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Synthesis of arylhalonium compounds [including (4-methylphenyl) phenylfluoronium] by the nuclear–chemical method

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Abstract—The nuclear–chemical method has been used for the synthesis of previously unknown multivalent fluorine derivatives, namely (4-methylphenyl)phenylfluoronium. The synthesis includes the ion-molecular reaction of free phenyl cations generated by tritium β-decay with 4-methylhalobenzenes. The influence of the halogen atom (F, Cl, Br, I) as well as effects of the methyl substituent on the yields of the corresponding halonium compounds have been investigated. © 2002 Elsevier Science Ltd. All rights reserved.

The organic derivatives of multivalent halogen atoms, especially organic halonium salts, are unusual and very interesting compounds in theoretical and practical aspects.[1] Of the known organic halonium compounds, the iodonium compounds have been the subject of most study.[2] Little is known about the less stable and more difficult to prepare organic bromonium, chloronium and fluoronium derivatives.

This present work is a continuation of our investigations in the field of multivalent organic halogen compounds, particularly fluorine derivatives. Use of the nuclear–chemical method has allowed us to prepare a number of previously unknown compounds. The procedure has even been used by us to prepare diphenylfluoronium.[3] However, even using free phenyl cations the yield of the diphenylfluoronium was limited.

$$C_6T_6 \xrightarrow{\beta^-} [C_6T_5He^+] \longrightarrow C_6T_5^+ + He$$

$$C_6T_5^+ + FC_6H_5 \longrightarrow [C_6T_5FC_6H_5]^+ \xrightarrow{An^-} [C_6T_5FC_6H_5]^+An^-$$

Scheme 1. Formation of diphenylfluoronium compounds.

The nuclear–chemical method of synthesis includes the generation of free phenyl cations from β-decay of pertritiated benzene.[4] The phenyl cations go on to react with the substrate molecule in a fashion shown in Scheme 1, using fluorobenzene as an example. In previous investigations, we chose to use phenyl derivatives of the larger halogen atoms. The larger halogen atoms, along with a careful choice of the counter ion (those with high stabilizing ability) like BF_4^-, ClO_4^- and I^- lead to the formation of diphenylhalonium salts.[5] However, in investigations using fluorobenzene, yields of the fluoronium compound never exceeded 6–7%.[3]

We decided to try and increase the yield of the fluoronium salt by altering the electron density on the investigated substrates. Previously, this approach had been used by Nesmeyanov in the synthesis of (4-phenyl)phenyl halonium compounds.[6] Unfortunately, this method proved unusable in the case with fluorine derivatives. Rather, we chose to use (4-methyl)phenyl halogen compounds. The presence of the methyl group, being electron donating, we assumed would increase the yields of the fluoronium compounds obtained by the nuclear–chemical method.

The main pathway of these reactions is the electrophilic attack of the free phenyl cation on an electron pair of the halogen atom. This leads to the formation of the halonium ion. Stabilization is provided by the counter

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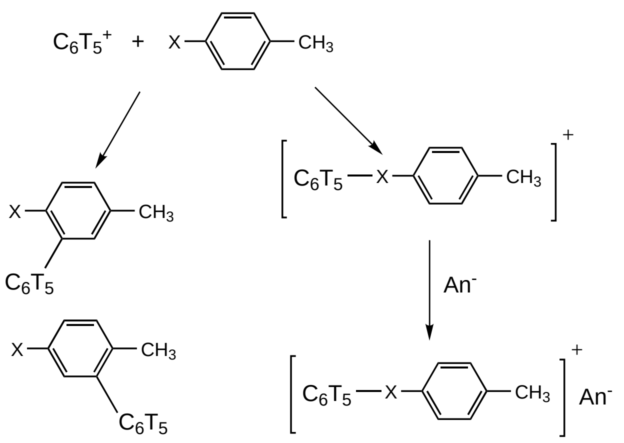
ion to form the halonium salt (**1**) (Scheme 2). Other processes can occur leading to formation of phenyl substituted halobenzenes (**2**) and biphenyl. In previous investigation (not including any with fluorine) we studied in detail the course of the electrophilic attack on the halogenated substrates, determined the yields of phenyl substituted products and their isomeric distributions.[5]

Nuclear–chemical syntheses were conducted according to the method described previously.[5] The only alteration in the procedure was the use of 4-methylphenyl halides instead of halobenzenes as substrates. The relative yields of the labeled products were determined by the ratio of the radioactivity of the investigated compound to the summary radioactivity of all tritiated products. Table 1 shows the yields obtained from using 4-methylphenyl halides, along with yields obtained using halobenzenes from previous studies.

In accordance with our proposal, the use of 4-methylfluorobenzene as a substrate in the nuclear–chemical synthesis more than doubled the yield of the fluoronium compound. The yield of the chloronium derivative is also significantly increased, while the yield of the bromonium compound was relatively unchanged. Yields of the iodonium compound actually decreased using the methyl substituted substrate. Similar results have been noticed during the study of isotopic effects, as well as photochemical and NQR analysis of diarylhalonium compounds.[7]



2 **1**

Scheme 2. Formation of 4-methylphenyl halonium compounds.

Table 1. Yields of tritium labeled halonium compounds using $C_6T_5^+$

Halogen	Substrate	Yield of halonium compound (%)
I	C_6H_5I	27[a]
	$4\text{-}CH_3C_6H_4I$	18
Br	C_6H_5Br	9[a]
	$4\text{-}CH_3C_6H_4Br$	11
Cl	C_6H_5Cl	8[a]
	$4\text{-}CH_3C_6H_4Cl$	22
F	C_6H_5F	6[b]
	$4\text{-}CH_3C_6H_4F$	16

[a] Ref. 5.

[b] Ref. 3.

As shown in Table 1, the use of an electron donating substituent at the 4-position of fluorobenzene has been used to significantly increase the yield of the diarylfluoronium compound. It is hoped that further investigations with tritium NMR and the use of other donor groups will provide better understanding and characterization of these unique organofluoronium compounds.

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