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Abstract

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REACTION OF DIPHENYLIODONIUM BOROFLUORIDE WITH ALIPHATIC AMINES

We have established earlier (^{1}) that, upon interaction of diphenyliodonium borofluoride with aromatic amines at room temperature, complex compounds are formed.

In the present work, the reaction of diphenyliodonium borofluoride with aliphatic amines was investigated. In this case we did not isolate complex compounds, since in the presence of aliphatic amines diphenyliodonium borofluoride decomposed rapidly even at room temperature. The main product of the reaction proved to be the hydrofluoroborate salt of the starting amine. Such results were observed when the reaction was carried out in various solvents both at room temperature and at the boiling point of the solvent.

We studied in greater detail the reaction of diphenyliodonium borofluoride with diethylamine in acetone, water, and an excess of the amine itself, and also with triethylamine in methyl alcohol, acetone, and without solvent in an excess of amine.

Trimethylamine was chosen by us because in this case formation of the amine salt by an exchange reaction between the salt of the arylation product and the starting amine is excluded; such a reaction is possible with primary and secondary amines, for example:

$$(C_2H_5)_2NH + (C_6H_5)_2IBF_4 \rightarrow C_6H_5\overset{+}{N}H(C_2H_5)_2BF_4{}^- + C_6H_5I,$$

$$C_6H_5\overset{+}{N}H(C_2H_5)_2BF_4{}^- + (C_2H_5)_2NH \rightarrow C_6H_5{-}N(C_2H_5)_2 + (C_2H_5)_2\overset{+}{N}H_2BF_4{}^-.$$

The reaction mixture was treated as follows. After completion of the reaction, water and ether were added to the reaction mixture.* The iodonium and ammonium salts passed into the aqueous solution, and all the other organic substances into the ether. The layers were separated; after several extractions with ether, a saturated aqueous solution of NaI was added to the aqueous solution, whereupon diphenyliodonium iodide, sparingly soluble in water, precipitated—in those cases in which not all of the $(C_6H_5)_2JBF_4$ had entered into the reaction. The aqueous solution was then evaporated to a small volume on a water bath; the residue was transferred to a Claisen flask and decomposed with alkali. The amine thus obtained was distilled off, dried, and identified. Usually after drying the amine had a good refractive index, which indicated the purity of the substance.

The ethereal solution was examined by thin-layer chromatography on aluminum oxide.** On the chromatograms iodobenzene was always readily detected. Spots corresponding to arylation products were either absent or very weak, which indicated the presence of only traces of the substance, since the method used is sufficiently sensitive (0.5-1 γ of amine is readily detected). The results of the experiments are given in Table 1.

As can be seen from the table, upon interaction of diphenyliodonium borofluoride with di- and triethylamine, arylation products are practically absent, while the hydrofluoroborate salts of the corresponding amines are formed in good yield.

* When the reaction was carried out in methyl alcohol or acetone, the solvent was first distilled off.

** The chromatograms were developed with iodine.

It should be noted that this direction of the reaction had not previously been observed by anyone. It was believed that diaryliodonium salts, on interaction with nucleophilic substances, in particular with amines, act as arylating agents. Thus, Beringer et al. (^{2}) used diaryliodonium bromides for the arylation of dimethylamine and piperidine in boiling aqueous solution. L. G. Makarova and A. N. Nesmeyanov (^{3}) carried out the reaction between trimethylamine and diphenyliodonium borofluoride in an ampoule at 220° and isolated, in low yield, the arylation product—dimethylaniline. In both cases, in the authors' opinion, the iodonium salts decompose heterolytically and an aryl cation is transferred to the amine.

We believe that in our case diphenyliodonium borofluoride, on interaction with fatty amines under mild conditions, decomposes homolytically. The reaction proceeds as follows. The diphenyliodonium cation reacts with the amine; in this process, at the expense of the free electron pair of the amine, a covalent bond between iodine and nitrogen is formed:

$$(C_6H_5)_2\overset{+}{J} + :NR_3 \rightarrow [(C_6H_5)_2J:NR_3]^+.$$

In the complex cation formed, the trivalent iodine atom has an electron decet, and such a state for iodine must be rather unstable. It is known, for example, that compounds of the type $(C_6H_5)_2JR$ are unstable and, even at low temperatures, readily decompose with formation of free radicals (^{7}). Recently compounds of the type $Ar_2J—S—Ar^1$ have been isolated, which on heating likewise undergo radical decomposition (^{8}).

