Tetrahedron, 1957, Vol. 1, pp. 145-157. Pergamon Press Ltd., London

# HETEROLYTIC DECOMPOSITION OF ONIUM COMPOUNDS (DIPHENYL HALOGENONIUM AND TRIPHENYLOXONIUM SALTS)

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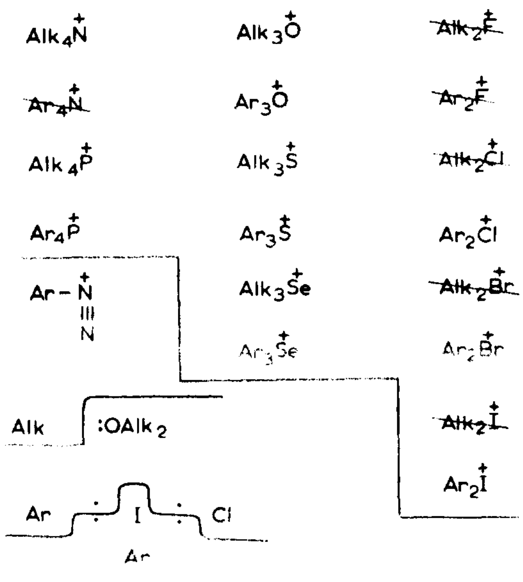
The present report deals with the investigation of various types of exchange of aromatic onium compounds. In Table 1 are listed the types of aliphatic and aromatic onium compounds known at present.

Table 1



One must add to them aryldiazonium salts, which may be considered as onium compounds of the nitrogen molecule. In exchange reactions, onium compounds, particularly ammonium[1] and oxonium,[2] transfer their aliphatic radicals to the attacking molecule heterolytically (Table 2).

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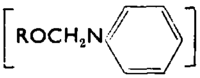
[1] A. E. Porai-Koshits Trudy Leningrad. Khim.-Technol Institute, Vypusk I (1934); D. N. Kursanov and V. N. Setkina *Izvest. Akad. Nauk. SSSR, Otdel. khim. nauk.* 190, 274 (1949); 386 (1950); *Doklady Akad. Nauk SSSR* **65**, 847 (1949); D. N. Kursanov, V. N. Setkina, and V. M. Rodionov *Izvest. Akad. Nauk SSSR. Otdel. khim. nauk.* 228 (1948); D. N. Kursanov and O. M. Shemyakina *Doklady Akad. Nauk SSSR* **62**, 341 (1948); E. Meyer C. A. **5**, 887 (1911); H. R. Snyder *et al.* *J. Amer. Chem. Soc.* **61**, 668, 2895 (1939); **66**, 200, 350 (1944); **67**, 38 (1945); **70**, 1703, 1857, 3855 (1948); **71**, 663 (1949); **73**, 970 (1951).

[2] H. Meerwein, G. Hinz, P. Hofmann, E. Kroning, and E. Pfeil *J. Prakt. Chem.* **147**, 257 (1937); H. Meerwein, E. Battenberg, H. Gold, E. Pfeil, and G. Willfang *J. Prakt. Chem.* **154**, 83 (1939).

TABLE 2

Heterolyse

| | | |
|---|---|---|
| $(C_6H_5)(CH_3)_2C_6H_5CH_2\overset{+}{N}\overset{-}{Cl} + HOC_6H_5$ | $\longrightarrow$ | $C_6H_5CH_2OC_6H_5$ |
|  $\overset{-}{Cl} + HOR$ | $\longrightarrow$ | $ROCH_2OR$ |
| $(C_2H_5)_3\overset{+}{O}\overset{-}{BF_4} + RCOOH$ | $\longrightarrow$ | $RCOOC_2H_5$ |
| $(C_2H_5)_3\overset{+}{O}\overset{-}{BF_4} + R_3N$ | $\longrightarrow$ | $[R_3\overset{+}{N}C_2H_5]\overset{-}{B}F_4$ |

On the other hand, it has been shown previously[3] and by our investigations that aromatic radicals are usually transferred homolytically as free phenyl radicals. Such, for example, is the method of synthesis of aromatic organo-mercuric compounds, discovered in 1929, when decomposing double diazonium salts and mercuric chloride

TABLE 3

| | | | | |
|---|---|---|---|---|
| $C_6H_5N_2HgCl_3$ | $+ Cu$ | $\longrightarrow$ | $C_6H_5HgCl$ | Nesmeyanov, 1929 |
| $C_6H_5N_2Cl$ | $+ Hg$ | $\longrightarrow$ | $C_6H_5HgCl$ | McClure, Lowy, 1931[21] |
| $(C_6H_5N_2)_2SnCl_6$ | $+ Sn$ | $\longrightarrow$ | $(C_6H_5)_2SnCl_2$ | Nesmeyanov, Kocheshkov, 1935 |
| $(C_6H_5N_2)_2PbCl_6$ | $+ Zn$ | $\longrightarrow$ | $(C_6H_5)_3PbCl$ | Nesmeyanov, Kocheshcov, 1935 |
| $C_6H_5N_2BF_4 + HgCl_2$ | $+ SnCl_2$ | $\longrightarrow$ | $C_6H_5HgCl$ | Dunker *et al.*, 1936[23] |
| $C_6H_5N_2Cl$ | $+ M_n$ | $\longrightarrow$ | $(C_6H_5)_{n-m}M_nCl_m$<br>$M = Hg, Sn, Sb, S, Se, Te, As$ | Waters, 1937-1939[4] |
| $C_6H_5N_2BiCl_4$ | $+ Cu$ | $\longrightarrow$ | $(C_6H_5)_3Bi$ | Gilman, 1939 |
| $C_6H_5N_2BiCl_4$ | $+ Bi$ | $\longrightarrow$ | $(C_6H_5)_3Bi$ | Nesmeyanov, Kocheshkov, 1940 |
| $C_6H_5N_2SbCl_4$ | $+ Zn$ | $\longrightarrow$ | $C_6H_5SbCl_2$<br>$(C_6H_5)_2SbCl$<br>$(C_6H_5)_3Sb$<br>$(C_6H_5)_3SbCl_2$ | Nesmeyanov, Kocheshkov, 1944 |
| $C_6H_5N_2BF_4$ | $+ Pb$ | $\longrightarrow$ | $(C_6H_5)_4Pb$ | Nesmeyanov, Kocheshkov, 1945 |
| $C_6H_5N_2BF_4$ | $+ Tl$ | $\xrightarrow{Cl'}$ | $(C_6H_5)_2TlCl$ | Nesmeyanov, Makarova, 1952[19] |
| $C_6H_5N_2BF_4 + SnCl_2$ | $+ Zn$ | $\longrightarrow$ | $(C_6H_5)_2SnCl_2$<br>$(C_6H_5)_3SnCl$<br>$C_6H_5SnCl_3$ | Nesmeyanov, Makarova, 1952[17] |
| $C_6H_5N_2BF_4$ | $+ MCl_3$ | $\xrightarrow[M = P,Sb,As]{OH'}$ | $C_6H_5MO(OH)_2 + (C_6H_5)_2MO(OH)$ | Doak, 1952-1954[29] |

