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Academician A. N. Nesmeyanov, T. P. Tolstaya, and L. S. Isaeva

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Abstract

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CHEMISTRY

Academician A. N. Nesmeyanov, T. P. Tolstaya, and L. S. Isaeva

PHENYLATION REACTIONS BY MEANS OF DIPHENYLBROMONIUM AND DIPHENYLCHLORONIUM SALTS

In the heterolytic arylation of bromobenzene and chlorobenzene with aryldiazonium borofluorides, we obtained a series of diarylhalogenonium salts, including diphenylbromonium and diphenylchloronium salts ([1]). In the present work we describe a procedure that makes it possible to increase the yield of these salts tenfold—from 0.6 to 6% of the theoretical yield (calculated on phenyldiazonium borofluoride). Investigation of the chemical properties of diphenylbromonium and diphenylchloronium salts showed us a complete analogy between their behavior and that of diphenyliodonium salts. All of them are excellent phenylating reagents, capable of phenylating both homolytically (halide salts) and heterolytically. Homolytic phenylation occurs, for example, under the action of the iodides, bromides, and chlorides of all three halogenonium compounds on metallic mercury, best in isopropyl alcohol, according to a scheme of the following type:

$$(C_6H_5)_2ClCl + Hg \rightarrow C_6H_5HgCl + C_6H_5Cl.$$

A surprising preliminary conclusion from the fact that this reaction exists is the existence of a covalent form of diphenylbromonium and diphenylchloronium halides, $(C_6H_5)_2Hal—Hal$, in which the central halogen atom must expand its octet to a decet. This question will be investigated by us further. Examples of heterolytic phenylation may be the phenylations described in the present work by diphenylbromonium and diphenylchloronium halides in aqueous solution of sodium nitrite with formation of nitrobenzene, potassium cyanide (benzonitrile), sodium azide (phenyl azide), and diethylamine (diethylaniline). Phenylation by diphenylbromonium and diphenylchloronium borofluorides also proceeds heterolytically. In this case it is no longer necessary to use water as the reaction medium. Pyridine, for example, in 85% yield forms, under the action of diphenylbromonium or -chloronium borofluoride, N-phenylpyridinium borofluoride. Diethylamine is phenylated in a similar manner. In all the cases studied, the behavior of all three diphenylhalogenonium compounds is identical.

As regards the interaction of diphenylhalogenonium salts with metals, interesting features should be noted here. With metallic mercury there interact, forming halogenophenylmercury, only the halides of diphenylhalogenonium compounds, but not the borofluorides, which can evidently be explained by the heterolytic character of the decomposition of the latter. With metallic thallium, however, the situation is exactly the reverse: a diphenylthallium salt is formed only with the borofluorides of the halogenonium compounds. The relationships here are completely identical with the results of the reaction of diazonium salts with these two metals. The explanation must evidently also be the same. Diazonium borofluoride also forms organometallic compounds with lead (2). To explain this result with diazonium salts, L. G. Makarova and we (3) proposed that metals, being nucleophilic reagents, are capable, like the anions OH', CN', etc.,

convert the diazonium cation into the diazo form, which decomposes homolytically:

$$C_6H_5 - \overset{+}{N} \equiv N : + OH' \longrightarrow C_6H_5 - N = N - OH$$

$$C_6H_5\overset{+}{N} \equiv N : + \text{metal} \longrightarrow C_6H_5 - N = N - \overset{+}{Me} \longrightarrow C_6H_5 - {\cdot}N = N^{+}Me$$

An analogous explanation for halogenonium salts will require the formation of a transition complex with metallic thallium containing the diphenylhalogenonium cation in covalent form (with a decet):

$$(C_6H_5)_2\ddot{Cl}^{+}\text{ thallium} \longrightarrow (C_6H_5)_2Tl^{+} + C_6H_5Cl$$

Mercury, sufficiently nucleophilic to effect the conversion of diazonium into the diazo form, is not capable of doing this with diphenylhalogenonium cations, whereas less noble elements accomplish both transformations. Confirmation of this point of view is provided by the fact that copper, for example, actually causes homolytic decomposition both of diazonium salts (the Gattermann reaction and a number of our works on the synthesis of organometallic compounds by the diazo method (4)) and of halogenonium salts, as follows from the present work. Thus, diphenylbromonium borofluoride in the presence of copper forms diphenyl at room temperature.

All the facts listed could also be explained by heterolytic decomposition of onium compounds with subsequent reduction of the phenyl cation by the metal to the free phenyl radical.

