Chemistry

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1962

SovietRxiv

Abstract

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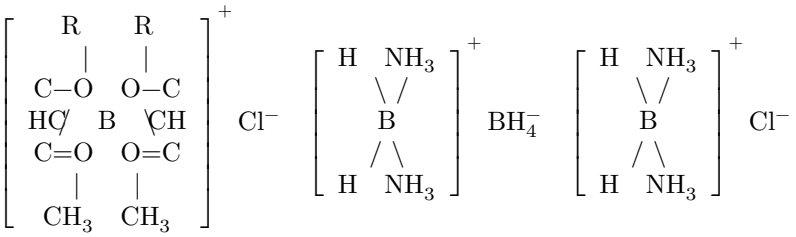
CATIONIC COMPLEXES OF BORON

(Presented by Academician B. A. Kazanskii, 26 IV 1962)

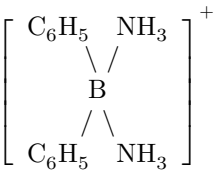
For boron compounds, as is known, the formation of neutral and anionic complexes is typical, whereas the capacity for forming cationic complexes has until now been considered uncharacteristic of boron. Among complex compounds of the latter type, until recently the known ones were boronium salts I, obtained by Dilthey and co-workers ([1]) by the action of 1,3-diketones (acetylacetone and benzoylacetone) on boron trichloride

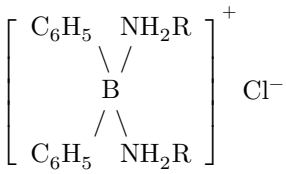


(I) (II) (III)

In 1958, Shultz and Perry ([2]) showed that the so-called "diamminodiborane" has the structure of boronium salt II. On treatment with hydrogen chloride in the presence of ammonia, compound II is converted into chloride III. As our investigations have shown, boron exhibits a considerably greater tendency to form insertion products than had previously been supposed.

A numerous series of boronium compounds is obtained by the action of ammonia or primary amines on diphenylboron chloride ([3], [4]) or di-*p*-tolylboron chloride. Investigation of the complex compounds of diphenylboron chloride with two molecules of ammonia or of a primary amine shows that they are typical boronium salts, having structures IV or V, respectively. Like Dilthey' s complexes, they react with tin tetrachloride to form salts VI ([5]), and with ferric chloride, as described in the present article, they give salts VII


(IV)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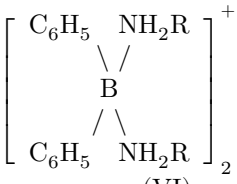
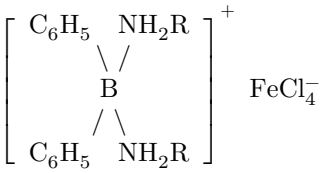

(VI)


(VII)

Following the nomenclature accepted in the chemistry of complex compounds, compounds IV and V may be called, respectively, diphenyl-diamine-boron chlo –

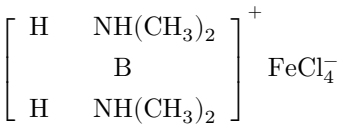
with diphenyl and diphenyl-di-(alkylamine)-boron chloride. However, it appears more convenient to adhere to another nomenclature, namely—to call salts of cationic boron complexes boronium salts, regarding them as derivatives of boronium $(H_2BA_2)^+$, where A is a molecule. Then compounds IV and V will be called, respectively: diphenyldiamminoboronium chloride and diphenyl-di-(alkylamine)-boronium chloride.

Boronium salts of another type were obtained by us starting from the recently synthesized complex compounds of alkylmercaptoboranes with amines. On treatment of an ethereal solution of hydrogen chloride with dimethylamine-methylmercaptoborane or dimethylamine-ethylmercaptoborane, di-(dimethylamine)-boronium chloride (VIII) is formed according to the following equation:

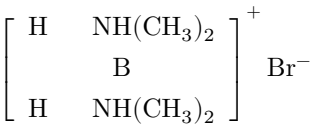
$$2RSBH_2 \cdot NH(CH_3)_2 + HCl \rightarrow \begin{bmatrix} H & NH(CH_3)_2 \\ & B \\ H & NH(CH_3)_2 \end{bmatrix}^+ Cl^- + \tfrac{1}{3}(RSBH_2)_3 + RSH$$

(VIII) $\qquad R = CH_3,\ C_2H_5$

Salt VIII is also formed on prolonged standing of a solution of dimethylamine-alkylmercaptoborane in carbon tetrachloride. With ferric chloride, salt VIII is converted into the tetrachloroferrate of di-(dimethylamine)-boronium (IX), which confirms its structure as a boronium compound. Di-(dimethylamine)-boronium bromide (X) is obtained by the interaction of dimethylamine-ethylmercaptoborane and bromoform.



(IX)



(X)

All the compounds obtained are relatively stable in air. They are insoluble in ether, petroleum ether, and benzene, but readily soluble in chloroform. With hydrochloric acid these boronium salts hydrolyze very slowly; with alkali and alcohols the hydrolysis proceeds rapidly and quantitatively.

As is known, amines behave toward diborane not as ammonia does: they form not boronium salts of type II, but addition products—alkylamine-boranes. Perry, Kodama, and Schulz ([6]) suggested that this difference is explained by steric hindrance preventing the placement of amine molecules in the cationic boron complex. As follows from the results of our investigation, boronium salts with coordinated molecules of a primary or secondary amine are capable of existing and, consequently, the different course of the reactions of diborane with ammonia and with amines is not associated with a steric effect.