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[3] M. Gomberg and W. E. Bachmann *J. Amer. Chem. Soc.* **46**, 2339 (1924); M. Gomberg and J. C. Pernert *J. Amer. Chem. Soc.* **48**, 1372 (1926); D. H. Hey and W. A. Waters *Chem. Rev.* **21**, 169 (1937); W. A. Waters *Chemistry of the free radicals* Oxford (1946).

[4] W. A. Waters *J. Chem. Soc.* 2007 (1937); 843, 1077 (1938); 864, 867 (1939).

with powdered metals,[4a] as well as a number of similar syntheses of organo-metallic compounds carried out at a later date (Table 3).[5]

This is the case also with diaryliodonium salts. Thus, diphenyliodonium chloride, under the action of a metal (mercury, selenium, tellurium), homolytically transfers its phenyl radical to form organo-metallic compounds.[6]

Whether the phenyl, transferred from ammonium or oxonium, would follow the alkyl ammonium and oxonium mechanism or the phenyl diazonium and iodonium one, could not be decided, tetra-aryl ammonium and triaryloxonium having been unknown.

In a series of investigations we have shown that it is possible to make diazonium and iodonium salts transfer their aromatic radical heterolytically. We have used this type of reaction to extend synthetic procedures as well as for obtaining new types of onium compounds such as diarylchloronium, diarylbromonium, and triaryloxonium.

To effect the heterolytic cleavage of phenyl from the iodonium and diazonium salts, it was necessary to decompose the salts of these onium cations with stable complex anions. In fact, it has been shown that phenyldiazonium and diphenyliodonium borofluorides do decompose heterolytically. In contrast to the corresponding chlorides, they do not form organo-mercuric compounds with metallic mercury. On the contrary the phenyl cation resulting from the decomposition of diphenyliodonium borofluoride[7] is fixed by a pair of free electrons of nitrogen, phosphorus, antimony, sulphur, and selenium in trimethylamine, pyridine, triphenylphosphine, triphenylarsine, triphenylstibine, diphenylsulphide, and diphenylselene, forming new onium borofluorides.

TABLE 4

$$(C_6H_5)_2\overset{+}{I}\overset{-}{B}F_4 + \left\{ \begin{array}{lcl} :N(CH_3)_3 & \longrightarrow & C_6H_5N(CH_3)_3BF_4 \\ :NC_5H_5 & \longrightarrow & [C_6H_5NC_5H_5]BF_4 \\ :P(C_6H_5)_3 & \longrightarrow & (C_6H_5)_4PBF_4 \\ :As(C_6H_5)_3 & \longrightarrow & (C_6H_5)_4AsBF_4 \\ :Sb(C_6H_5)_3 & \longrightarrow & (C_6H_5)_4SbBF_4 \\ :S(C_6H_5)_2 & \longrightarrow & (C_6H_5)_3SBF_4 \\ :Se(C_6H_5)_2 & \longrightarrow & (C_6H_5)_3SeBF_4 \end{array} \right.$$

All these reactions give excellent yields. It should be noted that in none of the conditions investigated did the phenyl from diphenyliodonium chloride react with

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[4a] A. N. Nesmeyanov *Zhur. Russ. khim. Obshch.* **61**, 1393 (1929); *Ber.* **62**, 1010 (1929); A. N. Nesmeyanov and E. I. Kahn *Zhur. Russ. khim. Obshch.*, **61**, 1407 (1929), *Ber.* **62**, 1018 (1929); A. N. Nesmeyanov and L. G. Makarova *Zhur. Obshchei. Khim.* **1**, 538 (1931); A. N. Nesmeyanov, N. Th. Glushnev, P. Th. Epifansky, and A. J. Flegontov *Zhur. Obshch. Khim.* **4**, 714, (1934); *Ber.* **67**, 130 (1934); A. N. Nesmeyanov *Uch. Zap. Mosk. Univ. ser. khim.* **3**, 291 (1934); A. N. Nesmeyanov and E. M. Toropova *Zhur. Obshchei Khim.* **4**, 664 (1934).

[5] A. N. Nesmeyanov, K. A. Kocheshkov, and V. A. Klimova *Zhur. Obshchei. Khim.* **6**, 167 (1936); *Ber.* **68**, 1877 (1935); K. A. Kocheshkov, A. N. Nesmeyanov, and N. K. Gipp *Zhur. Obshechei Khim.* **6**, 172 (1936); K. A. Kocheshkov and A. N. Nesmeyanov *Izvest. Akad. Nauk. Otdel. khim. nauk* 416 (1944); O. A. Reutov and O. A. Ptitsyna *Doklady Akad. Nauk.* **79**, 819 (1951); K. A. Kocheshkov, and A. N. Nesmeyanov *Zhur. Obshchei. Khim.* **6**, 144 (1936); T. K. Kozminskaya, M. M. Nadj and K. A. Kocheshkov *Zhur. Obshchei Khim.* **16**, 891, 897 (1946). Gilman and Svigoon *J. Amer. Chem. Soc.* **61**, 3586 (1939); Gilman and Yablunsky *J. Amer. Chem. Soc.* **63**, 949 (1941).

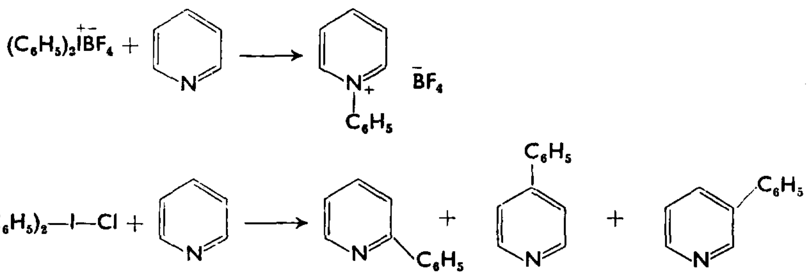
[6] R. B. Sandin, F. T. McClure and F. Irwin *J. Amer. Chem. Soc.* **61**, 2944 (1939).

