

ORGANOMETALLIC COMPLEXES CONTAINING ANTIMONY AND ALUMINUM

II. PREPARATION OF PENTAETHYLANTIMONY AND ITS REACTIONS WITH ALUMINUM COMPOUNDS, $\text{AlEt}_n\text{Cl}_{3-n}$

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INTRODUCTION

In connection with the characteristic effects of antimony compounds on Ziegler type catalysts for the polymerization of α -olefins, the reactions of some stable alkylantimony compounds, *e.g.*, triethylantimony dichloride, tetraethylstibonium chloride and triethylstibine, with aluminum compounds have previously been studied, and a variety of the complexes containing antimony and aluminum have been prepared¹.

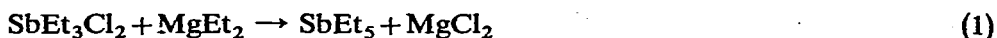
Pentaalkylantimonies are known generally as unstable compounds, and only the syntheses of pentamethylantimony and of some pentaalkenylantimony compounds have been reported^{2,3}.

We report here the synthesis of pentaethylantimony and the reactions of pentaethylantimony with various aluminum compounds, $\text{AlEt}_n\text{Cl}_{3-n}$, which resulted in the formation of new types of complexes containing antimony and aluminum.

RESULTS AND DISCUSSION

Preparation of pentaethylantimony and its properties

In order to search for a convenient method for the preparation of pentaethylantimony, some reactions of ethylantimony(V) halides with various metal alkyls were attempted. It was found that the reaction of triethylantimony dichloride with diethylmagnesium and that of tetraethylstibonium chloride with ethyllithium gave pentaethylantimony almost quantitatively according to the following equations:



The reaction of diethylzinc with tetraethylstibonium chloride afforded pentaethylantimony only in poor yield. The reaction of triethylaluminum with triethylantimony dichloride or tetraethylstibonium chloride yielded the stibonium complex salts predominantly as reported in the previous paper¹.

Pentaethylantimony is a yellow liquid with a boiling point of *ca.* 55.8°/0.19 mm. The distillation of this compound was difficult because of its thermal instability.

Thermal decomposition of pentaethylantimony yielded triethylstibine and an equimolar mixture of ethane and ethylene. The reaction may be represented as follows:



Nevertheless, the distillation of pentaethylantimony was made possible by keeping the still temperature as low as possible, using a short-necked column, and keeping the receiver temperature high enough to prevent the condensation of triethylstibine.

The IR spectrum of pentaethylantimony is shown in Fig. 1. The absorption

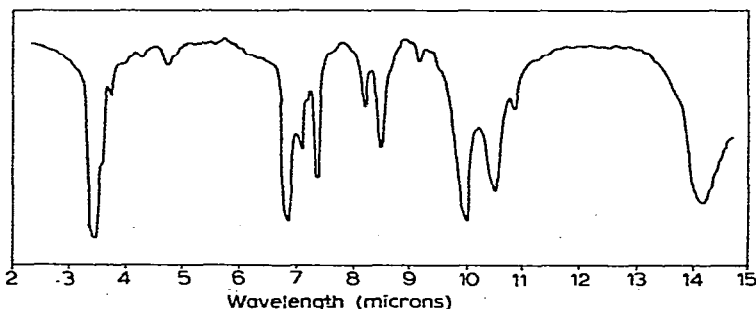
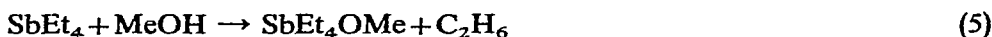


Fig. 1. IR spectrum of pentaethylantimony.

pattern is similar to that of triethylstibine, but the strong bands at 9.8 and 10.4 μ in triethylstibine, which may be assigned to C-C stretching vibrations, shift to 10.0 and 10.5 μ respectively in pentaethylantimony.

Pentaethylantimony reacted with methanol, as in the case of pentaarylantimony^{4,5}, to yield tetraethylantimony methoxide and ethane quantitatively.