Experimental Part

1. Tetrachloroferrate of diphenyl-di-(methylamine)-boronium. To a solution of 0.7 g of diphenyl-di-(methylamine)-boronium chloride ([3]) in 75 ml of abs. chloroform, 0.39 g of ferric chloride dissolved in 20 ml of abs. ether was added. The ether and most of the chloroform (to a volume of $\sim$ 7 ml) were distilled off from the reaction mixture. The precipitate that separated on standing, in the form of light-yellow prisms, was filtered off. Obtained: 0.77 g of tetrachloroferrate of diphenyl-di-(methylamine)-boronium (yield 70% of theory), m.p. 104–105° (sealed capillary).

Found, %: C 39.46, 39.31; H 5.03, 4.92; B 2.42, 2.53; N 6.56, 6.49;
Cl 33.30, 33.30

$$C_{14}H_{20}BN_2Cl_4Fe.$$

Calculated, %: C 39.57; H 4.74; B 2.54; N 6.58;
Cl 33.42

2. Tetrachloroferrate of diphenyl-di-(ethylamine)-boronium. Similarly, from 0.63 g of diphenyl-di-(ethylamine)-boronium chloride and 0.3 g of ferric chloride, 0.77 g (82.7% of theoretical) of diphenyl-di-(ethylamine)-boronium tetrachloroferrate was obtained as dark-orange rhombic prisms, m.p. 121-123° (sealed capillary).

Found, %: C 42.62, 42.28; H 5.55, 5.31; B 2.43, 2.44; N 6.49, 6.69; Cl 31.34, 31.47
$C_{16}H_{24}BN_2Cl_4Fe$. Calculated, %: C 42.41; H 5.33; B 2.38; N 6.18; Cl 31.26

3. Tetrachloroferrate of diphenyl-di-(isobutylamine)-boronium. Similarly, from 2 g of diphenyl-di-(isobutylamine)-boronium chloride and 0.93 g of ferric chloride, 1.2 g (41% of theoretical) of diphenyl-di-(isobutylamine)-boronium tetrachloroferrate was obtained, m.p. 91–93° (sealed capillary).

Found, %: C 46.80, 46.94; H 6.54, 6.56; B 2.13, 2.22; N 5.66, 5.70; Cl 27.66, 27.39
$C_{20}H_{32}BN_2Cl_4Fe$. Calculated, %: C 47.17; H 6.33; B 2.12; N 5.49; Cl 27.89

The obtained salts of tetrachloroferric acid are stable on storage in air. They dissolve readily in water, alcohol, and chloroform, with difficulty in ether, and are completely insoluble in isopentane.

4. Di-(dimethylamine)-boronium chloride. A) To a solution of 11.56 g (0.10 mole) of dimethylamine-ethylmercaptoborane [6] in 20 ml of absolute ether, with water cooling, 17.6 ml of a 2.83 *N* ethereal solution of hydrogen chloride (0.05 mole HCl) was slowly added dropwise. A white finely crystalline precipitate immediately began to separate. After 10 h the precipitate was filtered off, washed with absolute ether, and dried in vacuo to constant weight. Obtained 6.77 g (98% of theoretical) of di-(dimethylamine)-boronium chloride, m.p. 167–169°.

Found, %: C 34.73, 34.50; H 11.61, 11.41; B 7.98, 7.58; H_{act} 1.51, 1.50; N 20.38, 20.28; Cl 25.91, 26.04
$C_4H_{16}BN_2Cl$. Calculated, %: C 34.70; H 11.56; B 7.82; H_{act} 1.46; N 20.22; Cl 25.70

The mother liquor was kept in vacuo to remove ether; the residue (3.2 g) was distilled. Obtained 2.75 g (75% of theoretical) of the trimer of ethylmercaptoborane, b.p. 98–99° at 2 mm.

Found, %: B 13.92; H_{act} 2.53
$C_6H_{21}B_3S_3$. Calculated, %: B 14.62; H_{act} 2.72

B) 10.12 g (0.096 mole) of dimethylamine-ethylmercaptoborane was dissolved in 15.1 g of absolute CCl_4. On standing for one week, colorless crystals separated from the solution; these were filtered off, washed with absolute ether, and dried to constant weight. After recrystallization from a chloroform–ether mixture (1:5), the substance had m.p. 164.5–166° (sealed capillary). Yield 6.25 g (95% of theoretical).

5. Tetrachloroferrate of di-(dimethylamine)-boronium. To a solution of 0.39 g of di-(dimethylamine)-boronium chloride in 1.5 ml of absolute chloroform, a solution of 0.45 g of ferric chloride in 25 ml of absolute ether was added. Ether and 1/3 of the chloroform were distilled off in vacuo. On standing for 12

h, yellow-green crystals of di-(dimethylamine)-boronium tetrachloroferrate separated from the residue; after recrystallization from a chloroform–ether mixture (1:5), they had m.p. 62.5–63°.

Found, %: C 16.17, 16.28; H 5.48, 5.30
$C_4H_{16}BN_2FeCl_4$. Calculated, %: C 16.08; H 5.38

Yield 0.47 g (55% of theoretical).

6. **Bromide of di-(dimethylamine)-boronium.** 4.9 g (0.041 mole) of dimethylamine–ethylmercaptoborane was dissolved in 7 ml of absolute bromoform; the mixture warmed up. After 3 days, colorless crystals separated from the solution. They were filtered off and washed with absolute benzene. On dilution of the filtrate with benzene, a precipitate again separated. In all, 2.9 g (80% of theory) of bromide of di-(dimethylamine)-boronium was obtained, m.p. 155–156° (sealed capillary).

Found, %: C 26.36, 26.67; H 8.97, 8.95; B 5.89, 6.13; Br 43.77, 43.38
H_{act} 0.98, 1.07;

$C_4H_{16}BN_2Br$. Calculated, %: C 26.26; H 8.82; B 5.91; Br 43.69
H_{act} 1.10;

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Received
25 IV 1962

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