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Abstract

Full Text

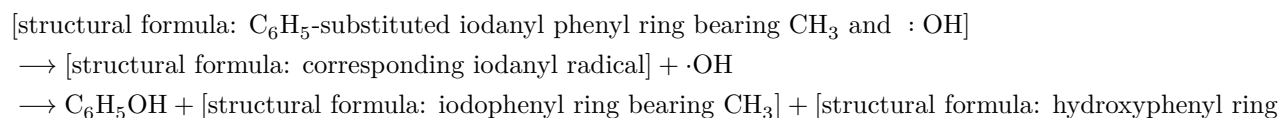
CHEMISTRY

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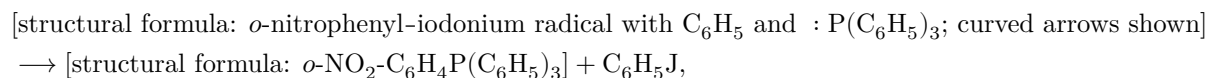
REACTIONS BETWEEN TRIPHENYLPHOSPHINE AND THE BOROFLUORIDES OF UNSYMMETRICAL DIARYLIODONIUM SALTS

It is known from the literature that unsymmetrical diaryliodonium salts behave differently depending on the type of decomposition. In those cases where diaryliodonium salts of the type $\text{ArAr}'\text{JX}$ decompose heterolytically, the direction of cleavage of the C—J bond is substantially influenced by the polar factor (^{1,2}). At the same time, reactions in which the electronic character of substituents in the aromatic nuclei Ar and Ar' has practically no effect on the direction of cleavage of the C—J bond in $\text{ArAr}'\text{JX}$ are ascribed a homolytic character (³).

The latter proposition, in our opinion, should be valid only in those cases where the diaryliodonium radical $\text{ArAr}'\text{J}\cdot$ formed upon decomposition of the diaryliodonium salt reacts with another radical, for example, with the hydroxyl radical (³):

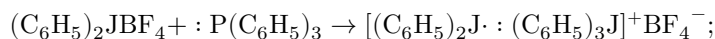


If, however, a diaryliodonium salt decomposes homolytically and the diaryliodonium radical reacts not with another radical but with a nucleophilic reagent, for example with $(\text{C}_6\text{H}_5)_3\text{P}$:

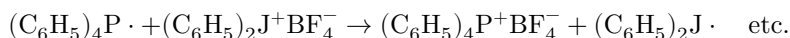
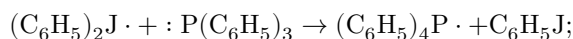
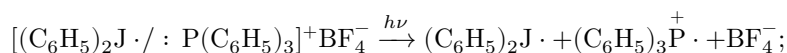


then the polar factor* should apparently exert the same influence on the direction of cleavage of the C—J bond in $\text{ArAr}'\text{JBF}_4$ as in the case of heterolytic reactions proceeding by the mechanism of bimolecular nucleophilic substitution S_N2 (¹). The present work is devoted to testing this assumption.

In a previous communication (5) we presented data indicating that the photochemical reaction between triphenylphosphine and diaryliodonium borofluoride is a chain radical process and proceeds according to the scheme:



* From studies on the arylation of aromatic compounds by radicals it is known that radicals are not absolutely "neutral" particles. In particular, the *n*-nitrophenyl radical exhibits certain electrophilic properties (4).



As can be seen from the scheme presented, one of the important stages in the formation of tetraphenylphosphonium salt consists in the interaction of a diaryliodonium radical with a nucleophilic agent—triphenylphosphine. Thus, the photochemical reaction between $(\text{C}_6\text{H}_5)_3\text{P}$ and $\text{ArAr}'\text{JBF}_4$ proved to be a very suitable object for testing the assumption stated by us above.

The tetrafluoroborates of the following unsymmetrical diaryliodonium salts were introduced into reaction with triphenylphosphine: *m*-nitrophenyliodonium, *p*-anisylphenyliodonium, *p*-anisyl-*m*-nitrophenyliodonium, *m*-carbomethoxyphenyl-phenyliodonium, *o*-nitrophenyl-phenyliodonium, and *p*-chlorophenyl-phenyliodonium. These reactions were carried out in acetone for 6–8 hours; the ratio of the starting reagents $(\text{C}_6\text{H}_5)_3\text{P} : \text{ArAr}'\text{JBF}_4$ was 1 : 1. The light source was a PRK-4 mercury lamp; the distance between the reaction test tube and the lamp was 30 cm. After the reaction had been carried out, the acetone was evaporated, and the residue was washed repeatedly with ether to remove aryl iodides and unreacted triphenylphosphine. Then the tetraarylphosphonium borofluorides were separated from the diaryliodonium borofluoride chromatographically,* as indicated in (5). For the separation of tetraarylphosphonium borofluorides of the types $(\text{C}_6\text{H}_5)_3\text{ArPBF}_4$ and $(\text{C}_6\text{H}_5)_3\text{Ar}'\text{PBF}_4$, which were obtained in some cases, we also used the method of thin-layer chromatography—

