

Reactions of Triarylbiomuth Bis(arenesulfonates)

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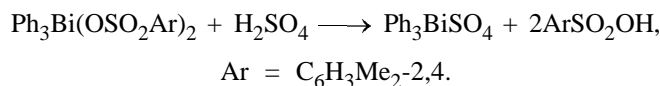
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Abstract—Reactions of triphenylbiomuth with sodium salts, acids, alkalies, and zinc are studied. In the first three cases Bi–O bond cleavage takes place, while zinc reduces the starting biomuth compounds to triphenylbiomuth.

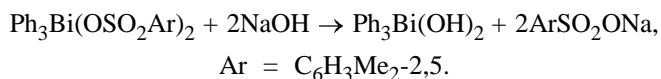
Triphenylbiomuth bis(arenesulfonates) have been synthesized by reaction of triphenylbiomuth carbonate with benzene and 4-methylbenzenesulfonic acids [1] and also by oxidative addition of triphenylbiomuth to 2,4- and 2,5-dimethylbenzenesulfonic acids in the presence of hydrogen peroxide [2, 3]. At the same time, the reactivity of triphenylbiomuth bis(arenesulfonates) has scarcely been studied. The only precedent is the reaction of triphenylbiomuth bis(benzenesulfonate) and bis(4-methylbenzenesulfonate) with alkali metal chlorides, leading to formation of triphenylbiomuth dichloride [1].

We showed that treatment with sulfuric acid of triphenylbiomuth bis(arenesulfonates) gives rise to Bi–O bond cleavage. Triphenylbiomuth sulfate and arenesulfonic acid were quantitatively isolated from the reaction mixture.

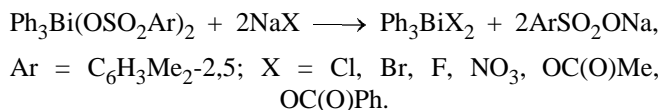


The Bi–O bonds are also easily cleaved under the action of alkalies. Hence, treatment with aqueous

potassium hydroxide or sodium alcoholate of alcoholic triphenylbiomuth bis(arenesulfonates) results in formation of triphenylbiomuth dihydroxide and potassium(sodium) arenesulfonate.



Substitution of arenesulfonyl groups on the biomuth atom also takes place in reactions of triphenylbiomuth bis(2,4- and bis(2,5-dimethylbenzenesulfonates) with sodium salts NaX in alcohol independent of the nature of X. With acetone instead of ethanol, the reaction pathway is the same.



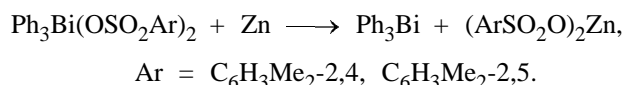
The yield of biomuth salts Ph_3BiX_2 reaches 98% (see table).

Zinc easily reduces triphenylbiomuth bis(arenesulfonates) to triphenylbiomuth. The second reaction

Products and yields of reactions of triphenylbiomuth bis(arenesulfonates) with salts, sulfuric acid, and zinc

