Preparation of Phenylalkyl Ethers and Phenyl Esters from Benzenediazonium Tetrafluoroborate with Alkoxytrimethylsilanes and Trimethylsilyl Esters[1]

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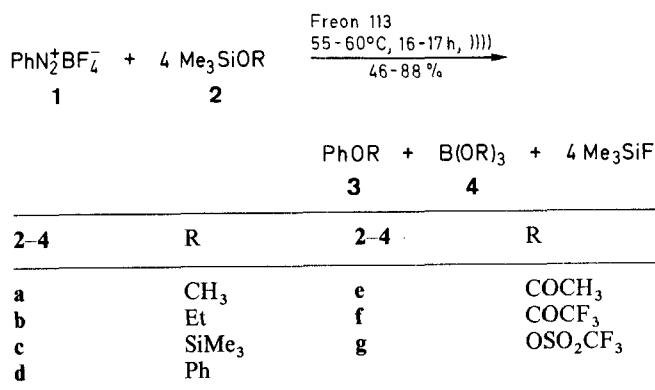
Sonication assisted reaction of benzenediazonium tetrafluoroborate with alkoxytrimethylsilanes and trimethylsilyl esters gives phenylalkyl ethers and phenyl esters, respectively, with trialkyl-(aryl) borates as byproducts. The scope of the reaction, experimental conditions and proposed mechanism are discussed.

Arenediazonium tetrafluoroborates are used for the preparation of aryl fluorides (Schiemann reaction),[2] unsymmetrical biaryls,[3] coupling reactions with aliphatic compound containing activated carbon–hydrogen bonds,[4] arylation of unsaturated compounds (Meerwein arylation reaction[5]), and various dediazoniative substitutions.[6-9] In these reactions either radical cation or highly reactive, metastable phenyl cation intermediates are proposed.

Structural effects on the stability of carbocations have been much studied and are now well understood. The carbocationic center in trivalent carbocations is generally planar (or close to planar) with a perpendicular vacant p orbital. It has been recognized that those carbocations in which the empty orbital has significant "s" character (e. g., sp^2 or sp) are extremely reactive and thus generally non-observable as persistent ions.

Within the last two decades, convincing evidence was obtained for the intervention of vinyl cations in solvolysis.[10,11] The intermediacy of phenyl cations in dediazoniation[12] of benzenediazonium ion has also been reported.[13]

We report now our observation that benzenediazonium tetrafluoroborate (1) under ultrasound irradiation readily undergoes reaction with low nucleophilicity alkoxytrimethylsilanes 2 to give phenylalkyl ethers/esters 3 and the corresponding trialkyl borates 4 in moderate to good yield.

$$PhN_2^+BF_4^- \; + \; 4\,Me_3SiOR \xrightarrow[46-88\,\%]{\substack{\text{Freon 113} \\ 55-60^\circ C,\ 16-17h,\ ))))}}$$

$$\underset{1}{} \qquad \underset{2}{}$$

$$PhOR \; + \; B(OR)_3 \; + \; 4\,Me_3SiF$$

$$\underset{3}{} \qquad \underset{4}{}$$

2-4	R	2-4	R
a	CH_3	e	$COCH_3$
b	Et	f	$COCF_3$
c	$SiMe_3$	g	OSO_2CF_3
d	Ph		

The ionic benzenediazonium tetrafluoroborate has been well-known to undergo Schiemann decomposition to give fluorobenzene, nitrogen and boron trifluoride.[14] The mechanism of the decomposition of the diazonium fluoroborates is not known with certainty, nor the reason for the unusual stability of these salts fully understood. Schiemann[15] proposed that the stability of these salts was due to the linking of an unstable diazonium cation with

Table 1. Phenyl Ethers 3a–d and Phenyl Esters 3e–g Prepared

| Product	Yield[a] (%)	bp (°C)/Torr	
		found	reported
3a	51	62–63/12	154/760[21]
3b	54	67–68/12	169–170/760[21]
3c	46[b]	83–84/28	81/23[22]
3d	61	73–74/1	259[21]
3e	66	64–66/2	196[21]
3f	88	54–56/12	42–44/15[23]
3g	82	67–68/12	67–68/15[24]

[a] Isolated yield.
[b] Diphenyl ether (7%) was obtained as a byproduct.

