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Synthesis and Studies of Chemical Properties of Arylthallium(III)bis(tetrafluoroborates)

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Abstract—Synthesis of arylthallium(III)bis(tetrafluoroborates) was carried out and their pyrolysis was studied. Synthetic procedure for preparation of fluoroaromatic compounds is developed.

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Arylthallium(III) salts are used in organometallic and organic synthesis. Carbon-thallium bond in the arylthallium(III) salts is fairly labile (E = 125 kJ mol^{-1}) suggesting an easy substitution of thallium fragment leading to the formation of various substituted arenes. Arylthallium(III) derivatives attract the attention first of all because they are inert with respect to various functional groups, and in the course of functionnalization the substituting group selectively occupies the position of thallium atom.

The aim of this work is the synthesis of arylthallium bis(tetrafluoroborates) and the investigation of their chemical properties.

We synthesized previously unknown arylthallium (III) bis(tetrafluoroborates) **I–III** by the reaction of arylthallium(III) dihydroxide with HBF_4 in ether at room temperature [reaction {1)].

$$ArTl(OH)_2 + 2HBF_4 \xrightarrow{\text{ether}} \underset{\textbf{I–III}}{ArTl(BF_4)_2} + 2H_2O, \quad (1)$$

Ar = C_6H_5 (**I**); 4-$CH_3C_6H_4$ (**II**); 3,4$(CH_3)_2C_6H_3$ (**III**).

Compounds **I–III** are insoluble in ether and precipitate as hygroscopic oils, and only after thorough drying over P_2O_5 in a vacuum at room temperature they gradually crystallize. All the attempts to purify compounds **I–III** by recrystallization failed because they gradually decompose on heating. That is why these substances were purified at room temperature by reprecipitation (see Experimental).

It was found that arylthallium bis(tetrafluoroborates) **I–III** while heating in argon without a solvent undergo the oxidative decomposition to give fluoroaromatic compounds **IV–VI**, thallium(I) tetrafluoroborate, and BF_3 [reaction (2)].

$$ArTl(BF_4)_2 \xrightarrow[t,\ ^\circ C]{\text{Ar}} \underset{\textbf{IV–VI}}{ArF} + TlBF_4 + BF_3, \quad (2)$$

ArF = C_6H_5F (**IV**), 4-$CH_3C_6H_4F$ (**V**), 3,4$(CH_3)_2C_6H_3F$(**VI**).

Yields of fluoroaromatic compounds are 55–70%. The developed procedure for the preparation of monofluoroaromatic compounds is interesting because the starting substances **I–III** can be synthesized considerably easy. Note that monofluoroaromatic compounds are usually prepared according to the Balz–Schiemann reaction [1–3]. Synthesis of monofluoroarenes by the reaction of arylthallium difluoride and boron trifluoride in boiling cyclohexane was reported [4]. 9-Fluorocarboranes with the B–F bond were synthesized by the reaction of carboranylthallium(III) bis(trifluoroacetates) with the boron trifluoride etherates [5]. Hence, the developed synthesis of fluoroaromatic compounds supplements the Balz–Schiemann method.

In the course of the reaction (2) thallium converts from the trivalent state to univalent, and gaseous boron trifluoride is evolved. For improving the yields of fluoroarenes **IV–VI** the starting tetrafluoroborates **I–III** should be thoroughly dried. Hence, pyrolysis of arylthallium(III) bis(tetrafluoroborates) can be successfully used for the selective introduction of fluorine in the aromatic ring.

As known, arylthallium bis(trifluoroacetates) undergo disproportionation in acetone at 56°C to give diarylthallium(III) trifluoroacetate [6]. We have shown that arylthallium(III) bis(tetrafluoroborates) synthesized behave analogously [reaction (3)].

$$PhTl(BF_4)_2 \xrightarrow[56°C]{\text{acetone}} \underset{\textbf{VII}}{Ph_2TlBF_4} + TlBF_4. \qquad (3)$$

EXPERIMENTAL

IR spectra of compounds **I–III** were registered on a Specord-80 spectrometer in mineral oil and hexachlorobutadiene.

Arylthallium dihydroxides were synthesized according to [7].

