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Journal of Fluorine Chemistry 89 (1998) 31–34

JOURNAL OF FLUORINE CHEMISTRY

Synthesis of arylperfluoroalkyl ethers by direct fluorination

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Received 14 June 1996; accepted 25 October 1997

Abstract

Arylperfluoroalkyl ethers ArOCF$_2$CF$_2$X (X = F, OC$_3$F$_7$) were prepared from vinyl ethers ArOCF = CFX by reaction with elemental fluorine at low temperatures. The best solvent for fluorination was a mixture of chloroform and fluorotrichloromethane. Yields were improved by adding ethanol to the solvent mixture. The starting olefins were prepared by decarboxylation of the acid salts ArOCF$_2$CF$_2$CO$_2$Na (X = F) or by reaction of areneoxides with perfluoropropylvinyl ether (X = OC$_3$F$_7$).

Keywords: Arylperfluoroalkyl ethers; Arylfluorovinyl ethers; Direct fluorination

1. Introduction

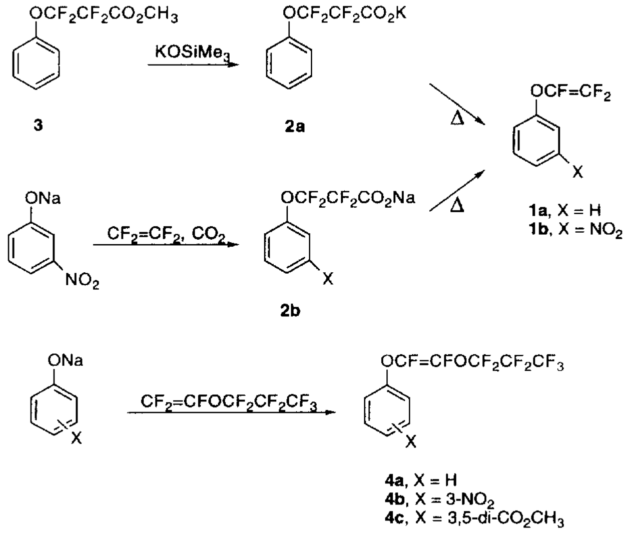
Arylperfluoroalkyl ethers are very stable compounds with applications as high temperature fluids [1], intermediates and, most recently, as precursors to fluorinated condensation polymers [2,3]. Although there are several syntheses of aryltrifluoromethyl ethers reported [1,4], analogs with larger fluoroalkyl groups are less easily prepared. Arylperfluoroalkyl esters, ArOCOR$_f$, react with SF$_4$ to give the corresponding ethers [1], but this route requires availability of the fluorinated acids and use of costly SF$_4$. Arylpentafluoroethyl ethers have been prepared by chlorination of ArOCH$_2$CF$_3$ to ArOCCl$_2$CF$_3$ and fluorine/chlorine exchange [5,6]. Synthesis of the starting ethers can be difficult, conditions required for chlorination and fluorination may be incompatible with many functional groups and the use of chlorinated intermediates can be undesirable for environmental reasons.

We now describe a new synthesis of arylperfluoroalkyl ethers by selective fluorination of the corresponding arylperfluorovinyl ethers with elemental fluorine. Also described is a convenient method for production of aryl trifluorovinyl ethers. Syntheses of novel fluorinated diamines and polyimides from some of these products have been described elsewhere [3].

2. Results and discussion

2.1. Vinyl ether synthesis

The precursors for our fluorinations were the aryltrifluorovinyl ethers **1a,b** and the longer chain difluorovinyl ethers **4a–c**. The latter compounds are easily prepared [7] in high yield by reaction of sodium areneoxides with perfluoropropylvinyl ether (Scheme 1). Aryltrifluorovinyl ethers have been prepared by direct reaction of sodium areneoxides with tetrafluoroethylene [8]. However, this reaction can be difficult to control, and we found that substantial amounts of the saturated 1,1,2,2-tetrafluoroethyl ethers and other products from further reactions of **1** with the nucleophile were also formed. The vinyl ethers have also been prepared by reaction of areneoxides with 1,2-dibromotetrafluoroethane to give 2-bromotetrafluoroethyl ethers, followed by elimination of 'BrF' using zinc [9]. This procedure worked well for the



Scheme 1.

