. It was found that the compounds, SnA_2, were also obtained by the reaction of stannous chloride with HA in the presence of triethylamine. The results are summarized in Table I and II.

Volatilities of these compounds suggest their monomeric strucure which is also supported by molecular-weight measurements and solubilities in organic solvents. The product, SnA_2, exhibited two IR bands in the region of 1600-1500 cm^{-1}. The upper band ($1600 cm^{-1}$, $1567 cm^{-1}$) is atrributed to the chelated carbonyl group and the lower band to the double bond of the chelate ring. The disappearance[6)] of the absorption band at 2780 cm^{-1} in stannous bis(N.N-dimethylaminoethoxide) shows that the lone pair of nitrogen electrons is no longer present. In the NMR spectra of stannous bis(acetylacetonate) and bis(ethylacetoacetate), methyl protons of $-O-C-CH_3$ displayed a singlet at $\delta=1.77$ ppm and $\delta = 1.80$ ppm, respectively. This indicates the equivalence of the both methyl groups. In stannous bis(N.N-dimethylaminoethoxide) and bis(N.N-diethylaminoethoxide), the proton chemical shift of methyl and methylene attached to nitrogen was shifted to lower field than that of the corresponding aminoethanol. On the basis of the above IR and NMR results, therefore, it may be concluded that tin atom has a four-coordination and forms 2 six-membered ring structure.

Table I. Physical and Analytical Data of Reaction Products of $Sn(OC_2H_5)_2$

Products	% yield of refined product	B.P. (°C) [mmHg]	Mol. Wt.! Found (Calcd.)	Analysis (%) Sn(Total) (Calcd.)	Sn(II)
$Sn(O\underset{CH_3}{C}=CHCOCH_3)_2$	86.9	101	332	36.9	36.4
		[0.15]	(317)	(37.9)	
$Sn(O\underset{CH_3}{C}=CHCOOC_2H_5)_2$	78.5	121-123	380	31.0	30.9
		[0.13]	(377)	(31.5)	
$Sn(OCH_2CH_2\underset{CH_3}{N}CH_3)_2$	89.1	100-105	313	40.2	37.5
		[0.3-0.4]	(295)	(40.2)	
$Sn(OCH_2CH_2\underset{C_2H_5}{N}C_2H_5)_2$	85.6	124.5-128.3	357	34.0	32.5
		[0.028-0.032]	(347)	(33.8)	

! Determined by cryoscopic method in benzene at a concentration of 0.5-1.0g/30ml.

Table II. IR and NMR Spectra of Stannous Chelate Compounds

	IR $(cm^{-1})^a$			NMR $(\delta)^b$					
	Sn-O	C=O	C=C	$C\underline{H}_3$	$-C\underline{H}$	$C\underline{H}_3CH_2$	$CH_3C\underline{H}_2$	$C\underline{H}_2O$	$C\underline{H}_2N$
$Sn(O\underset{CH_3}{C}=CHCOCH_3)_2$	407	1567	1509	1.77 (s)	5.19 (s)				
$Sn(O\underset{CH_3}{C}=CHCOOC_2H_5)_2$	417	1600	1515	1.80 (s)	5.09 (s)	1.40 (t)	4.04 (q)		
$Sn(OCH_2CH_2\underset{CH_3}{N}CH_3)_2{}^c$	583			2.11 $(2.05)^d$ (s)				4.14 $(3.58)^d$ (t)	2.38 $(2.27)^d$ (t)
$Sn(OCH_2CH_2\underset{C_2H_5}{N}C_2H_5)_2$	586					0.86 $(0.86)^d$ (t)	2.67 $(2.28)^d$ (q)	4.15 $(3.52)^d$ (t)	2.50 $(2.47)^d$ (t)

a) Measured in a liquid film with a Hitachi EPI-S2 spectrometer.

b) Benzene solution ; TMS internal standard. s = singlet, t = triplet, q = quartet.

c) A characteristic absorption band of $N-CH_3$ group of N,N-dimethylaminoethanol at 2780 cm^{-1} was not found in this compound.

d) The corresponding chemical shift of the aminoethanol.

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