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BIS(DICHLOROSTIBINO)METHANE

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Although bis(diorganostibino)methanes $(R_2Sb)_2CH_2$ (R = CH_3 or C_6H_5) have recently been prepared[1,2], a useful compound such as $(X_2Sb)_2CH_2$ (X = halogen) has not yet been prepared. It was found that bis(diphenylstibino)methane (I) reacts easily with dry hydrogen chloride in chloroform to give bis(dichlorostibino)-methane (II) almost quantitatively.

$$\underset{\text{(I)}}{[(C_6H_5)_2Sb]_2CH_2} \underset{C_6H_5MgBr}{\overset{HCl}{\rightleftharpoons}} \underset{\text{(II)}}{(Cl_2Sb)_2CH_2} \xrightarrow{CH_3MgI} \underset{\text{(III)}}{[(CH_3)_2Sb]_2CH_2}$$

(II) is a colorless crystalline compound and easily hydrolyzed on solution. As shown above, methylation or phenyl-ation of (II) was successful by using corresponding Grignard reagents in the presence of N,N,N',N'-tetramethylethylenediamine.

Experimental

All the reactions were carried out under dry nitrogen atmosphere and nitrogen was bubbled into the solvents just before use.

Preparation of (II)

Bis(diphenylstibino)methane[2] (20 g, 35.3 mmol) was dissolved in 100 ml of $CHCl_3$ and dry hydrogen chloride was bubbled into the solution at 0° for 30 min. The white precipitate

was recrystallized from dry benzene containing dry hydrogen chloride to give 13.0 g (92 %) of colorless crystals of (II); m.p. >152° decomp. (Found: C, 3.27; H, 0.50; Cl, 35.22; Sb, 60.20 $CH_2Cl_4Sb_2$ calcd.: C, 3.01; H, 0.50; Cl, 35.51; Sb, 60.98 %.)
A tentative assignment of the IR spectrum (in Nujol or hexachlorobutadiene mull) is as follows: CH str., 2980 w and 2910 w; CH_2 scis., 1328 m; CH_2 wag., 1090 w; CH_2 twist., 983 s; CH_2 rock., 620 vs; Sb-C-Sb asym.str., 577 vs; Sb-C-Sb sym.str., 564 vs; Sb-Cl str., 323 vs,br and 297 vs,br; other weak bands, 1155, 932 and 928 cm^{-1}.
The PMR spectrum (ca. 3 wt % in benzene using TMS as an internal standard): τ(Sb$C\underline{H}_2$Sb), 8.15 ppm.

This compound is not flammable and not oxidized in air, but was hydrolyzed easily to give an oxide, $(OSb)_2CH_2$; m.p. >260° decomp. (Found: C, 4.35; H, 0.90 $CH_2O_2Sb_2$ calcd.: C, 4.15; H, 0.70 %.)

When an equimolar amount of N,N,N',N'-tetramethylethylenediamine to Mg was added to RMgX (R = CH_3 or C_6H_5; X = I or Br) in ether, brown precipitate appeared. To this mixture ether solution of (II) was added. The yields of (I) and (III) were 55 and 38 %, respectively. Without addition of the amine, the yields were only 2-3 %. (I) and (III) were identical with the compounds prepared by the previous methods[2].

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References

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