Reference and Notes

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(2) Present address: Department of Chemistry and Physics, St. Mary's College, Notre Dame, Indiana 46556.

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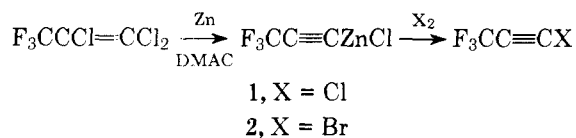
Perfluoroacetylenic Ethers[1]

S. Trofimenko, R. W. Johnson, and J. K. Doty

*Contribution No. 76-22 from the Plastic Products and Resins Department,
E. I. du Pont de Nemours & Co., Wilmington, Delaware 19898*

The first examples of perfluoroacetylenic ethers, $CF_3C{\equiv}COCF_3$ and $CF_3C{\equiv}COCF_2CF_2CF_3$, were synthesized via several routes starting with $CF_3CCl{=}CCl_2$. They homopolymerize at room temperature and have been copolymerized with other perfluoro monomers.

In the course of our work on fluorocarbon polymers the need arose to investigate perfluoroalkoxyacetylenes, a hitherto unknown class of compounds. As a starting point for their synthesis we chose $CF_3CCl{=}CCl_2$, a commercially available material,[2] which can be readily converted to $CF_3C{\equiv}CZnCl$ by zinc dust in dimethylacetamide.[3] Halogenation of this species[4] yielded $CF_3C{\equiv}CCl$ (**1**) and $CF_3C{\equiv}CBr$ (**2**), respectively, which have been made before less conveniently or in lower yields[5-7] by other routes. The IR and Raman spectra of both **1** and **2** have been reported,[8,9] as has the microwave spectrum of **1**.[10]

$$CF_3CCCl{=}CCl_2 \xrightarrow[\text{DMAC}]{\text{Zn}} F_3CC{\equiv}CZnCl \xrightarrow{X_2} F_3CC{\equiv}CX$$

$$1, X = Cl$$
$$2, X = Br$$

Despite the reported high-yield replacement of Cl^- in **1** by $(F_3C)_3C^-$,[11] the direct halide replacement by R_fO^- in **1** or **2** did not appear very promising because of the known poor nucleophilicity of R_fO^- and the equilibrium[12]

$$R_fCF_2O^- \rightleftharpoons R_fCFO + F^-$$
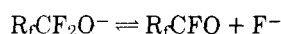
Furthermore, in view of the established mode of trans addition to acetylenes[13,14] and, hence, also of trans elimination, the intermediate vinylic carbanion would be expected to eliminate R_fO^- rather than Cl^-. On the other hand, conducting the reaction in the presence of a proton source should trap the
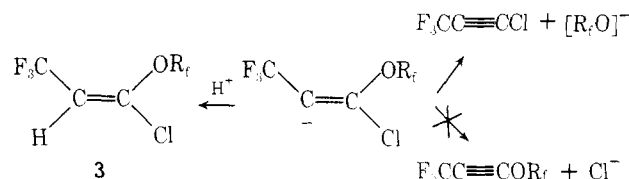
carbanion and give rise to the perfluoroalkoxy vinyl ether (**3**).

Indeed, when **1** was treated with "$AgOCF_3$", made in situ from AgF, COF_2, and HF in adiponitrile, compound **3**, bp 49–50 °C, was obtained in about 45% yield. There was no evidence for CF_3O^- addition to the 2 position. Compound **3** was a single isomer, identified as trans (H, OCF_3) by NMR spectroscopy. Treatment with strong base under drastic conditions converted it only to **1** (Scheme I). Irradiation in the presence of a trace of bromine converted **3** to a 50:50 cis/trans mixture. This mixture, upon being passed through soda lime at 210 °C, yielded both **1** and $CF_3C{\equiv}COCF_3$ (**4**), although in low yields and conversions thus confirming the trans elimination mechanism, though not providing a convenient synthetic path to **4**.

Compound **3** was readily converted to the dibromo derivative **5**, which evolved bromine during distillation at atmospheric pressure, but which could be distilled undecomposed in vacuo. Triethylamine converted **5** cleanly to a cis/trans mixture of **6**. No dehydrochlorination was observed.