Table 2. Trialkylborates 4a–g Formed in the Reaction of Benzenediazonium Tetrafluoroborate with Alkoxytrimethylsilanes and Trimethylsilyl Esters

Product	Yield[a] (%)	bp (°C)/Torr		^{11}B-NMR (Et$_2$O·BF$_3$), δ	
		found	reported	found	reported
4a	66	68–69/760	68–69/760[25]	18.3	18.3[25]
4b	63	117–118/760	117–118/760[26]	17.8	17.6[26]
4c	74	98–99/28	184/760[27]	14.5	15.1[27]
4d	71	105–106/0.8	96–97/0.1[28]	15.7	16.5[28]
4e	76	59–61/12	54–56/10[29]	1.7	1.6[30]
4f	79	53–55/12	45–46/10[30]	1.3	1.5[30]
4g	77	78–81/1.2	68–73/0.5[31]	−1.2	−1.1[31]

[a] Isolated yield.

the complex fluoroborate anion, the breaking down of the fluoroborate complex to boron trifluoride and fluoride anion requiring approximately the same amount of energy as is given off by the decomposition of the cation. The amount of energy required was calculated by De Boer and Van Liempt[16] to be about 70 kcal mol^{-1}. Much work has been done on the mechanism of the decomposition of the diazonium salts in general,[17] however, little has been done directly with the fluoroborates.

The proposed mechanism for the reaction of benzenediazonium tetrafluoroborate with alkoxy trimethylsilane is as follows:
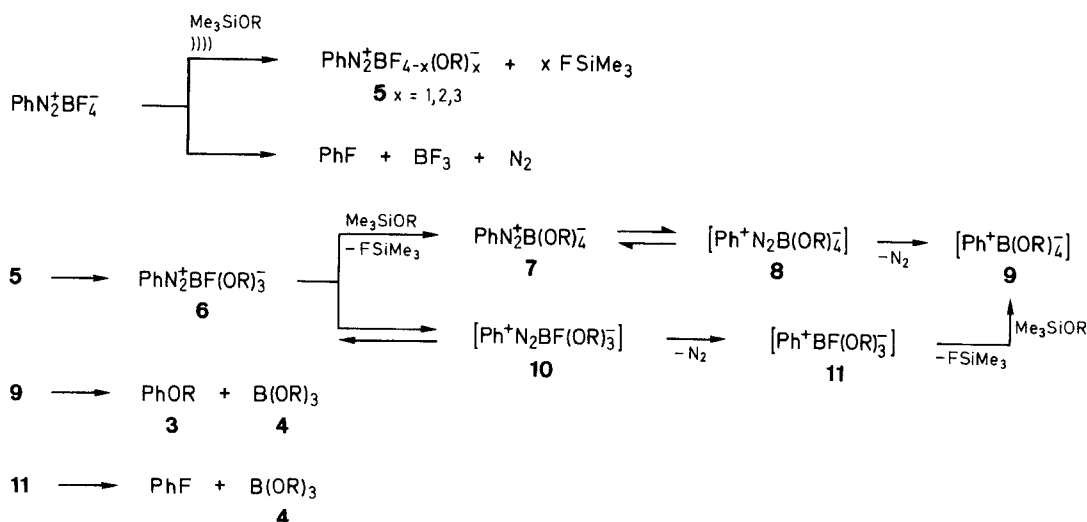
When the reaction of benzenediazonium tetrafluoroborate (1) with alkoxytrimethylsilane was attempted in stirred 1,1,2-trichlorotrifluoroethane (Freon-113) solution, fluorobenzene was found to be the predominant product formed via the well-known Schiemann reaction. Presumably, the tight Ph$^+$BF$_4^-$ ion pair is unable to break apart under these conditions and leads to the formation of fluorobenzene.

However, when the reaction of 1 with alkoxytrimethylsilane was carried out in Freon 113 under ultrasound irradiation, it resulted in the formation of the corresponding phenylalkyl ethers (and trialkyl borates) in moderate to good yield. Sonication (i.e. ultrasound irradiation),[18] found effective in promoting organometallic reactions, is believed to bring about the initial step of the reaction, i.e. fluoride–alkoxy exchange of the tetrafluoroborate with the exothermic formation of fluorotrimethylsilane helping the process. The formation enthalpy of silicon–fluoride bonding in fluorotrimethylsilane is about 160 kcal/mol^{-1},[19] which is sufficient to drive the reaction to completion forming phenylalkyl ether and trialkyl borate.

A control experiment was conducted by reacting boron trifluoride with alkoxytrimethylsilanes (R = methyl, ethyl and phenyl) in Freon-113 under ultrasound irradiation at 55–60 °C. Even prolonged reaction time did not give any ethers and trialkyl borates, clearly suggesting that the initial stage of the reaction involves the tetrafluoroborate, and boron trifluoride does not take place in it. In addition the fluoride–alkoxy exchange is a thermodynamically favorable process, although the proposed intermediates 5–11 have not been observed in ^{11}B-NMR spectrometry.