[7] L. G. Makarova, and A. N. Nesmeyanov *Izvest. Akad. Nauk SSSR. Otdel. khim. nauk* 617 (1945).

triphenylarsine, triphenylstibine, diphenylsulphide, diphenylselene, but reacted with triphenylphosphine to form tetraphenyl-phosphonium in 40% yield.

The reaction with pyridine is the most definite indication of the ionic or radical decomposition. The phenyl cation formed by decomposing diphenyliodonium borofluoride results in the formation of the *N*-phenylpyridinium salt in 88% yield,[7] whilst the phenyl radical formed during the decomposition of diphenyliodonium and phenyldiazonium chlorides enters the pyridine nucleus[10a].

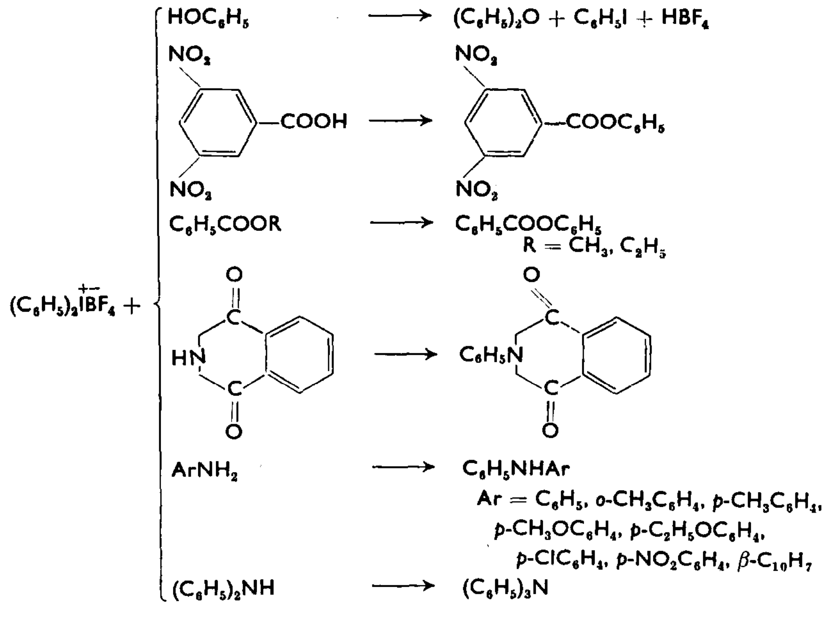
TABLE 5



The phenyl resulting from diphenyliodonium borofluoride also adds on the free pair of electrons of oxygen and nitrogen, thus phenylating the phenolic, carboxylic, and carbethoxylic oxygen and the nitrogen of amides[8] and amines[9]

Decomposition of diphenyliodonium borofluoride in phenol leads to diphenyloxide.

TABLE 6



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[8] A. N. Nesmeyanov and L. G. Makarova *Uch. Zap. Mosk. Univ.* 132, 109 (1950).
[9] L. G. Makarova *Izvest. Akad. Nauk SSSR, Otdel. khim. nauk* 741 (1951).
[10a] R. B. Sandin and R. K. Brown *J. Amer. Chem. Soc.* 69, 2253 (1947).

In capronic, benzoic, and 3,5-dinitrobenzoic acids it yields the corresponding phenyl esters. In the alkyl benzoate and phosphate, re-esterification takes place.

Decomposition of diphenyliodonium borofluoride in methyl and ethyl benzoate and in methyl, ethyl, *n*-propyl, and *n*-butyl phosphate results in the formation of the corresponding phenyl esters.

Decomposition of diphenyliodonium borofluoride in phthalimide leads to *N*-phenyl phthalimide, and decomposition in primary and secondary aromatic amines gives respectively secondary and tertiary amines.

Phenyl, resulting from diphenyliodonium borofluoride, does not add to triphenylamine or to triphenylbismuth.

The decomposition of aryldiazonium borofluorides was first observed to take place heterolytically in the benzene nucleus containing substituents.[10b] Phenyldiazonium borofluoride and other aryldiazonium borofluorides were decomposed in benzene derivatives containing meta-orienting substituents. Homolytic decomposition of aryldiazonium borofluorides should have led to the aryl radical entering the substituted benzene derivative mainly in ortho- and para-positions to any substituent. But if decomposition of aryldiazonium borofluorides takes place heterolytically, generating an aryl cation, then the latter should be affected by the usual orienting influence of the substituent in the benzene ring, and, being an electrophilic reagent, it has in this case to enter the benzene nucleus primarily in the meta-position to the meta-orienting group.

Decomposition of aryldiazonium borofluorides in a benzene derivative containing the following meta-orienting substituents, nitro group, quaternary ammonium nitrogen, carbalkoxy group, trifluoromethyl and acetyl groups, leads mainly to aryl occupying the meta-position to these meta-orientants.

In contrast to the decomposition of iodonium, the majority of diazonium decomposition reactions investigated resulted in poor yields of products formed by aryl cations entering the aromatic nucleus. In the benzene ring the meta-orienting influence of the substituents listed above is quite evident. Though, in some cases some ortho- and para-isomers were isolated, their amount was substantially less than that of meta-isomers. Low yields of benzene nucleus substitution products depend on the fact that the main reaction always proceeds following Schiemann with fluorobenzene formation and that in addition large amounts of the so-called "diazoresin" are formed.

Yet, on the whole, the general picture of the decomposition of diazonium borofluoride seems as convincing as that of diphenyliodonium borofluorides.

When the following aryldiazonium borofluorides are decomposed in nitrobenzene, aryl occupies the meta-position to the nitro group, the only biphenyl derivative isolated being in each case the respective meta-nitrobiaryl (Table 7).

The ultra-violet analysis of fractions containing nitrobiaryls showed the mixture to contain over 90% meta-derivatives.

Phenyldiazonium borofluoride decomposition in phenyl-trimethylammonium borofluoride has revealed (together with the predominance of products of meta-substitution) the formation of a smaller amount of a para-isomer (the reaction products were isolated as dimethylaminodiphenyls). The ratio of the meta-isomer to the para-isomer can be approximately calculated as 3 : 1.