Scheme I

$$F_3CCH=CClOCF_3 \xrightarrow[210\ °C]{\text{soda lime}} F_3CC\equiv COCF_3 + F_3CC\equiv CCl$$
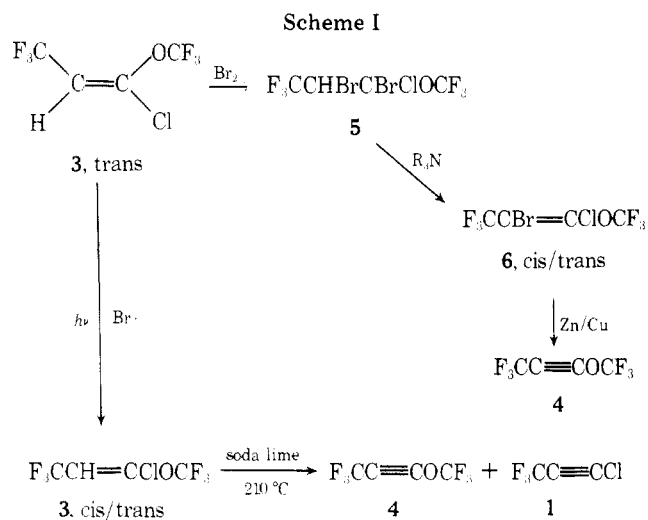
When **6** was treated with zinc–copper couple[15] in diglyme, the desired perfluoroalkoxyacetylene (**4**) was formed and distilled out of the reaction vessel, along with small amounts of **1**. In addition, $CF_3C\equiv CZnCl$ was formed, as evidenced by the appearance of the characteristic 2150 cm^{-1} infrared band in the solution, and the formation of $CF_3C\equiv CH$ (identified by IR) upon adding water. Yields of crude **4** averaged 45–50%. It appears that only one isomer of **6** is converted to the desired product.

By contrast, under identical dehalogenation conditions neither **8** (obtained as a cis/trans mixture from **3** via chlorination to **6** and dehydrochlorination) nor **9** produced any **4**.
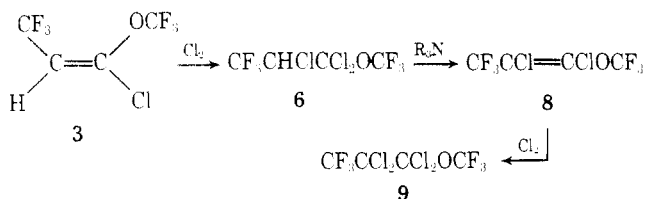

Because the boiling points of **4** and **1** were too close for their convenient separation (0 and 3 °C, respectively) we decided to replace OCF_3 by a larger perfluoroalkoxy group. Replacing CF_2O by CF_3CF_2CFO in the original synthetic scheme, the analogous series of compounds, **10**, **11**, and **12**, was obtained. The 1-perfluoropropoxy-3,3,3-trifluoropropyne (**12**) boiled around 50 °C and was easily separated from **1**, although some yield losses occurred during redistillation because it polymerized in the pot.
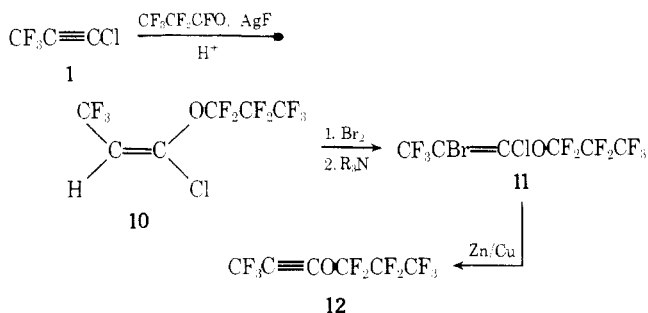
As yields of **12** averaged about 46%, again probably arising from just one of the **11** isomers, a synthesis was sought which would overcome this drawback.

The readily prepared $CF_3C\equiv CBr$ (**2**) behaved differently toward R_fO^- than **1**: while **13**, the bromo analogue of **10**, was formed in very small yield, the major product was the ketene acetal **14**, bp 118 °C.

Formation of **14** probably proceeds via addition of R_fO^- to **13**, yielding a carbanion capable of rotating around the single bond, and hence of eliminating Br^-.

$$\xrightarrow{OH^-} CF_3C\equiv COCF_2CF_2CF_3$$
12
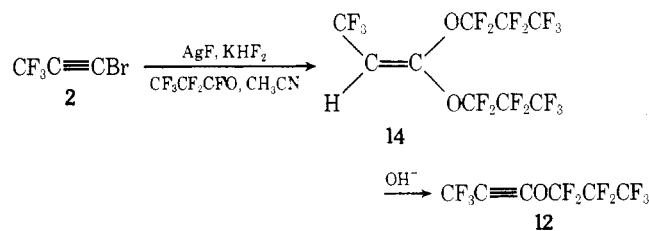
Reaction of **14** with molten KOH was clean, affording a 30:70 mixture of **12** and starting material per pass, which could be easily separated by distillation for recycling of **14**. This approach constitutes the most convenient synthesis of **12**.

The perfluorinated acetylenic ethers **4** and **12** are colorless liquids (bp 0 and 50 °C, respectively) characterized by a strong $C\equiv C$ band at 2315 and 2299 cm^{-1}, respectively. They can be stored unchanged at -80 °C, but they homopolymerize slowly at room temperature to polymers which are transparent, probably due to plasticization by lower oligomers. Drying in vacuo produces white powders of high chemical and thermal stability.

