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Supporting Information

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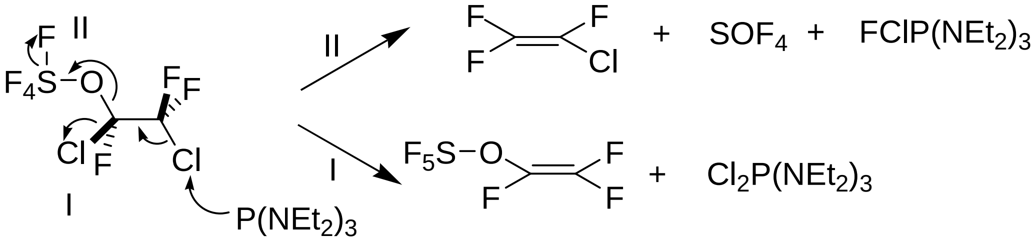
Synthesis of Pentafluorosulfur Trifluorovinyl Ether and Its Facile Rearrangement to 2-Pentafluorosulfurdifluoroacetyl Fluoride

*Libin Du, Bevan Elliott, Luis Echegoyen, Darryl D. DesMarteau,**



Scheme S1. A possible dehalogenation mechanism of $SF_5OCFClCF_2Cl$ (**2**) using $P(NEt_2)_3$ (**3**). Route I shows the generation of **1** through dehalogenation. A chlorine atom and a SF_4O group are lost sequentially to generate the major side product CF_2=CFCl in Route II.

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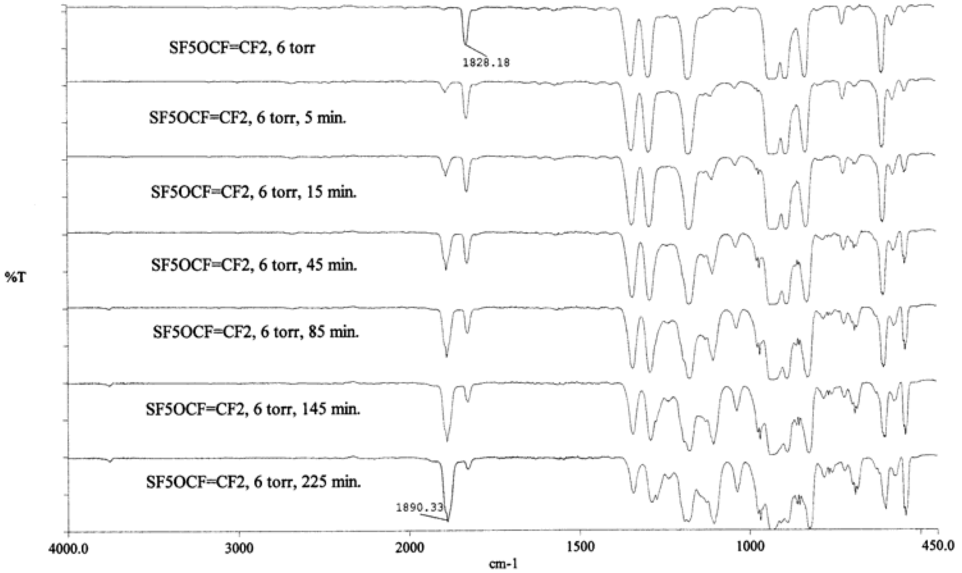

Figure S1. IR spectra showing the rearrangement of $SF_5OCF{=}CF_2$ to $SF_5CF_2C(O)F$. Infrared spectra were recorded on a Perkin-Elmer Spectrum 2000 series FTIR in a 10 cm path length glass gas cell fitted with AgCl windows. The initial pressure in the IR Cell was 6 torr (approximately 8 kPa).

The transition of the vinyl functionality (1828 cm^{-1} for C=C stretch) of the vinyl ether (**1**) to the carbonyl group (1890 cm^{-1} for C=O stretch) of acid fluoride (**3**) can be easily identified. The rearrangement shown in Figure S1 is almost complete after 145 min. The small peak at approximately 1835 cm^{-1} in the bottom spectrum is probably a combination band of **3** rather than the C=C stretch band of **1** which had by then been completely consumed by the rearrangement and other side reactions**.**

