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PREPARATION OF ASYMMETRICAL TERTIARY STIBINES, $(C_6H_5)(CH_3)RSb$ AND $[(C_6H_5)(CH_3)Sb]_2(CH_2)_n$

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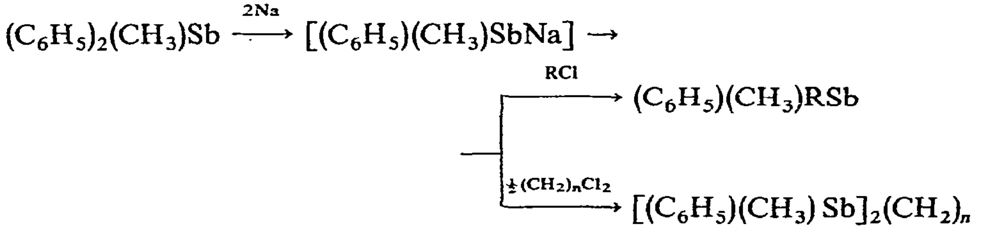
SUMMARY

Six asymmetrical tertiary stibines, $(C_6H_5)(CH_3)RSb$ [$R=C_2H_5$, $(CH_3)_2CH$ and $C_6H_5CH_2$] and $[(C_6H_5)(CH_3)Sb]_2(CH_2)_n$ ($n=1$, 3 and 4) were prepared in about 60% yield by the reaction of $(C_6H_5)_2(CH_3)Sb$ with sodium in liquid ammonia and the subsequent reaction with RCl and $(CH_2)_nCl_2$, respectively. $[(C_6H_5)(CH_3)Sb]_2(CH_2)_3$ was also prepared by the reaction of $[(C_6H_5)_2Sb]_2(CH_2)_3$ with sodium and CH_3Cl in the same solvent. The existence of the stable invertomers of newly prepared asymmetrical tertiary stibines was shown by PMR data.

INTRODUCTION

Some asymmetrical triarylstibines[1,2] have been prepared by the reaction of phenylmagnesium halides with diarylchlorostibines R'R''ClSb, which were obtained by the diazonium reaction. However, alkyl-substituted analogues are not known[3].

Here we wish to report on the preparation of the asymmetrical tertiary stibines, $(C_6H_5)(CH_3)RSb$ (R = alkyl) and $[(C_6H_5)(CH_3)Sb]_2(CH_2)_n$ ($n=1$, 3 and 4) via the cleavage reaction of $(C_6H_5)_2(CH_3)Sb$ with sodium in liquid ammonia as shown below.



$$(C_6H_5)_2(CH_3)Sb \xrightarrow{2Na} [(C_6H_5)(CH_3)SbNa] \rightarrow \begin{cases} \xrightarrow{RCl} (C_6H_5)(CH_3)RSb \\ \xrightarrow{\frac{1}{2}(CH_2)_nCl_2} [(C_6H_5)(CH_3)Sb]_2(CH_2)_n \end{cases}$$

PMR data are submitted to show the existence of the stable invertomers of these asymmetrical stibines.

EXPERIMENTAL

All the reactions were carried out under a dry nitrogen atmosphere, and nitrogen was bubbled into the solvents just before use. Since essentially the same procedure was used to prepare all of the tertiary stibines, only typical experiments will be described. Since all the tertiary stibines except $[(C_6H_5)_2Sb]_2(CH_2)_3$ are easily oxidized in air, analyses were performed on the dihalides obtained by adding sulfuryl chloride or bromine to the stibine in dichloromethane at 0°. The PMR spectra were measured in $CDCl_3$ using Japan Electron Optics JNM-3H-60 or JNM-PS-100 spectrometers, and the data (δ) are given in ppm downfield from TMS.

Preparation of $(C_6H_5)_2(CH_3)Sb$ *and* $[(C_6H_5)_2Sb]_2(CH_2)_3$

$(C_6H_5)_2(CH_3)Sb$. To a solution of $(C_6H_5)_3Sb$ (75 g, 0.21 mol) in liquid ammonia (1 l), sodium (9.7 g, 0.42 mol) was added with stirring, and the stirring was continued for 6 h. After ammonium chloride (11.2 g, 0.21 mol) was added to consume the phenylsodium, methyl chloride gas was bubbled into the dark red solution of $(C_6H_5)_2SbNa$[4,5]. The reaction took place immediately. After the ammonia was allowed to boil off, water (200 ml), THF (200 ml) and benzene (70 ml) were added to dissolve the residue. The organic layer was separated and dried with anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residual liquid was distilled to give 36.5 g (60%) of colorless $(C_6H_5)_2(CH_3)Sb$: b.p. 115–120°/1 mmHg (lit[6]. b.p. 98–105.5/5×10^{-5} mmHg); PMR 1.11 (s, $SbCH_3$), 7.10–7.50 (m, aromatic).