However, the passivity of the triphenyloxonium cation toward metals described in our preceding article (5) (owing to the obvious inability of oxygen to expand its octet to a decet) would appear to support the hypothesis set forth above.

Data from crystallographic study and X-ray structural analysis of halogenonium salts will be published by T. L. Khotsyanova. It is interesting to note here that diphenylbromonium iodide is isomorphous with diphenyliodonium bromide.

Experimental Part

Preparation of diphenylbromonium salts. To 100 ml of bromobenzene at 80–90° (bath temperature), with stirring, a solution of 10.8 g of phenyldiazonium borofluoride in 300 ml of acetone was added over the course of an hour (the latter distills off during the reaction). Thirty minutes after addition of the diazonium solution, the reaction is complete. After cooling, the combined reaction mixture from 9 experiments was treated 4 times with water; the aqueous extracts were extracted several times with ether. From the first aqueous extract (50 ml), 1.7 g of diphenylbromonium borofluoride was isolated by freezing. From the 2nd, 3rd, and 4th aqueous extracts (100 ml each), and also from the residue of the 1st aqueous extract after isolation from it of $[(C_6H_5)_2Br]BF_4$, upon addition of solid NaJ, 10.2 g of diphenylbromonium iodide was obtained (m.p. 81–82° after reprecipitation from CH_3OH with abs. ether).

Diphenylbromonium borofluoride was reprecipitated twice from CH_3OH with ether and recrystallized from abs. ethanol. These are colorless crystals with decomp. point 120–121°, stable at room temperature.

$C_{12}H_{10}BrBF_4$. Found %: C 44.97; 44.93; H 3.12; 2.95
Calculated %: C 44.92; H 3.15

The total yield of both diphenylbromonium salts was 6.6% of theory.

Table 1

Reactions of diphenylbromonium and diphenylchloronium salts *

Starting salt, g	Reagent, ml or g	Solvent, ml	Reaction conditions	Reaction product: formula	m.p., °C	Yield, %
$[(C_6H_5)_2Br]J$^20.14	Metallic mercury1.0 ml	n-C_3H_7OH2.5	Boiling5-7 min	C_6H_5HgJ^1	270.5	29
0.16	1.5 ”	1.5	Shaking at room temperature 30 min	Same	270 (*)	45

Starting salt, g	Reagent, ml or g	Solvent, ml	Reaction conditions	Reaction product: formula	m.p., °C	Yield, %
3.3	2.0 ”	Water15	Boiling2 h	””	270.5	2.4
$[(C_6H_5)_2Br]Br$	1.5 ”0.3	n-C_3H_7OH3	Shaking at room temperature 30 min	C_6H_5HgBr^1	280 (^7)	41
$[(C_6H_5)_2Cl]J$	1.5 ”^4	3	Same, 15 min	C_6H_5HgJ^1	270	26^5
$[(C_6H_5)_2Cl]Br$	1.5 ”^6	Aqueous n-C_3H_7OH3	”” 30 ”	C_6H_5HgBr^1	280	66^5
$[(C_6H_5)_2Cl]Cl$	1.5 ”^6	3	”” 30 ”	C_6H_5HgCl^1	260 (^8)	15^5
$[(C_6H_5)_2Cl]BF_4$2.2	Metallic thallium2.4 g	Acetone15	”” 38 h	$(C_6H_5)_2TlBF_4$^7	–	9.5
$[(C_6H_5)_2Br]BF_4$5	6.0 ”	20	”” 36 ”	Same^8	–	11.4
$[(C_6H_5)_2J]BF_4$4.8	4.0 ”	25	”” 42 ”	Same^8	–	6
$[(C_6H_5)_2Br]BF_4$2	Metallic copper2.0 g	10	”” 3 ”	$C_6H_5OH^9$ $C_6H_5{-}C_6H_5$	69-70	17.552
0.91	0.95 ”	Water20	”” 3 ”	$C_6H_5OH^9$ $C_6H_5{-}C_6H_5$	69-70	77traces
2	2.0 ”	Dry cyclohexanone15	”” 3 ”	$C_6H_5OH^9$ $C_6H_5{-}C_6H_5$	69-70	462
$[(C_6H_5)_2Br]J$0.8	$NaNO_2$2.5 g	Water30	Boiling3 h	$C_6H_5NO_2$^10		54^11
$[(C_6H_5)_2Cl]J$	1.3 ”^4	15	Same, 1 h	Same		31^11
$[(C_6H_5)_2Br]J$	$NaN_3$2.5 g	30	”” 3 ”	$C_6H_5N_3$^10		55^11
$[(C_6H_5)_2Cl]J$	1.3 ”^4	15	”” 1.5 ”	Same		49^11
$[(C_6H_5)_2Br]Cl$	KCN6.3 g	120	”” 2 ”	C_6H_5CN^12		21
3.0	$(C_2H_5)_2NH$18 ml		”” 5 ”	$C_6H_5N(C_2H_5)_2$^13		14.5
3.0	9.0 ”	Water10	”” 5 ”	Same		20
$[(C_6H_5)_2Cl]J$	7.0 ”^4	8	”” 1.5 ”	””		70.5

