Fluorine Chemistry

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Synthesis of Pentafluorosulfanyl Trifluorovinyl Ether and Its Facile Rearrangement to Difluoro(pentafluorosulfanyl)acetyl Fluoride**

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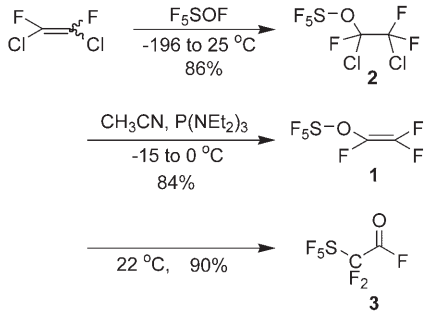
Amorphous fluoropolymers, such as teflon AF, hyflon AD, and cytop, have attractive properties as optical materials for use in a variety of applications.[1] However, their application as soft polymer pellicles in 157-nm microlithography failed because of photochemical degradation.[2,3] The degradation was thought to be a result of β scission of the cyclic ether structures in the polymer chains. In exploratory research on potential alternative amorphous fluoropolymers, a polymer based on $F_5SOCF{=}CF_2$ (**1**) seemed promising for two main reasons: 1) the bulkiness of the SF_5 group might effectively prevent crystallinity in the co-polymer with tetrafluoroethylene (TFE), and 2) its linear structure might be less prone to β scission under UV irradiation. Other perceived advantages included high fluorine content and expected high thermal stability. The polymerization of SF_5-substituted vinyl ethers had not been previously reported.

Four partially fluorinated SF_5-substituted vinyl ethers were previously prepared through dehydrohalogenation using KOH.[4] However, an attempt to dehalogenate $F_5SOFClC{-}CF_2Cl$ (**2**) to prepare **1** did not succeed.[5] Herein, we report the first synthesis of **1** with reasonable yields through the dechlorination of **2** using hexaethyl phosphorus triamide $P(NEt_2)_3$. Quite unexpectedly, **1** undergoes a facile rearrangement at 22 °C to give difluoro(pentafluorosulfanyl)acetyl fluoride $F_5SF_2CC({=}O)F$ (**3**). Two intermediate free radicals in the rearrangement were readily identified by EPR and a plausible mechanism is proposed.

The preparation of **1** is summarized in Scheme 1. The addition reaction of F_5SOF to $FClC{=}CFCl$ led to **2** in high yields (caution: this reaction can be explosive, and a small scale reaction and careful control of the temperature are essential). Repeated attempts to dehalogenate **2** using zinc dust failed, despite the fact that this method has been widely used to prepare many other related compounds.[6] The dehalogenation was subsequently carried out using $P(NEt_2)_3$ which had been used to prepare some unusual halogenated olefins.[7] The ^{19}F NMR spectrum of **1** with 95 % purity is shown in Figure 1. The only major impurity seen in the spectrum is $F_2C{=}CFCl$, which was assumed to be generated by a loss of the F_5SO unit rather than the Cl atom of **2**. The spectrum shows the strongly overlapped AB_4 pattern for the SF_5 group and the $^2J_{AB}$ coupling constant was not readily determined. Often the AB_4 patterns of SF_5 groups are well resolved.[4,5,8]



Scheme 1. Synthesis of pentafluorosulfanyl trifluorovinyl ether and its rearrangement to difluoro(pentafluorosulfanyl)acetyl fluoride.

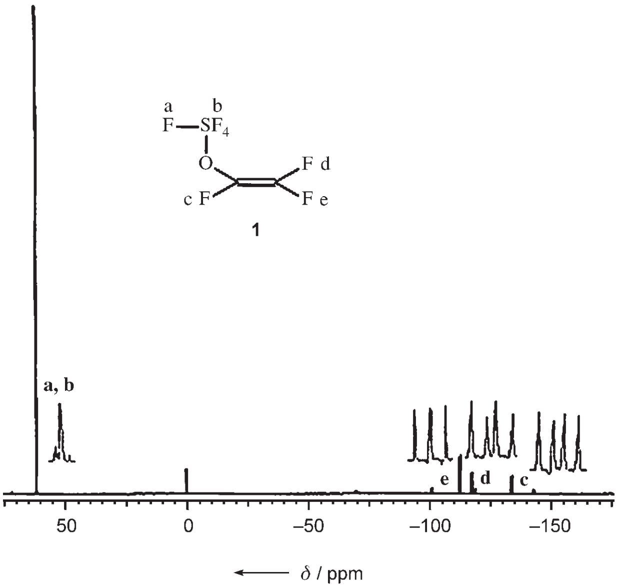


Figure 1. ^{19}F NMR spectrum of pentafluorosulfanyl trifluorovinyl ether, recorded on a Bruker AC 200 spectrometer. The sample (in $CDCl_3$ as solvent and $CFCl_3$ as reference) was sealed in a 4-mm NMR tube, which was contained in a regular 5-mm NMR tube for the measurement.