Initial compounds	Reaction products (%)
$\text{Ph}_3\text{Bi}(\text{OSO}_2\text{C}_6\text{H}_3\text{Me}_{2-2,4})_2 + \text{NaF}$	Ph_3BiF_2 (87), $\text{NaOSO}_2\text{C}_6\text{H}_3\text{Me}_{2-2,4}$ (98)
$\text{Ph}_3\text{Bi}(\text{OSO}_2\text{C}_6\text{H}_3\text{Me}_{2-2,5})_2 + \text{NaF}$	Ph_3BiF_2 (93), $\text{NaOSO}_2\text{C}_6\text{H}_3\text{Me}_{2-2,5}$ (97)
$\text{Ph}_3\text{Bi}(\text{OSO}_2\text{C}_6\text{H}_3\text{Me}_{2-2,5})_2 + \text{NaCl}$	Ph_3BiCl_2 (97), $\text{NaOSO}_2\text{C}_6\text{H}_3\text{Me}_{2-2,5}$ (92)
$\text{Ph}_3\text{Bi}(\text{OSO}_2\text{C}_6\text{H}_3\text{Me}_{2-2,5})_2 + \text{NaBr}$	Ph_3BiBr_2 (89), $\text{NaOSO}_2\text{C}_6\text{H}_3\text{Me}_{2-2,5}$ (92)
$\text{Ph}_3\text{Bi}(\text{OSO}_2\text{C}_6\text{H}_3\text{Me}_{2-2,5})_2 + \text{NaNO}_3$	$\text{Ph}_3\text{Bi}(\text{NO}_3)_2$ (88), $\text{NaOSO}_2\text{C}_6\text{H}_3\text{Me}_{2-2,5}$ (95)
$\text{Ph}_3\text{Bi}(\text{OSO}_2\text{C}_6\text{H}_3\text{Me}_{2-2,5})_2 + \text{NaOC}(\text{O})\text{CH}_3$	$\text{Ph}_3\text{Bi}(\text{O}_2\text{CCH}_3)_2$ (92), $\text{NaOSO}_2\text{C}_6\text{H}_3\text{Me}_{2-2,5}$ (97)
$\text{Ph}_3\text{Bi}(\text{OSO}_2\text{C}_6\text{H}_3\text{Me}_{2-2,5})_2 + \text{NaOC}(\text{O})\text{Ph}$	$\text{Ph}_3\text{Bi}(\text{O}_2\text{CPh})_2$ (98), $\text{NaOSO}_2\text{C}_6\text{H}_3\text{Me}_{2-2,5}$ (97)
$\text{Ph}_3\text{Bi}(\text{OSO}_2\text{C}_6\text{H}_3\text{Me}_{2-2,4})_2 + \text{H}_2\text{SO}_4$	Ph_3BiSO_4 (94), $\text{HOSO}_2\text{C}_6\text{H}_3\text{Me}_{2-2,4}$ (96)
$\text{Ph}_3\text{Bi}(\text{OSO}_2\text{C}_6\text{H}_3\text{Me}_{2-2,4})_2 + \text{KOH}$	$\text{Ph}_3\text{Bi}(\text{OH})_2$ (62), $\text{KOSO}_2\text{C}_6\text{H}_3\text{Me}_{2-2,4}$ (98)
$\text{Ph}_3\text{Bi}(\text{OSO}_2\text{C}_6\text{H}_3\text{Me}_{2-2,5})_2 + \text{NaOH}$	$\text{Ph}_3\text{Bi}(\text{OH})_2$ (72), $\text{NaOSO}_2\text{C}_6\text{H}_3\text{Me}_{2-2,5}$ (91)
$\text{Ph}_3\text{Bi}(\text{OSO}_2\text{C}_6\text{H}_3\text{Me}_{2-2,4})_2 + \text{Zn}$	Ph_3Bi (96), $\text{Zn}[\text{OSO}_2\text{C}_6\text{H}_3\text{Me}_{2-2,4}]_2$ (95)
$\text{Ph}_3\text{Bi}(\text{OSO}_2\text{C}_6\text{H}_3\text{Me}_{2-2,5})_2 + \text{Zn}$	Ph_3Bi (95), $\text{Zn}[\text{OSO}_2\text{C}_6\text{H}_3\text{Me}_{2-2,5}]_2$ (95)

product is the zinc salt of the corresponding acid. The yields of the products are close to quantitative.



The starting compounds were prepared by oxidative addition of triphenylbismuth with arenesulfonic acids in the presence of hydrogen peroxide [2, 3].

Thus, we established that Bi–O bonds in triphenylbismuth bis(arenesulfonates) are easily cleaved under the action of sulfuric acid, bases, salts, and metallic zinc.

EXPERIMENTAL

The IR spectra were recorded on a Hitachi-215 spectrometer (suspension in Vaseline oil).

The reactions were carried out in evacuated glass ampules by the following typical procedures.

