The Reactions of the Dimers of Hexafluoropropene with *O*-Nucleophiles

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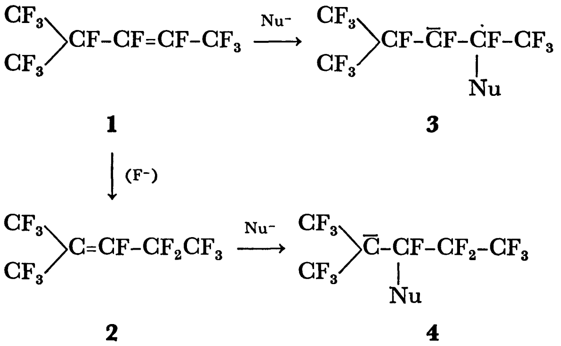
The reactions of the dimers of hexafluoropropene with alcohols and phenol in the presence of triethylamine, and with sodium alkoxides and phenolate were carried out. Of the two dimers, perfluoro-2-methyl-2-pentene (Dimer **2**) was much more reactive than perfluoro-4-methyl-2-pentene (Dimer **1**). While the dimer **2** and *O*-nucleophiles gave various addition and substitution products very easily, the dimer **1** reacted only with sodium alkoxides to give trialkoxylated products.

Hexafluoropropene is known to oligomerize readily in the presence of a base or a fluoride ion, giving a mixture of its dimers and trimers.[1-4] The dimers are composed of perfluoro-4-methyl-2-pentene (**1**) and perfluoro-2-methyl-2-pentene (**2**), the former being predominant. However, because of the negative hyperconjugation and the electron-withdrawing inductive effect of the trifluoromethyl groups adjacent to the double bond, **2** is thermodynamically more stable than **1**, and the latter is converted into **2** by heating with potassium fluoride.[2-5] Further, **2** is likely to be more susceptible to the nucleophilic attack than **1**, because the supposed anionic intermediate, **4**, must be more stable than another intermediate, **3**.



We wish to report several results derived from the reactions of these dimers with alcohols and phenol.

Results and Discussion

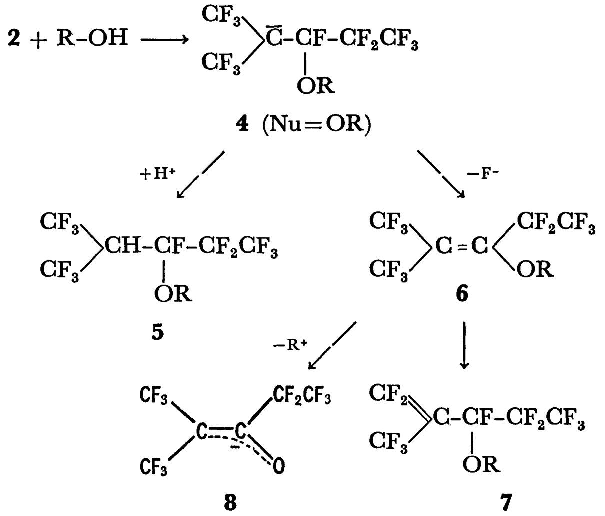
Reactions with Alcohols and Phenol in the Presence of Triethylamine. While the dimer **1** was unsusceptible to methanol under basic conditions, even when heated for a prolonged time, the dimer **2** and methanol in the presence of an equimolar amount of triethylamine reacted readily at −10—0 °C. They gave a mixture of addition and substitution products [**5** : **6** (R=Me)= 1 : 1; total, 44%], together with highly boiling products. These by-products seem to have resulted from further reactions of **6**. For example, a reactive terminal olefin, **7**, or a dealkylated ambident anion, **8**, might be formed[6] and might then react further with alcohol to give other products.

When a catalytic amount of triethylamine was used in the above reaction, the adduct, **5**, was obtained in a good yield (69%), together with a trace of the substituted product, **6**.

