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Ion-molecular reactions of free phenylium ions, generated by tritium β-decay with Group V–VII elements

N. E. Shchepina,[b,d,*] V. D. Nefedov,[a] M. A. Toropova,[a] V. V. Avrorin,[a]
Scott B. Lewis[c] and Bruce Mattson[d]

[a]*Department of Radiochemistry, St-Petersburg University, St. Petersburg, Russia*
[b]*Laboratory of Radiochemistry, Natural Sciences Institute of Perm University, Perm, Russia*
[c]*Department of Chemistry, James Madison University, MSC 7701, Harrisonburg, VA 22807, USA*
[d]*Department of Chemistry, Creighton University, Omaha, NE 68178, USA*

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Abstract

Generation of free phenylium ions, obtained by tritium β-decay and their ion-molecular reactions with Group V–VII elements are described. The elaborated nuclear–chemical method has been used for the synthesis of tritium-labeled organic derivatives containing these Group V–VII elements. © 2000 Elsevier Science Ltd. All rights reserved.

Phenylium ions have generated interest since first being postulated in 1942.[1] To this day they continue to be a subject of study both experimentally[2] and theoretically.[3] In our continuing interest[4] in phenylium ions[5] generated by tritium β-decay[6] from pertritiated benzene,[7] we wish to report our result of the electrophilic reactions between phenylium ions with phenyl and methylphenyl substituted derivatives of Group V–VII elements. The organoelement compounds from such reactions have a wide spectrum of applications: from traditional areas of chemistry, biology and medicine to the new technologies—room temperature ionic liquids, used as solvents.[8]

All ion-molecular reactions were carried out according to the procedure described previously[4] in sealed glass ampoules containing the source of phenylium ions (pertritiated benzene), substrate (organoelement compound) and an inorganic salt. The ampoules were opened and solvent (CH_3CN) added after an accumulation time of no less than 10 days, at which time the reaction mixtures were then subjected to TLC or HPLC analysis. 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 the obtained products.

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* Corresponding author.

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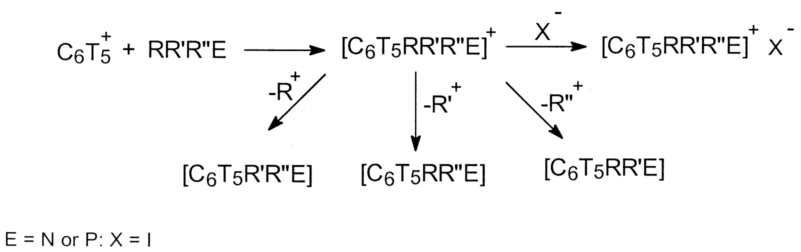
We have used this method to successfully obtain tritium-labeled phenyl-substituted derivatives of all the main subgroup V–VII elements using tetrafluoroborate as the counter ion (Table 1). In order to establish the structure of the tetraphenylammonium and diphenylfluoronium compounds, the isomorphic co-crystallization method was used.[9] Since the quantity of the radioactive products is extremely small, we have used the specific radiochemical methods for the identification of the unknown compounds. The similarity of the chromatographic behavior of the synthesized compounds with their isomorphic carries[10] as well as the stability of the crystallization coefficients with the change of micro- and macro-components ratios[11] revealed the identity of the molecular structures of the obtained tritiated onium derivatives. Also listed in Table 1 are the yields of tritiated substrates that resulted from the fragmentation of the original onium cations.

Table 1
Yields of tritiated organic derivatives of Group V–VIIa elements

E	$[C_6T_5(C_6H_5)_3E]^+$ BF_4^-	$C_6T_5(C_6H_5)_2E$	E	$[C_6T_5(C_6H_5)_2E]^+$ BF_4^-	$C_6T_5(C_6H_5)E$	E	$[C_6T_5(C_6H_5)E]^+$ BF_4^-
N	4	5	O	5	3	F	6
P	40	6	S	13	10	Cl	(a)
As	16	21	Se	22	21	Br	(a)
Sb	31	18	Te	43	34	I	(a)
Bi	11	22					

(a) see reference 4

In a separate set of experiments, the ion-molecular reactions of free phenylium ions reacted with phenyl- and methylphenyl-substituted derivatives of nitrogen and phosphorus were investigated using iodide as the counter ion. For these reactions, we proposed and obtained a spectrum of mixed organoelement derivatives (Scheme 1).



Scheme 1. (a) $R = R' = R'' = C_6H_5$; (b) $R = CH_3$, $R' = R''C_6H_5$; (c) $R = R' = CH_3$, $R'' = C_6H_5$

The yields of the labeled compounds obtained from these reactions with the substituted nitrogen and phosphorus compounds are listed in Table 2. In addition, the yields from the heterolytic destruction of the onium cations and the yields of tritiated biphenyl are listed in Table 2. The small yields of the previously unknown tetraphenylammonium and difficult to prepare methyltriphenylammonium compounds are the result of high steric difficulties in these compounds.[12]

Table 2
Yields of tritium labeled products from substituted nitrogen and phosphorus compounds

	$[C_6T_5RR'R''E]^+ I^-$	$C_6T_5(C_6H_5)_2E$	$C_6T_5CH_3C_6H_5E$	$C_6T_5(CH_3)_2E$	$C_6T_5C_6H_5$
C_6T_6 $(C_6H_5)_3N/KI$	6	2	-	-	20
C_6T_6 $(C_6H_5)_3P/KI$	45	3	-	-	16
C_6T_6 $CH_3(C_6H_5)_2N/KI$	7	5	25	-	17
C_6T_6 $CH_3(C_6H_5)_2P/KI$	25	3	15	-	28
C_6T_6 $(CH_3)_2C_6H_5N/KI$	26	-	6	31	8
C_6T_6 $(CH_3)_2C_6H_5P/KI$	25	-	33	5	18

The successful synthesis of the tetraphenylammonium and methyltriphenylammonium compounds can be attributed to the smaller steric size of the free phenylium ion generated by the β-decay process.[13] These reactions were also run under very mild conditions, which may account for our ability to isolate these compounds with multiple large substituents.

The interesting result from the data in Table 2 is the difference in the heterolytic dissociation of the mixed methylphenyl-substituted cations of nitrogen and phosphorous. Steric interactions of ammonium cation lead to the dissociation of them by fragmentation of a large phenyl group. On the contrary, in the case of the phosphonium cations with smaller steric interactions the direction of fragmentation is changed completely to the well-known and preferable fragmentation of a methyl cation.[14]

The results presented herein bring to the forefront one of the main advantages of the ion-molecular method: mild reaction conditions that allow for the synthesis of compounds that are otherwise difficult to prepare. We have shown that even the tetraphenylammonium cation is assessable by this method.

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