

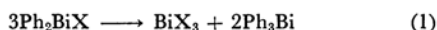
Bismuth-Carbon Cleavage on Complex Formation

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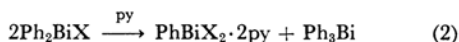
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Numerous investigations have been concerned with the preparation of triarylbismuths from diarylbismuth halides. Gilman et al.¹⁾ have reported that the reaction of diphenylbismuth halides with hydrazine hydrate in refluxing alcohol gave triphenylbismuth and inorganic bismuth halides according to;



However, we have obtained monophenylbismuth compounds together with triphenylbismuth by the reactions of diphenylbismuth halides with pyridine at room temperature.



These compounds correspond to the hypothetical intermediate substances of the conversion reaction 1. Hartmann et al.²⁾ have assumed that analogous compounds are formed in the decomposition reactions of para-substituted phenylbismuth compounds.

Experimental.—Phenylbismuth Halides.— Ph_2BiX and PhBiBr_2 were prepared by the reaction³⁾ of Ph_3Bi and BiX_3 ($\text{X}=\text{Cl}, \text{Br}$), and purified by the recrystallization from dry benzene.

Phenylbismuth Dibromide Pyridine Ad-

1) H. Gilman and H. L. Yablunsky, *J. Am. Chem. Soc.*, **62**, 665 (1940).

2) H. Hartmann, G. Habenicht and W. Reiss, *Z. Anorg. Allg. Chem.*, **317**, 54 (1962).

3) H. Gilman, H. L. Yale, *Chem. Revs.*, **30**, 281 (1942).

duct.—Method 1: A solution of 3 g. Ph_2BiBr in 50 ml. of dry pyridine was added dropwise to 150 ml. of petroleum ether. After filtering 0.2 gr. of white solid (A), m. p. 143–146°C, the filtrate was kept standing for a day at room temperature, and 1.1 gr. of pale yellow needle-like crystals (B) of $\text{PhBiBr}_2 \cdot 2\text{py}$ was obtained, m. p. 145–146°C. Yield (A+B) 62%.

Found: Bi, 34.72; C, 31.93; H, 2.33; N, 4.65; Br, 26.42. Calcd. for $\text{C}_6\text{H}_5\text{BiBr}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$: Bi, 34.59; C, 31.81; H, 2.50; N, 4.64; Br, 26.46%.

Removal of the solvents under reduced pressure from the mother liquor gave 1.3 gr. of white solid, which was recrystallized from ethanol to give Ph_3Bi , m. p. 77–78°C. Yield 87%.

Method 2: On addition of a solution of PhBiBr_2 (1 g.) in 40 ml. of pyridine to 150 ml. of petroleum ether, a creamy precipitate of $\text{PhBiBr}_2 \cdot 2\text{py}$ (m. p. 145–146°C) was obtained almost quantitatively.

The infrared spectra and the mixed melting point showed that the complexes prepared by methods 1 and 2 were identical.

Phenylbismuth Dichloride Pyridine Adduct.

—White needle crystals of $\text{PhBiCl}_2 \cdot 2\text{py}$ (m. p. 136–137°C) was prepared by the same procedure (method 1) used for the bromide. Yield 77%.

Found: Bi, 40.67; C, 37.83; H, 2.80; N, 5.46; Cl, 13.77. Calcd. for $\text{C}_6\text{H}_5\text{BiCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$: Bi, 40.56; C, 37.30; H, 2.93; N, 5.44; Cl, 13.76%.

From the mother liquor a 95% yield of Ph_3Bi was obtained.