Chemistry

Academician A. N. NESMEYANOV, T. P. TOLSTAYA, and L. S. ISAEVA

1958

SovietRxiv

Abstract

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SYNTHESIS OF AROMATIC ORGANOMETALLIC COMPOUNDS OF BISMUTH THROUGH DIAZO COMPOUNDS

Until now, the synthesis of organometallic compounds by decomposition with metal powders of double diazonium salts (the method of double diazonium salts), proposed by one of us ([1]), has been carried out for the preparation of organometallic compounds of: Hg ([1]), Tl ([2]), Sn ([3]), Pb ([4]), Sb ([5]), Bi ([6–9]). It was also shown that higher yields of organometallic compounds of Pb ([10,11]), Sn ([12]), and Tl ([2]) were obtained on decomposition of aryldiazonium borofluorides, and not of double diazonium salts with the halide of the given metal. The results of the synthesis of organobismuth compounds, carried out by decomposition of double salts of bismuth trichloride and diazonium chlorides with copper ([6]), zinc dust, or metallic bismuth ([7–9]), were not always satisfactory.

In systematically studying the decomposition of diarylbromonium borofluorides by metal powders, we established a close analogy between the results of these reactions (formation of organometallic compounds) and the results of analogous reactions with aryldiazonium borofluorides. In a number of cases it was precisely the diarylbromonium borofluorides that led to a better result than the diarylbromonium halides. We shall report on this separately. In the case of decomposition of diphenylbromonium salts by metallic bismuth, triphenylbismuth was obtained only from the borofluoride.

We applied this experience to the decomposition of aryldiazonium salts. The analogy was confirmed. Decomposition of aryldiazonium borofluorides in acetone with powdered metallic bismuth (obtained by precipitation of the metal through the action of zinc dust on an acetone solution of bismuth trichloride) led, after the action of ammonia—disproportionation—to good yields of triarylbismuth (30–50–70%) for various aromatic radicals. Thus were obtained: triphenylbismuth, tri-*p*-tolylbismuth, tri-*o*-tolylbismuth, dichloro-tri-*m*-tolylbismuth, tri-*p*-bromophenylbismuth, tri-*p*-chlorophenylbismuth, dichloro-tri-*p*-chlorophenylbismuth, dichloro-tri-*p*-carbethoxyphenylbismuth, tri-*p*-ethoxyphenylbismuth, dichloro-tri-*m*-nitrophenylbismuth, and dichloro-tri-*p*-nitrophenylbismuth.

This method for the synthesis of organobismuth compounds through diazo compounds should at present be considered the best. A possible explanation of the

reaction mechanism is given in ([13]).

Experimental Part

The reactions were carried out in a three-necked flask with a Witt stirrer, a reflux condenser, and a thermometer reaching to the bottom of the flask.

Metallic bismuth. Powdered bismuth was obtained by the action of 20 g of zinc dust on 60 g of bismuth trichloride in acetone. After successive washing with water, hydrochloric acid (15%), water, alcohol, ether, and drying in air, 37 g of freshly reduced metallic bismuth was isolated.

Triphenylbismuth ($(C_6H_5)_3Bi$). To 9.6 g (0.05 mole) of phenyldiazonium fluoroborate in 100 ml of dry acetone, with vigorous stirring, 10.5 g (0.05 g-at.) of freshly prepared metallic bismuth was added. Decomposition of the diazonium salt begins immediately and after 15 min becomes vigorous. The temperature of the reaction mixture rises to 30–35°. To avoid a further rise in temperature, the reaction mixture was cooled to 25°. After another 15 min the evolution of nitrogen had ceased. After 10 min of stirring, the reaction mixture was treated successively with 85 ml of concentrated ammonia solution and 330 ml of water. After standing for an hour the precipitate was filtered off, washed with water, dried in air, and extracted with benzene in a Soxhlet apparatus. The residue after distilling off the benzene crystallized. Weight of crude product 5.05 g (69% of theory). Resinification was slight; after recrystallization from alcohol, m.p. 77–78°.

According to the literature: m.p. 78° (14).