Starting salt, g	Reagent, ml or g	Solvent, ml	Reaction conditions	Reaction product: formula	m.p., °C	Yield, %
$[(C_6H_5)_2Br]BF_4$ 1.5	9.0	–	"" 3 "	""		70
$[(C_6H_5)_2Cl]BF_4$ 0.75	4.5	–	"" 3 "	""		88
0.4	C_5H_5N 1.5 ml	–	Sealed tube, 206°	$[C_5H_5NC_6H_5]BF_4$	176-177 (^12)	85
$[(C_6H_5)_2Br]BF_4$ 0.5	1.5	–	Same, 213°	Same	176.5-177.5	84.5

* A number of experiments were carried out with the participation of L. V. Lisitskaya.

Notes

^1 After symmetrization with sodium stannite, diphenylmercury with m.p. 124-125° (125° (^9)) was obtained.

^2 Diphenylbromonium and -chloronium borofluorides do not react with metallic mercury.

[3] Identified as diphenylmercury, m.p. 124-125°.

[4] Obtained under the above-described conditions from 0.5 g of diphenylchloronium borofluoride and, because of its extreme instability, introduced into the reaction without preliminary purification.

[5] Calculated for diphenyliodonium borofluoride.

[6] A solution of 0.2 g of diphenylchloronium borofluoride in a minimal amount of water, saturated with sodium bromide or lithium chloride, was introduced into the reaction.

[7] Identified as $(C_6H_5)_2TlCl$. (Found, %: C 37.00; 36.93; H 2.62; 2.72. $C_{12}H_{10}TlCl$. Calculated, %: C 36.58; H 2.56.)

[8] Identified as $(C_6H_5)_2TlCl$. (Found, %: C 36.50; 36.52; H 2.87; 2.95.)

[9] Identified as tribromophenol, m.p. 92°. A mixed sample with an authentic specimen showed no depression of the melting point.

[10] After reduction and diazotization, identified as benzolazo-β-naphthol, m.p. 128.5-129.5° (128.5-129.5° ([10])).

[11] The yield is given for benzolazo-β-naphthol, calculated on the starting salt.

[12] Identified as benzoic acid; the yield is also given for this product, calculated on the starting diphenylbromonium iodide.

[13] Identified as 4′-nitro-4-diethylaminoazobenzene, m.p. 150-151.5° (151° (11)); the yield is also given for this product, calculated on the starting salt.

Preparation of diphenylchloronium salts. From 10.8 g of phenyldiazonium borofluoride (in 300 ml of acetone) and 100 ml of chlorobenzene, under the above-described conditions, 0.14 g (1% of theory) of diphenylchloronium borofluoride was obtained. After reprecipitation from CH_3OH with abs. ether, it has decomp. temp. 109.5-110° and consists of colorless crystals, readily soluble in water, alcohol, and acetone, and insoluble in ether.

Found, %:	C 52.13; 52.09;	H 3.76; 3.71
$C_{12}H_{10}ClBF_4$. Calculated, %:	C 52.12;	H 3.65

From the residue of the 1st, and also from the 2nd, 3rd, and 4th aqueous extracts, on addition of a solution of $NaHgJ_3$, a further 1.05 g of $[(C_6H_5)_2Cl]HgJ_3$, difficultly soluble in water, was precipitated; thus, the total yield of diphenylchloronium borofluoride was 3.3% of theory.

Diphenylchloronium iodide was precipitated by adding solid NaJ to a concentrated aqueous solution of diphenylchloronium borofluoride cooled to 0°. After recrystallization from CH_3OH within the temperature limits from +20 to −70°, the salt consists of very unstable colorless crystals with decomp. temp. 56-57.5°, readily soluble in water, lower alcohols, and acetone, and insoluble in ether.

Found, %:	C 44.96; 45.11;	H 3.27; 3.34
$C_{12}H_{10}ClJ$. Calculated, %:	C 45.52;	H 3.16.

Institute of Organoelement Compounds
Academy of Sciences of the USSR

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