$(C_6H_5)_2(CH_3)SbBr_2$. This compound was recrystallized from dichloromethane/petroleum ether; m.p. 147–148°. (Found: C, 34.81; H, 3.02. $C_{13}H_{13}Br_2Sb$ calcd.: C, 34.64; H, 2.91%.) PMR 2.99 (s, $SbCH_3$), 7.40–7.60 and 8.00–8.23 (m, aromatic).

TABLE 1

PROPERTIES OF ASYMMETRICAL TERTIARY STIBINES AND THEIR DERIVATIZED DIHALIDES

Tertiary stibines	*B.p.* (°*C/mmHg*)	*Derivatized dihalides*	*M.p.* (°*C*)	*Analysis found (calcd.)* (%)	
				C	*H*
$(C_6H_5)(CH_3)RSb$		$(C_6H_5)(CH_3)RSbX_2$			
$R=C_2H_5$	74–75/2.5	X=Br	44–45	27.11 (26.89)	3.34 (3.26)
$(CH_3)_2CH$	84–85/4	Br	62–63	29.02 (28.82)	3.43 (3.63)
$C_6H_5CH_2$	135–136/2	Br	132–133	36.35 (36.18)	3.21 (3.25)
$[(C_6H_5)(CH_3)Sb]_2(CH_2)_n$[a]		$[X_2(C_6H_5)(CH_3)Sb]_2(CH_2)_n$			
$n=1$	130–168/10^{-2}	X=Cl	163	30.89 (30.87)	3.14 (3.11)
		F[b]	120–121	35.05 (34.79)	3.34 (3.50)
3	130–180/10^{-2}	Cl	148.5–149.5	33.41 (33.38)	3.71 (3.63)
4	100–157/10^{-2}	Cl	198.5–199.5	34.54 (34.55)	3.94 (3.87)

[a] A yellow color could not be removed by repeated distillations (See ref. 5).

[b] Obtained from the reaction of $[Cl_2(C_6H_5)(CH_3)Sb]_2CH_2$ with AgF in moist acetone.

$[(C_6H_5)_2Sb]_2(CH_2)_3$. This compound was prepared in 60% yield by the reaction of $(C_6H_5)_2SbNa$ with a 0.5 molar amount of $(CH_2)_3Cl_2$ and recrystallized from acetone, m.p. 52–53°. (Found: C, 54.69; H, 4.62. $C_{27}H_{26}Sb_2$ calcd.: C, 54.60; H, 4.41%.) PMR 1.94 [s, $Sb(CH_2)_3Sb$], 7.00–7.60 (m, aromatic).

$[Cl_2(C_6H_5)_2Sb]_2(CH_2)_3$. This compound was recrystallized from dichloromethane/methanol; m.p. 137–137.5°. (Found: C, 43.83; H, 3.50. $C_{27}H_{26}Cl_4Sb_2$ calcd.: C, 44.07; H, 3.56%.) PMR 3.00–3.50 [m, $Sb(CH_2)_3Sb$], 7.45–7.65 and 7.97–8.30 (m, aromatic).

Preparation of asymmetrical tertiary stibines $(C_6H_5)(CH_3)RSb$ [$R = C_2H_5$, $(CH_3)_2CH$, $C_6H_5CH_2$, $(CH_2)_nSb(CH_3)(C_6H_5)$ ($n = 1, 3, 4$)]

All the compounds were obtained in ca. 60% yields from the reaction of the corresponding alkyl chloride or dichloroalkane with $(C_6H_5)(CH_3)SbNa$ prepared

TABLE 2

PMR DATA[a] OF ASYMMETRICAL TERTIARY STIBINES AND THEIR DERIVATIZED DIHALIDES

Tertiary stibines	*δ (ppm)*	*J (Hz)*	*Derivatized dihalides*	*δ (ppm)*	*J (Hz)*	*Assignment*
$(C_6H_5)(CH_3)RSb$			*$(C_6H_5)(CH_3)RSbX_2$*			
$R=C_2H_5$	0.90 (s)		X=Br	2.71 (s)		$SbCH_3$
	1.30 (m)			1.71 (t)	7.5[b]	SbC_2H_5
				3.23 (q)	7.5[b]	
$(CH_3)_2CH$	0.95 (s)		Br	2.73 (s)		$SbCH_3$
	1.21 (d)	7.5[c]		1.75 (d)	6.8[c]	$C(CH_3)_2$
	1.26 (d)	7.5[c]				
	1.90 (m)			3.85 (m)	6.8[c]	SbCH
$C_6H_5CH_2$	0.95 (s)		Br	2.49 (s)		$SbCH_3$
	2.96 (d)	12.0[d]		4.61 (s)		$SbCH_2$
	3.06 (d)	12.0[d]				
$[(C_6H_5)(CH_3)Sb]_2(CH_2)_n$[f]			*$[X_2(C_6H_5)(CH_3)Sb]_2(CH_2)_n$*			
$n=1$[g]	0.91 (s)		X=Cl	2.83 (s)		$SbCH_3$
	1.45 (d)	11.3[d]		4.20 (s)		$SbCH_2Sb$
	1.50 (d)	11.3[d]				
	1.50 (d)					
			F[g]	2.00 (m)		$SbCH_3$
				2.90 (qui)	6.0[e]	$SbCH_2Sb$
3	0.83 (s)		Cl	2.48 (s)		$SbCH_3$
	1.64 (m)			3.00 (m)		$Sb(CH_2)_3Sb$
4	0.84 (s)		Cl[h]			$SbCH_3$
	1.63 (m)					$Sb(CH_2)_4Sb$

