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Arylation of Aryl- and Diarylbismuth Arenesulfonates with Pentaarylantimony

V. V. Sharutin, I. V. Egorova, I. I. Pavlushkina, and T. K. Ivanenko

Blagoveshchensk State Pedagogical University, Blagoveshchensk, Russia

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Abstract—Pentaarylantimony Ar_3Sb (Ar = Ph, *p*-Tol) arylates diarylbismuth arylsulfonates Ar_2BiOSO_2Ar' (Ar' = C_6H_4Me-4; $C_6H_3Me_2$-2,4, $C_6H_3Me_2$-2,5) in ether at 20°C (48 h) to form triarylbismuth in yields of up to 95%. The second reaction product is tetraarylantimony arenesulfonate. The reaction of pentaphenylantimony with phenylbismuth bis(arenesulfonate) $PhBi(OSO_2Ar')_2$ under the same conditions leads to formation of diphenylbismuth arenesulfonate and tetraphenylantimony arenesulfonate in yields of up to 90%.

It is khown that radical redistribution reactions are characteristic of pentaarylantimony and pentaphenylbismuth. These compounds are effective arylating agents for organic derivatives of tin(IV), antimony(V), and bismuth(V) [1–8]. Proceeding with studies on arylating properties of pentaarylantimony we have investigated its reactions with aryl- and diarylbismuth(III) arenesulfonates.

It was shown that the reaction of pentaarylantimony with diphenylbismuth arenesulfonate involves redistribution of radicals between the antimony and bismuth atoms to give triarylbismuth and tetraarylantimony arenesulfonates in yields of up to 95%.

$$Ar_5Sb + Ar_2BiOSO_2Ar' \longrightarrow Ar_3Bi + Ar_4SbOSO_2Ar',$$

$$Ar = Ph,\ p\text{-Tol};\ Ar' = C_6H_4Me\text{-}4,\ C_6H_3Me_2\text{-}2,4,\ C_6H_3Me_2\text{-}2,5.$$

The reactions between the above-mentioned reagents proceed in ether at 20°C for 48 h. Therewith, disappearance of crystals of the starting diarylbismuth arenesulfonate and crystallization of tetraarylantimony arenesulfonate take place.

The reaction of pentaphenylantimony with phenylbismuth bis(arenesulfonate) under similar conditions results in quantitative formation of tetraphenylantimony arenesulfonate and diphenylbismuth arenesulfonate.

$$Ph_5Sb + PhBi(OSO_2Ar')_2 \longrightarrow Ph_2BiOSO_2Ar' + Ph_4SbOSO_2Ar',$$

$$Ar' = C_6H_4Me\text{-}4,\ C_6H_3Me_2\text{-}2,4,\ C_6H_3Me_2\text{-}2,5.$$

Hence, it was shown that pentaarylantimony is an effective arylating agent not only for bismuth(V), but also for bismuth(III) organic derivatives.

EXPERIMENTAL

The IR spectra were recorded on a Hitachi-215 spectrometer for suspensions in Vaseline oil between NaCl plates.

Reaction of diphenylbismuth 4-methylbenzenesulfonate with pentaphenylantimony. A mixture of 1.10 g of pentaphenylantimony and 1.16 g of diphenylbismuth 4-methylbenzenesulfonate in 20 ml of ether was kept for 48°C at 20°C. Coarse crystals formed and were filtered off, washed with hexane, dried, and weighted. Tetraphenylantimony 4-methylbenzenesulfonate, 120 g (93%) was obtained, mp 165°C. The IR spectrum of this compound is identical to the IR spectrum of a compound prepared from pentaphenylantimony and 4-methylbenzenesulfonic acid. The ethereal and hexane solutions were evaporated, and the solid residue was recrystallized from ethanol. Triphenylbismuth, 0.92 g (96%), was obtained, mp 78°C.

Reaction of di-*p*-tolylbismuth 4-methylbenzenesulfonate with penta-*p*-tolylantimony. A mixture of 1.15 g of penta-*p*-tolylantimony and 1.12 g of di-*p*-tolylbismuth 4-methylbenzenesulfonate in 20 ml of ether was kept for 48 h at 20°C. Coarse crystals formed and were filtered off, washed with hexane, dried, and weighted. Tetra-*p*-tolylantimony 4-methylbenzenesulfonate, 1.30 g (99%) was obtained, mp 143°C. The IR spectrum of this compound is identical to the IR spectrum of a compound prepared from penta-*p*-tolylantimony and 4-methylbenzenesulfonic acid. The ethereal and hexane solutions were evaporated, and the solid residue was re crystallized from ethanol. Tri-*p*-tolylbismuth, 0.93 g (97%), was obtained, mp 118°C.

Reaction of phenylbismuth bis(2,5-dimethylbenzenesulfonate) with pentaphenylantimony. A mixture of 1.15 g of pentaphenylantimony and 1.49 g of phenylbismuth bis(2,5-dimethylbenzenesulfonate) in 30 ml of ether was kept for 48 h at 20°C. The solvent was removed, and the residue extracted with toluene. The crystals insoluble in toluene were filtered off and dried. Diphenylbismuth 2,5-dimethylbenzenesulfonate, 1.20 g (97%), was obtained, mp 215°C. The IR spectrum of this compound was identical to the IR spectrum of the diphenylbismuth 2,5-dimethylbenzenesulfonate prepared from triphenylbismuth and 2,5-dimethylbenzenesulfonic acid. After evaporation of the toluene, 1.32 g (95%) of tetraphenylantimony 2,5-dimethylbenzenesulfonate was obtained, mp 142°C. The IR spectrum of this compound was identical to the IR spectrum of the tetraphenylantimony 2,5-dimethylbenzenesulfonate prepared from pentaphenylantimony and 2,5-dimethylbenzenesulfonic acid.

Reaction of phenylbismuth bis(2,4-dimethylbenzenesulfonate) with pentaphenylantimony was performed in a similar way. Diphenylbismuth 2,4-dimethylbenzenesulfonate (98%), mp 210°C, and tetraphenylantimony 2,4-dimethylbenzenesulfonate (98%), mp 209°C, were obtained.

Reaction of phenylbismuth bis(4-methylbenzenesulfonate) with pentaphenylantimony was performed in a similar way. Diphenylbismuth 4-methylbenzenesulfonate (95%), mp 190°C, and tetraphenylantimony 4-methylbenzenesulfonate (93%), mp 165°C, were obtained.

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