This facile homopolymerization of **4** and **12** is in contrast to the homopolymerization of hexafluoro-2-butyne (HFB), where catalysis (γ irradiation,[16] triphenylphosphine,[17] fluoride ion,[18,19] transition metal complexes,[20] or nitrosyl hexafluorophosphate[21]) and generally harsher conditions are necessary.

Compared to $(HFB)_n$,[20] the homopolymers of **4** and **12** exhibit somewhat lower thermal stability (10% weight loss at 470 and 420 °C, respectively, vs. 540 °C for $(HFB)_n$).

The copolymerization of **12** with various fluoromonomers was also investigated. It would be expected that this monomer would be more amenable toward polymerization than HFB, because the $-OC_3F_7$ group is known to offer less resistance to polymerization than the $-CF_3$ group. This study focused on polymerization at high pressures (500–4000 atm) using perfluoropropionyl peroxide (3P) initiator at 25 °C. In order to carry out these polymerizations on a small scale, the monomers and 3P were charged into a platinum tube, sealed, and inserted into a vessel which could be pressurized with nitrogen. Since the platinum tubing readily collapsed, the 500–4000-atm pressure was transferred to the contents of the tube.

Copolymers of **12** containing 50 and 67% HFB were prepared at 4000 atm in quantitative conversion to clear transparent materials. However, these polymers proved to be similar to $(HFB)_n$ and $(12)_n$ in that they were very thermally stable (1% weight loss at 400 °C N_2 atmosphere) and showed no signs of flow in attempts to compression mold samples at temperatures up to 400 °C.

Attempts to copolymerize **12** with tetrafluoroethylene, hexafluoropropene, and $CF_2=CFOR_f$ ($R_f = CF_3$, C_3F_7) have been moderately successful and represent the first time that tetrafluoroethylene and the fluorovinyl ethers have been copolymerized with any perfluoroacetylene. Copolymers of tetrafluoroethylene have been prepared which contain 20, 50, and 60% of **12**. They are more transparent and stiffer than Teflon; moreover, these materials flow well under compression molding conditions at 300 °C, in contrast to all other polymers prepared from perfluoroacetylenes.

Thermal analysis results indicated these materials to be genuine copolymers. TGA showed very similar stability for all copolymer samples. Degradation began at $\sim$350 °C compared to 460 °C for polytetrafluoroethylene in a N_2 atmosphere. DTA/DSC at high sensitivities detected transition temperatures or melting of small amounts of crystallites. The copolymer containing 2% **12** shows a melting peak (318–324 °C) a few degrees below that of Teflon, as expected for copolymer. All copolymers of **12** with tetrafluoroethylene decomposed at temperatures $>$500 °C.

Inherent viscosities have been determined in fluorocarbon oil, Freon E2, which was a solvent for these polymers. The copolymers of **12** with tetrafluoroethylene had inherent viscosities as high as 1.2. The viscosity data suggest that the molecular weight of these copolymers is independent of polymerization pressure and dependent on 3P concentration. Higher conversion of monomers is observed at increased pressure (4000 atm).

Copolymers of **12** containing 50% hexafluoropropene CF_2=$CFOCF_3$ and CF_2=$CFOC_3F_7$ have been prepared. All of these copolymers were much less stable than those based on tetrafluoroethylene. The CF_2=$CFOC_3F_7$ copolymer began to show weight loss at about 200 °C in a N_2 atmosphere with distinct phase transitions in the 60–70 °C region. The other two copolymers were somewhat more thermally stable with a 1% weight loss at about 250 °C and phase transitions in the 75–120 °C region. None of these copolymers showed melting points and they were completely decomposed at temperatures in excess of 500 °C. In contrast to the copolymerization with tetrafluoroethylene, the molecular weights and conversions of copolymers based on the other perfluoromonomers showed a dependence on polymerization pressure.

While structural studies on copolymers containing **12** are not conclusive, it is probable that the polymer chain is linear and contains double bonds. In support of this, infrared and Raman spectra of all copolymers showed the presence of carbon–carbon double bonds in the 1600–1725-cm^{-1} region.

Experimental Section

The following chemicals were purchased and used as received: perfluoropropionyl fluoride from PCR Inc., CF_3CCl=CCl_2 from Columbia Organic Chemicals Co., Inc., and AgF from Ozark-Mahoning Co.

NMR spectra are referred to internal CFCl$_3$.