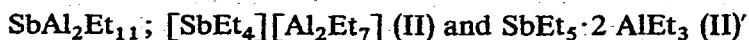


Pentaethylantimony was fairly stable to water but was oxidized easily with atmospheric oxygen.

Reactions of pentaethylantimony with aluminum compounds, $\text{AlEt}_n\text{Cl}_{3-n}$

Pentaethylantimony was found to react with various aluminum compounds, such as triethylaluminum, diethylaluminum chloride, ethylaluminum dichloride, and aluminum chloride, to give various complexes containing antimony and aluminum which were insoluble in the hydrocarbon used as reaction medium. The results of the reactions are summarized in Tables 1 and 2. The formulas of the complexes were postulated on the basis of the elemental analysis and the amounts of ethane, tetraethylstibonium ion and pentaethylantimony which were liberated on hydrolysis.

The reaction of pentaethylantimony with triethylaluminum gives two complexes with the composition of SbAlEt_8 and $\text{SbAl}_2\text{Et}_{11}$, respectively, for which two types of formulas can be postulated as shown below, since both tetraethylstibonium ion and pentaethylantimony were liberated on hydrolysis.



The former are ionic stibonium complex salts and the latter are simple adducts. The formulas of these complexes were not determined exactly by measurement of active ethyl groups because it is uncertain that all the ethyl groups bound to aluminum

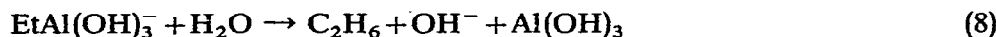
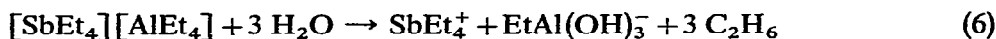
TABLE I

REACTIONS OF SbEt_5 WITH $\text{Et}_n\text{AlCl}_{3-n}$

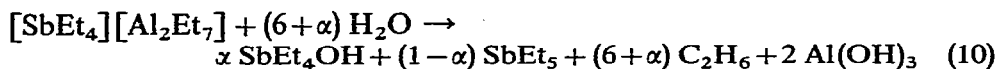
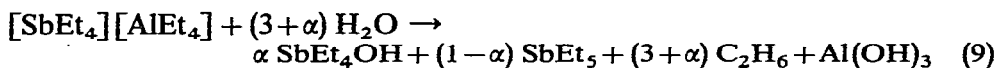
SbEt_5 (g)	$\text{AlEt}_n\text{Cl}_{3-n}$		$\text{AlEt}_n\text{Cl}_{3-n}/$ SbEt_5 molar ratio	Reaction temp. (°C)	<i>n</i> -Hexane-insoluble product	
	Formula	<i>g</i>			<i>g</i>	Appearance
57.85	AlEt_3	14.46	0.59	10 ~ 40	48.16	White crystals
19.14	AlEt_3	24.51	2.99	10 ~ 40	30.15	Colorless liquid
40.21	AlEt_2Cl	12.10	0.66	-20 ~ 30	32.81	Pale yellow liquid
18.70	AlEt_2Cl	25.32	3.00	-20 ~ 30	34.55	Colorless liquid
8.10	AlEtCl_2	2.57	0.59	-20 ~ 30	7.39	Pale yellow liquid
3.30	AlEtCl_2	4.70	2.99	-20 ~ 30	5.20	White crystals
8.40	AlCl_3	2.80	0.67	20 ~ 60	7.95 ^a	Pale yellow soft crystals
2.70	AlCl_3	3.03	3.00	20 ~ 60	5.23 ^a	Reddish orange liquid

^a Benzene-insoluble portion.

atom yield ethane on hydrolysis. It is conceivable that some of the ethyl groups bound to aluminum do not give ethane on hydrolysis but yield pentaethylantimony as follows:



If four and seven ethyl groups are bound to aluminum in complexes (I) and (II) respectively, the overall reactions can be written as follows:



The reactions (7) and (8) may proceed competitively. Then, SbEt_4OH , SbEt_5 and ethane are obtained as final products. The material balances of the hydrolysis of the complexes SbAlEt_8 and $\text{SbAl}_2\text{Et}_{11}$ are well accounted for by eqns. (9) and (10) respectively, and the value of α was calculated as about 0.30 in both cases. On the other hand, even if three and six ethyl groups are bound to aluminum in adducts (I) and (II) respectively, the presence of SbEt_4^+ ion in the hydrolyzates can be also explained by the simple substitution of the ethyl group bound to antimony with OH^- ion. The NMR spectrum of the complex $\text{SbAl}_2\text{Et}_{11}$ showed that six ethyl groups were bound to aluminum and the rest to antimony. This fact supports the

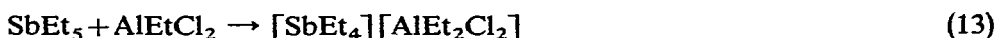
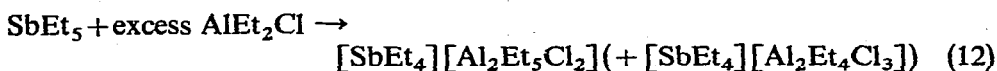
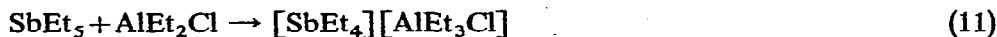
TABLE 2
ANALYSIS OF THE n-HEXANE-INSOLUBLE PRODUCTS

$AlEt_nCl_{3-n}$	$AlEt_nCl_{3-n}$ $SbEt_5$ molar ratio	Analysis found (calcd.) (%)					Hydrolysis			Proposed formula
		Sb	Al	Cl	C	H	Et_0	$SbEt_4^+$	$SbEt_5$	
$AlEt_3$	0.59	31.62 (31.94)	7.73 (7.08)	0 (0)	49.90 (50.40)	10.34 (10.58)	25.5 (uncertain)	18.6 (uncertain)	46.7 (uncertain)	$[SbEt_4][AlEt_4]$ or $SbEt_5 \cdot AlEt_3$
$AlEt_2$	2.99	25.09 (24.58)	10.97 (10.89)	0 (0)	53.12 (53.34)	10.87 (11.19)	38.2 (uncertain)	18.8 (uncertain)	32.6 (uncertain)	$[SbEt_4][Al_2Et_7]$ or $SbEt_5 \cdot 2 AlEt_3$
$AlEt_2Cl$	0.66	30.82 (31.41)	7.08 (6.96)	10.02 (9.15)	43.16 (43.38)	9.05 (9.10)	19.1 (22.5)	61.0 (61.4)	0 (0)	$[SbEt_4][AlEt_3Cl]$
$AlEt_2Cl$	3.00	22.55 (23.25)	11.05 (10.92)	17.96 (18.55)	39.27 (39.08)	8.19 (8.20)	22.9 (25.1)	45.3 (45.5)	0 (0)	$[SbEt_4][Al_2Et_5Cl_2]$ + $[SbEt_4][Al_2Et_4Cl_3]^a$
$AlEtCl_2$	0.59	30.19 (30.90)	6.95 (6.85)	18.57 (18.00)	36.24 (36.58)	7.66 (7.67)	11.4 (14.7)	58.6 (60.4)	0 (0)	$[SbEt_4][AlEt_2Cl]$
$AlEtCl_2$	2.99	29.05 (29.93)	6.97 (6.63)	34.54 (34.87)	23.70 (23.62)	5.05 (4.95)	1.3 (0)		0 (0)	$[SbEt_4][AlCl_4]$
$AlCl_3$	0.67	29.63 (30.41)	6.86 (6.74)	26.09 (26.57)	30.20 (29.97)	6.39 (6.29)	5.6 (7.3)	60.4 (59.5)	0 (0)	$[SbEt_4][AlEtCl_3]$

