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Abstract

Full Text

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TRIPHENYLOXONIUM SALTS

By diazo decomposition of aryldiazonium fluoroborates in bromobenzene or chlorobenzene, we have recently for the first time succeeded in obtaining a series of diarylbromonium and diarylchloronium salts ([1]). In the present work we describe the application of this same method to the preparation of previously unknown tertiary aromatic oxonium salts.

In contrast to Meerwein' s trialkyloxonium salts ([2]), triphenyloxonium salts are very stable compounds, with decomposition temperatures above 150°. All the salts described in this work, except the chloride and bromide, are poorly soluble in water. In contrast to Meerwein' s salts, and also to chloronium and bromonium salts, triphenyloxonium salts enter into the phenylation reaction only very sluggishly. Thus, triphenyloxonium chloride, bromide, iodide, and fluoroborate do not phenylate metallic mercury under any of the conditions tested; the fluoroborate does not react with copper or thallium. Phenylation of such anions as NO_2' and N_3' requires many hours' boiling of aqueous solutions. It can be carried out in only 25–27% yield. Compounds containing atoms with free electron pairs are phenylated more readily. Pyridine, for example, is phenylated at nitrogen in 90% yield. Phenylation of diethylamine occurs only in the presence of water and proceeds in 60% yield.

Experimental Part

1. Preparation of triphenyloxonium fluoroborate. To 150 g of diphenyl oxide at 80–90° (bath temperature), with vigorous stirring, there was added over the course of one hour a solution of 10.5 g of phenyldiazonium fluoroborate in 300 ml of acetone (which during the reaction is continuously distilled off). To complete the reaction, the mixture was heated for another 30 min., and after cooling was treated 4 times with 50% aqueous acetone (10 ml each time). The aqueous-acetone extracts were extracted with ether, and after removal of the latter (and of acetone) in vacuo, water-insoluble triphenyloxonium fluoroborate separates from the solution in an amount of 0.38 g (2% of theoretical, calculated on phenyldiazonium fluoroborate). The salt was purified by reprecipitation from acetone with ether. These are colorless crystals, m.p. 226°, readily soluble in acetone, less soluble in alcohols, insoluble in cold water and ether.

Found	% :	C	64.61;	64.46;	H 4.56;	4.65
$C_{18}H_{15}BF_4O$. Calculated	% :	C	64.73;		H 4.52	

2. Other triphenyloxonium salts–see Table 1).

Phenylation reactions with triphenyloxonium fluoroborate.

Reaction with sodium nitrite in aqueous medium. A solution of 1 g of triphenyloxonium fluoroborate and 2.5 g of $NaNO_2$ in 30 ml of water was boiled for 25 hours, after which 0.51 g of unreacted material was isolated from the reaction···

Table 1

Salt anion	Obtained from:	Yield, %	Mp., °C	C, %	H, %	halide, %	N, %	metal, %
Cl'*	$[(C_6H_5)_3O]Cl$ and acetone	63	193–194	67.68; 67.75 / 67.60	5.90 / 6.00	11.60 / 11.09		
Br'***	$[(C_6H_5)_3O]BF_4$ and NaBr	72	182–182.5	65.86; 65.88 / 66.09	4.78; 4.68 / 4.62	24.55; 24.20 / 24.42		
J'	$[(C_6H_5)_3O]BF_4$ and NaJ	93	177–178	57.91; 57.99 / 57.78	4.03; 4.03 / 4.03	34.31; 34.07 / 33.92		
HgJ'_3	$[(C_6H_5)_3O]BF_4$ and $NaHgJ_3$	92	156–157	26.15; 26.27 / 26.09	1.97; 2.01 / 1.82			
$(C_6H_5)_4B$	$[(C_6H_5)_3O]BF_4$ and $(C_6H_5)_4BNa$	80	~165	89.22; 89.33 / 89.02	6.17; 6.36 / 6.23			
$PtCl''_6$	$[(C_6H_5)_3O]BF_4$ and H_2PtCl_6	74	184–185	47.79; 47.83 / 47.92	3.17; 3.35 / 3.35			21.75; 21.64 / 21.63
$Cr_2O''_7$	$[(C_6H_5)_3O]J$ and $K_2Cr_2O_7$	42	~180 (darkens)	61.66; 61.56 / 60.84	4.40; 4.44 / 4.25			14.78; 14.62 / 14.63
$C_6H_2(NO_2)_3O'$	$[(C_6H_5)_3O]BF_4$ and $C_6H_2(NO_2)_3OH$	83	155–157	60.44; 60.36 / 60.63	3.63; 3.65 / 3.60		9.47; 9.19 / 8.84	
JCl'_4	$[(C_6H_5)_3O]J$ and Cl_2	94	167–171	41.95 41.99 / 41.91	2.90 2.91 / 2.93	51.32 51.64 / 55.06		

* Crystallizes with 2 molecules of water.
** Above the line–found, below the line–calculated.

Fig. 1. Absorption spectra of triphenyloxonium salts

Figure 1: Fig. 1. Absorption spectra of triphenyloxonium salts

*** Crystallizes with 1.5 molecules of water. The analysis of the anhydrous salt is given.

···of triphenyloxonium borofluoride. The nitrobenzene formed as a result of the reaction was not isolated, but was reduced in the usual way (by the action of 1 g of metallic tin in 3 ml of conc. hydrochloric acid) to aniline. The latter was identified in the form of benzeneazo-β-naphthol, the yield of which was 0.09 g (25% of theory, calculated on the triphenyloxonium borofluoride that entered into the reaction), mp 128–129° (128.5–129.5° (3)).

Reaction with sodium azide in aqueous medium. A solution of 0.5 g of triphenyloxonium borofluoride and 2 g of NaN_3 in 30 ml of water was boiled for 14.5 h. The phenyl azide formed in this process was reduced with sodium (0.5 g) in alcohol (8 ml) to aniline. The latter was diazotized and coupled with β-naphthol. The yield of benzeneazo-β-naphthol was 0.1 g (27% of theory, calculated on triphenyloxonium borofluoride), mp 128.5–129.5°.

Reaction with diethylamine in aqueous medium. A mixture of 0.25 g of triphenyloxonium borofluoride, 15 ml of diethylamine, and 6 ml of water was boiled for 8.5 h. The diethylaniline formed was coupled with *p*-nitrophenyldiazonium. The yield of 4-nitro-4′-diethylaminoazobenzene was 0.13 g (59% of theory, calculated on triphenyloxonium borofluoride), mp 149–150° (151° (4)).

Reaction with pyridine. A solution of 0.2 g of triphenyloxonium borofluoride in 2 ml of pyridine was boiled for 4 h. On cooling it dis-

was added with abs. ether. The yield of the N-phenylpyridinium borofluoride that separated in this process was 0.13 g (89% of theoretical). M.p. 177.5-178.5° after recrystallization from alcohol (178-179° [5]). The filtrate from $[C_5H_5N^+C_6H_5]B^-F_4$ was washed several times with 5% hydrochloric acid and dried over $CaCl_2$. After evaporation of the ether, 0.05 g of diphenyl ether remained.

Fig. 1. Absorption spectra of triphenyloxonium salts*. 1-4–salts of triphenyloxonium: 1–chloride, 2–bromide, 3–iodide, 4–borofluoride, 5–sodium iodide; $c_M = 1 \cdot 10^{-3}$; $d = 0.5$ cm; solvent–ethanol.

* The spectra were recorded in the optical laboratory of the Institute of Organoelement Compounds on an FP-1 spectrophotometer designed by V. I. Dianov-Klokov.

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