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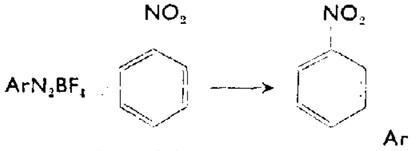
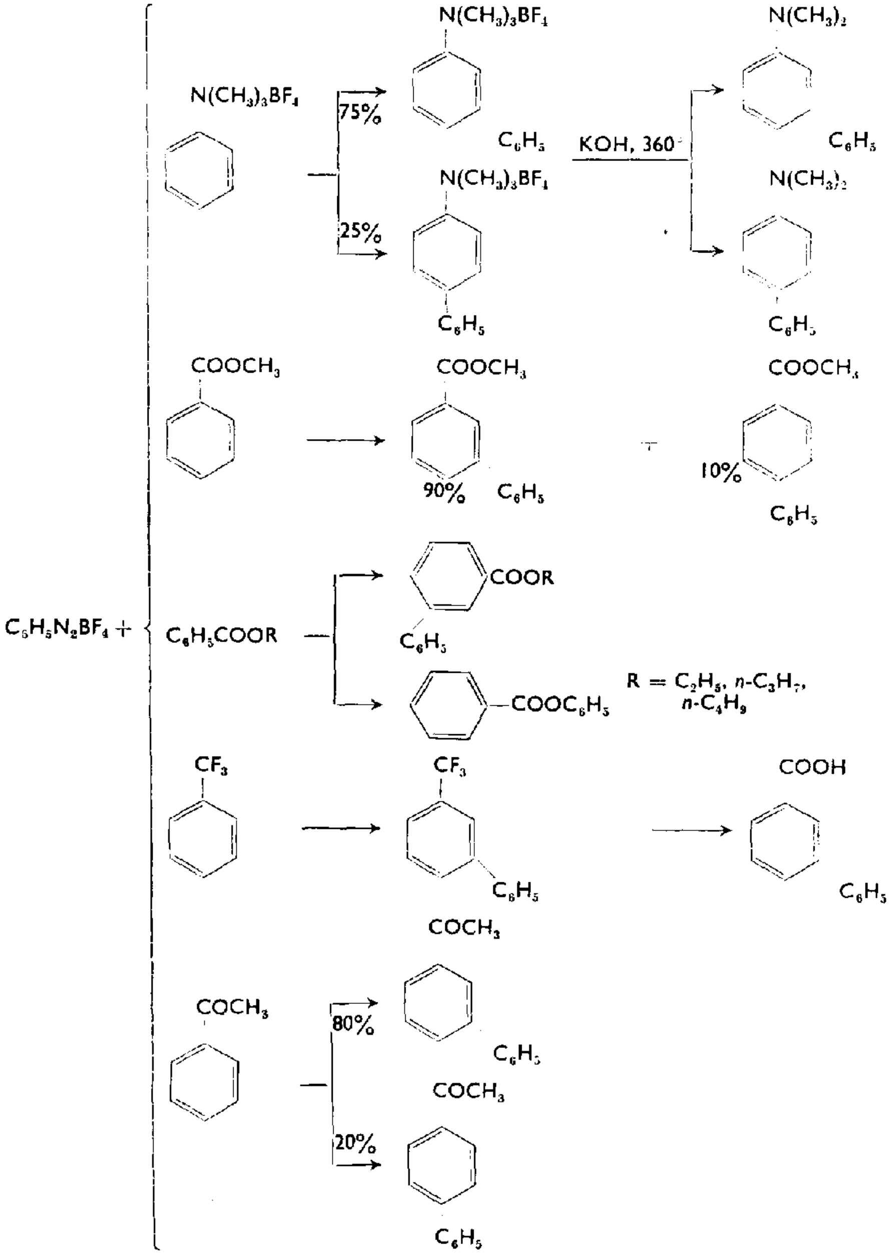
[10b] A. N. Nesmeyanov and L. G. Makarova *Izvest. Akad. Nauk SSSR, Otdel. khim. nauk* 213 (1947).

TABLE 7*



Ar = $C_6H_5$, $p$-$CH_3C_6H_4$,
$p$-$CH_3OC_6H_4$, $p$-$ClC_6H_4$,
$o$-$CH_3O_2CC_6H_4$, $p$-$C_2H_5O_2CC_6H_4$



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* The figures represent the percentage ratio of isomers in the reaction product (but not the yield).

Phenyldiazonium borofluoride being decomposed in methyl, ethyl, *n*-propyl, *n*-butyl, benzoates, phenyl occupies the meta-position to the carbalkoxy group.

The reaction of phenyldiazonium borofluoride with ethyl, *n*-propyl, *n*-butyl benzoates leads after saponification to meta-diphenylcarboxylic acid.

Decomposition in methyl benzoate, besides phenyl occupying predominantly the meta-position, resulted also in some para-isomer formation. Phenyldiazonium borofluoride decomposition in the ethyl, *n*-propyl, *n*-butyl benzoates brought about, in addition, re-esterification and, just as in the case of diphenyliodonium, phenyl benzoate was formed, probably due to phenyl cation affecting the carbethoxy-group.

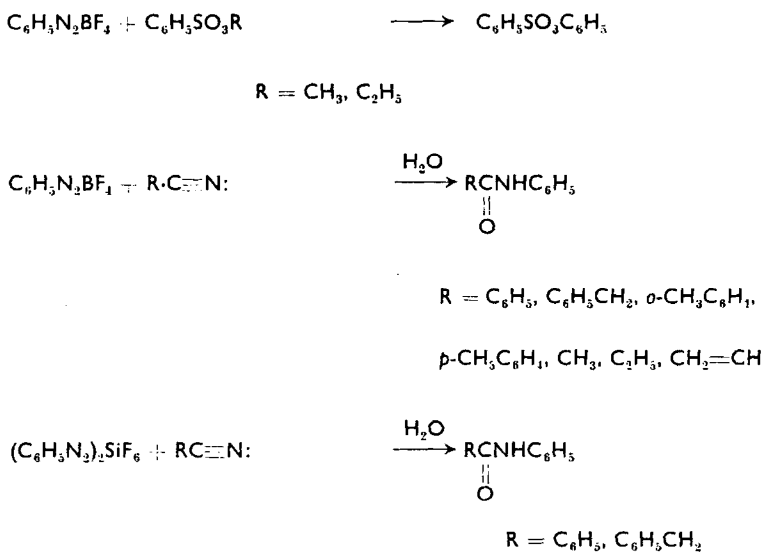
The phenyl cation from phenyldiazonium borofluoride also occupied the meta-position to the trifluoromethyl-group of benzotrifluoride. The only diphenylcarboxylic acid isolated after hydrolysis was the meta-acid.