[a] In $CDCl_3$ at 23°; δ ppm downfield from internal TMS. Aromatic protons were observed at about 7.0–7.6 ppm in tertiary stibines and at about 7.3–7.7 and 8.0–8.3 ppm in derivatized dihalides. Multiplicity: (s), singlet; (d), doublet; (t), triplet; (q), quartet; (qui), quintet; (m), multiplet. [b] $J(CH_3\text{–}CH_2)$. [c] $J(CH_3\text{–}CH)$. [d] $J(H_A\text{–}H_B)$. [e] $J(CH_2\text{–}F)$. [f] The yellow liquids showed a small broad singlet at 1.00–1.12 ppm due to an impurity. The peak scarcely appeared in the pale yellow liquid of $[(C_6H_5)(CH_3)Sb]_2CH_2$ obtained by reduction from $[Cl_2(C_6H_5)(CH_3)Sb]_2CH_2$ (see ref. 5). [g] At 100 MHz. [h] Not measured because of the limited solubility in $CDCl_3$.

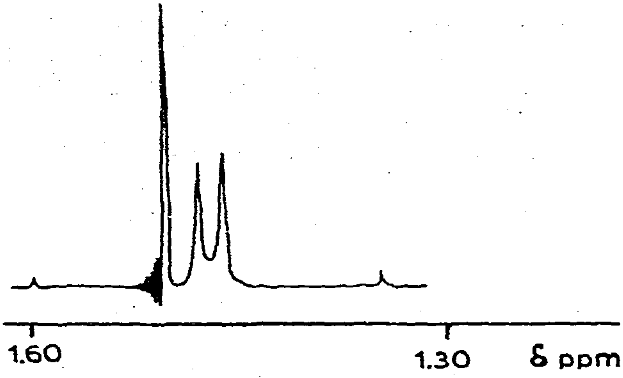


Fig. 1. PMR Spectrum of methylene group in $[(C_6H_5)(CH_3)Sb]_2CH_2$ (b.p. 130–168°/10^{-2} mmHg) in $CDCl_3$ solution at 23°.

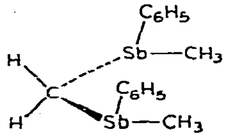
in 14 h from $(C_6H_5)_2(CH_3)Sb$* and sodium. $[(C_6H_5)(CH_3)Sb]_2(CH_2)_3$ was prepared also from the reaction of $[(C_6H_5)_2Sb]_2(CH_2)_3$ with sodium and CH_3Cl.

Properties and the PMR data of the asymmetrical stibines and their dihalides thus obtained are listed in Tables 1 and 2, respectively. The PMR spectrum of the methylene group in $[(C_6H_5)(CH_3)Sb]_2CH_2$ is shown in Fig. 1.

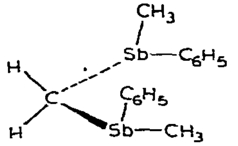
RESULTS AND DISCUSSION

The asymmetrical tertiary stibines, $(C_6H_5)(CH_3)RSb$ and $[(C_6H_5)(CH_3)Sb]_2$-$(CH_2)_n$ were obtained in fairly good yields via cleavage of a phenyl group in $(C_6H_5)_2$-$(CH_3)Sb$ with sodium.

As shown in Table 2, the PMR spectra of phenylmethylbenzylstibine and phenylmethylisopropylstibine in $CDCl_3$ at 23° showed an AB quartet for the benzyl methylene group and two doublets for the isopropyl methyl groups, which are expected for asymmetrical compounds. In methylene bis(phenylmethylstibine) a singlet and an AB quartet for the methylene group were observed as shown in Fig. 1. These are reasonably assigned to the racemic and the *meso* forms, respectively.



meso



racemic

The above observations, which are consistent with the calculations** of both Weston[7] and Keopple *et al.*[8], suggest that the rates of the pyramidal inversion of our asymmetrical tertiary stibines are very slow on the PMR time scale.

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* Asymmetrical stibines were not obtained from $(C_6H_5)_2RSb$ [$R=(CH_3)_2CH$, $C_6H_5CH_2$ and $CH_2Sb(C_6H_5)_2$]. The details of these reactions will be published.

** The calculated barrier to the pyramidal inversion for trimethylstibine was reported to be 26.7 (ref. 7) and 25 kcal/mol (ref. 8). A lower limit to the barrier for diisopropyl-*p*-tolylstibine was determined[9] to be 26 kcal/mol from its PMR spectrum.

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