Compounds with a covalent bond between iodine and nitrogen, in their stability, apparently should be analogous to the above-mentioned compounds. It is probable that the cation formed in our case also decomposes homolytically:

$$[(C_6H_5)_2J : NR_3]^+ \rightarrow (C_6H_5)_2\dot{J} + \overset{+}{\dot{N}}R_3$$

$$(C_6H_5)_2\dot{J} \downarrow$$

$$C_6H_5{}^{\cdot} + C_6H_5J$$

As a result, a nitrogen ion-radical* is obtained, which, by abstracting hydrogen from the solvent, is converted into the ammonium cation $R_3\overset{+}{N}H$. The latter reacts with BF_4^-, giving the amine hydrofluoroborate salt:

$$R_3\overset{+}{N}H + BF_4^- \rightarrow R_3NHBF_4.$$

With such a course of the reaction, the almost complete absence of arylation products in the reaction mixture becomes understandable, since their formation requires the collision of two free radicals, C_6H_5 (or $(C_6H_5)_2J\cdot$) and $\overset{+}{\dot{N}}R_3$, the probability of which is small.

To confirm the correctness of the mechanism given above, we carried out the reaction between diphenyliodonium borofluoride and triethylamine in boiling benzene in the presence of metallic mercury, which was used as a scavenger of free phenyl radicals. As a result of this reaction we obtained diphenylmercury, which we converted into phenylmercuric chloride (yield 6%). Diphenylmercury, in our opinion, could have been formed only by the reaction of phenyl radicals with mercury, since L. G. Makarova and A. N. Nesmeyanov ([3]) showed that diphenyliodonium borofluoride with metallic mercury gives no organomercury compounds.

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* Cases of formation of nitrogen ion-radicals are known in the literature. For example, it is believed that the reaction between amines and benzoyl peroxide ([9]) proceeds through the stage of formation of the ion $[C_6H_5COO : NR_3]^+$, which decomposes homolytically with formation of $R_3\overset{+}{\dot{N}}$.

The formation of free radicals in the course of the reaction is also indicated by the fact that, when the reaction was carried out in benzene and in water, diphenyl was detected chromatographically in the reaction mixture. In addition, when the reaction was carried out in methyl alcohol, benzene was proved spectroscopically among the reaction products.* Consequently, our assumption concerning a free-radical mechanism of the reaction is apparently correct.

Let us note that during thermal decomposition of diphenyliodonium borofluoride in the presence of nucleophilic substances, heterolytic cleavage probably occurs, with an aryl cation being transferred to the nucleophilic agent. It is precisely this reaction, it seems to us, that accounts for the formation of the arylation product upon heating $(C_6H_5)_2JBF_4$ with trimethylamine to 220°. However, alongside the heterolytic reaction under these conditions, the radical reaction established in the present work must also proceed, leading to the hydrogen borofluoride salt of the amine taken.

Indeed, carrying out the reaction of diphenyliodonium borofluoride with triethylamine at 220°, we obtained the hydrogen borofluoride salt of triethylamine, from which the free amine, identified in the form of the picrate, was isolated. At the same time, an arylation product—diethylaniline—was detected chromatographically in the reaction mixture.

Table 1.

Reactions of diphenyliodonium borofluoride with amines

Starting amine	Amount (g), amine	Amount (g), $(C_6H_5)_2JBF_4$	Ratio $(C_6H_5)_2BF_4$ to amine, mol	Solvent	Solvent volume (ml)	Reaction temp. (°C)	Reaction time (h)	Unreacted $(C_6H_5)_2JBF_4$ (%)	Yield (%), arylation product	Yield (%), amine from salt
$(C_2H_5)_2NH$	3.2	0.49	1:30	–	–	20	7	65	no	a)
$(C_2H_5)_2NH$	3.9	6	1:3	Acetone	30	20	2	0	traces	696)
$(C_2H_5)_2NH$	5.9	10	1:3	Water	75	100	4.5	0	no	48)
$(C_2H_5)_3N$	4.7	6	1:3	Acetone	30	20	2	0		54)
$(C_2H_5)_3N$	8.8	10	1:3	Methanol	15	65	2	0		60)
$(C_2H_5)_3N$	16.6	3	1:20	–	–	80–85	8	5		55)
$(C_2H_5)_3N$	1.5	3	1:1.7	–	–	218	0.25	48		14)

Notes. a) The amount of amine formed upon decomposition of the salt was not determined.
) n_D^{18} 1.3900; literature data (4): n_D^{18} 1.3873.) n_D^{18} 1.3870; literature data (4): n_D^{18} 1.3873.
) n_D^{20} 1.3971; literature data (5): n_D^{20} 1.4003.) n_D^{20} 1.3992; literature data (5): n_D^{20} 1.4003; triethylamine was converted into the picrate, m.p. 174–175°; literature data (6): m.p. 174.5°.
) n_D^{20} 1.4006; literature data (5): n_D^{20} 1.4003.) Identified in the form of the picrate, m.p. 170°; literature data (6): m.p. 174.5°.

Thus, the data obtained by us indicate that the nature of the decomposition of diphenyliodonium borofluoride upon interaction with amines may be either homolytic or heterolytic and depends to a large extent on the reaction conditions.

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* Benzene was detected in the alcohol distillate.

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

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