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Pyrolysis of benzenediazonium bis(trifluoromethanesulfonyl)methide

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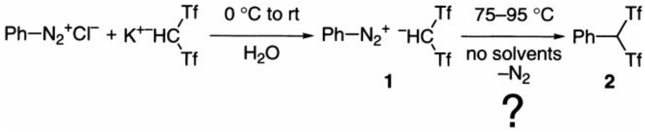
Abstract

The pyrolysis of benzenediazonium bis(trifluoromethanesulfonyl)methide in the absence of solvents did not give the carbon arylation product, $PhCH(SO_2CF_3)_2$, but the oxygen phenylation product, $PhO(CF_3)S(O)=CHSO_2CF_3$, in good yield. In contrast, the pyrolysis of the same compound in acetonitrile gave the acetonitrile-inserted compound, $PhNH(Me)C=C(SO_2CF_3)_2$, quantitatively. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Pyrolysis; Benzenediazonium bis(trifluoromethanesulfonyl)methide; Acetonitrile

1. Introduction

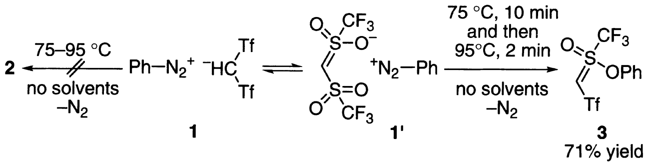
Zhu reported a new synthetic route to phenyl bis(trifluoromethanesulfonyl)methane (**2**) in this journal in 1993 [1]. According to that report, **2** has been prepared in 73% yield by the pyrolysis of benzenediazonium bis(trifluoromethanesulfonyl)methide (**1**) obtained from the reaction of benzenediazonium chloride with potassium bis(trifluoromethanesulfonyl)methide (Eq. (1)). This synthetic route was very attractive to us as a general method for the preparation of various aryl bis(perfluoroalkanesulfonyl)methanes. Unfortunately, however, we were never be able to detect the desired compound **2** in our crude products obtained with the pyrolysis of **1** following his procedure. Here, we would like to report some unexpected results found in the course of our reinvestigation of the pyrolysis of **1**.



(1)

2. Results and discussion

Benzenediazonium bis(trifluoromethanesulfonyl)methide (**1**) (mp. 74°C (decd.)) was easily obtained as a light brown precipitate from the reaction of benzenediazonium chloride with potassium bis(trifluoromethanesulfonyl)methide in high yield essentially according to Zhu's procedure [1,2]. Pyrolysis of **1** in the absence of solvents at temperatures of 75–95°C gave only the oxygen arylation product **3** as a white solid in place of the desired carbon arylation product **2** (Eq. (2)). Lack of the production of **2** was confirmed by comparing ^1H and ^{19}F NMR spectra of crude compounds with those of an authentic sample **2**, prepared by photolysis of phenyliodonium bis(trifluoromethanesulfonyl) methide according to his procedure [3]. The ^{19}F NMR spectrum of **2** showed a singlet at δ −71.9. Zhu reported that only the carbon arylation product **2** was obtained in 76% yield by pyrolysis of **1** under the same conditions as above, even though his X-ray structure analysis of **1** indicates the real structure of **1** in solid state is rather like **1′** in which the positive nitrogen is closer to the oxygen than to the carbon atom [1,2]. The new compound **3** was identified by ^1H and ^{19}F NMR and GC-MS spectral analyses. The ^{19}F NMR spectrum of **3** consists of two peaks with an intensity of 1:1 at δ −75.1 and −79.9 corresponding to the expected two different CF_3 groups.



(2)

Zhu has reported that pyrolysis of benzenediazonium tris(trifluoromethanesulfonyl)methide gives two products (Eq. (3)): the phenyl cation formed attacks both the carbon

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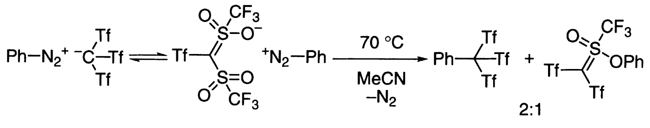
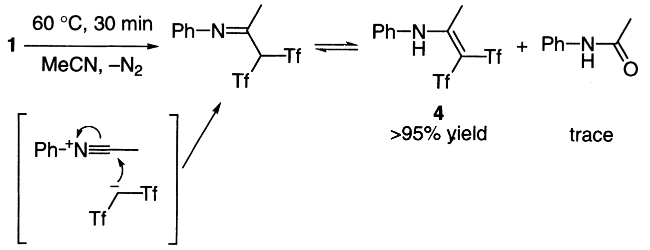
and the oxygen atom in the tris(trfluoromethanesulfonyl)methide anion [4]. In the case of $PhN_2^+C(SO_2F)_3^-$, pyrolysis under the same conditions has given only $PhO(F)S(O)=C(SO_2F)_2$ and no $(FSO_2)_3CPh$ has been detected [5].



