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ALKYL CLEAVAGE OF TERTIARY PHENYLALKYLSTIBINES WITH SODIUM

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Recently we have reported that one phenyl group in diphenylmethylstibine was cleaved with sodium in liquid ammonia, and subsequent treatment with alkylchlorides gave asymmetrical tertiary stibines $(C_6H_5)(CH_3)RSb$ (R= Alkyl) in fairly good yields (1). Here we wish to report an interesting alkyl cleavage reaction found in tertiary phenylalkylstibines with the same reagent.*

As shown in Table 1, the cleavage of the alkyl group was found in the diphenylalkylstibines, $(C_6H_5)_2RSb$ [R= C_2H_5, $(CH_3)_2CH$ and $C_6H_5CH_2$], and $[(C_6H_5)_2Sb]_2CH_2$**, and the cleavage of the phenyl group was also observed in $(C_6H_5)_2(C_2H_5)Sb$. It is worth noting that the alkyl cleavage was found to occur in all the phenyldialkylstibines listed. The results suggest that the cleavage of the isopropyl (or benzyl) group is preferred to those of the phenyl and methyl groups, and the phenyl group in phenyldialkylstibines is difficult to be cleaved.

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* With lithium in THF, one phenyl group was cleaved in diphenylalkylphosphines, and in phenyldialkylphosphines a complex reaction took place but characterizable products were not obtained (2). Similarly, with potassium in dioxane, one aryl group was cleaved in diarylalkylarsines but in aryldialkylarsines no reaction occurred (3).

** In $[(C_6H_5)_2Sb]_2(CH_2)_3$ (1) and $[(C_6H_5)_2E]_2(CH_2)_n$ [E= P(4), As(5)], only one of the phenyl groups attached to each metal atom was cleaved with sodium in liquid ammonia.

Table 1

Cleavage Reaction of Tertiary Phenylalkylstibines

Starting material	Reaction time (h) with Na	Alkyl-chloride	Product stibine	Product % yield
Ph_2EtSb	15	MeCl	Ph_2MeSb PhMeEtSb	30 25
$Ph_2{}^iPrSb$	15	MeCl	Ph_2MeSb	58
Ph_2BzSb	15	MeCl	Ph_2MeSb	30
$(Ph_2Sb)_2CH_2$	3.5	MeCl	Ph_2MeSb	29
$PhMe_2Sb$	5	BzCl	PhMeBzSb	43
PhMeEtSb	10	BzCl	PhMeBzSb PhEtBzSb	29 24
$PhMe{}^iPrSb$	10	BzCl	PhMeBzSb	58
PhMeBzSb	10	^iPrCl	$PhMe{}^iPrSb$	56

Me= CH_3, Et= C_2H_5, ^iPr= $(CH_3)_2CH$, Bz= $C_6H_5CH_2$ and Ph= C_6H_5.

Experimental

All the reactions were carried out under a dry nitrogen atmosphere and nitrogen was bubbled into the solvents just before use. The tertiary stibines prepared here are easily oxidized in air, and analyses were performed on their derivatized dibromides obtained by adding bromine in dichloromethane at 0°. The PMR spectra were measured on a Japan Electron Optics JNM-3H-60 spectrometer, and the data are given in δ ppm downfield from internal TMS in $CDCl_3$.

Starting materials

$(C_6H_5)_2RSb$ [R= C_2H_5, $(CH_3)_2CH$, $C_6H_5CH_2$ and $(C_6H_5)_2SbCH_2$(6)] were prepared from $(C_6H_5)_3Sb$, sodium and the corresponding alkylchlorides in 50-70 % yields.