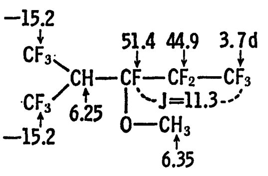
Ethanol reacted with the dimer **2** more moderately. In the presence of an equimolar amount of triethylamine, they gave a mixture of addition and substitution products, **5** and **6** (R=Et), in a ratio of 2 : 5; the total yield was rather good (71%). When the mixture was treated with aqueous potassium hydroxide, **6** was obtained as a pure product.

With a catalytic amount of triethylamine, ethanol and the dimer **2** did not react at low temperatures. At room temperature, however, they gave the substitution product (**6**) and that alone. The prevailing formation of **6** in this case is presumed to be due to the bulky OEt group, which prefers the sp^2 carbon of **6** rather than the sp^3 carbon of **5**.

This was supported by the results of the reaction between the dimer **2** and phenol. This weak and bulky nucleophile, in the presence of triethylamine, also reacted readily with **2** in diethyl ether, thus giving the substitution product, **6** (R=Ph), exclusively (65%).

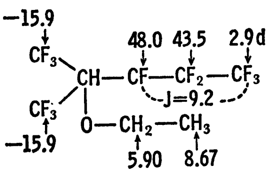


The structures of the products described above were established from various spectral data, especially the ^{19}F NMR. The chemical shifts and some of the coupling constants were as follows:*

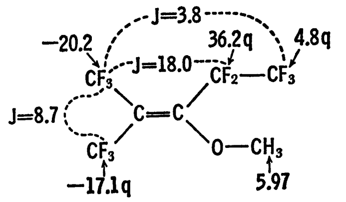


5 (R=Me)

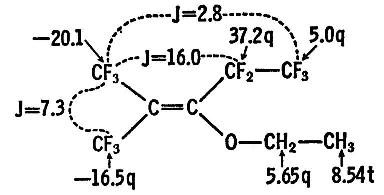
* All the ^{19}F NMR chemical shifts throughout this article are given in δ ppm from external trifluoroacetic acid. The PMR chemical shifts and the coupling constants are given in τ and Hz, as usual. All were taken in neat.



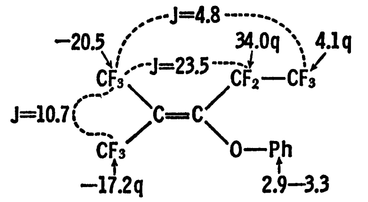
5 (R=Et)



6 (R=Me)

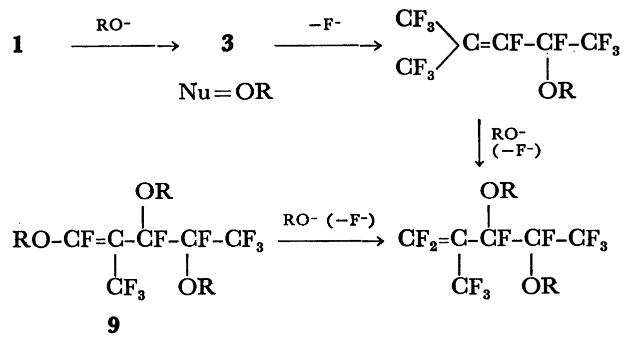


6 (R=Et)



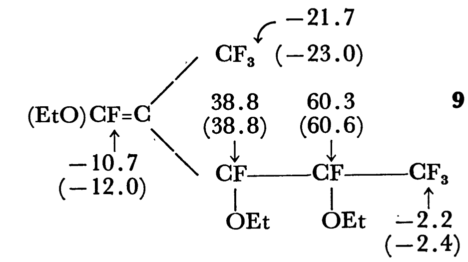
6 (R=Ph)

The Reactions with Sodium Alkoxides and Phenoxide. Althouth the dimer **1** did not react with alcohols in the presence of a base, it was readily attacked by sodium alkoxides at low temperatures from −10 to 0 °C. When three moles of sodium ethoxide in ethanol were used, a triethoxy-substituted product, **9**, was obtained. The reaction seemed to proceed according to an S_N-2′-like mechanism as follows:



The crude product of this reaction partly decomposed on distillation *in vacuo*, probably because it contains a small amount of an addition product containing the EtO–CF_2–CH⟨ group, which is hydrolyzed easily to an ester, EtO–C(=O)–CH⟨.