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PII S0022-1139(98)00082-7

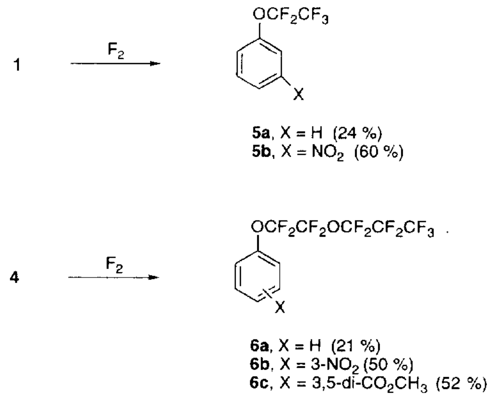
synthesis of the unsubstituted compound **1a**, but the zinc reduction seemed likely to be troublesome with the nitroderivative **1b**.

We adopted a third procedure for the synthesis of aryltrifluorovinyl ethers **1a,b**. The known [10] 3-phenoxy-2,2,3,3-tetrafluoropropionic acid, methyl ester was converted to its potassium salt (**2a**) using potassium trimethylsilanoate [11] and pyrolyzed as the dry salt to afford **1a** in good yield. Conjugate addition of sodium 3-nitrophenoxide to tetrafluoroethylene and carbon dioxide afforded the carboxylate salt **2b**. Pumping on the crude product was sufficient to remove a small amount of the saturated 1,1,2,2-tetrafluoroethyl ether byproduct. Pyrolysis of this salt afforded the vinyl ether **1b** in 46% overall yield from 3-nitrophenol.

2.2. *Direct fluorination of the vinyl ethers*

In the past, we [12] and others [13] have shown that fluorine can be successfully added to many types of double bonds by suppressing as much as possible any undesirable radical processes. However, it is also known that fluorine can react with aromatic rings, usually resulting in formation of complex mixtures especially if higher than few percent conversions are required [14,15]. One of our goals was to find conditions under which the olefinic moiety will react with fluorine in marked preference to the aromatic ring.

Some of the tools for controlling radical reactions are low temperature, low concentration of the reactants, especially fluorine, and polar solvents. We carried out the addition reactions across the double bond of arylperfluorovinyl ethers, by using 1.5% F_2 in N_2 which proved to be a reasonable compromise between an even lower concentration and the time required to convert practical amounts of olefin into the corresponding perfluoroalkyl derivatives. Increasing the fluorine concentrations to 4% or more resulted in similar products although in noticeably lower yields. The solvent of choice was a 1:1 mixture of $CFCl_3$ and $CHCl_3$ which allowed us to carry the reactions at −78°C and provided a reasonably polar environment. The yields could be considerably improved, sometimes by tens of percents, if ethanol was added periodically to the reaction mixture, amounting eventually of up to 3-fold excess based on the reacting olefin. The ethanol increased the polarity of the reaction media and may have also served as a good acceptor to the negative pole of the F_2 molecule thus, encouraging electrophilic reaction. A similar behavior pattern was noted with electrophilic substitution of inactivated hydrogen atoms with fluorine [16] and with the in situ generated BrF reacting with olefins [17] and aromatic compounds [18]. The increase of the electrophilicity of the fluorine molecule helps avoid unselective radical reactions on the aromatic rings. Nevertheless, we have always found some unidentified polymeric and other residues containing aromatic rings substituted by –F, $-CCl_3$, –OH, $-CCl_2CCl_3$ and other groups resulting from radical reactions. The importance of the deactivation of the aromatic group was reflected in the differences in the reaction outcome between substrates **1b** and **4b** and the corresponding nitro-free derivatives **1a** and **4a**. With the deactivated rings, it was not necessary to closely monitor the reaction and up to a 3-fold excess of fluorine could be used in order to achieve a full conversion and obtain **5b** and **6b** in greater than 60% yield (Scheme 2). With the more sensitive substrate **1a**, only 1 mol/equiv fluorine had to be used and the phenylperfluoroethyl ether (**5a**) was obtained only in a moderate yield. With a somewhat more deactivated ring, as in compound **4b**, an excess of fluorine could be used, but the yield of the product **6b** did not improve much. Other solvent systems were also tested. With $CFCl_3$, $CFCl_3$/MeOH and CH_3CN, the yields were lower by 10–30% compared to $CFCl_3$:$CHCl_3$:EtOH. With propionitrile and mixtures of $CFCl_3$:$CHCl_3$:EtOH in the presence of oxygen, yields of the reactions dropped to no more than 5%.