(3)

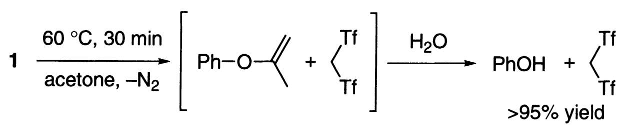
The solvent effect was investigated for the pyrolysis of **1** at 60°C. Unfortunately, no **2** was detected in toluene, *N*,*N*-dimethylformamide, or acetonitrile, and only a trace amount of **2** was detected by ^{19}F NMR spectrum in acetone, nitromethane, ethyl acetate, or THF.

Very interestingly, the pyrolysis of **1** gave another novel compound **4** quantitatively when heated in acetonitrile at 60°C (Eq. (4)). In this reaction, bis(trifluoromethanesulfonyl)methide anion reacted with an ammonium ion intermediate which was generated by nucleophilic attack of the nitrogen atom in acetonitrile to the phenyl cation formed. A trace amount of acetanilide, which would be obtained by hydrolysis of the same intermediate, was also detected. Other nitriles such as isobutyronitrile also reacted with **1** to afford compounds analogous to **4**. As fas as we know, there have been no reports on the production of nitrile-inserted compounds like **4** by the pyrolysis of arenediazonium bis(trifluoromethanesulfonyl)methide [1], arenediazonium tris(trifluoromethanesulfonyl)methide [4], or arenediazonium bis(trifluoromethanesulfonyl)imide [4].



(4)

The pyrolysis of **1** in dry acetone gave phenol and bis(trifluoromethanesulfonyl)methane in quantitative yields, respectively (Eq. (5)). In this reaction, 2-pheoxypropene as an intermediate may be generated by nucleophilic attack of the oxygen atom in acetone to phenyl cation formed.



(5)

In conclusion, phenyl[bis(trifluoromethanesulfonyl)]methane **2** was never be able to be obtained in isolatable yield by the pyrolysis of **1** despite Zhu's report of success in 1993 [1]; its isomeric product **3** was obtained in good yield. Furthermore, we have found that acetonitrile was quantitatively inserted into **2** to give **4** during the pyrolysis of **1**. The novel structure of **4** is fascinating as a ligand bearing a new functional group for a metal ion.

3. Experimental

Melting points were measured on a Yanaco apparatus and are uncorrected. All reactions were carried out in an ordinary glass-ware. Bis(trifluoromethanesulfonyl)methane was prepared from trimethylsilylmethyl lithium and trifluoromethanesulfonic anhydride according to the literature method [6]. All other reagents were commercially available and were purified before use as appropriate. IR spectra were obtained on a FTIR-8100 Shimadzu spectrophotometer using thin films on NaCl plates or KBr films. ^{19}F NMR and ^1H NMR spectra were recorded on a Varian Gemini 300 instrument using $CFCl_3$ ($\delta = 0$) and Me_4Si ($\delta = 0$) as internal standards, respectively, and $CDCl_3$ as a lock solvent. Low-resolution mass spectra were obtained by direct insertion for CI (isobutane) on a Shimadzu GC-MS instrument (GC-17A and QP-5000). Elemental analyses were performed at the School of Agriculture, Nagoya University.

3.1. Preparation of benzenediazonium bis(trifluoromethanesulfonyl)methide (1)

Zhu's procedure [1] was modified as follows: A solution consisting of water (5 ml) and pottasium bis(trifluoromethanesulfonyl)methide (1.3 mmol), synthesized from the reaction of bis(trifluoromethanesulfonyl)methane (0.136 g, 1.3 mmol) with potassium carbonate (0.09 g, 0.65 mmol), was added dropwise to a 10 ml schlenk flask charged with a solution of phenyldiazonium chloride in water prepared by treatment of aniline (130 µl, 1.4 mmol), water (0.5 ml), hydrochloric acid (1 M, 3.1 ml) and sodium nitrite (0.11 g, 1.56 mmol) at −3°C (ice water–NaCl bath). After being stirred at −3°C for 0.5 h, the reaction mixture was warmed to room temperature and stirred for 1 h. The light brown precipitate was filtered off, washed with water (2 ml), and dried under vacuum at ambient temperature to give the pure product (0.35 g, 70% yield). Mp. 74°C (decd.); IR (KBr) 3098 (s), 2307 (s), 1574 (s), 1464 (m), 1350 (vs), 1333 (vs), 1314 (s), 1246 (m), 1167 (vs), 1101 (vs), 965 (vs), 930 (w), 849 (w), 752 (s), 664 (m), 637 (w), 604 (vs), 563 (m), 527 (m), 504 (s) cm^{-1}; ^1H NMR ($CDCl_3 + CD_3OD$, 300 MHz) δ 7.94 (t, $J = 8$ Hz, 2H), 8.25 (t, $J = 8$ Hz, 1H), 8.36 (d, $J = 8$ Hz, 2H); ^{19}F NMR ($CDCl_3$+ CD_3OD, 282 MHz) δ −80.6.