Table 1

Results of the photochemical reaction between triphenylphosphine and $\text{ArAr}'\text{JBF}_4$

Starting salts	Phosphonium salt obtained	Yield, %	m.p., °C	Results of analysis
$\text{ArAr}'\text{JBF}_4$	$(\text{C}_6\text{H}_5)_3\text{ArPBF}_4$			
$m\text{-O}_2\text{NC}_6\text{H}_4$ C_6H_5	$\text{JBF}_4(\text{O}_2\text{NC}_6\text{H}_4)(\text{C}_6\text{H}_5)_3\text{PBF}_4$	48	192-193	Found %: C 61.42; H 4.28 Calculated %: C 61.17; H 4.06
$o\text{-O}_2\text{NC}_6\text{H}_4$ C_6H_5	$\text{JBF}_4(\text{O}_2\text{NC}_6\text{H}_4)(\text{C}_6\text{H}_5)_3\text{PBF}_4$	26	209-210	Found %: C 60.97, 60.74; H 4.28, 4.33 Calculated %: C 61.17; H 4.06
$m\text{-O}_2\text{NC}_6\text{H}_4$ $n\text{-CH}_3\text{OC}_6\text{H}_4$	$\text{JBF}_4(\text{O}_2\text{NC}_6\text{H}_4)(\text{C}_6\text{H}_5)_3\text{PBF}_4$	50	192-193	
$m\text{-C}_2\text{H}_5\text{OCOC}_6\text{H}_5$ C_6H_5	$\text{JBF}_4(\text{OCOC}_6\text{H}_5)(\text{C}_6\text{H}_5)_3\text{PBF}_4$	48	191-192	Found %: C 65.05, 65.21; H 5.05, 5.04 Calculated %: C 65.07; H 4.85
$n\text{-CH}_3\text{OC}_6\text{H}_4$ C_6H_5	$\text{JBF}_4(\text{CH}_3\text{OC}_6\text{H}_4)(\text{C}_6\text{H}_5)_4\text{PBF}_4^*$	40	340	
$n\text{-CH}_3\text{OC}_6\text{H}_4$ C_6H_5	$\text{JBF}_4(\text{CH}_3\text{OC}_6\text{H}_4)(\text{C}_6\text{H}_5)_3\text{PBF}_4^*$	7	196	
$n\text{-ClC}_6\text{H}_4$ C_6H_4	$\text{JBF}_4(\text{C}_6\text{H}_5)_4\text{PBF}_4^*$	40	350	
$n\text{-ClC}_6\text{H}_4$ C_6H_4	$\text{JBF}_4(n\text{-ClC}_6\text{H}_4)(\text{C}_6\text{H}_5)_3\text{PBF}_4^*$	43	198-199	

* For all the indicated compounds, a mixed melting-point test with authentic substances was determined. No depression of the melting point was observed.

* The preparative method of thin-layer chromatography on aluminum oxide was used.

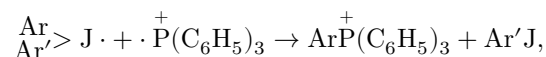
chromatography on aluminum oxide (layer thickness 3-4 mm, solvent—*n*-butyl

alcohol : petroleum ether*). The results we obtained are given in Table 1.

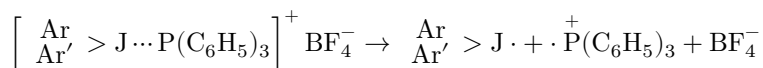
As can be seen from the data in Table 1, in the photochemical reaction between diaryliodonium borofluorides and triphenylphosphine, polar factors have a substantial effect. In most cases phosphonium salts are obtained only with the more electron-accepting substituent. In the reaction of *p*-anisylphenyliodonium borofluoride with triphenylphosphine, although both phosphonium salts are formed, here too the salt with the more electron-accepting radical, $(\text{C}_6\text{H}_5)_4\text{PBF}_4$, is obtained predominantly. And only in the decomposition of the *p*-chlorophenyl-phenyliodonium salt, in which the radicals are close in their electronegativity, are the phosphonium salts obtained in nearly equivalent amounts.

Thus, the results obtained confirm the correctness of our earlier suggestion concerning the influence of polar factors on the direction of cleavage of the C–I bond in the case of homolytic decomposition of diaryliodonium salts, if the latter react with nucleophilic agents. Consequently, on the basis of the decomposition products of unsymmetrical diaryliodonium salts alone, one cannot judge the mechanism of the reactions, since identical results are obtained both in heterolytic and in homolytic decomposition of $\text{ArAr}'\text{JBF}_4$, if the latter react with nucleophilic agents.