Decomposition of phenyldiazonium borofluoride in acetophenone resulted in phenyl occupying essentially the meta-position to the acetyl group, a para-substitution product being also formed, though to a lesser extent.

We have isolated meta- and para-phenylacetophenones as such, and part of the meta- and para-phenylacetophenone mixture was subjected to the iodoformic reaction. The resulting mixture of meta- and para-diphenylcarboxylic acids was separated owing to the difference in solubilities of their sodium salts, the resulting acids being identified. By this procedure we have also determined the predominance of meta-isomer formation. Thus, even with a relatively weak meta-orientant, i.e. the acetyl group, the phenyl from the phenyldiazonium borofluoride occupied mainly the meta-position, showing in this case also a different behaviour from the phenyl derived from the homolytically decomposing phenyl source.

Decomposition of phenyldiazonium borofluoride in methyl and ethyl benzene

TABLE 8



$$C_6H_5N_2BF_4 + C_6H_5SO_3R \longrightarrow C_6H_5SO_3C_6H_5$$

$$R = CH_3,\ C_2H_5$$

$$C_6H_5N_2BF_4 + R{\cdot}C{\equiv}N: \xrightarrow{H_2O} \underset{\underset{O}{\|}}{RC}NHC_6H_5$$

$$R = C_6H_5,\ C_6H_5CH_2,\ o\text{-}CH_3C_6H_4,$$
$$p\text{-}CH_3C_6H_4,\ CH_3,\ C_2H_5,\ CH_2{=}CH$$

$$(C_6H_5N_2)_2SiF_6 + RC{\equiv}N: \xrightarrow{H_2O} \underset{\underset{O}{\|}}{RC}NHC_6H_5$$

$$R = C_6H_5,\ C_6H_5CH_2$$

sulphonates did not give products resulting from phenyl entering the benzene ring of these esters. The phenyl attack was directed to the sulphalkoxy group and the only reaction product in both cases was phenyl benzenesulphonate in good yield.

Decomposition of phenyldiazonium borofluoride in nitrile medium leads to the addition of phenyl to nitrogen.[11] Hydrolysis of nitrilium borofluorides not isolated by us results in anilides of corresponding acids, the yield of benzanilide, starting for example from benzonitrile, being up to 40%. Similarly starting from benzylcyanide, phenylacetanilide was obtained. A similar reaction was carried out with ortho- and para-toluo-, propio-, and acrylonitriles.

The production of anilides by the reaction of diazo-compounds with nitriles is well known. Hanby and Waters,[12] when decomposing phenyldiazonium chloride in acetonitrile, observed the formation of a mixture consisting of benzene, acetophenone, and 10% acetanilide. Here the phenyl radical attacks alternatively the carbon or the nitrogen of the nitrile group or the α-attached hydrogen. In our case the phenyl cation attack took place on the nitrogen atom.

A number of similar results were obtained by us in decomposing aryldiazonium fluorosilicate.[13]

Without going into details, it may be mentioned that this excludes any specific role of boron trifluoride.

To prove the heterolytic mechanism of phenyldiazonium borofluoride decomposition, a reaction with compounds involving a double carbon-carbon bond was carried out.[8] It was supposed that the phenyl cation would add at the polar double bond, following Markovnikov rule and being acted upon by acrylic acid, should form different products from those obtained under the action of aryl radicals in the Meerwein-Koelsch reaction.

The decomposition of phenyldiazonium borofluoride in ethyl crotonate results in phenyl occupying the α-position to the ethoxycarbonyl group to yield (after saponification) methylatropic acid.[8] On the other hand, the decomposition in the same medium of phenyldiazonium chloride in the Meerwein-Koelsch reaction leads to phenyl occupying the β-position, to form α-chloro-β-phenylisobutyric acid.[14]

During the decomposition of phenyldiazonium borofluoride in methyl acrylate the phenyl attacks the α-carbon and the carboxylic oxygen. The main reaction products formed were atropic acid (after saponification) and phenyl acrylate.

The Meerwein-Koelsch reaction of phenyldiazonium chloride with methyl acrylate yields α-chloro-hydrocinnamic acid ester.[15]

Decomposition of phenyldiazonium borofluoride in methyl-methacrylate also results in different products from those formed with phenyldiazonium chloride,[16] α-methylcinnamic acid being formed after hydrolysis in the latter case.

As a result of this reaction, benzyl-acrylic acid was obtained (after saponification) and 5-hydroxy-2-methyl-hydrindenone, a product of further conversion of the phenylmethacrylate.

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[11] L. G. Makarova and A. N. Nesmeyanov *Izvest. Akad. Nauk. SSSR, Otdel. khim. nauk* 1019 (1954).

[12] W. E. Hanby and W. A. Waters *J. Chem. Soc.* 1792, (1939).

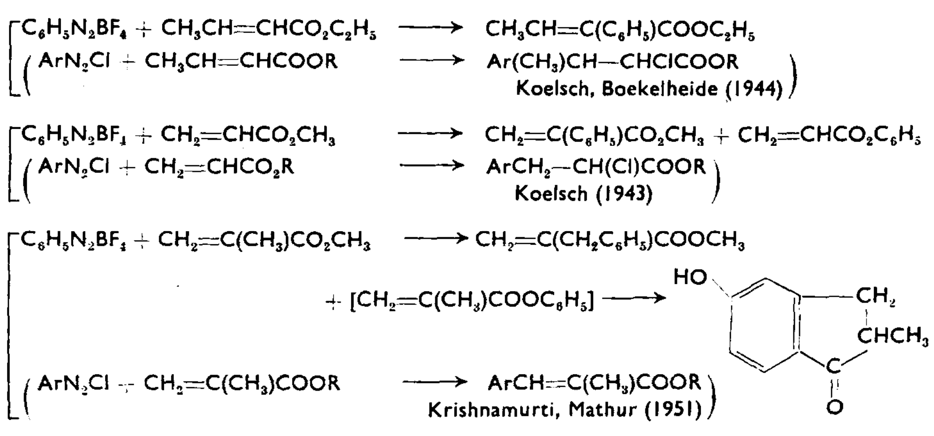
[13] L. G. Makarova and M. K. Matveeva *Izvest. Akad. Nauk. SSSR, Otdel. khim. nauk* 435 (1956).