^a Calculated for $[SbEt_4][AlEt_2Cl]_{1.74}(AlEt_3)_{0.38}Cl$.

latter structure (I) and (II). The electrical conductivity of the complex $\text{SbAl}_2\text{Et}_{11}$ was measured to be $3.64 \times 10^{-3} \text{ } \Omega/\text{cm}$ at 20° . This result suggests that these complexes consist of certain ionic structures. It is difficult to consider the presence of two or more different structures in these complexes since the crystalline complex SbAlEt_8 shows a fairly sharp melting point of $54\text{--}56^\circ$. The clarification of the structures and the nature of the chemical bonds in the complexes remain as future problems.

The reactions of pentaethylantimony with diethylaluminum chloride and with ethylaluminum dichloride yielded stibonium complex salts which were proved by infrared spectra and analysis to be identical with those prepared by the reactions of tetraethylstibonium chloride with aluminum compounds or by the other reactions reported in the previous paper¹. These reactions can be written as follows:



The crystalline complex $[\text{SbEt}_4][\text{AlCl}_4]$ was proved also by X-ray analysis to be identical with that prepared before¹. The following reaction was reported in the previous work¹:



Reaction (14) is noted as a reaction similar to that shown by equation (15).

The reaction of pentaethylantimony with aluminum chloride gave a similar stibonium complex salt through the alkylation of aluminum chloride as follows:



EXPERIMENTAL

General comments

All reactions were carried out under an atmosphere of dry and oxygen-free nitrogen.

Tetraethylstibonium chloride and triethylantimony dichloride were prepared by the method previously described¹. Ethyllithium and diethylmagnesium were prepared by known procedures. Ethylaluminum compounds supplied from Texas Alkyls Corp. were used without further purification. All solvents were refluxed over sodium ribbon, distilled and stored over a molecular sieve.

Analytical methods common to the previous work were described before¹. Pentaethylantimony, which was liberated on hydrolysis of the solid sample, was extracted with ether from the hydrolyzate. The NMR spectrum was measured at room temperature without any solvent using a Varian A-60 spectrometer operating at 60 Mc. The ethyl groups bound to antimony and aluminum showed proton chemical shifts as follows: $\text{CH}_2(\text{Sb})$, 151; $\text{CH}_3(\text{Sb})$, 92; $\text{CH}_2(\text{Al})$, 21; $\text{CH}_3(\text{Al})$, 64 cps. All values were given with tetramethylsilane as the external standard. The signal areas of the above two types of ethyl groups were compared to determine the molar

ratio of the ethyl groups bound to each metallic atom. X-ray powder diffractometry was accomplished under nitrogen atmosphere with a Shimadzu diffractometer GX-1 by use of a scintillation counter and Cu-K α radiation.

Reaction of tetraethylstibonium chloride with ethyllithium

Tetraethylstibonium chloride (0.0284 mole) was added to a n-hexane solution containing an equimolar amount of ethyllithium in a 200 ml glass ampoule at room temperature. The ampoule was sealed and shaken at 60° overnight. The reaction mixture was filtered from 1.4 g of a grayish-white powder, and the filtrate was hydrolyzed with 100 ml of water at room temperature. The n-hexane phase of the hydrolyzate was extracted with water several times, dried over calcium chloride, and evaporated under reduced pressure. There remained 5.71 g of liquid product. The liquid product (2.69 g) was distilled under reduced pressure using a short-necked simple distillation flask, and pentaethylantimony (b.p. 55.8°/0.19 mm) was obtained in 85% yield. (Found: C, 44.50; H, 9.32; Cl, 0.00; Sb, 45.58. C₁₀H₂₅Sb calcd.: C, 44.90; H, 9.44; Sb, 45.59%.)