The crude product was then treated with an aqueous potassium hydroxide solution prior to distillation. The yield of the purified product thus obtained was 32%. This triethoxylated product was composed of two isomers in a ratio of 2 : 3; they were separated by means of a preparative gas chromatography. These isomers gave almost identical patterns in their IR, ^{19}F, and ^1H NMR and mass spectra. In the IR spectra, both compounds gave a strong absorption band at 1675 cm^{-1} due to the C=C double bond. In the mass spectra, strong peaks at *m/e* 333 (M^+−OEt), 233 (M^+−CF(OEt)–CF_3), and 137 ($O=\overset{+}{C}-C(CF_3)=C=O$) were observed for each isomer. The ^{19}F NMR chemical shifts are shown below. From these results, we assigned for the *E* and *Z* isomers to them, though we could not ascertain which was which.



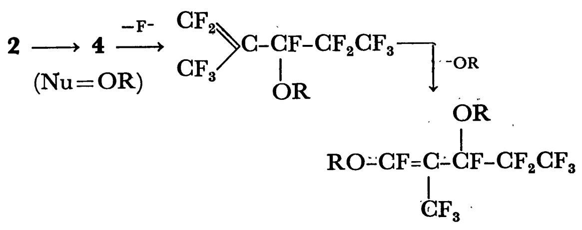
9 (R=Et)

(The values in parentheses are of the minor component)

Even when the reaction was carried out using an equimolecular amount of sodium ethoxide, the triethoxy compound was formed. This means that the second and the third steps of the above scheme proceed very fast, and that the first alkoxylation is the rate-determining step.

In the same manner, the dimer **1** and sodium methoxide gave similar trimethoxylated products, also composed of two isomers. Although the attempt to separate them from each other was unsuccessful, even by means of preparative gas chromatography, the IR and NMR spectra of the mixture supported the structure **9** (R=Me).

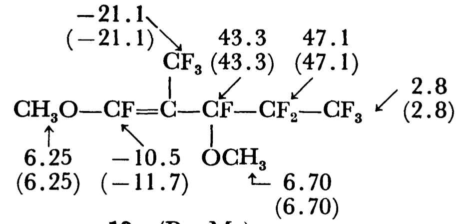
The dimer **2**, in contrast with **1**, gave dialkoxy compounds in a reaction with sodium alkoxide. The dimer **2** with a 2.2-molar amount of sodium ethoxide in ethanol below 0 °C yielded a diethoxy substituted product, **10** (R=Et). Vacuum distillation after treatment with an aqueous sodium hydroxide solution gave a pure compound in a 52% yield. The reaction path seemed to be as follows:



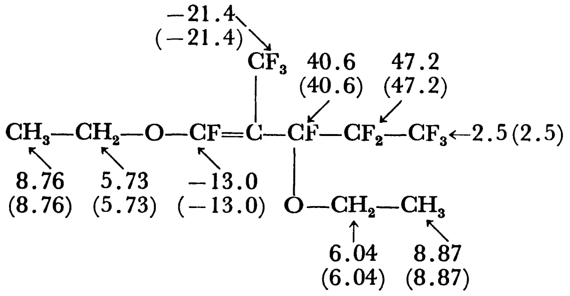
10

This ethoxylated product was also a mixture of two isomers in a ratio of 1 : 3. Since the IR, NMR and mass spectra of the mixture strongly supported the structure **10**, these two compounds are also presumed to be *E* and *Z* isomers. Sodium methoxide gave a similar dimethoxy substituted product in a 51% yield. This was also a mixture of two isomers (1 : 3). The

^{19}F NMR spectra for these products are shown below.



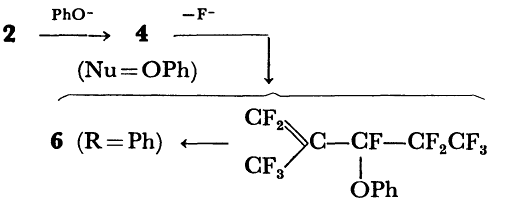
10 (R=Me)



10 (R=Et)

(The values in parentheses are of the minor component)

Sodium phenoxide, a weaker nucleophile than sodium alkoxide, was unreactive to the dimer **1**. However, the dimer **2** in diethyl ether reacted even below 0 °C, giving a mixture of monophenoxylated internal and terminal olefins, **6**(R=Ph) and **11**(2 : 11), in a total yield of 70%.



