CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR O. A. REUTOV, G. A. ERTEL, and O. A. PTITSYNA

1960

SovietRxiv

Abstract

Full Text

CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR O. A. REUTOV, G. A. ERTEL, and O. A. PTITSYNA

ISOTOPIC EXCHANGE REACTION BETWEEN DIARYLIODONIUM BOROFLUORIDES AND ARYL IODIDES LABELED WITH J^{131}

A. N. Nesmeyanov and co-workers ($^{1-4}$) investigated the thermal decomposition of aryldiazonium and diaryliodonium borofluorides in the presence of various organic compounds, establishing thereby that the indicated borofluorides decompose heterolytically with formation of aryl cations

$$\mathrm{Ar}:\mathrm{N}_2^+\mathrm{BF}_4^- \rightarrow \mathrm{Ar}_2^+ + \mathrm{N}_2 + \mathrm{BF}_4^-,$$

$$\overset{\mathrm{Ar}:}{}\mathrm{J}^+\mathrm{BF}_4^- \rightarrow \mathrm{Ar}^+ + \mathrm{ArJ} + \mathrm{BF}_4^-.$$

The latter attack the sites of greatest electron density in organic molecules.

Thus, L. G. Makarova and A. N. Nesmeyanov (^{4}) showed that, upon thermal decomposition of diphenyliodonium borofluoride in the presence of pyridine, trimethylamine, triphenylphosphine, triphenylarsine, triphenylstibine, diphenyl sulfide, and diphenyl selenide, borofluorides of the corresponding onium compounds are formed.

By decomposing phenyldiazonium borofluoride in chlorobenzene and bromobenzene, A. N. Nesmeyanov and co-workers obtained salts of diphenylchloronium (^{2}) and diphenylbromonium (^{1}).

$$\mathrm{C_6H_5N_2BF_4 + C_6H_5X \rightarrow (C_6H_5)_2X^+BF_4^- + N_2}.$$

It should be noted that the diphenyliodonium salt was obtained by them when phenyldiazonium borofluoride was decomposed not in pure iodobenzene, but in its mixture with acetone (^{3}). In pure iodobenzene, diphenyliodonium salts are not formed.

Salts of diphenyliodonium (^{5}) and diphenylbromonium (^{3}) are also formed, as A. N. Nesmeyanov showed, upon spontaneous decomposition of double salts of phenyldiazonium iodide with mercuric iodide or phenyldiazonium bromide with mercuric bromide. In all cases, phenylhalogenonium compounds were formed in essentially one and the same way: the phenyl cation, arising upon decomposition of phenyldiazonium borofluoride in the presence of a halobenzene, is added to the halogen atom at the expense of the unshared electron pair of the latter. Obviously, the phenyl cation formed upon decomposition of diaryliodonium borofluoride must behave in a completely analogous manner. These considerations led us to the conclusion that it should be possible to carry out the isotopic exchange reaction described in the present work between diaryliodonium borofluorides and aryl iodides.

The isotopic exchange reaction studied by us may be represented by the following equation:

$$\mathrm{Ar_2J^+BF_4^-} + \mathrm{ArJ^*} \rightleftarrows \mathrm{Ar_2J^{*+}BF_4^-} + \mathrm{ArJ} \quad (\mathrm{J^*} = \mathrm{J^{131}}).$$

The radioactive aryl iodides required for the reaction were obtained by thermal decomposition of diaryliodonium iodide whose anion contained iodine labeled with J^{131}.

To obtain radioactive diaryliodonium iodide, the halide salt of iodonium was ground with moist silver oxide, the silver halide was filtered off, and to the resulting aqueous solution of diaryliodonium hydroxide there was added an aqueous solution of radioactive iodine in the form of potassium iodide, sodium iodide, or elemental iodine. Then a solution of nonactive potassium iodide was added until complete precipitation of the diaryliodonium iodide.

The activity of the aryliodide labeled with J^{131}, obtained by the method described above, was determined as follows. An accurately weighed sample (20 mg) of the aryliodide was placed on a standard filter 2 cm in diameter, dissolved in one drop of acetone, and coated with a lacquer of Plexiglas in dichloroethane. After drying, the filter was placed in a tracing-paper envelope and the activity was measured on a B-2 apparatus using an end-window counter of the SI-2B type.

The diaryliodonium borofluorides used by us in the reaction were obtained by the method described by L. G. Makarova and A. N. Nesmeyanov$^{(4)}$ for diphenyliodonium borofluoride.

Table 1

Ar_2JBF_4	m.p., °C	decomp. temp., °C	Found, % C	Found, % H	Found, % F	Calculated, % C	Calculated, % H	Calculated, % F	Yield, %
$(C_6H_5)_2JBF_4$	136	210	39.11 39.19	2.65 2.68	21.04 21.54	39.17	2.74	20.68	79
$(n\text{-}ClC_6H_4)_2JBF_4$	181.5 −182	224	33.14 33.15	1.57 21.73		33.0	1.73		27
$(n\text{-}BrC_6H_4)_2JBF_4$	193.5	217	28.03 28.01	1.55 1.53	14.65 14.60	27.41	1.53	14.45	4

