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Ion-molecular reactions of free phenylium ions, generated by tritium β-decay with bidentate arenes

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Abstract

Generation of free phenylium ions, obtained by tritium β-decay and their ion-molecular reactions with bidentate arenes are described. The elaborated nuclear-chemical method has been used for the synthesis of tritium labeled organic derivatives using halobenzenes. Two alternative pathways for interaction of the phenylium ion with the bidentate arene, addition to the lone pair of the halogen or substitution on the aromatic ring, were revealed. © 1999 Elsevier Science Ltd. All rights reserved.

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Carbocations are an important class of intermediates in many types of organic reactions.[1] Aryl cations[2] have generated much interest since first postulated by Waters[3] and to this day continue to generate much experimental[4] and theoretical[5] interest.

The elaborated nuclear-chemical method gives the unique opportunity for free carbocations based on the consequences of tritium β-decay from tritiated compounds.[6] This paper describes the generation of free phenylium ions[7] generated by tritium β-decay from per tritiated benzene[8] and their ion-molecular reactions with halobenzenes. The investigated bidentate arenes in our study have the ability to use either the lone pair of electrons on the halogen atom or a pair of electrons from the adjoining aromatic ring as the nucleophilic site.

Our investigations of the ion-molecular reactions of halobenzenes on salt surfaces produced a variety of products. Among the products found were the stabilized halonium cations as well as tritiated halobenzenes from fragmentation of the initially formed halonium cations. In addition, a large proportion of products were derived from the interaction of the phenylium ion with electron density of the aromatic ring (Scheme 1).

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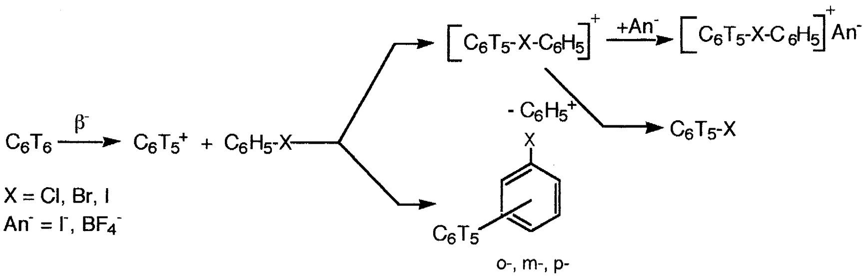

Scheme 1. Products produced during the ion-molecular reaction of phenyl cations with halobenzenes

This interaction with the aromatic ring was especially evident during reactions of the phenylium ion with chloro- and bromobenzene. The yields of the tritium labeled isomers of the various biphenylhalogen compounds and their isomeric distributions are presented in Table 1. Work done using bidentate arenes in the liquid and gas phases produced similar distributions of products in the liquid phase while producing mostly *meta*-isomers in the gas phase.[9]

Table 1
Tritium labeled products from the ion-molecular reactions of $C_6T_5^+$ with halobenzenes (liquid phase)

X	Yields, %							Isomeric Distribution in Ph_2-X, %$^{(b)}$		
	$[Ph_2X]^+ BF_4^{-(a)}$	Ph-X	Ph-Ph	Ph_2X						
				o-	m-	p-	Σ	o-	m-	p-
Cl	8	11	8	10	5	12	27	25	13	62
Br	9	27	9	7	4	11	25	19	19	61
I	27	52	18	4	4	7	15	18	18	64

(a) Accumulation times for diphenylhalonium derivatives were in the solid phase at liquid nitrogen temperatures. Products were then identified by TLC. (b) Represents reactivity per carbon

Instability of aliphatic halonium derived cations leads to rapid dissociation of the cations.[10] However, in performing the ion-molecular reactions on the surface of the salt with phenylium ions, we were able to see the halonium ions stabilized by an anion of choice (Table 1). A portion of these halonium cations do undergo fragmentation leading to the formation of tritiated halobenzenes (Table 1). The decrease in C–X bond energy according to the series C–Cl>C–Br>C–I causes a significant increase in the yields of tritiated halobenzenes in the opposite direction: Ph–I>Ph–Br>Ph–Cl.

As mentioned, the second mode of electrophilic attack by the phenylium ion was realized by simultaneous formation of tritiated halobiphenyl compounds in these reactions (Table 1). During electrophilic aromatic substitution reactions of halobenzenes, the preferable *ortho*- and *para*-directing influence of the halogen is well known theoretically and experimentally.[11] The formation of all three possible regioisomers, with a preference for *para*-substitution, was revealed from our investigations. These results (Table 1; isomeric distribution) are identical to those obtained from nitration reactions of halobenzenes.[11b] In the absence of a solvent, the cation is unable to derive any stabilization from a solvent shell.[12] Thus, this example, using free tritium labeled phenylium ions generated by β-decay, indicates a true preference for *ortho*- and *para*-substitution.

The elaborated ion-molecular method, generation of cations by β-decay of tritiated hydrocarbons, has two important advantages over generation of cations via more typical methods: (1) With the use of such nuclear-chemical methods one can carry out many one-step syntheses of tritium labeled compounds of interest;[13] among these are examples of previously unknown onium compounds of fluorine.[13b] (2) The ion-molecular method provides a unique opportunity to investigate the mechanism of electrophilic substitution and addition reactions with an unusual intermediate — a free tritiated carbocation.

This particular investigation, using tritiated phenylium ions, provided direct evidence for the formation of tritiated halonium ions formed from halobenzenes as well as tritiated halobiphenyls. The tritiated halobiphenyls came from EAS type reactions on the π cloud of the halobenzene. In the absence of any solvent stabilization of the cation, a preference for *ortho*- and *para*-substitution was realized, indicating a true preference for substitution at these positions with halobenzenes.

General experimental for nuclear-chemical synthesis: All ion-molecular reactions were carried out in sealed glass ampoules containing the source of phenylium ions (per tritiated benzene), the nucleophile of choice and an inorganic salt containing the desired anion (KI, KBF_4). The nucleophile of choice was dissolved in benzene and added to the ampoule with the salt present. The solvent was removed under reduced pressure to coat the salt and finally, 1 μL of C_6T_6 was added (0.2 equivalents based on nucleophile). The ampoules were sealed cold and kept between 5–25°C during the accumulation time (typically 10 days). The ampoules were then opened, solvent was added (acetone or CH_3CN) and the mixture subjected to TLC and HPLC analysis.

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