1-Chlorotrifluoropropyne (1). To a slurry of CF_3 C≡CZnCl made from 1 mol of CF_3CCl=CCl_2 by the literature method[3] and stirred in a flask equipped with a −80 °C reflux condenser was added chlorine (44 mL at −80 °C, 1 mol) by passing it over the surface. Chlorine was absorbed exothermally and the flask had to be externally cooled to maintain the temperature at 10–30 °C. When all chlorine had reacted, the −80 °C condenser was replaced by a water-cooled condenser. The mixture was heated to 90–100 °C, and the volatiles were passed through the water condenser to a −80 °C trap. Redistillation on a cold still gave **1**, bp ~3–4 °C in 40–50% yields. Its vapor IR spectrum was in accord with literature data.[8]

Trifluoro-1-bromopropyne (2). To a slurry of CF_3C≡CZnCl made from 1 mol of CF_3CCl=CCl_2 was added dropwise, at 10–20 °C, 1 mol of bromine. After completion of the addition the flask was connected to a vacuum source through a −80 °C trap and the product was distilled over while the flask was warmed slowly to 50 °C. The crude product obtained in ~60% yields was purified by redistillation on a spinning band column. It boils at 24–25 °C and polymerizes slowly at room temperature, but keeps well at −80 °C. The IR spectrum agreed with literature data.[8]

(*E*)-1-Trifluoromethoxy-1-chloro-3,3,3-trifluoropropene (3). A mixture of 120 mL of adiponitrile (acetonitrile was equally good, but it codistilled with the product), 40 g of silver oxide, 2.0 mL of water, 40 mL (at −80 °C) of CF_3C≡CCl, and 150 g of carbonyl fluoride was loaded into a 320-mL autoclave and shaken for 2 h at 75 °C. After venting off low boilers, the reaction mixture was distilled, and material having bp 40–60 °C was collected. This liquid was stirred overnight with a saturated sodium bicarbonate solution (to remove acyl fluoride impurities characterized by an IR band at 1850 cm^{-1}). The organic layer was separated, run through a short column of alumina, and finally fractionated on an efficient spinning band column. Yields of the cut, bp 49–50 °C, d_{25} = 1.467 g/mL, averaged 40 g (45%).

Similar results were also obtained using Cu$_2$O instead of Ag$_2$O in the above procedure.

Anal. Calcd for C_4HClF_6O: C, 22.4; H, 0.47; Cl, 16.6; F, 53.1; mol wt, 214. Found: C, 22.4; H, 0.52; Cl, 16.6; F, 52.9; mol wt (parent mass spectrum peak), 214.

^{1}H NMR: quartet (*J* = 6.8 Hz) at 4.70 ppm. ^{19}F NMR: quartet (*J* = 1.8 Hz) at 57.8 ppm and a doublet of quartets (*J* = 6.8, 1.8 Hz) at −60.0 ppm in 1:1 ratio assigned to the OCF$_3$ and CF$_3$ groups, re-

spectively. IR (in CCl$_4$): 3077 (w), 1710 (w), 1670 (vs), 1400 (vs), 1300–1100 (vs), 1080 (m), 910 (m), 855 (s), 720 (w) cm^{-1}.

3 (cis/trans). Irradiation of the pure *E* isomer CF_3CH=$CClOCF_3$, to which a few drops of bromine was added, with a sunlamp gave within 2 h a roughly 50:50 mixture of cis/trans isomers as evidenced by: (a) GC showing the appearance of a lower boiling component at 84 mm, the starting material being at 91 mm; (b) boiling point of the mixture dropping to 46–49 °C; and (c) the ^{19}F NMR spectrum showing, in addition to the starting material, two new peaks in a 1:1 ratio, a singlet at −59.0 ppm and a doublet (*J* = 6.5 Hz) at −60.4 ppm.

Fractional distillation of this mixture gave a lower boiling cut somewhat enriched in the cis isomer (60:40).

(*E*)-1-Perfluoro-*n*-propoxy-1-chloro-3,3,3-trifluoropropene (10). A mixture of 26 g of silver fluoride, 14 g of sodium bifluoride, 120 mL of adiponitrile, 35 mL (at −80 °C) of CF_3C≡CCl, and 170 g of perfluoropropionyl fluoride was shaken in a 330-mL autoclave for 2 h at 90 °C. Distillation gave 7 mL (20%) of unreacted CF_3C≡CCl, along with 63 g of liquid, bp 80–90 °C, corresponding to a conversion of 80% and a yield of 72%. The liquid was stirred overnight in aqueous sodium acetate and then separated, run through a short alumina-packed column, and redistilled. The main cut has bp 88–90 °C, d_{25} = 1.583 g/mL. It was a single isomer, as shown by GC and NMR data.

Anal. Calcd of $C_6HClF_{10}O$: C, 22.9; H, 0.32; Cl, 11.3; F, 60.4. Found: C, 23.0; H, 0.55; Cl, 11.3; F, 60.5.

^{19}F NMR has peaks at −62.0 (3 F), −83.4 (3 F), −86.4 (2 F), and −131.3 ppm (2 F) (J_{f-H} = 7.5 Hz), consistent with structure **10**. IR (in CCl$_4$): 3125 (w), 1670 (vs), 1330 (vs), 1300–1100 (vs), 1060 (vs), 1040 (vs), 980 (vs), 970 (s), 855 (s, br), 806–730 (vs), 697 (s, br) cm^{-1}.