[14] C. F. Koelsch and V. Boekelheide *J. Amer. Chem. Soc.* **66**, 412 (1944).

[15] C. F. Koelsch *J. Amer. Chem. Soc.* **65**, 57 (1943).

[16] P. L'Ecuyer and Ch. A. Olivier *Canad. J. Research* **28**, 648 (1950); M. Krischnamurti and K. B. Lal Mathur *J. Indian. Chem. Soc.* **28**, 507 (1951).

TABLE 9



I

$C_6H_5N_2BF_4 + CH_3CH{=}CHCO_2C_2H_5 \longrightarrow CH_3CH{=}C(C_6H_5)COOC_2H_5$

$(ArN_2Cl + CH_3CH{=}CHCOOR \longrightarrow Ar(CH_3)CH{-}CHClCOOR$ Koelsch, Boekelheide (1944))

II

$C_6H_5N_2BF_4 + CH_2{=}CHCO_2CH_3 \longrightarrow CH_2{=}C(C_6H_5)CO_2CH_3 + CH_2{=}CHCO_2C_6H_5$

$(ArN_2Cl + CH_2{=}CHCO_2R \longrightarrow ArCH_2{-}CH(Cl)COOR$ Koelsch (1943))

III

$C_6H_5N_2BF_4 + CH_2{=}C(CH_3)CO_2CH_3 \longrightarrow CH_2{=}C(CH_2C_6H_5)COOCH_3$

$+ [CH_2{=}C(CH_3)COOC_6H_5] \longrightarrow$

$(ArN_2Cl + CH_2{=}C(CH_3)COOR \longrightarrow ArCH{=}C(CH_3)COOR$ Krishnamurti, Mathur (1951))

Table 3 records the comparative data of the synthesis of organo-metallic (and organo-element) compounds through double diazonium salts and the homolytic synthesis of the same compounds obtained from diazonium chloride and a metal. In cases where the double salt procedure with the same metal results in a poor yield (as, for example, in the synthesis of organo-lead and tin compounds) and the direct action of diazonium halide on a metal also gives little or no result, diazonium borofluorides give good results.

Thus, as has been shown, it is possible to obtain a 40% yield of organo-tin compounds[17] (reaction N 12), up to 30% of organo-lead compounds[18] (reaction N 10) as well as organo-thallium compounds[10] (reaction N 11), formerly not available through diazo-compounds.

The table suggests two parallels. First, a parallel between the direct attack of the decomposing diazonium halides on the free metal in Waters[20, 12] and McClure[21] reactions and our reactions of organo-metallic syntheses through double diazonium salts. It is concluded that in both cases homolytic reactions of identical mechanism are involved. Secondly, there is a parallel between diazonium borofluoride syntheses and all our syntheses through onium borofluoride compounds mentioned above. This analogy seems in both cases to demand a heterolytic mechanism.[22]

One can, however, hardly imagine a heterolytic mechanism of synthesis of an organo-metallic compound by diazonium borofluoride acting on a free metal. If it were homolytic, why should diazonium borofluoride prove successful in cases where its chloride failed? It is impossible at present to come to any conclusions. The following correlations can be of some help in elucidating this point.

Iodonium and diazonium borofluorides behave essentially in a similar way. But there is a difference in their behaviour in reactions where both borofluorides are acted on by a base, as, for example, by pyridine.

It has already been mentioned above that iodonium borofluoride as a result of an

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[17] A. N. Nesmeyanov and L. G. Makarova *Doklady Akad. Nauk SSSR* **87**, 421 (1952).
[18] A. N. Nesmeyanov and L. G. Makarova *Izvest. Akad. Nauk SSSR, Otdel. khim. nauk* 380 (1954).
[19] A. N. Nesmeyanov and L. G. Makarova *Doklady Akad. Nauk SSSR* **87**, 417 (1952).
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obviously heterolytic decomposition up to 90%, forms with pyridine *N*-phenylpyridinium borofluoride. On the other hand, phenyldiazonium borofluoride behaves with pyridine like phenyldiazonium or diphenyliodonium chloride forming a mixture of $\alpha$- and $\gamma$-phenylpyridines.

For obvious reasons we are dealing with a homolytic reaction. Pyridine like the hydroxyl ion appears first to convert the diazonium cation into a diazo-compound, which is then homolytically decomposed. Since this conversion, like that of diazonium hydroxide into diazo-hydrate, is impossible for the diphenyliodonium cation, diphenyliodonium borofluoride in all cases decomposes heterolytically.

For this reason, in contrast to diphenyliodonium chloride, it does not give with metallic mercury any organo-mercuric compound. In the Dunker reaction,[23] phenyldiazonium borofluoride forms phenylmercury chloride similar to the formation of the latter from phenyldiazonium chloride and mercury in the McClure reaction.[21] Thus we are led to assume that free metal acts on the diazonium cation as electron-releasing reagent, similar to a base, causing it to decompose homolytically with a previous conversion into a diazo-form.

This assumption is supported by the decomposition of aryldiazonium borofluoride in nitrobenzene in the presence of large amounts of powdered copper, the process without copper resulting, as already stated above, in an almost pure meta-nitrobiaryl. Copper induces the process to run along the homolytic mechanism, as seen by exclusive formation of ortho- and para-nitrobiaryl. A similar difference is to be observed in the results of decomposition of phenyldiazonium borofluoride in ethyl benzoate in the presence or absence of powdered copper. In the latter case the decomposition seems to run heterolytically, as it leads to re-esterification, yielding phenyl benzoate, and to formation of metaphenyl benzoate. With copper, due to homolysis, the phenyl radical attacks the aromatic nucleus, yielding ethyl paraphenylbenzoate as the main reaction product.

As a new result of heterolysis of aryldiazonium borofluoride, one may mention the transfer of the phenyl cation to the free electron pair of bromine, chlorine, and oxygen in bromobenzene, chlorobenzene, and diphenyloxide respectively, to yield previously unknown cations of diphenylbromonium,[24] diphenylchloronium,[25] and triphenyloxonium.[26] Gradually introducing phenyldiazonium borofluoride into an excess of halogen benzene at 60° and mixing until the diazo-compound is completely decomposed, one obtains in a 0·55% of theory yield diphenyl halogenonium borofluoride which is extracted by water. From the water extract it is precipitated with chloroplatinic acid or with sodium tetraphenylborate and in the case of diphenylbromonium cation with an iodine ion as well. The reaction being carried out in the same way, by introducing the acetone solution of phenyldiazonium borofluoride into the halogenbenzene at about 80°, it is possible to raise the yield up to 6% of theory.