Reaction of triphenylbismuth bis(2,5-dimethylbenzenesulfonate) with sodium fluoride. A solution of 1.5 g of triphenylbismuth bis(2,5-dimethylbenzenesulfonate) in ethanol was mixed with a solution of 0.16 g of sodium fluoride in water. A finely dispersed precipitate formed. The solvent was removed, and the residue was extracted with toluene. The toluene was evaporated to leave 0.82 g (93%) of triphenylbismuth difluoride, mp 125°C. The weight of the toluene-insoluble sodium 2,5-dimethylbenzenesulfonate with mp >250°C was 0.75 g (97%). The IR spectra of the obtained compounds were identical with those of the authentic samples.

Reaction of triphenylbismuth bis(2,5-dimethylbenzenesulfonate) with sodium acetate. A mixture of 0.70 g of triphenylbismuth bis(2,5-dimethylbenzenesulfonate) and 0.14 g of sodium acetate in 20 ml of toluene was heated for 15 min at 90°C. The finely dispersed precipitate was washed with toluene and dried to obtain 0.35 g (97%) of sodium 2,5-dimethylbenzenesulfonate, mp >250°C. Removal of the solvent and crystallization from chloroform gave 0.44 g (92%) of triphenylbismuth diacetate, mp 187°C (with decomposition). The IR spectra of the obtained compounds were identical with those of the authentic samples.

Reaction of triphenylbismuth bis(2,4-dimethylbenzenesulfonate) with sulfuric acid. A mixture of 0.50 g of triphenylbismuth bis(2,4-dimethylbenzenesulfonate) and 10 ml of ethanol was treated with 0.13 ml of 98% sulfuric acid (1:4 molar ratio).

Crystals formed and were filtered off, washed with water and ethanol, and dried to obtain 0.31 g (94%) of triphenylbismuth sulfate, mp >280°C. IR spectrum, ν , cm^{-1} : 1250 v.s., 1120 v.s., 980 v.s. The aqueous-ethanolic extracts were evaporated in a dessicator with concentrated sulfuric acid to obtain 0.26 g (96%) of 2,4-dimethylbenzenesulfonic acid, mp 47°C.

Reaction of triphenylbismuth bis(2,4-dimethylbenzenesulfonate) with potassium hydroxide. A solution of 0.07 g of potassium hydroxide in 10 ml of ethanol was added to 0.50 g of triphenylbismuth bis(2,4-dimethylbenzenesulfonate) in 10 ml of ethanol. A precipitate formed and was washed with water and ethanol, and dried to obtain 0.18 g (62%) of triphenylbismuth dihydroxide. IR spectrum, ν , cm^{-1} : 3440 v.s., 3050 s., 1640 s., 1560 s., 1470 s., 1430 s., 1005 s., 990 s., 830 s., 730 v.s., 690 v.s. mp >250°C. The obtained triphenylbismuth dihydroxide was treated with ethanolic hydrochloric acid. The solvent was removed, and the residue was extracted with toluene and then with ethanol. The toluene extracts were evaporated to obtain triphenylbismuth dihydrochloride, mp 158°C. Evaporation of the ethanol extracts gave 0.27 g (98%) of potassium 2,4-dimethylbenzenesulfonate, mp >250°C. IR spectrum, ν , cm^{-1} : 1200 v.s., 1095 s., 1030 v.s.

Reaction of triphenylbismuth bis(2,5-dimethylbenzenesulfonate) with zinc. A mixture of 0.35 g of triphenylbismuth bis(2,5-dimethylbenzenesulfonate) and 0.50 g of zinc powder in 10 ml of acetone was kept for 24 h at room temperature. Colorless crystals formed. The solvent was removed, and the residue was extracted with petroleum ether and ethanol. The ether extract was evaporated to obtain 0.18 g (95%) of triphenylbismuth, mp 77°C. Evaporation of the ethanol solution gave 0.18 g (95%) of zinc bis(2,5-dimethylbenzenesulfonate), mp > 250°C. IR spectrum, ν , cm^{-1} : 1145 v.s., 1100 v.s., 960 s. This IR spectrum is identical to the IR spectrum of zinc bis(2,5-dimethylbenzenesulfonate) prepared from zinc and 2,5-dimethylbenzenesulfonic acid.

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