Scheme 2.

3. Experimental details

^1H NMR spectra were recorded at 300 MHz with $CDCl_3$ as solvent and Me_4Si as internal standard. The ^{19}F NMR spectra were measured at 188.2 MHz and are reported in parts per million upfield from $CFCl_3$, which also served as internal standard. Mass spectra were measured with a VG micromass 7070 H instrument. UV spectra were measured on Cary-5 using EtOH as a solvent.

3.1. *Phenyltrifluorovinyl ether (**1a**)*

3-Phenoxy-2,2,3,3-tetrafluoropropionic acid, methyl ester [10] (50.4 g, 0.2 mol) in 50 ml of ether was added to a suspension of 25.7 g (0.2 mol) potassium trimethylsilanoate in 500 ml of ether at room temperature resulting in a mild exotherm. After stirring for 22 h at room temperature, the white precipitate was collected and dried at 0.05 mm Hg giving 59 g of the potassium 3-phenoxy-2,2,3,3-tetrafluoropropionate. A 44.7 g (0.16 mol) portion of this product was placed in a 500 ml round-bottomed flask connected to a cold trap and heated in a 150°C oil bath at 0.025 mm Hg to remove volatile contaminants. A clean trap was attached to the flask and the flask contents were heated in an oil bath to 240°C resulting in rapid gas evolution. After gas evolution ceased, the title product (**1a**) (23.2 g, 82%) was isolated from the trap as a colorless liquid. ^{1}H NMR ($CDCl_3$) 7.1–7.5. ^{19}F NMR ($CDCl_3$) −117.9 (1F, dd), −125.7 (1F, dd), −132.8 (1F, dd).

3.2. *3-Nitrophenyltrifluorovinyl ether (**1b**)*

A solution of 69.6 g (0.5 mol) 3-nitrophenol in 100 ml of THF was added dropwise over 2.5 h at 10°C to a suspension of 14.9 g (0.62 mol) of sodium hydride in 300 ml of THF. The resulting suspension was stirred overnight at room temperature, then transferred to a 1-l Hastelloy autoclave. The autoclave was closed, cooled in dry ice and acetone, evacuated and charged with 36 g of carbon dioxide and 55 g (0.55 mol) of tetrafluoroethylene. This mixture was agitated at 100°C for 5 h. The autoclave was cooled to room temperature and vented. The contents were filtered and the filtrate was concentrated under vacuum to a solid. The solid was dried at 100°C and 0.01 mm Hg providing 6.5 g of $ArOCF_2CF_2H$ in a cold trap. The residual solid was placed in a round-bottomed flask and evacuated to about 0.25 mm Hg through a cold trap. The flask was heated in an oil bath to 250°C giving 73.0 g of liquid in the trap. Distillation of this liquid through a 16-in. spinning band column gave 50.2 g (46% yield) of **1b**, bp 68°C at 1.0 mm Hg. ^{1}H NMR ($CDCl_3$) 7.48 (1H, m); 7.60 (1H, t); 7.97 (1H, m); 8.10 (1H, m). ^{19}F NMR ($CDCl_3$) −118.3 (1F, dd), −125.1 (1F, dd), −137.1 (1F, dd). Anal. Calcd. for $C_8H_4F_3NO_3$: C, 43.85; H, 1.84; N, 6.39; F, 26.01. Found: C, 43.74; H, 2.01; N, 6.23; F, 25.97%.