3.2. Preparation of compound 2 by photolysis of phenyliodobenzene bis(trifluoromethanesulfonyl)methide

Compound **2** was prepared according to the known procedure [3]. White solid; mp. 105°C; TLC (hexane-EtOAc, 1:1), $R_f = 0.13$; IR (KBr) 2950 (m), 1495 (w), 1458 (w), 1381 (s), 1242 (s), 1219 (s), 1184 (s), 1102 (s), 806 (m), 695 (m), 660 (m), 608 (m), 585 (m), 544 (m), 507 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 5.97 (s, 1H), 7.54–7.68 (m, 5H); ^{19}F NMR (CDCl$_3$, 282 MHz) δ −71.9.

3.3. Preparation of compound **3** *by pyrolysis of* **1** *in the absence of solvents*

Compound **1** (0.192 g, 0.5 mmol) was placed in a 10 ml schlenk flask equipped with a drying tube. After heating at 60°C for 30 min, the release of N$_2$ ceased. After being cooled, the residue was sublimed under vacuum (100°C, 0.6 torr) to give a white solid (0.171 g, 0.48 mmol). TLC (hexane-EtOAc, 8:1)$R_f = 0.09$; Mp. 90–91°C; IR (KBr) 3054 (m), 1605 (w), 1581 (w), 1483 (w), 1460 (w), 1368 (s), 1308 (s), 1255 (s), 1230 (s), 1196 (s), 1156 (s), 1121 (s), 1071 (w), 1021 (w), 1009 (w), 970 (s), 918 (w), 876 (s), 831 (s), 777 (s), 746 (w), 685 (w), 648 (s), 621 (m), 600 (m), 571 (m), 563 (m), 509 (s), 496 (m), 475 (w) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 4.25 (s, 1H), 7.31–7.34 (m, 2H), 7.48–7.58 (m, 3H); ^{19}F NMR (CDCl$_3$, 282 MHz) δ −79.9 (s, 3F), −75.1 (s, 3F); GC-MS(CI) *m/z* 357 (MH$^+$), 265 (MH$^+$−C$_6$H$_4$O), 210 (M$^+$−C$_6$H$_5$−CF$_3$), 185 (CF$_3$SO$_2$SFH$^+$), 113 (S$_2$O$_3$H$^+$). Anal. Calcd for C$_{11}$H$_9$NO$_4$F$_6$S$_2$: C, 33.25; H, 2.28; N, 3.53. Found: C, 33.23; H, 2.29; N, 3.55.

3.4. Preparation of compound **4** *by pyrolysis of* **1** *in acetonitrile*

Compound **1** (0.192 g, 0.5 mmol) and acetonitrile (2 ml) were placed in a 10 ml schlenk flask equipped with a drying tube. After heating at 60°C for 30 min, the release of N$_2$ ceased. After being cooled, the residue was purified by column chromatography on silica gel as eluents, hexane-EtOAc, 10:1 to 8:1 giving a white solid (0.195 g, 0.49 mmol). White solid; mp. 84°C; TLC (hexane-EtOAc, 8:1) $R_f = 0.13$; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 2.53 (s, 3H), 7.18–7.21 (m, 2H), 7.51–7.55 (m, 3H); ^{19}F NMR (CDCl$_3$, 282 MHz) δ −76.8; GC-MS (CI) *m/z* 398 (MH$^+$), 305 (M$^+$ − PhNH), 266 (CF$_3$SO$_2$SO$_2$CF$_3$$^+$), 131 (M$^+$−2CF$_3SO_2$). Anal. Calcd for C$_{11}H_9NO_4F_6S_2$: C, 33.25; H, 2.28; N, 3.53. Found: C, 33.23; H, 2.29; N, 3.55.

3.5. Preaparation of phenol by pyrolysis of **1** *in acetone*

Compound **1** (0.192 g, 0.5 mmol) and dry acetone (2 ml) were placed in a 10 ml schlenk flask equipped with a drying tube. After heating at 60°C for 30 min, the release of N$_2$ ceased. After being cooled, the residue was purified by column chromatography on silica gel as eluents, hexane-EtOAc, 8:1 to give phenol (0.047 g, 0.5 mmol). TLC (hexane-EtOAc, 8:1) $R_f = 0.06$.

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