The vinyl ether **1** was quickly found to be unstable at 22 °C and plans to use it as a co-monomer in polymerization with TFE had to be abandoned. Its facile rearrangement to **3** at room temperature was evident in both NMR and IR spectra. A sample of **1** (3 mmol) sealed in an approximately 40-mL

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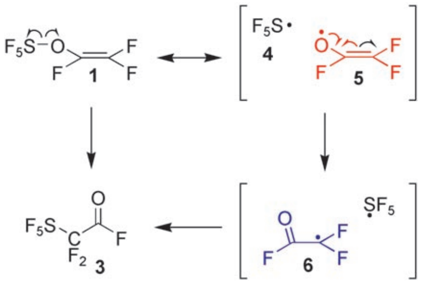
sample tube gave 2.7 mmol of pure **3** (90 %) after 12 h at 22 °C. A sample of neat **1** (0.5 mmol) for EPR was completely decomposed after 2 h at 22 °C.

A proposed radical mechanism for the rearrangement is shown in Scheme 2. The process is comprised of a homolytic cleavage of the S–O bond of **1**, followed by a rearrangement of an oxygen-centered radical **5** to a more-stabilized carbon-centered radical **6**, and then a recombination of the radicals **4** and **6**. An intermolecular mechanism was proposed to account for the related thermal rearrangement (at 260 °C) of $F_3CO(F)C{=}CF_2$ into $F_3CF_2CC({=}O)F$, based on the analysis of the side products.[9,10] In **1**, the process is more likely intramolecular in nature based on the high yields and the EPR study. Comparison of the outwardly similar fluorinated vinyl ethers, $F_3COCF{=}CF_2$ (very stable) and $H_3COFC{=}CF_2$[11] (explosive) indicates the disparate properties of this compound class.



Scheme 2. Proposed radical mechanism of the pentafluorosulfanyl trifluorovinyl ether rearrangement.

The rearrangement shown in Scheme 2 is supported by EPR. The experimental spectrum (top, Figure 2), was closely matched by the simulated spectrum (bottom, Figure 2) and is consistent with the proposed mechanism. Five spectroscopic lines having additional second-order splittings were fitted using four equivalent F nuclei with a hyperfine splitting of 144.0 G and a *g* value of 2.00290 (black in the simulated spectrum). This spectrum is identical to that from an earlier study of the SF_5 radical, in which electron spin on four equivalent equatorial F nuclei was observed with no resolvable coupling to the axial F nucleus.[12–14]

A second hyperfine pattern is also visible in the spectrum. This pattern, a triplet of doublets with 1:2:1 relative line intensities and a *g* value of 2.00318, can be simulated by electron spin on two equivalent F nuclei (58.2 G) and a single F nucleus (5.0 G) (blue in the simulated spectrum). This spectrum, with hyperfine values well within the typical range of known primary and secondary F hyperfine splittings, corresponds well with the radical **6**. This radical has not been previously identified. No evidence for radical **5** or other radical species was observed in the EPR, probably because of its rapid intramolecular electron transfer and conversion into **6**.

A related interesting rearrangement of $F_5SOClC{=}CFH$ (*cis*/*trans*) has been reported.[4] The rearranged product was believed to be $F_5SOHC{=}CFCl$ based on the NMR and IR spectroscopic data,[4] although a possible mechanism of the rearrangement was not proposed. However, we have prepared $F_5SOHC{=}CFCl$ (*cis* and *trans*) and the spectroscopic data are totally different from those reported;[4] the previously reported ^{19}F NMR and IR spectroscopic data are consistent with that expected for $F_5SCFHC({=}O)Cl$ and not the alkene. The reported rearrangement was probably similar to the rearrangement of **1**. Among a series of other SF_5-substituted vinyl ethers we have prepared, several also undergo the same type of rearrangement, but with different reaction rates.[15]