1,1-Bis(perfluoro-*n*-propoxy)-3,3,3-trifluoropropene (14). A 330-mL shaker tube was charged with 50.8 g (0.4 mol) of AgF, 15.6 g (0.2 mol) of KHF$_2$, and 100 mL of acetonitrile. After cooling and evacuation, 34 g (0.2 mol) of CF_3C≡CBr and 133 g (0.8 mol) of perfluoropropionyl fluoride were distilled in. After reaction at 100 °C for 2 h, excess perfluoropropionyl flouride was vented into a trap and saved for later recycle. The residue was filtered to remove solids. This crude product consisted of two layers, an upper layer consisting primarily of acetonitrile and a lower layer which was nearly pure CF_3CH=$C(OC_3F_7)_2$. The lower layer was washed with aqueous sodium acetate, dried in an alumina column, and distilled on a spinning band column (bp 118 °C). Typical yields were 45%, but the system was not optimized.

^{19}F NMR CF_3ªCH=$C(OCF_2$ᵈCF_2ᵉCF_2ᵇ$)(OCF_2$ᶜCF_2ᵉCF_3ᵇ$)$: a, −59.6 (3 F); b, −81.8 (6 F); c, −84.0 (2 F); d, −86.3 (2 F); e, −130.0 ppm (4 F). ^{1}H NMR: unresolved four-line pattern at 5.1 ppm. IR (gas): 3100 (vw), 1720 (m), 1340 (m), 1250 (s), 1150 (s), 1100 (m), 1030 (w), 1010 (w), 990 (m), 750 (w) cm^{-1}. Mass spectrum: parent peak at *m/e* 464, plus other peaks consistent with CF_3CH=$C(OC_3F_7)_2$.

2,3,3-Trichloro-3-trifluoromethoxy-1,1,1-trifluoropropane (7). To 21.4 g (0.1 mol) of CF_3CH=$CClOCF_3$ stirred under a −80 °C condenser and irradiated with a sunlamp was added 6 mL of chlorine (at −80 °C, an excess). Uptake of chlorine was rapid, as evidenced by the disappearance of the C=C band in the IR. After a few hours, the solution was distilled, and the main cut, bp 105–110 °C, was obtained in 23.4 g (82.1%) yield. Redistillation afforded a pure product boiling at 109–110 °C.

Anal. Calcd for $C_4HCl_3F_6O$: C, 16.8; H, 0.35; Cl, 37.2; F, 40.0. Found: C, 16.8; H, 0.39; Cl, 37.3; F, 39.7.

^{1}H NMR: quartet (*J* = 7.7 Hz) at 5.50 ppm. ^{19}F NMR: singlet at −56.2 ppm and doublet (*J* = 7.7 Hz) at −68.8 ppm assigned to OCF$_3$ and CF$_3$, respectively.

2,3-Dichloro-1-trifluoromethoxy-3,3,3-trifluoropropene (8). To a solution of 28.5 g (0.1 mol) of $CF_3CHClCCl_2OCF_3$ in 40 mL of *o*-dichlorobenzene was added 14 g (excess) of diisopropylethylamine (triethylamine is equally good). The solution was heated and volatiles were distilled out on a spinning band column. The cut bp 60–72 °C was collected and obtained in 24.2 g (97%) yield. Pure product boils at 72–73 °C, d_{25} = 1.581 g/mL. GC shows the presence of two isomers in about 55:45 ratio.

Anal. Calcd for $C_4Cl_2F_6O$: C, 19.3; H, 0.00; Cl, 28.5; F, 45.8. Found: C, 19.6; H, 0.00; Cl, 28.4; F, 45.9.

^{19}F NMR showed two isomers present: *trans*-dichloro, singlets at −60.1 and −65.2 ppm; *cis*-dichloro, quartets (*J* = 2 Hz) at −61.0 and −65.2 ppm. IR (in CCl$_4$): 1630 (vs), 1300–1100 (vs), 1005, 990 (s), 893–885 (s), 844 (s), and 702 (vs) cm^{-1}.

1,1,2,2-Tetrachloro-1-trifluoromethoxy-3,3,3-trifluoropropane (9). A mixture of 12.5 g (0.05 mol) of CF_3CCl=$CClOCF_3$ and 2.8 mL (at −80 °C) of chlorine was stirred under a −80 °C condenser and irradiated with a sunlamp for 2 h, at which time the yellow color

had faded and no C=C band was present in the IR. Distillation gave a little unreacted starting material, then the product, bp 130 °C, d_{25} = 1.739 g/mL, obtained in 13 g (82%) yield.

Anal. Calcd for $C_4Cl_4F_6O$: C, 15.0; H, 0.00; Cl, 44.4; F, 35.6. Found: C, 15.0; H, 0.10; Cl, 44.0; F, 35.8.