$(C_6H_5)_2(C_2H_5)Sb$: $(C_6H_5)_3Sb$ (17.6 g, 0.05 mol) was added to sodium (2.3 g, 0.1 mol) in liquid ammonia (300 ml) and stirring was continued for 6 h. Ammonium chloride (2.7 g, 0.05 mol) was added and ethylchloride gas was bubbled into the dark red solution. The reaction took place immediately. After the ammonia was allowed to boil off, water (50 ml) and THF or ether (80 ml) were added to dissolve the residue. The organic layer was separated and dried with anhydrous sodium sulfate. The solvent was removed in vacuo and the residual liquid was distilled to give 8.7 g (50 %) of colorless $(C_6H_5)_2(C_2H_5)Sb$: b.p. 123-124°/0.5 mm; PMR 1.03-2.06 (m, SbC_2H_5), 7.05-7.61 (m, aromatic).

$(C_6H_5)_2(C_2H_5)SbBr_2$: m.p. 156-157° [m.p. 158° (7)]. (Found: C, 36.34; H, 3.34. $C_{14}H_{15}Br_2Sb$ calcd.: C, 36.18; H, 3.25 %.) PMR 1.80 [t, C-CH_3; J(CH_2-CH_3) 7.5 Hz], 3.48 (q, $SbCH_2$), 7.27-7.72 and 7.88-8.32 (m, aromatic).

$(C_6H_5)_2[(CH_3)_2CH]Sb$: b.p. 127-128°/0.5 mm [b.p. 167-169°/6-7 mm (8)]. PMR 1.27 [d, $(CH_3)_2C$; J(CH-CH_3) 7.5 Hz], 2.25 (m, SbCH), 7.00-7.51 (m, aromatic).

$(C_6H_5)_2[(CH_3)_2CH]SbBr_2$: m.p. 155-156°. (Found: C, 37.62; H, 3.64. $C_{15}H_{17}Br_2Sb$ calcd.: C, 37.62; H, 3.58 %.) PMR 1.78 [d, $(CH_3)_2C$; J(CH-CH_3) 6.8 Hz], 3.96 (m, SbCH), 7.15-7.50 and 7.77-8.10 (m, aromatic).

$(C_6H_5)_2(C_6H_5CH_2)Sb$: b.p. 179-180°/0.5 mm [b.p. 224-225°/15-17 mm (9)]. PMR 3.10 (s, $SbCH_2$), 6.80-7.50 (m, aromatic).

$(C_6H_5)_2(C_6H_5CH_2)SbBr_2$: m.p. 121-122°. (Found: C, 43.24; H, 3.28. $C_{19}H_{17}Br_2Sb$ calcd.: C, 43.31; H, 3.25 %.) PMR 4.86 (s, $SbCH_2$), 7.15-7.50 and 7.60-7.95 (m, aromatic).

$(C_6H_5)(CH_3)RSb$ [R= CH_3, C_2H_5(1), $(CH_3)_2CH$(1) and $C_6H_5CH_2$(1)] were prepared from $(C_6H_5)_2(CH_3)Sb$.

$(C_6H_5)(CH_3)_2Sb$: b.p. 74-75°/3.5 mm [b.p. 95-97°/10 mm (10)]. PMR 0.95 (s, $SbCH_3$), 7.10-7.60 (m, aromatic).

$(C_6H_5)(CH_3)_2SbBr_2$: m.p. 108-109°. (Found: C, 24.60; H, 2.93. $C_8H_{11}Br_2Sb$ calcd.: C, 24.72; H, 2.85 %.) PMR 2.80 (s, $SbCH_3$), 7.10-7.60 and 7.85-8.15 (m, aromatic).

Cleavage of tertiary phenylalkylstibines

All the reactions were carried out by the practically same procedure to that of the preparation of the starting materials. The results are summarized in Table 1. The products and the derivatized bromides were identified by comparison of the PMR and IR spectra with the authentic samples. The two stibines obtained from $(C_6H_5)_2(C_2H_5)Sb$ were separated by distillation. However, the products from $(C_6H_5)(CH_3)(C_2H_5)Sb$ and benzylchloride were not separated by distillation, and the yields were assumed by the PMR spectrum of the brominated mixture.

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