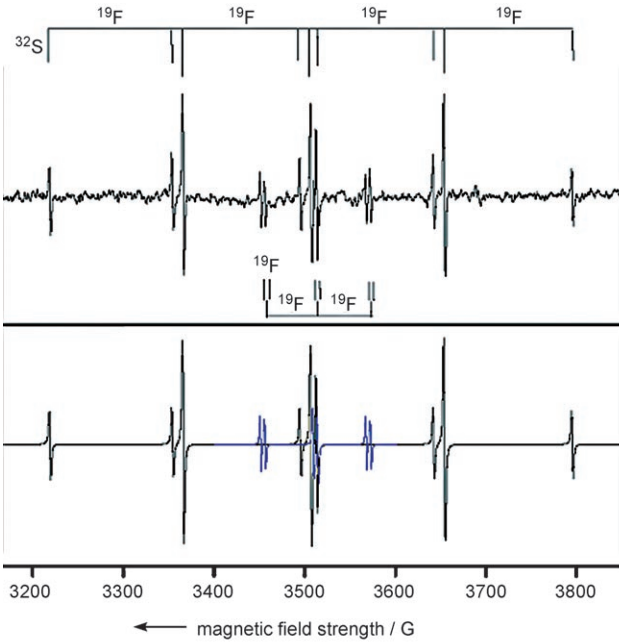


Figure 2. EPR spectra of the rearrangement of **1**; top: the experimental spectrum recorded on a Bruker EMX spectrometer; bottom: simulated spectrum (calculated by Bruker SimFonia). Neat liquid samples of **1** were placed in a 3-mm I.D. tubes, degassed, and sealed. X-band first derivative absorption was then recorded at 22 °C. Signal intensity decreased after 2 hours.

The EPR study suggests that the intermediate radicals **4** and **6** have reasonably long lifetimes, a property which can potentially be utilized to initiate radical polymerizations. Preliminary experiments demonstrated that **1** readily initiated polymerization of TFE or vinylidene fluoride (VDF).

In summary, we have reported the first successful synthesis of **1** using the atypical but effective dehalogenation reagent $P(NEt_2)_3$. An EPR study identified two long-lived radical intermediates in the facile but unexpected rearrangement of **1**. We believe the detection of both radicals in a homolysis reaction is quite rare, as is their recombination to form a rearranged product in high yield.

Experimental Section

2: FClC=CFCl (20.2 mmol, 12 % $F_2C{=}CCl_2$) was vacuum transferred into a stainless-steel bomb (150 mL) cooled to −196 °C. Then SF_5OF (6.4 mmol) was condensed on the upper walls of the reactor, which was allowed to warm slowly in a dewar from −196 °C to 22 °C. The reactor was then cooled to −196 °C and further SF_5OF (6.8 mmol) added and the warming repeated. This cycle was repeated five times to add a total of 32.2 mmol of SF_5OF. Vacuum fractional condensation through traps at −96 and −196 °C, followed by reseparation of the −96 °C trap through a −78 °C trap, gave **2** (14 mmol) contaminated with traces of $F_5SOCl_2C{-}CF_3$ and $F_5SOF_2C{-}CFCl_2$. IR and NMR spectroscopic data of **2** corresponded with those reported.[5]

1: Dry CH_3CN (15 mL) was introduced into a predried flask (250 mL). The starting material **2** (3.2 mmol) was then condensed into the flask through a vacuum line. The flask was immersed into an ethanol/H_2O bath at −15 °C. Compound **2** (1.1 mL, 3.2 mmol) was slowly injected into the flask over 5 min. The resulting mixture warmed to 0 °C over 30 min. A fractional vacuum condensation was carried out using 3 traps at −75, −88, and −196 °C, respectively. The compound **1** (2.7 mmol), contaminated with minor impurities, was collected at −196 °C. The unreacted starting material **2** and CH_3CN were collected in the other 2 traps. ^{19}F NMR (188.3 MHz, $CDCl_3$, 25 °C, $CFCl_3$): $\delta = 61.6$ (m, 5F; SF_5), −133.9 (ddm, $^3J(F,F) = 109$, $^3J(F,F) = 74$ Hz, 1F; CF_2), −117.5 (ddm, $^2J(F,F) = 72$ Hz, 1F; CF_2), −112.6 ppm (dd, 1F; CF). IR (gas phase, 6 torr): $\nu = 1828$ (s, $\nu_{C=C}$), 1343, 1292, 1175 (s, ν_{C-F}), 933, 890, 832 (s, ν_{S-F}), 722 (m), 607 (s), 577 (m), 538 cm^{-1} (w).

3: The vinyl ether **1** (3.0 mmol) was vacuum transferred into a glass tube (ca. 40 mL) at −196 °C fitted with a glass-teflon valve. The tube was then immersed in an ethanol bath at −30 °C and allowed to warm slowly to 22 °C (over around 4 h). The tube was then held at room temperature for 12 h. A mixture of the main product **3** along with minor side products was obtained. GC separation yielded pure **3** (2.7 mmol, 90 %). ^{19}F NMR (188.3 MHz, $CDCl_3$, 25 °C, $CFCl_3$,) $\delta =$ 62.1–65.3 (quintet of m, $^2J(F,F) = 150.6$ Hz, 1F; SF), 42.0–42.9 (dm, $^4J(F,F) = 4.4$ Hz, 4F; SF_4), −91.9 (m, $^3J(F,F) = 2.3$, $^3J(F,F) = 4.4$ Hz, 2F; CF_2), 21.4 ppm (septet, 1F; $C(O)F$). IR (gas phase, 15 torr): $\nu =$ 1890 (s, $\nu_{C=O}$), 1285, 1232, 1132 (s, ν_{C-F}), 902, 869, 765 (s, ν_{S-F}), 680 (s), 614 (m), 576 (m), 523 cm^{-1} (w).

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