Reaction of triethylantimony dichloride with diethylmagnesium

An ethereal solution containing about 1.5 moles of diethylmagnesium was placed into a 3 l four-necked glass flask equipped with a mercury-sealed stirrer, a reflux condenser, a thermometer and an addition funnel. Triethylantimony dichloride (0.75 mole) was added dropwise with stirring at room temperature over a 1 h period. As the reaction proceeded, a white solid was precipitated. After the reaction mixture had been refluxed for 1.5 h, 200 ml of water was added at room temperature over a 30 minute interval. The ether phase of the hydrolyzate was extracted with water several times, dried over sodium sulfate, and evaporated under reduced pressure. Pentaethylantimony (b.p. 50.5°/0.14 mm) was obtained in 80% yield. (Found: C, 44.51; H, 9.71; Cl, 0.00; Sb, 45.54. C₁₀H₂₅Sb calcd.: C, 44.97; H, 9.44; Cl, 0.00; Sb, 45.59%.)

Reaction of tetraethylstibonium chloride with diethylzinc

To a suspension of 5.46 g (0.020 mole) of tetraethylstibonium chloride in 6 ml of n-hexane was added 2.47 g (0.020 mole) of diethylzinc dropwise at room temperature. The reaction mixture was kept at 70° for 30 minutes, and left overnight at room temperature. The mixture consisting of a small quantity of crystals and two liquid layers was hydrolyzed. The n-hexane phase of the hydrolyzate was extracted with water, dried, and evaporated as described in the previous experiment. There remained 1.9 g (36% yield) of pentaethylantimony, which was identified by its IR spectrum.

Alcoholysis of pentaethylantimony

Pentaethylantimony (18.8 g, 0.0705 mole) and 30 ml of methanol were mixed at room temperature. An exothermic reaction took place, evolving a large amount of gas which was proved by gas chromatography to be almost pure ethane, and the reaction mixture became homogeneous and colorless. After the reaction mixture had been left overnight, volatile material and the unreacted methanol were removed from the mixture at 50°/5 mm. There remained 17.7 g (94% yield) of a colorless liquid, (C₂H₅)₄Sb(OCH₃). (Found: C, 40.62; H, 8.67; O, 5.27; Sb, 46.00. C₉H₂₃OSb calcd.:

C, 40.18; H, 8.62; O, 5.94; Sb, 45.26%.) This product dissolved in methanol and water.

Reactions of pentaethylantimony with aluminum compounds, $AlEt_nCl_{3-n}$

Into a 50 ml glass ampoule equipped with a magnetic stirrer and an addition funnel were placed an aliquot of pentaethylantimony and 10 ml of n-hexane. The ethylaluminum compound was added dropwise with stirring over a 20 minute period. The reaction conditions are given in Table 1. After having stood overnight at room temperature, the resulting mixture was extracted with n-hexane repeatedly, leaving an insoluble product. In the case of the reaction with aluminum chloride, pentaethylantimony dissolved in 10 ml of dry benzene was added to a suspension of aluminum chloride in benzene. The reaction mixture was extracted with benzene.

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SUMMARY

Pentaethylantimony has been prepared by the reactions of ethylantimony(V) chlorides with diethylmagnesium and with ethyllithium. Pentaethylantimony reacts with methanol to give tetraethylantimony methoxide.

A series of the organometallic complexes shown by the formulas of $[SbEt_4] \cdot [AlEt_nCl_{4-n}]$ and $[SbEt_4][Al_2Et_nCl_{7-n}]$ has been prepared by the reactions of pentaethylantimony with various aluminum compounds, $AlEt_nCl_{3-n}$. The exact structures of the complexes $[SbEt_4][AlEt_4]$ and $[SbEt_4][Al_2Et_7]$, obtained by the reaction of pentaethylantimony with triethylaluminum, have not been clarified yet. The simple adduct structures $SbEt_5 \cdot AlEt_3$ and $SbEt_5 \cdot 2 AlEt_3$, respectively, may be also taken for these complexes. The complexes obtained by the reactions of pentaethylantimony with aluminum compounds having at least one chlorine atom are confirmed to be stibonium complex salts.

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