Tri-*p*-tolylbismuth ($(p\text{-}CH_3C_6H_4)_3Bi$). From 10.3 g (0.05 mole) of *p*-tolyldiazonium fluoroborate and 21 g (0.1 g-at.) of metallic bismuth in 100 ml of dry acetone, under the conditions of the preceding experiment, 4.66 g (58% of theory) of crude tri-*p*-tolylbismuth was obtained. After recrystallization from alcohol, 4 g (50% of theory) of a substance with m.p. 115–117° was isolated. After a second recrystallization from alcohol its m.p. was 118–119°.

According to the literature: m.p. 116–117° (6); 119–120° (8).

Tri-*o*-tolylbismuth ($(o\text{-}CH_3C_6H_4)_3Bi$). From 10.3 g (0.05 mole) of *o*-tolyldiazonium fluoroborate and 21 g (0.1 g-at.) of metallic bismuth in 100 ml of dry acetone, under the conditions of the synthesis of triphenylbismuth, but with extraction by chloroform, tri-*o*-tolylbismuth was obtained. After recrystallization from *n*-octane, 4.28 g (54% of theory) of a substance with m.p. 125–130° was isolated. After recrystallization from abs. methyl alcohol, m.p. 130–131°.

According to the literature: m.p. 130–131° (8).

Found, %: C 52.24; 52.38; H 4.48; 4.47
$C_{21}H_{21}Bi$. Calculated, %: C 52.28; H 4.41

Tri-*p*-ethoxyphenylbismuth ((p-$C_2H_5OC_6H_4)_3Bi$). 11.8 g (0.05 mole) of p-ethoxyphenyldiazonium fluoroborate was decomposed with 24 g (0.11 g-at.) of metallic bismuth in 100 ml of dry acetone under the conditions of the preceding experiment. After recrystallization from a mixture of alcohol and ether, 2.54 g (27% of theory) of tri-p-ethoxyphenylbismuth with m.p. 86–87° was obtained. On subsequent recrystallization from abs. methyl alcohol, the substance had m.p. 87–88°.

According to the literature: m.p. 73° (15).

Found, %: C 50.40; 50.51; H 4.80; 4.85
$C_{24}H_{27}BiO_3$. Calculated, %: C 50.35; H 4.75

Tri-*p*-bromophenylbismuth ((p-$BrC_6H_4)_3Bi$). From 13.5 g (0.05 mole) of p-bromophenyldiazonium fluoroborate and 16 g (0.08 g-at.) of metallic bismuth in 100 ml of dry acetone, under the conditions of the preceding experiment with preliminary heating of the reaction mixture, there was isolated (after recrystallization from a mixture of n-octane and chloroform) 4.42 g (40% of theory) of tri-p-bromophenylbismuth with m.p. 125–130°. After recrystallization from a mixture of acetone and ethyl acetate, 3.45 g (31% of theory) of a substance with m.p. 140–142° was obtained. Subsequent recrystallization from ethyl acetate gave tri-p-bromophenylbismuth with m.p. 147–148°.

According to the literature: m.p. 148–149° (9).

Tri-*p*-chlorophenylbismuth ((p-$ClC_6H_4)_3Bi$). From 11.3 g (0.05 mole) of p-chlorophenyldiazonium fluoroborate and 14 g (0.07 g-at.) of metallic bismuth in 100 ml of dry acetone, under the conditions of the synthesis of tri-p-bromophenylbismuth, there was obtained (after two recrystallizations from a mixture of chloroform and ethanol (1:1)) 2.84 g (31% of theory) of tri-p-chlorophenylbismuth with m.p.

100–102°. After recrystallization from a mixture of n-octane and chloroform, the melting point of the substance was 115–116°.

According to the literature: m.p. 116° (16).

The resinous residue after isolation of the main reaction product was dissolved in chloroform, and chlorine was passed through the solution, cooled with snow, for 15 min. The residue after evaporation of the chloroform was recrystallized from a mixture of n-octane and chloroform. This gave 1.74 g (17% of theory) of trichlorinated tri-p-chlorophenylbismuth, m.p. 148–150°. After a second recrystallization from the same solvents, m.p. 170°.

According to the literature: m.p. 141° (16), 170° (17).