3.3. *Difluorovinyl ethers*

Vinyl ether **4a** was prepared as described previously [7]. The nitro-derivative **4b** was prepared in the same way and isolated in 84% yield as an oil by Kugelrohr distillation at 110–120°C at 5 mm Hg. The mixture of *cis:trans* isomers could be partially separated by distillation through an 18-in. spinning band column. The lower boiling material (64–66°C at 0.2 mm Hg) was enriched in the *cis* isomer. ^{19}F NMR ($CDCl_3$) −81.8 (3F), −85.8 (2F), −130.4 (2F), −116.3 (1F, d, J = 51 Hz), −121.6 (1F, d, J = 51 Hz). Higher boiling material (70–73°C at 0.25 mm Hg) was enriched in the *trans* isomer. ^{19}F NMR ($CDCl_3$) −81.8 (3F), −85.8 (2F), −130.4 (2F), −123.9 (1F, d, J = 113 Hz), −127.9 (1F, d, J = 113 Hz). Both isomers had identical proton NMR spectra. ^{1}H NMR ($CDCl_3$) 7.45 (1H, m), 7.62 (1H, m), 7.95 (1H, m), 8.15 (1H, m). Compound **4c** was prepared in the same way and isolated by Kugelrohr distillation at 95–105°C and 0.15 mm Hg as an oily *cis:trans* mixture in 89% yield. ^{19}F NMR ($CDCl_3$) −81.7 (3F), −85.8 (2F), −129.9 and −130.0 (2F), −115.9 (0.5F, d, J = 50 Hz), −122.0 (0.5F, d, J = 50 Hz), −123.4 (0.5F, d, J = 113 Hz), −128.5 (0.5F, d, J = 113 Hz). ^{1}H NMR ($CDCl_3$) 3.97 (6H, s), 7.95 (2H, s), 8.55 (1H, s). Anal. Calcd. for $C_{15}H_9O_6F_9$: C, 39.49; H, 1.99; F, 37.48. Found: C, 40.26; H, 2.10; F, 36.4%.

3.4. *General procedure for working with fluorine*

Fluorine is a strong oxidizer and very corrosive. An appropriate vacuum line made from copper or Monel in a well ventilated area should be constructed for working with this element. We usually use higher than 95% technical grade fluorine purchased from Air Products. The vacuum line is equipped with secondary containers of a known volume made also from copper or Monel. Pressure gauges constructed especially for work with fluorine (Matheson or Air Products) are attached to the line. All possible outlets of the system, including the one connected to the oil pump, are guarded by soda–lime traps so no fluorine escapes to the atmosphere. The secondary cylinders are first evacuated and then charged with nitrogen to a positive pressure of about 5 psi. The nitrogen flow is stopped and F_2 is allowed to pressurize the system to whatever is the desired final concentration. The system is then charged again with N_2 up to 60 psi. The main fluorine and nitrogen cylinders are then completely disconnected. The reactions themselves can be carried out in glass vessels whose outlets are connected to soda–lime traps. A simple gas bubbler fitted at the end of this trap can give a fair idea of the bubbling rate of the gas through the reaction mixture although this can be accurately measured if needed. If elementary precautions are taken, work with fluorine is relatively simple.

3.5. *General olefin fluorinating procedure*

The olefin was dissolved in a cold (−78°C) mixture of $CFCl_3$:$CHCl_3$:EtOH (1:1:0.05) and well stirred by a vibromixer. Diluted (1.5%) F_2 in N_2 was passed through the solution and the concentration of EtOH was maintained by periodically adding additional 2–4 ml. Upon completion, the reaction was washed with aqueous bicarbonate, chromatographed on silica gel using hexane as eluent and finally distilled under reduced pressure.

3.6. *Pentafluoroethoxybenzene (**5a**)*

Olefin **1a** (10.5 g, 60 mmol) was dissolved in cold (−78°C) 300 ml $CFCl_3$ containing 5 ml ethanol. A full conversion was achieved after 60 mmol of fluorine were passed through. The reaction was worked up, chromatographed and distilled as described above. The product was identified as **5a**, 24% yield; bp 118–121°C; UV (EtOH) 267 nm, e = 159, 260 nm, e = 240, 255 nm, e = 216, 250 nm, e = 154; ^{1}H NMR 7.5–7.2 (m); ^{19}F NMR −85.2 (3F, s), −86.7 (2F, s); MS *m/e* Found: 212.0216, Calcd. for $C_8H_5F_5O$: 212.0260.

3.7. *Pentafluoroethoxy-3-nitrobenzene (**5b**)*

Olefin **1b** (30 g, 116 mmol) was dissolved in 800 ml of cold (−78°C) $CFCl_3$:$CHCl_3$ (1:1) containing 10 ml ethanol. A full conversion was achieved after 280 mmol of fluorine were bubbled through the reaction mixture. During this time, an additional total of 25 ml of EtOH were added periodically to the reaction mixture. The reaction was worked-up as described above and distilled in 60% yield; bp 70°C at 4.2 mm Hg; UV (EtOH) 251 nm, *e* = 7454; ^{1}H NMR 8.3–8.1 (2H, m), 7.7–7.5 (2H, m); ^{19}F NMR −86.4 (3F, s), −88.5 (2F, s); MS *m/e* Found: 257.0110, Calcd. for $C_8H_4F_5NO_3$: 257.0111; Anal. Calcd. for $C_8H_4F_5NO_3$: C, 37.37; H, 1.57; F, 36.94; N, 5.45. Found: C, 37.34; H, 1.60; F, 36.69; N, 5.26%.