General procedure for preparation of arylthallium bis(tetrafluoroborates) (I–III). To a solution of 0.05 mol of the corresponding arylthallium hydroxide in 50 ml of ether 0.12 mol of aqueous HBF_4 was added under intense stirring. After dissolution of the precipitate and the formation of the oily product the reaction mixture was stirred for 10 min. After that the oils obtained were separated from ether, placed in the broad beaker, and evacuated. After removing the admixtures of ether compounds **I–III** were dried over P_2O_5 in a vacuum for a week at room temperature in the darkness. In the course of handling they gradually crystallized. Tetrafluoroborates **I–III** are well soluble in water, ethanol, acetonitrile, and DMF, and poorly soluble in ether. They are insoluble in the nonpolar solvents. Compounds **I–III** were purified by reprecipitation. They were dissolved in acetonitrile, and the solutions obtained were added to ether or to 3:1 ether–pentane. The precipitates formed were dried at room temperature in a vacuum for 2 days over P_2O_5.

Phenylthallium bis(tetrafluoroborate) (I). Yield 81.2%, decomposition temperature 113–115°C. IR spectrum, ν, cm^{-1}: 3060, 2960, 2930 (C–H_{ar}); 1548, 1476, 1440 (C=C_{ar}); 1040 (B–F), 768, 756, 720, 704, 676 [δ(C–H_{ar})]. Found, %: C 15.75, H 1.01, Tl 44.87. $C_6H_5B_2F_8Tl$. Calculated, %: C 15.84, H 1.11, Tl 44.91.

***p*-Tolylthallium bis(tetrafluoroborate) (II)**. Yield 70%, decomposition temperature 105–109°C. IR spectrum, ν, cm^{-1}: 3068, 3064, 3020 (C–H_{ar}); 2962, 2862 (CH_3); 1628, 1488, 1464 (C=C_{ar}); 1032 (B–F); 790, 756, 726, 724 [δ(C–H_{ar})]. Found, %: C 17.81, H 1.43, Tl 43.62. $C_7H_7B_2F_8Tl$. Calculated, %: C 17.92; H 1.50, Tl 43.57.

3,4-Dimethylphenylthallium bis(tetrafluoroborate) (III). Yield 74.4%, decomposition temperature 67–74°C. IR spectrum, ν, cm^{-1}: 3062, 3013 (C–H_{ar}); 2958 (CH_3), 1628, 1488 (C=C_{ar}); 1052 (B–F); 850, 804, 776, 749 [δ(C–H_{ar})]. Found, %: C 19.82, H 1.83, Tl 42.32. $C_8H_9B_2F_8Tl$. Calculated, %: C 19.89, H 1.88, Tl 42.30.

General procedure for preparing fluoroaromatic compounds IV–VI. The installation for distillation was connected with a vessel for washing of gases filled with aqueous NaF solution and flushed with dry argon. After that 0.05 mol of tetrafluoroborate **I–III** was placed into the flask and the system was additionally flushed with argon. The flask was heated at 70–90°C when the liberation of gaseous products began. Fluoroaromatic compounds were condensed in the condenser and collected in the receiver. Boron trifluoride was absorbed with sodium fluoride solution. At the end of the process reaction temperature was increased to 115–155°C and maintained for additional 30 min. After that the installation was flushed with argon and gradually cooled. Fluoroaromatic compounds were additionally purified by distillation The residue after pyrolysis containing thallium(I) tetrafluoroborate and the tarry products was treated with water, filtered, and thallium(I) salt was isolated.

Fluorobenzene (IV). Yield 55%, bp 85°C, n_D^{20} 1.4652, published data [4]: bp 84.5°C, n_D^{20} 1.4650.

4-Fluorotoluene (V). Yield 65%, bp 117°C, n_D^{20} 1.4678, published data [4]: bp 116°C, n_D^{20} 1.4670.

3,4-Dimethylfluorobenzene (VI). Yield 70%, bp 151°C, n_D^{20} 1.4857, published data [4]: bp 151.5°C, n_D^{20} 1.4864.

Diphenylthallium tetrafluoroborate (VII). A solution of 1.656 g of compound **I** in 20 ml of acetone was refluxed for 0.5 h. After that the volatile substances were distilled off, and the residue was three times treated with hot 9:1 benzene–ethanol. Solvent was distilled off, the precipitate was filtered off, washed with benzene, and dried in a vacuum at 50°C to give 0.350 g (44%) of compound **VII**, mp 304–306°C. IR spectrum, ν, cm^{-1}: 3050, 2964, 2952 (C–H_{ar}); 1581, 1479, 1433 (C=C_{ar}); 765, 725, 686 [δ(C–H_{ar})], 1035 (B–F). Diphenylthallium tetrafluoroborate **VII** prepared by us using the exchange reaction between Ph_2TlCl and $TlBF_4$ in aqueous pyridine; after crystallization from 9:1 benzene–ethanol it melted at 306–308°C, and its IR spectrum was identical to that obtained in the above-described experiment.

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