Dichlorinated tri-*m*-tolylbismuth ((m-$CH_3C_6H_4)_3BiCl_2$). 20.6 g (0.1 mole) of m-tolyldiazonium borofluoride was decomposed under the conditions of the synthesis of tri-o-tolylbismuth with 21 g (0.1 g-atom) of metallic bismuth. The

reaction product was extracted with chloroform, and chlorine was passed into the chloroform solution with cooling. The residue that crystallized after evaporation of the chloroform was recrystallized from *n*-octane; its weight was 6.8 g (37% of theory), m.p. 144–147°. After two recrystallizations from *n*-octane and then from alcohol, dichlorinated tri-*m*-tolylbismuth melts at 151–153°.

According to the literature: m.p. 132–133° (18).

Found: % C 45.35; 45.44; H 3.65; 3.83

$C_{21}H_{21}BiCl_2$. Calculated: % C 45.58; H 3.83

Dichlorinated tri-*p*-carbethoxyphenylbismuth (($(p\text{-}C_2H_5OCOC_6H_4)_3BiCl_2$). 13.5 g (0.05 mole) of *p*-carbethoxyphenyldiazonium borofluoride in 100 ml of dry acetone was decomposed under the above-described conditions with 12 g (0.06 g-atom) of metallic bismuth. After chlorine had been passed through, the chloroform solution was evaporated to a minimum volume, and 3.9 g (29% of theory) of crude dichlorinated tri-*p*-carbethoxyphenylbismuth was precipitated from it by addition of a three- to fourfold volume of alcohol. After recrystallization from a mixture of *n*-octane with ethyl acetate, 2.75 g (20% of theory) of a substance with m.p. 134–137° was isolated. Subsequent double recrystallization from the same solvents gave dichlorinated tri-*p*-carbethoxyphenylbismuth with m.p. 138–139°.

Found %: C 44.83; 44.91; H 3.68; 3.78

$C_{27}H_{27}BiCl_2O_6$. Calculated %: C 44.60; H 3.74.

Dichlorinated tri-*p*-nitrophenylbismuth (($(p\text{-}NO_2C_6H_4)_3BiCl_2$). From 12 g (0.05 mole) of *p*-nitrophenyldiazonium borofluoride and 23 g (0.11 g-atom) of metallic bismuth under the conditions of the synthesis of dichlorinated tri-*p*-carbethoxyphenylbismuth, 0.8 g (5.5% of theory) of crude dichlorinated tri-*p*-nitrophenylbismuth was obtained. After recrystallization from a mixture of acetone with alcohol, m.p. 160–161° (decomp.).

Found %: N 6.31; 6.37

$C_{18}H_{12}BiCl_2N_3O_6$. Calculated %: N 6.5

Dichlorinated tri-*m*-nitrophenylbismuth (($(m\text{-}NO_2C_6H_4)_3 \cdot BiCl_2$). To 18 g (0.075 mole) of *m*-nitrophenyldiazonium borofluoride in 150 ml of dry acetone was added 34 g (0.16 g-atom) of metallic bismuth. In the cold the reaction proceeds sluggishly; therefore the reaction mixture was heated for 2 h to 50–56°. Further treatment was carried out as in the preceding experiment. 3.7 g (26% of theory) of crude dichlorinated tri-*m*-nitrophenylbismuth was isolated. After double recrystallization from ethyl acetate and chloroform, m.p. 131–132°.

According to the literature: m.p. 132–134° (18)*.

$C_{18}H_{12}BiCl_2N_3O_6$. Found, %: C 33.50; 33.43; H 2.08; 2.04; N 6.48
Calculated, %: C 33.47; H 1.87; N 6.50

Institute of Organoelement Compounds
Academy of Sciences of the USSR

Moscow State University
named after M. V. Lomonosov

Received
30 VI 1958

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* Dichlorotri-*m*-nitrophenylbismuth was first obtained by Supniewski and Adams (18) from tri-*m*-nitrophenylbismuth dinitrate, but the authors mistak-

enly regarded it as dichlorotri-*p*-nitrophenylbismuth. Later Vorländer (19) was able to prove that the initial dinitrate has a meta structure. Our method confirms Vorländer' s point of view.

Note: Figure translations are in progress. See original paper for figures.

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