IR (in CCl_4): 1300–1200 (vs, br), 1100 (vs), 1020 (s), 935 (m), 910 (w, br), 855 (s, vs), 813 (s, br sh to 730), 702 (s) cm^{-1}.

1-Chloro-1,2-dibromo-1-trifluoromethoxy-3,3,3-trifluoropropane (5). A mixture of 10.7 g (0.05 mol) of $CF_3CH=CClOCF_3$ and 8 g (0.05 mol) of bromine was stirred and irradiated with a sunlamp until the red color disappeared. The product boiled around 140 °C (atm) with evolution of bromine, but could be distilled undecomposed at 59–60 °C (35–36 mm), yield 15 g (82%), d_{25} = 2.100 g/mL.

Anal. Calcd for $C_4HBr_2ClF_6O$: C, 12.8; H, 0.27; Cl, 9.47; Br, 42.7. Found: C, 13.0; H, 0.39; Cl, 9.99; Br, 42.3.

1-Chloro-2-bromo-1-trifluoromethoxy-3,3,3-trifluoropropene (6). A mixture of 90 mL (0.6 mol) of $CF_3CH=CClOCF_3$ and 34 mL (excess) of bromine was stirred and irradiated with a sunlamp for 3 h (a test of a small sample showed at this time disappearance of the C=C band in the IR and a shift of the C–H band from 3125 to 2985 cm^{-1}). The whole solution was then slowly added to a stirred mixture of 30 mL of o-dichlorobenzene, 500 mL of water, and 100 mL of triethylamine. After the exothermic reaction subsided, the two-phase mixture was stirred for 2 h; then the organic layer was separated and washed twice with dilute hydrochloric acid. It was then run through a bed of alumina and was finally fractionated on a spinning band column. After recovery of 10 g of starting material, the main cut boiled at 86–87 °C. The overall yield was 149 g (83.5%), d_{25} = 1.833 g/mL.

Anal. Calcd for C_4BrClF_6O: C, 16.3; H, 0.00, Br, 27.2; Cl, 12.1. Found: C, 16.4; H, 0.09, Br, 26.5; Cl, 12.1.

IR (in CCl_4): 1620 (vs), 1300–1100 (vs), 968 (vs), 876 (vs), 830 (s), 820–706 (br), 696 (s) cm^{-1}.

1-Chloro-2-bromo-1-perfluoro-n-propoxy-3,3,3-trifluoropropene (11). A mixture of 174 g (0.55 mol) of $CF_3CH=CClOCF_2CF_2CF_3$ and 29 mL (excess) of bromine was irradiated with a sunlamp for 2 h. The crude mixture was then diluted with 200 mL of o-dichlorobenzene, placed along with 400 mL of water into a 1 L flask, and 88 mL (excess) of triethylamine was added dropwise to the stirred solution. After stirring overnight, the organic phase was washed twice with dilute HCl; then it was run through a short alumina column. Fractionation on a spinning band column gave 17.5 g of recovered starting material, bp 85–80 °C; the remainder boiled at 121–125 °C, d_{25} = 1.844 g/mL, and was obtained in 185 g (94%) overall yield at a conversion of 90%.

Anal. Calcd for $C_6BrClF_{10}O$: C, 18.4; H, 0.00; Br, 20.7; Cl, 9.02; F, 48.3. Found: C, 18.4; H, 0.28; Br, 22.0; Cl, 8.79; F, 48.1.

IR (in CCl_4): 1620 (vs), 1330 (vs), 1300–1120 (vs), 1100 (vs), 1030 (w), 990 (vs), 948 (w), 935 (m), 851 (m), 830 (m), 806–719 (m, br), 697 (s) cm^{-1}.

Trifluoromethoxy-3,3,3-trifluoropropyne (4). To a suspension of 75 g of zinc–copper couple[12] in 250 mL of dry diglyme, stirred at 120 °C, was added dropwise 50 mL of $CF_3CBr=CClOCF_3$. After a short induction period, the reaction commenced and proceeded exothermally, so that the temperature stayed at ∼140 °C without external heat application. Volatiles were trapped in a −80 °C trap and purified by fractionation. The main product, bp −1 to 0 °C, was obtained in 18 mL (∼50%) yield.

Its IR spectrum has very strong bands at 2326, 1300, 1250, 1160, and 1110 cm^{-1}, with weaker bands at 1366, 1028, and 935 cm^{-1}. The C≡C band is clearly distinguishable from that of $CF_3C\equiv CCl$ at 2257 cm^{-1}, which was also present along with $CF_3CBr=CClOCF_3$ and $CF_3CH=CClOCF_3$, as a minor component in the crude first distillate.

The residual reaction mixture had a strong band at 2150 cm^{-1}, ascribed to $CF_3C\equiv CZnX$, since addition of water resulted in the evolution of gas identified as $CF_3C\equiv CH$ (by IR).