Diphenylbromonium compounds are typical salts with a colourless cation, more soluble than the corresponding diphenyliodonium salts. Chloride, bromide, nitrate, nitrite, sulphate, acetate, borofluoride, and a number of others are soluble in water.

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TABLE 10

| | | | F. (dec.) |
|---|---|---|---|
| $C_6H_5\overset{+}{N_2}\overset{-}{BF_4}$ | ⟶ | $(C_6H_5)_2\overset{+}{Br}\overset{-}{BF_4} + N_2$ | 120–121° |
| $C_6H_5Br$ | | $(C_6H_5)_2\overset{+}{Br}\overset{-}{Br}$ | 82–83° |
| | | $(C_6H_5)_2\overset{+}{Br}\overset{-}{I}$ | 81–82° |
| | | $(C_6H_5)_2\overset{+}{Br}\overset{-}{HgI_3}$ | 108–109° |
| | | $[(C_6H_5)_2\overset{+}{Br}]_2\overset{--}{PtCl_6}$ | 160° |
| | | $(C_6H_5)_2\overset{+}{Br}\overset{-}{B}(C_6H_5)_4$ | 165° |
| $p\text{-}CH_3C_6H_4\overset{+}{N_2}\overset{-}{BF_4}$ | ⟶ | $(p\text{-}CH_3C_6H_4)(C_6H_5)\overset{+}{Br}\overset{-}{BF_4}$ | 78° |
| $C_6H_5Br$ | | $(p\text{-}CH_3C_6H_4)(C_6H_5)\overset{+}{Br}\overset{-}{I}$ | 81–82° |
| | | $(p\text{-}CH_3C_6H_4)(C_6H_5)\overset{+}{Br}\overset{-}{HgI_3}$ | 110–111° |
| | | $[(p\text{-}CH_3C_6H_4)(C_6H_5)\overset{+}{Br}]_2\overset{--}{PtCl_6}$ | 152° |
| | | $(p\text{-}CH_3C_6H_4)(C_6H_5)\overset{+}{Br}\overset{-}{B}(C_6H_5)_4$ | ~135° |
| $o\text{-}CH_3C_6H_4\overset{+}{N_2}\overset{-}{BF_4}$ | ⟶ | $(o\text{-}CH_3C_6H_4)(C_6H_5)\overset{+}{Br}\overset{-}{BF_4}$ | 112–113° |
| $C_6H_5Br$ | | $(o\text{-}CH_3C_6H_4)(C_6H_5)\overset{+}{Br}\overset{-}{I}$ | 65–66° |
| | | $(o\text{-}CH_3C_6H_4)(C_6H_5)\overset{+}{Br}\overset{-}{HgI_3}$ | 92° |
| | | $[(o\text{-}CH_3C_6H_4)(C_6H_5)\overset{+}{Br}]_2\overset{--}{PtCl_6}$ | 142° |
| $2,4\text{-}(CH_3)_2C_6H_3\overset{+}{N_2}\overset{-}{BF_4}$ | ⟶ | $[2,4\text{-}(CH_3)_2C_6H_3](C_6H_5)\overset{+}{Br}\overset{-}{BF_4}$ | 104–105° |
| $C_6H_5Br$ | | $[2,4\text{-}(CH_3)_2C_6H_3](C_6H_5)\overset{+}{Br}\overset{-}{I}$ | 66° |
| $p\text{-}ClC_6H_4\overset{+}{N_2}\overset{-}{BF_4}$ | ⟶ | $(p\text{-}ClC_6H_4)(C_6H_5)\overset{+}{Br}\overset{-}{HgI_3}$ | 97–98° |
| $C_6H_5Br$ | | $[(p\text{-}ClC_6H_4)(C_6H_5)\overset{+}{Br}]_2\overset{--}{PtCl_6}$ | 137–138° |
| $p\text{-}C_2H_5OOCC_6H_4\overset{+}{N_2}\overset{-}{BF_4}$ | ⟶ | $[(p\text{-}C_2H_5OOCC_6H_4)(C_6H_5)\overset{+}{Br}]_2\overset{-}{HgI_3}$ | 79° |
| $C_6H_5Br$ | | $[(p\text{-}C_2H_5OOCC_6H_4)(C_6H_5)\overset{+}{Br}]_2\overset{--}{PtCl_6}$ | 127° |
| | | $(p\text{-}C_2H_5OOCC_6H_4)(C_6H_5)\overset{+}{Br}\overset{-}{B}(C_6H_5)_4$ | 142–144° |
| $\beta\text{-}C_{10}H_7\overset{+}{N_2}\overset{-}{BF_4}$ | ⟶ | $(\beta\text{-}C_{10}H_7)(C_6H_5)\overset{+}{Br}\overset{-}{I}$ | 77° |
| $C_6H_5Br$ | | | |

Iodide, chloroplatinate, and tetraphenylborate are sparingly soluble. The two latter salts are stable at room temperature. The chloroplatinate decomposes at 159·5° and tetraphenylborate at 164–165°. Iodide is not stable, decomposing in 1–2 days into a mixture of bromo- and iodobenzene. It decomposes at 81–82°. Diphenylchloronium salts are considerably less stable. The action of an iodine ion on borofluoride solution leads to the formation of diphenylchloronium iodide, which decomposes at 56–57°. Chloroplatinate decomposes at 142·5–143°, tetraphenylborate at 160–161°.

In the Tables 10 and 11, are listed all diarylbromonium and diarylchloronium salts which we have obtained and are at present investigating.

Thus, by introducing the acetone solution of diazonium borofluoride, into diphenyl oxide at 80–90°, after half an hour's heating at the same temperature triphenyloxonium borofluoride is obtained from the water extract, after removing acetone and cooling. It is an extremely stable compound, decomposing at 226°.