*3.8. (1,1,2,2-Tetrafluoro-(2-heptafluoropropoxy)ethoxy)-benzene (**6a**)*

Olefin **4a** (80 g, 235 mmol, *cis + trans*) was dissolved in cold (−78°C) 600 ml $CFCl_3$: $CHCl_3$ (1:1) containing 16 ml ethanol. A full conversion was achieved after 770 mmol of fluorine were passed through the solution. During this time, an additional total of 30 ml of EtOH were added periodically. Upon completion, the reaction was worked up, chromatographed and distilled as described above. The product was identified as **6a**, 21% yield; bp 112°C at 180 mm Hg; UV (EtOH) 267 nm, *e* = 144, 261 nm, *e* = 231, 255 nm, *e* = 219, 250 nm, *e* = 157; ^{1}H NMR 7.5–7.1 (m); ^{19}F NMR −80.4 (3F, t, $J = 7$ Hz), −83.5 (2F, narrow m), −86.9 (2F, s), −87.1 (2F, narrow m), −129.0 (2F, s); MS *m/e* Found: 378.0071, Calcd. for $C_{11}H_5F_{11}O_2$: 378.0114; Anal. Calcd. for $C_{11}H_5F_{11}O_2$: C, 34.94; H, 1.33; F, 55.27. Found: C, 35.07; H, 1.30; F, 54.60.

*3.9. 1-(1,1,2,2-Tetrafluoro-(2-heptafluoropropoxy)ethoxy)-3-nitrobenzene (**6b**)*

Olefin **4b** (37 g, 96 mmol, *cis + trans*) was dissolved in cold (−78°C) 600 ml $CFCl_3$:$CHCl_3$ (1:1) containing 10 ml ethanol. A full conversion was achieved after 300 mmol of fluorine were passed through. During this time, an additional total of 25 ml of EtOH were added periodically to the reaction mixture. Upon completion, the reaction was worked-up as described above and distilled. The product was identified as **6b**, 50% yield; bp 69°C at 0.5 mm Hg; UV (EtOH) 251 nm, *e* = 7981; ^{1}H NMR 8.3–8.1 (2H, m), 7.7–7.5 (2H, m); ^{19}F NMR −81.9 (3F, t, $J = 7$ Hz), −85.0 (2F, narrow m), −88.47 (2F, narrow m), −88.8 (2F, s), −130.5 (2F, s); MS *m/s* Found: 422.9984, Calcd. for $C_{11}H_4F_{11}NO_4$: 422.9965; Anal. Calcd. for $C_{11}H_4F_{11}NO_4$: C, 31.22; H, 0.95; F, 49.39; N, 3.31. Found: C, 31.16; H, 0.91; F, 48.77; N, 3.18.

*3.10. 5-(1,1,2,2-tetrafluoro-(2-heptafluoropropoxy)ethoxy)-isophthalic acid, dimethyl ester (**6c**)*

Olefin **4c** (63 g, 138 mmol, *cis + trans*) was dissolved in cold (−78°C) 700 ml $CFCl_3$:$CHCl_3$ (1:1) containing 10 ml ethanol. A full conversion was achieved after 330 mmol of fluorine were passed through. During this time, an additional total of 50 ml of EtOH were added periodically to the reaction mixture.

Upon completion, the reaction was worked-up as described above and distilled. The product was identified as **6c**, 52% yield; bp 90°C at 0.25 mm Hg; ^{1}H NMR 8.65–8.06 (3H, m), 3.98 (6H, s); ^{19}F NMR −81.72 (3F, t, $J = 7$ Hz), −84.88 (2F, m), −88.27 (2F, m), −88.4 (2F, s), −130.3 (2F, s); Anal. Calcd. for $C_{15}H_9F_{11}O_6$: C, 36.46; H, 1.84; F, 42.29. Found: C, 36.57; H, 1.92; F, 41.58%.

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