1-Perfluoro-n-propoxy-3,3,3-trifluoropropyne (12). (A) To 20 g of zinc–copper couple stirred along with 0.2 g of anhydrous $ZnCl_2$ in 100 mL of dry diglyme at 150 °C was added dropwise 20 mL (37 g, 0.094 mol) of $CF_3CBr=CClOC_3F_7$. Heating was maintained at such a rate that steady distillation took place and material having bp 40–55 °C was collected. The distillate was combined with about 2 mL of liquid collected in the −80 °C trap behind the receiver. The combined liquids were washed with 150 mL of cold aqueous sodium acetate solution and, after a further water wash, were passed through a short alumina column. The product was obtained in 12 g (46%) yield. Careful fractionation on a spinning band column gave a heart cut, bp 49–50 °C, which was 99% pure by GC. In the course of distillation about half of the product polymerized in the pot.

^{19}F NMR spectrum was consistent with the structure,

$F_3^aCC\equiv COCF_2^bCF_2^cCF_3^d$: a, −52.8 (3 F); b, −131.2 (*J* = 1 Hz, 2 F); c, −88.7 (*J* = 15.1, Hz, 2 F); d, −84.3 (*J* = 15.5 Hz, 3 F) ppm.

(B) A 500-mL flask was fitted with an N_2 inlet, mechanical stirrer, syringe port, and an outlet to a 50 mL dry ice cooled receiver. The system was purged with nitrogen and charged with 300 g of KOH pellets. After heating to 220–240 °C (molten KOH), the nitrogen flow was turned off and 30 mL of $CF_3CH=C(OC_3F_7)_2$ was added dropwise via syringe. After 15 min a slow nitrogen flow was used to drive over all fluorocarbons into the receiver. The product was a 30:70 mixture of $CF_3C\equiv COC_3F_7$ and unconverted $CF_3CH=C(OC_3F_7)_2$; yields were around 95%.

After repeating the above step several times, the combined products were dried by passage through a short alumina column into a distillation flask. A simple still was used to collect the $CF_3C\equiv COC_3F_7$ boiling at 50–52 °C and the $CF_3CH=C(OC_3F_7)_2$ boiling at 116–118 °C.

Since normal fractional distillation of $CF_3C\equiv COC_3F_7$ results in extensive polymerization, the product was redistilled on a spinning band column as a 30–50% solution in Rimar 101, a fluorocarbon solvent of bp 100 °C which is primarily c-$(CF_2CF_2CF_2CF(C_4F_9)O)$. Pure product boils at 51.5–52 °C.

IR (in CCl_4): 2300 (vs), 1360 (m), 1330 (vs, br), 1260–1060 (vs), 980 (vs), 948 (vs), 893 (w), 873 (vw), 806–714 (s, br) cm^{-1}.

Poly(trifluoromethoxy-3,3,3-trifluoropropyne) (4)$_n$. Freshly redistilled $CF_3C\equiv COCF_3$ (about 13 mL) was sealed in a heavy-walled ampule. On standing at room temperature over the weekend, the contents solidified. The ampule was cooled to −80 °C and opened, and the volatiles were distilled out. About 2 mL of liquid was collected, the IR of which showed, apart from unreacted $CF_3C\equiv COCF_3$, the presence of $CF_3CH=CClOCF_3$ and of carbonyl-containing impurities (1820, 1720 cm^{-1}).

The polymer, obtained in 16 g yield, does not melt on a block up to 320 °C. It sublimes without melting in a Bunsen flame when the spatula reaches red heat. The polymer is amorphous under the microscope and has a C=C absorption at 1670–1640 cm^{-1} in the IR.

Poly(perfluoropropoxy-1-perfluoropropyne) (12)$_n$. Pure samples of $CF_3C\equiv COCF_2CF_2CF_3$ polymerized on standing for 24 h at room temperature to transparent, slightly reddish solids. Drying in vacuo at 230 °C gave a colorless solid.

Anal. Calcd for $C_6F_{10}O$: F, 68.4. Found: F, 68.4.

No glass transition was noted between −120 and 380 °C; 10% weight loss occurs at 420 °C under N_2 and at 380 °C in air.

General Procedure for High-Pressure Polymerization. Small-scale polymerizations at 500–4000 atm were carried out in platinum tubes. Platinum tubing of 13-mm diameter was cut to the desired length (20 cm) and sealed at one end. The tube was flamed out while attached to a vacuum line, cooled to 25 °C, and filled with nitrogen. After further cooling in wet ice/acetone, the required amount of perfluoropropionyl peroxide solution in F-113 was syringed into the chilled tube. After freezing the 3P/F-113 solution in liquid nitrogen, the tube was evacuated and the appropriate monomers were distilled in via the vacuum line system. The top was then pinched off with a C clamp and melt sealed.

The cold platinum tube was then transferred to a shaker tube, pressurized with nitrogen to the desired pressure, and allowed to stand at 25 °C for 24 h. Since the platinum tube readily collapsed, the pressure was transferred to the contents within the tube.