Moreover, it seems to us that the data obtained in the present work rule out the possibility of formation of tetraarylphosphonium salts directly as a result of interaction of the radicals $\text{ArAr}'\text{J}\cdot$ and $(\text{C}_6\text{H}_5)_3\text{P}^+$:



formed in the homolytic decomposition of the complex



In fact, if phosphonium salts of the type $\text{Ar}(\text{C}_6\text{H}_5)_3\text{PBF}_4$ were formed by interaction of the radicals $(\text{C}_6\text{H}_5)_3\text{P}^+$ and $\text{ArAr}'\text{J}\cdot$, then the influence of the electronic character of the substituents Ar and Ar' in $\text{ArAr}'\text{J}\cdot$ on the direction of cleavage of the C–I bond either should have been practically absent (3), or the less electron-accepting radical from $\text{ArAr}'\text{J}\cdot$ would have been transferred preferentially to phosphorus, since on phosphorus, in addition to the unpaired electron, there is also a positive charge.

Thus, the data obtained in the present work on the photochemical decomposition of unsymmetrical diaryliodonium salts in the presence of triphenylphosphine are in good agreement with the chain radical mechanism proposed earlier (5).

For comparison we investigated the thermal reaction between triphenylphosphine and $\text{ArAr}'\text{JBF}_4$. The reaction was carried out with the following

diaryliodonium borofluorides: *m*-nitrophenyl-phenyliodonium, *p*-anisyl-phenyliodonium, *p*-anisyl-*m*-nitrophenyliodonium, and *m*-carbethoxyphenyl-phenyliodonium.

* The ratio of *n*-butyl alcohol to petroleum ether was varied depending on the salts of phosphonium being separated. Thus, in the case of separation of $(C_6H_5)_4PBF_4$ and $(C_6H_5)_3(p-CH_3OC_6H_4)PBF_4$ it was 3 : 2, and in the separation of a mixture of $(C_6H_5)_4PBF_4$ and $(C_6H_5)_3(p-ClC_6H_4)PBF_4$, 5 : 4. Under these separation conditions triphenylarylophosphonium borofluoride had R_f 0.42-0.50, while $(C_6H_5)_4PBF_4$ remained at the point of application.

The reactions were carried out according to the following procedure. An equimolecular mixture of diaryliodonium borofluoride and triphenylphosphine was heated in the dark for 10 h in *n*-propyl alcohol at 97°. After completion of the reaction, the propyl alcohol was distilled off, and the residue was treated in the same way as in the case of the photochemical reaction between triphenylphosphine and diaryliodonium salts of the type $ArAr'JBF_4$. The results of the thermal reaction are given in Table 2.

Table 2

Results of the thermal reaction between $(C_6H_5)_3P$ and $ArAr'JBF_4$

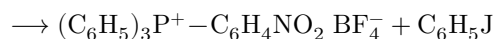
Starting salt $ArAr'JBF_4$	Salt obtained $(C_6H_5)_3ArPBF_4$	Yield, %	M.p., °C
$m-O_2NC_6H_4 \setminus \left. \begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix} \right\} JBF_4$	$m-O_2NC_6H_4)(C_6H_5)_3PBF_4$	45	190
$m-O_2NC_6H_4 \setminus \left. \begin{matrix} C_6H_5 \\ n-CH_3OC_6H_4 \end{matrix} \right\} JBF_4$	$m-O_2NC_6H_4)(C_6H_5)_3PBF_4$	44	192
$m-C_2H_5OCOC_6H_4 \setminus \left. \begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix} \right\} JBF_4$	$m-C_2H_5OCOC_6H_4)(C_6H_5)_3PBF_4$	20	
$n-CH_3OC_6H_4 \setminus \left. \begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix} \right\} JBF_4$	$(C_6H_5)_4PBF_4$	17	343
$n-CH_3OC_6H_4 \setminus \left. \begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix} \right\} JBF_4$	$n-CH_3OC_6H_4)(C_6H_5)_3PBF_4$	6	196

Comparing the data for the thermal reaction (Table 2) with the results of the photochemical reaction between triphenylphosphine and diaryliodonium salts (Table 1), it can be seen that they are practically identical. In both cases, the radical with the more electron-accepting substituent is transferred predominantly (or exclusively) to triphenylphosphine.

However, as we indicated above, on the basis of the decomposition products of $ArAr'JBF_4$ alone it is impossible to judge the reaction mechanism, in particular the mechanism of the thermal reaction between triphenylphosphine and

diaryliodonium borofluorides. Such results could be obtained in two cases. First, if in the thermal reaction nucleophilic substitution occurs at the carbon atom bonded to iodine, and the diaryliodonium salt decomposes heterolytically, as proposed by L. G. Makarova and A. N. Nesmeyanov (6):

[[unclear: structural scheme showing attack of $P(C_6H_5)_3$ on the nitrophenyl ring of a diaryliodonium tetrafluoroborate]]



Second, if the thermal reaction, like the photochemical reaction, proceeds by a chain radical mechanism according to the scheme given above. At present, further investigations of the mechanism of the thermal reaction of diaryliodonium borofluoride with triphenylphosphine are being carried out.

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

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