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LETTERS TO THE EDITOR

New Method of Synthesis of Tetraphenylbismuth Aroxides

V. V. Sharutin, I. V. Egorova, and T. V. Tsiplukhina

Blagoveshchensk State Pedagogical University, Blagoveshchensk, Russia

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It is known that bismuth compounds of the general formula Ph_4BiOR (R = SiPh₃, C_6F_5 , C_6Cl_5) are synthesized from pentaphenylbismuth and hydroxyl-containing compounds [1, 2]. We devised a new method of synthesis of tetraphenylbismuth aroxides, involving reaction of pentaphenylbismuth with triphenylbismuth diaroxides. The method was exemplified by the synthesis of 2,4,6-tribromophenoxy- and (2,4,6-trichlorophenoxy)tetraphenylbismuth in yields of up to 46% from triphenylbismuth diaroxides and pentaphenylbismuth.

$$Ph_{5}Bi + Ph_{3}Bi(OAr)_{2} \longrightarrow 2Ph_{4}BiOAr,$$

Ar = C_{6}H_{2}Br_{2}-2,4,6, C_{6}H_{2}Cl_{2}-2,4,6.

The reactions were performed at room temperature in an aromatic hydrocarbon. Therewith, the solution changed color from violet (characteristic of pentaphenylbismuth solutions) to yellow within 2 min. The melting points and IR spectra of the synthesized tetraphenylbismuth aroxides were coincident with those of the same compounds synthesized from pentaphenylbismuth and phenols.

The starting triphenylbismuth diaroxides were prepared by a procedure previously applied to the synthesis of triphenylbismuth diacylates [3]. Like in the referred work, the oxidative addition of phenols to triphenylbismuth successfully proceeds in the presence of hydrogen peroxide in ether, providing the target products in 54% yields.

$$\begin{split} \text{Ph}_3\text{Bi} + 2\text{HOAr} + \text{H}_2\text{O}_2 &\longrightarrow \text{Ph}_3\text{Bi}(\text{OAr})_2 + 2\text{H}_2\text{O}, \\ \text{Ar} &= \text{C}_6\text{H}_2\text{Br}_3\text{-}2\text{,}4\text{,}6, \ \text{C}_6\text{H}_2\text{Cl}_3\text{-}2\text{,}4\text{,}6. \end{split}$$

According to preliminary X-ray diffraction data, the bismuth atoms in bis(2,4,6-tribromophenoxy)triphenylbismuth and (2,4,6-tribromophenoxy)tetraphenylbismuth have a trigonal bipyramidal coordination, and the aroxyl ligands are axial.

Bis(2,4,6-tribromophenoxy)triphenylbismuth. To a mixture of 0.50 g of triphenylbismuth and 0.76 g of 2,4,6-tribromophenol in 15 ml of ether, 0.13 ml of 31% aqueous hydrogen peroxide was added. The resulting mixture was left to stand at 20°C for 24 h. The solvent was removed, and the residue was treated with 20 ml of hexane to isolate 0.67 g (54%) of bis-(2,4,6-tribromophenoxy)triphenylbismuth, mp 118°C. The residue was treated with 20 ml of toluene to isolate 0.15 g (22%) triphenylbismuth dibromide, mp 125°C.

Bis(2,4,6-trichlorophenoxy)triphenylbismuth was obtained in a similar way, yield 48%, mp 113°C.

Reaction of pentaphenylbismuth with 2,4,6-tribromophenol. A mixture of 0.50 g of pentaphenylbismuth and 0.28 g of tribromophenol in 20 ml of benzene was stirred for 1–2 min. The solution got yellow. It was diluted with 10 ml of hexane, filtered, and the solvent was removed to obtain 0.56 g (80%) of (2,4,6-tribromophenoxy)tetraphenylbismuth, mp 133° C.

(2,4,6-Trichlorophenoxy)tetraphenylbismuth was obtained in a similar way, yield 83%, mp 132°C.

Reaction of pentaphenylbismuth with bis(2,4,6-**tribromophenoxy)triphenylbismuth.** A mixture of 0.16 g of pentaphenylbismuth and 0.29 g of bis(2,4,6-tribromophenoxy)triphenylbismuth in 20 ml of benzene was stirred for 1–2 min. The solution got yellow. It was diluted with 10 ml of hexane, filtered, and the solvet was removed to obtain 0.20 g (46%) of (2,4,6-tribromophenoxy)tetraphenylbismuth.

(2,4,6-Trichlorophenoxy)tetraphenylbismuth was obtained in a similar way, yield 38%, mp 132°C.

The IR spectra were measured on a Hitachi-215 spectrophotometer (suspension in mineral oil between NaCl plates).

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