We also found that trimethylsilyl esters, such as trimethylsilyl acetate, trifluoroacetate, and trifluoromethanesulfonate react similarly with benzenediazonium tetrafluoroborate to give the corresponding phenyl esters and boron tris(acetate/trifluoroacetate, trifluoromethanesulfonate) and phenyl trifluoromethanesulfonate, tris(trifluoroacetate) (Tables 1, 2).

In summary, the present method represents a novel extension of existing methodology of dediazonative arylation to the preparation of arylalkyl ethers and aryl esters.

All chemicals used are commercially available and distilled prior to use. GC analyses were carried out on a Varian Model 3700 Gas Chromatograph using quartz-silica capillary column coated with DB-1. Mass spectroscopic analyses were performed on a Finnigan Incos-50 GC-MS spectrometer. NMR spectra were recorded on a Varian VAX-200 superconducting NMR spectrometer. All known products gave satisfactory analysis and spectral data (in comparison with authentic samples).

Benzenediazonium tetrafluoroborate was prepared according to literature procedure.[7]

Anisole (3a); Typical Procedure:

To an ice-cold dispersion of benzenediazonium tetrafluoroborate (3.84 g, 20 mmol) in freshly distilled Freon-113 (50 mL) is slowly added, under N_2 atmosphere, a solution of methoxytrimethylsilylane (8.32 g, 80 mmol) in freshly distilled Freon-113 (10 mL). The suspension is placed in an ultrasound bath[20] and the agitated mixture is very slowly heated to 55°C via application of an external coil (*Caution!* fast heating leads to predominant formation of fluorobenzene via Balz–Schiemann decomposition). The mixture is refluxed overnight under ultrasound agitation at 55°C (ca.16 h). The slightly reddish mixture is fractionally distilled to afford anisole (3a); yield: 1.13 g (51%) and the corresponding trimethyl borate 4a; yield: 1.37 g (66% based on benzenediazonium tetrafluoroborate) as colorless liquids. The physical and spectral data of anisole 3a and 4a are consistent with those given in the literature (Tables 1, 2).

Phenyl Acetate (3e); Typical Procedure:

To an ice-cold dispersion of benzenediazonium tetrafluoroborate (3.84 g, 20.0 mmol) in freshly distilled Freon-113 (50 mL) is slowly added a solution of trimethylsilyl acetate 10.56 g, 80 mmol) in freshly distilled Freon-113 (10 mL) under N_2 atmosphere. After the addition of trimethylsilyl acetate has been completed, the reaction suspension is placed in an ultrasound device[20] and the agitated mixture is very slowly heated to 55°C (*Caution!* fast heating leads to predominant formation of fluorobenzene via Balz–Schiemann decomposition) via application of an external coil. The mixture is maintained at reflux under ultrasound agitation at 55°C overnight (ca.16 h). The slightly redish mixture is fractionally distilled to afford phenyl acetate (3e); yield: 1.80 g (66% based on benzenediazonium tetrafluoroborate) and the corresponding boron triacetate 4e; yield: 2.85 g (76% yield based on benzenediazonium tetrafluoroborate) as colorless liquids. The physical and spectral data of 3e and 4e were consistent with those given in the previous literature (Tables 1, 2).

3f:

^{13}C-NMR (50 MHz, CDCl$_3$): δ = 160.43 (s, $J_{C,F}$ = 44 Hz), 144.61 (s), 135.99 (d), 130.32 (d), 127.14 (d), 114.37 (q, $J_{C,F}$ = 280 Hz).

^{19}F-NMR (188 MHz, PhCF$_3$): δ = − 52.987.

GC/MS: m/z = 190 (M$^+$, 50.5), 162 (20.6), 96 (16.8), 93 (24.2), 77 (42.7), 69 (63.0), 65 (100.0).

3g:

^{13}C-NMR (50 MHz, CDCl$_3$): δ = 149.70 (s), 130.24 (d), 128.39 (d), 121.26 (d), 118.12 (q, $J_{C,F}$ = 247 Hz).

^{19}F-NMR (188 MHz, C$_6$H$_5$CF$_3$): δ = − 53.145.

GC/MS (70 eV): m/z = 226 (M$^+$, 42.1), 162 (17), 96 (15.1), 93 (53.9), 77 (40.1), 65 (100).

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