Ar_2JBF_4	m.p., °C	decomp. temp., °C	Found, % C	Found, % H	Found, % F	Calculated, % C	Calculated, % H	Calculated, % F	Yield, %
(n-$CH_3C_6H_4$)$_2JBF_4$	106.5 −108	216	42.07 42.08	3.51 3.68	18.99 19.42	42.46	3.56	19.19	35
(n-$CH_3OC_6H_4$)$_2JBF_4$	187	209	39.09 38.95	3.12 2.98	18.13 18.23	39.29	3.30	17.76	69
(m-$O_2NC_6H_4$)$_2JBF_4$	199	224	31.43	1.79		31.47	1.76		74
(m-$C_2H_5OCOC_6H_4$)$_2JBF_4$	93	124	42.30 42.18	3.67 3.71		42.22	3.54		9

Table 1 gives the Ar_2JBF_4 compounds synthesized by us for the first time, their melting points, analyses, and yields. It turned out that the isotope-exchange reaction under consideration takes place only near the decomposition temperature of the diaryliodonium borofluoride.

To determine the degree of exchange, accurately weighed samples of equimolecular amounts of diaryliodonium borofluoride and aryliodide labeled with J^{131} were introduced into a ground-glass test tube. The test tube was closed with a 25-cm-long tube, the end of which terminated in a capillary, and was placed in a thermostat with compressor oil. In the thermostat the reaction mixture was kept for a definite time at a constant temperature lying within the range 180–200° (depending on the decomposition temperature of the diaryliodonium borofluoride).

After the reaction had ended, the test tube was cooled, the contents were washed many times with ether to remove the aryliodide, and the residue was dissolved in boiling water, and the solution was filtered. The filtrate was evaporated to a small volume and cooled. The precipitated diaryliodonium borofluoride was filtered off, washed with water and ether, and dried in a vacuum desiccator.

The activity of the diaryliodonium borofluoride was measured analogously to the determination of the activity of the aryliodide. The yield of diaryliodonium borofluoride obtained as a result of the isotope-exchange reaction was determined in parallel with the activity determination. For this purpose the aqueous solution of Ar_2JBF_4 was evaporated to dryness, and the remaining iodonium salt was weighed.

We studied the isotope-exchange reactions of diphenyliodonium borofluoride with iodobenzene, di-*p*-chlorophenyliodonium borofluoride with *p*-chloroiodobenzene, di-*p*-bromophenyliodonium borofluoride with *p*-bromoiodobenzene, di-*p*-tolyliodonium borofluoride with *p*-iodotoluene, di-*p*-anisyliodonium borofluoride with *p*-iodoanisole, di-*m*-carbethoxyphenyliodonium borofluoride with ethyl *m*-iodobenzoate, and di-*m*-nitrophenyliodonium borofluoride with *m*-iodonitrobenzene.

Table 2

Ar	Temp., °C	Duration, h	Degree of exchange, %	Yield, %
C_6H_5	198–202	2	36	66
p-ClC_6H_4	200	2	24	83
p-ClC_6H_4	200	4	49	64
p-BrC_6H_4	200	2	8	85
p-BrC_6H_4	200	4	27	62
p-BrC_6H_4	200	6	30	–
p-$CH_3C_6H_4$	199	4	16	26
p-$CH_3OC_6H_4$	181	2	8	89
p-$CH_3OC_6H_4$	181	4	17	85
p-$CH_3OC_6H_4$	192.5	2	16	76
p-$CH_3OC_6H_4$	192.5	4	26	53
m-$C_2H_5OCOC_6H_4$	181	1	9	45
m-$O_2NC_6H_4$	183	4	4	83
m-$O_2NC_6H_4$	192	4	5	60
m-$O_2NC_6H_4$	200	1	0	79

* Average from a series of experiments carried out under optimal conditions.

Table 2 gives the conditions of our experiments (temperature and reaction time), as well as the degree of exchange and the yield of diaryliodonium borofluorides. Since the thermal stability of borofluorides of different diaryliodonium compounds differs appreciably, we were unable to conduct all experiments at one and the same temperature. Therefore, from our experiments, any conclusion about the influence of the nature of the substituent in the para or meta position of the benzene ring on the rate of the isotope-exchange reaction can be drawn only in the following cautious form: substituents of the second type retard the reaction under consideration. This circumstance is apparently due to a decrease in the electron density on the iodine atom in molecules XC_6H_4J, where X is an electronegative substituent. Naturally, attack of the iodine atom by the aryl cation will be hindered.

For unsubstituted phenyl and for those cases in which the benzene ring contains a substituent of the first type, the reaction gives diaryliodonium borofluorides with sufficiently high activity. In this connection, the isotope-exchange reaction under consideration can be recommended as a convenient method for obtaining diaryliodonium salts labeled with the isotope J^{131}.

Moscow State University
named after M. V. Lomonosov

Received
6 V 1960

REFERENCES CITED

1. A. N. Nesmeyanov, T. P. Tolstaya, L. S. Isaeva, DAN, **104**, 872 (1955).
2. A. N. Nesmeyanov, T. P. Tolstaya, DAN, **105**, 95 (1955).
3. A. N. Nesmeyanov, T. P. Tolstaya, DAN, **128**, 726 (1959).
4. L. G. Makarova, A. N. Nesmeyanov, Izv. AN SSSR, OKhN, 1945, 617.
5. A. N. Nesmeyanov, *Zs. anorg. u. allgem. Chem.*, **178**, 300 (192).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.