After removal from the shaker tube, the platinum tubes were refrozen in liquid nitrogen, opened, and attached to a vacuum line. The tube was allowed to warm up under vacuum and any volatiles were condensed in a trap for analysis. Finally, the tube was cut open to remove any polymer. The results are summarized (see Table I in supplementary material).

Volatiles were analyzed by IR, checking for the presence of –C≡C– and –C=C– absorptions in the region of 2440–2220 and 1640–1590 cm^{-1}, respectively.

All viscosity measurements were carried out at 30 °C in Freon E2. In all cases very dilute solutions (∼0.015 g/L) were employed.

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Effects of Bridgehead Substituents on the Mass Spectral Fragmentation Pathways for the 9-Methyl-9-azabicyclo[3.3.1]nonane Framework

Herman O. Krabbenhoft[1]

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109

The mass spectral fragmentations of the 9-methyl-9-azabicyclo[3.3.1]nonane nucleus functionalized at a bridgehead position with H (1), OH (2), OCH₃ (3), OCOCH₃ (4), NHCH₃ (5), Cl (6), and CN (7) are reported. The productions of the base ions were found to be strongly dependent on the nature of the bridgehead substituent. For the parent amine 1 the base ion is formed by α cleavage of the 1,2 bond, loss of cyclopropane (carbons 2, 3, and 4), and loss of hydrogen from carbon 6. For the bridgehead hydroxy and methylamino derivatives the most abundant ions arise from α scission of the 1,2 bond, loss of ethylene (carbons 2 and 3), and loss of hydrogen from carbon 5. Bridgehead methyl ether 3 gives rise to its base peak via α cleavage of the 1,2 bond, loss of cyclopropane, and loss of the O-methyl group. Acetate 4 takes part in a Hofmann–Loeffler type abstraction of an acetyl hydrogen by the initially generated nitrogen radical cation (in concert with the expulsion of ketene), followed by α cleavage of the 1,2 bond and loss of cyclopropane in route to its base peak. The α-amino chloride merely expels chlorine to produce its base ion. The 1-cyano derivative 7 forms its base peak by cleavage of the 4,5 bond, formation of an iminium radical by attack of the carbon radical (produced from the previous α cleavage) on the cyano carbon, homolytic scission of the bond between carbon 1 and the iminium carbon, and finally cleavage of the 2,3 bond. Other less important fragmentation sequences are also discussed.

Investigations focused on the performance of bridgehead functionalized bridged bicyclic compounds have proven to be of tremendous value in the elucidation of the relationships between structure and reactivity.[2,3] During the last few years heterobicyclic materials (in which the heteroatom is adjacent to the bridgehead carbon atom which bears the bridgehead functionality) have been subjected to various theoretical and experimental tests, the results of which have provided some very interesting postulates pertaining to the relative degrees of stabilization (or destabilization) by resonance and/or induction via the heteroatom.[4–6] In this report, the substantial effects of a bridgehead substituent on the electron-impact-induced fragmentation patterns for the 9-methyl-9-azabicyclo[3.3.1]nonane (granatanine) system (1–7) are described.[7,8]

1, X = H
2, X = OH
3, X = OCH₃
4, X = OCOCH₃
5, X = NHCH₃
6, X = Cl
7, X = CN
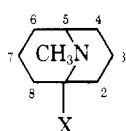
Previous reports concerned with interpretations of the mass spectra of compounds in the granatanine system have dealt exclusively with substrates having functionality at the 3 position.[9] In all cases, homolytic cleavage of a carbon–carbon bond adjacent to the nitrogen was shown to be the primary fragmentation process leading ultimately to the production of the base ion.[10] In a recent report from this laboratory it was disclosed that, with certain 1-alkoxy-9-methyl-9-azabicyclo[3.3.1]nonanes, the Hofmann–Loeffler hydrogen-abstraction process can compete effectively with the usual α-cleavage mechanism.[11] For three of the compounds whose mass spectra have been examined in the present study, scission of the 1,2 bond does *not* ultimately result in the formation of the base ion. Furthermore, for the remaining four compounds, wherein cleavage of the 1,2 bond is the predominant initial fragmentation step, the nature of the bridgehead substituent exerts considerable influence on subsequent fragmentations, particularly those leading to the base ions.

Results and Discussion

Table I collects the relative intensity data for the important ions derived from electron impaction of the various bridgehead functionalized 9-methyl-9-azabicyclo[3.3.1]nonanes 1–7.[12] Inspection of the data reveals that two fragmentation pathways are common to all of the compounds investigated; these sequences are outlined in Chart I. Following α cleavage to produce a′, cyclopropane (or its equivalent) is expelled to provide radical cation b, which in turn goes on to cation c by the loss of a hydrogen atom.[13] In support of the process involving the expulsion of cyclopropane (a′ → b), appropriate