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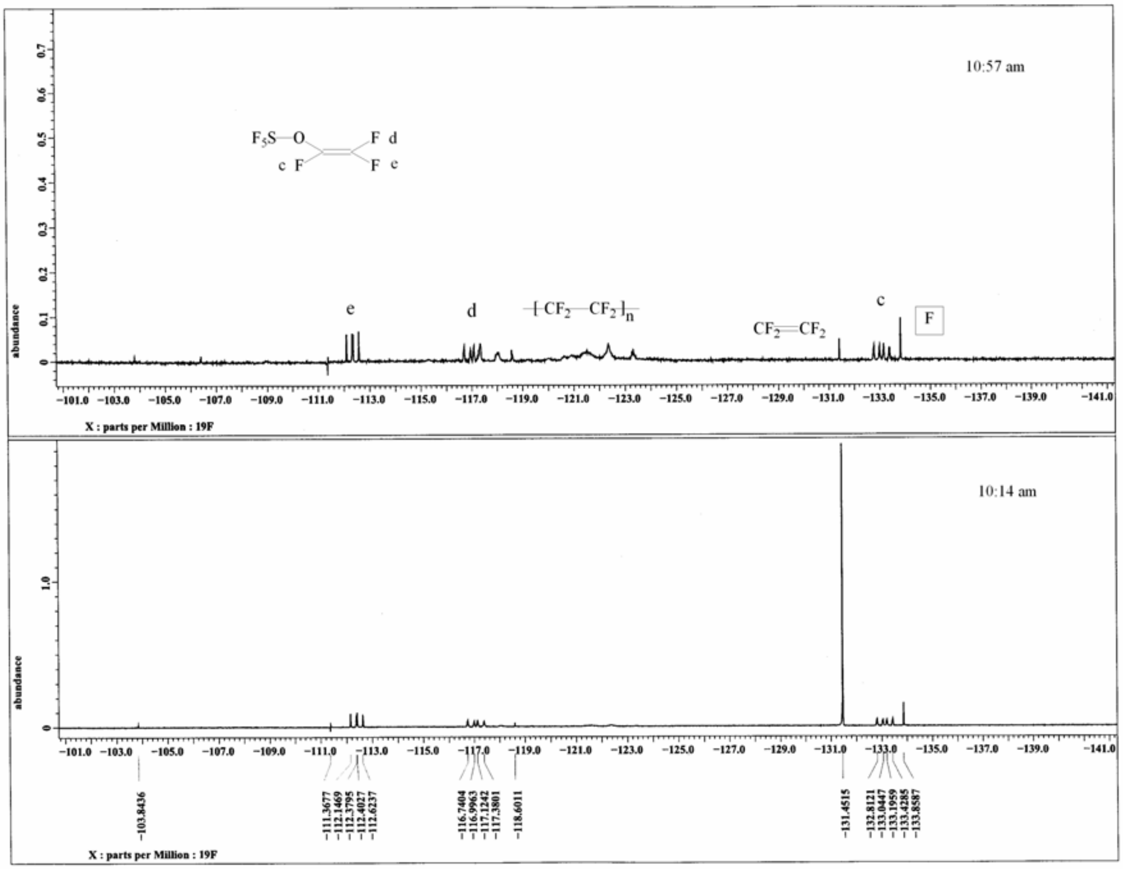

Figure S2. ^{19}F NMR spectra of a mixture of $SF_5OCF{=}CF_2$ and TFE measured at room temperature. NMR spectra were recorded on a JOEL 300 MHz Spectrometer. All the samples (**1** and TFE), solvent (CCl_4) and reference (FC11) were sealed in a 4mm NMR tube which was contained in a regular 5 mm NMR tube with deuterated D_2O.

A homopolymerization of TFE using **1** as the initiator in a sealed NMR tube is shown above. After approximately 40 minutes, more than 97 % of the added TFE was consumed with growing of new peaks at around -120 ppm, presumably belonging to TFE oligomers or low molecular weight PTFE. The reason why the TFE oligomers could be dissolved in the solvent is probably related to its low molecular weight and the end groups resulting from the addition of SF_5 and $CF_2C(O)F$. The majority of the PTFE obtained was insoluble--visible as a continuous precipitation of white solid throughout the polymerization. The rearranged product, **3**, was barely seen during the polymerization and was only noticed after the TFE was almost consumed. The successful homopolymerization of TFE using **1** as an initiator at room temperature could be extended to other SF_5 vinyl ethers that can undergo a similar rearrangement (unpublished results). In addition, the half-life of the process could be made adjustable by changing the substituents of the vinyl ethers.

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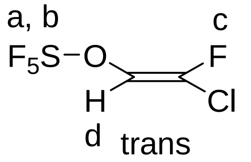
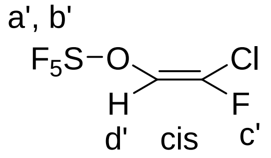
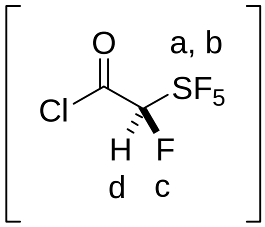
Table S1. Comparison of spectra data reported in literature[4] and obtained in this study[15]

		
Reported spectra data[4]	δc = -165.14 ppm; δd = 5.65 ppm; ^3Jcd = 47.0 Hz; C=C stretch: 1786 cm-1 (s)	δc’ = -89.07 ppm; δ’d = 5.96 ppm; ^3Jc’d’ = 13.2 Hz; C=C stretch: 1683 cm-1 (m)
		
Spectra data obtained in this study[14]	δc = -89.6 ppm; δd = 7.0 ppm; ^3Jcd = 14.5 Hz; C=C stretch: 1693 cm-1 (s)	δc’ = -108.7 ppm; δd’ = 7.7 ppm; ^3Jc’d’ = 3.0 Hz; C=C stretch: 1693 cm-1 (m)

The reported NMR and IR data for $SF_5OCH=CFCl$ (both *trans* and *cis*) do not match with that obtained in this study (see Table S1). The data set for *trans* isomer is not reasonable and is more likely to be from the acid chloride compound shown in the bracket in Table S1.