TABLE 11

| | | | F. (dec.) |
|---|---|---|---|
| $C_6H_5\overset{+}{N_2}\overset{-}{B}F_4$ | ⟶ | $(C_6H_5)_2\overset{+}{Cl}\overset{-}{B}F_4 + N_2$ | 109·5–110° |
| | | $(C_6H_5)_2\overset{+}{Cl}\overset{-}{I}$ | 56–57° |
| $C_6H_5Cl$ | | $(C_6H_5)_2\overset{+}{Cl}\overset{-}{B}(C_6H_5)_4$ | 161° |
| | | $[(C_6H_5)_2\overset{+}{Cl}]_2\overset{--}{Pt}Cl_6$ | 143° |
| $p\text{-}CH_3C_6H_4\overset{+}{N_2}\overset{-}{B}F_4$ | ⟶ | $(p\text{-}CH_3C_6H_4)(C_6H_5)\overset{+}{Cl}\overset{-}{Hg}I_3$ | 93–94° |
| $C_6H_5Cl$ | | $[(p\text{-}CH_3C_6H_4)(C_6H_5)\overset{+}{Cl}]_2\overset{--}{Pt}Cl_6$ | 139° |
| | | $(p\text{-}CH_3C_6H_4)(C_6H_5)\overset{+}{Cl}\overset{-}{B}(C_6H_5)_4$ | 127° |
| $o\text{-}CH_3C_6H_4\overset{+}{N_2}\overset{-}{B}F_4$ | ⟶ | $(o\text{-}CH_3C_6H_4)(C_6H_5)\overset{+}{Cl}\overset{-}{Hg}I_3$ | 64° |
| $C_6H_5Cl$ | | $[(o\text{-}CH_3C_6H_4)(C_6H_5)\overset{+}{Cl}]_2\overset{--}{Pt}Cl_6$ | 123–124° |
| $2,4\text{-}(CH_3)_2C_6H_3\overset{+}{N_2}\overset{-}{B}F_4$ | ⟶ | $[2,4\text{-}(CH_3)_2C_6H_3](C_6H_5)\overset{+}{Cl}\overset{-}{Hg}I_3$ | 83° |
| $C_6H_5Cl$ | | $[[2,4\text{-}(CH_3)_2C_6H_3](C_6H_5)\overset{+}{Cl}]_2\overset{--}{Pt}Cl_6$ | 144° |
| $p\text{-}C_2H_5OOCC_6H_4\overset{-}{N_2}\overset{-}{B}F_4$ | ⟶ | $[(p\text{-}C_2H_5OOCC_6H_4)(C_6H_5)\overset{+}{Cl}]_2\overset{-}{Hg}I_4$ | 58·5–60° |
| $C_6H_5Cl$ | | $[(p\text{-}C_2H_5OOCC_6H_4)(C_6H_5)\overset{+}{Cl}]_2\overset{--}{Pt}Cl_6$ | 106·5–108° |
| | | $(p\text{-}C_2H_5OOCC_6H_4)(C_6H_5)\overset{+}{Cl}\overset{-}{B}(C_6H_5)_4$ | 121–124° |
| $C_6H_5\overset{+}{N_2}\overset{-}{B}F_4$ | ⟶ | $(p\text{-}ClC_6H_4)(C_6H_5)\overset{+}{Cl}\overset{-}{Hg}I_3$ | 84° |
| $p\text{-}ClC_6H_4Cl$ | | $[(p\text{-}ClC_6H_4)(C_6H_5)\overset{+}{Cl}]_2\overset{--}{Pt}Cl_6$ | 119–120° |

In Table 12 are listed some representatives of this previously unknown type of tertiary aromatic oxonium salts which we have obtained.

TABLE 12

| | | | F. (dec.) |
|---|---|---|---|
| $C_6H_5\overset{+}{N_2}\overset{-}{B}F_4$<br>$(C_6H_5)_2O$ | ⟶ | $(C_6H_5)_3\overset{+}{O}\overset{-}{B}F_4$ | 226° |
| | | $(C_6H_5)_3\overset{+}{O}\overset{-}{Br}$ | 182–182·5° |
| | | $(C_6H_5)_3\overset{+}{O}\overset{-}{I}$ | 177–178° |
| | | $(C_6H_5)_3\overset{+}{O}\overset{-}{Hg}I_3$ | 156–157° |
| | | $(C_6H_5)_3\overset{+}{O}\overset{-}{B}(C_6H_5)_4$ | ~165° |
| | | $[(C_6H_5)_3\overset{+}{O}]_2\overset{--}{Pt}Cl_6$ | 184–185° |
| | | $[(C_6H_5)_3\overset{+}{O}]_2\overset{--}{Cr_2}O_7$ | 177–178° darkened |
| | | $(C_6H_5)_3\overset{+}{O}C_6H_2(NO_2)_3\overset{-}{O}$ | 155–157° |

It is rather striking that decomposition of phenyl-diazonium borofluoride into iodobenzene leaves no traces in diphenyliodonium salt. On the other hand, the homolytic decomposition of phenyldiazoacetate in iodobenzene gives a small amount of diphenyliodonium salt. In contrast, decomposition of diazophenyl acetate in chloro- and bromobenzene does not lead to any diphenylhalogenonium salts. Thus, the path to diarylchloronium and diarylbromonium consists in the heterolytic transfer of the phenyl cation to the aromatic halogen.

Finally, it may be recalled that the first to discover bromonium and chloronium salts were Sandin and Hey,[27] who in 1952 described the reaction leading to the formation of cyclic *o,o'*-diphenylene halogenonium in aqueous solution, a reaction similar to the reaction of Mascarelli,[28] which had enabled him to produce diphenylene iodonium.

Up to the present we have studied to some extent only the reactions of diphenylchloronium and diphenylbromonium salts. These compounds, less stable than iodonium salts, especially as far as diphenylchloronium salts are concerned, behave, on the whole, very similarly to diphenyliodonium salts. Their borofluorides in any medium, and their iodides in aqueous medium phenylate amines, converting for example, diethylamine into diethylaniline, pyridine into *N*-phenyl-pyridinium borofluoride. Sodium nitrite is phenylated into nitrobenzene, potassium cyanide into benzonitrile, etc. Diphenylbromonium and diphenylchloronium borofluorides do not react with metallic mercury. On the other hand, the iodides of these cations form with metallic mercury in alcoholic-medium phenylmercuryiodide, this time due to a homolytic reaction. It is difficult to explain the homolytic reaction otherwise than due to the formation of a covalent form of diphenylhalogenonium iodide, the bromine or chlorine octette being thus extended to a decette.

Thus, new halogenonium salts, just as iodonium ones, enable one to arylate arbitrarily according to either heterolytic or homolytic mechanism, these reactions taking place in milder conditions, than those of iodonium salts. If it were possible to find conditions for producing diarylchloronium and diarylbromonium salts in a higher yield, these salts would undoubtedly serve as excellent arylating reagents.[29]

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