(**11**)

These phenoxylated olefins were separated from each other by means of preparative gas chromatography, and their structures were elucidated from their IR and ^{19}F NMR spectra. The IR spectrum for **11** revealed the presence of the terminal double bond by its absorption at 1725 cm^{-1}, whereas that for **6** (R=Ph) showed the absorption due to the internal double bond at 1647 cm^{-1}. As for the ^{19}F NMR spectra, **11** gave the characteristic signals for CF_2=, which appeared at −15.0 and −17.7 ppm.

When a mixture of these two isomers (**6** : **11**=3 : 1) was treated with a catalytic amount of triethylamine in diethyl ether at room temperature, only **6** (R=Ph) was obtained. This means that the internal olefin (**6**) is thermodynamically more stable than the terminal olefin (**11**), as was previously known, and that the latter is easily converted into the former.

Experimental

Reaction of Perfluoro-2-methyl-2-pentene (Dimer 2) with Methanol in the Presence of Triethylamine. Into a mixture of the dimer **2** (9.0 g, 0.03 mol) and methanol (15 ml), was added dropwise a solution of triethylamine (3.03 g, 0.03 mol) in methanol (15 ml) at −10—0 °C. After 10 min of stirring at 0 °C, the reaction mixture was poured into dilute hydrochloric acid; the oily matter thus separated was washed with water and dried over magnesium sulfate. Distillation at an ordinary pressure gave an oil (4.2 g, 44%), bp 96—102 °C, which was a mixture of 2-trifluoromethyl-3-methoxy-1,1,1,3,4,4,5,5,5-nonafluoropentane (**5**, R=Me) and 2-trifluoromethyl-3-methoxy-1,1,1,4,4,5,5,5-octafluoro-2-pentene (**6**, R=Me) in a ratio of 1 : 1, based on the ^{19}F NMR spectrum.

When a catalytic amount of triethylamine (0.5 g, 0.005 mol) was used in this procedure, the addition product **5** (6.8 g, 69%), bp 98—99 °C, was obtained exclusively.

Found: F, 68.4%. Calcd for $C_7H_4F_{12}O$: F, 68.7%. IR: 2980 (C-H), 1150—1300 (C-F) cm^{-1}. MS: *m/e* 313 (M^+-F), 293 (M^+-HF_2), 259 ($M^+-CH_4F_3$), 213 ($M^+-C_2F_5$), 193 ($M^+-C_2HF_6$).

Reaction of the Dimer 2 with Ethanol in the Presence of Triethylamine. When ethanol instead of methanol was used in the procedure described above, it gave a mixture of 2-trifluoromethyl-3-ethoxy-1,1,1,3,4,4,5,5,5-nonafluoropentane (**5**, R=Et) and 2-trifluoromethyl-3-ethoxy-1,1,1,4,4,5,5,5-octafluoro-2-pentene (**6**, R=Et) (2 : 5), bp 110—115 °C (71%).

After the mixture (6.11 g, **5** : **6**=2 : 3) had been stirred with diethyl ether (20 ml) and a 30% aqueous potassium hydroxide solution (7 ml) for 5.5 h at room temperature, the ethereal layer was separated and washed with dilute hydrochloric acid and water successively. After being dried over magnesium sulfate, the solvent was removed and the residue was subjected to distillation, giving pure **6** (R=Et), bp 113—116 °C, in a yield of 58% (3.5 g).

Found: F, 64.2%. Calcd for $C_8H_5F_{11}O$: F, 64.1%. IR: 1635 (C=C), 1100—1400 (C-F) cm^{-1}.

Reaction of the Dimer 2 with Phenol in the Presence of Triethylamine. Into a solution of the dimer **2** (6.0 g, 0.02 mol) in diethyl ether (15 ml) was added portionwise a solution of phenol (1.88 g, 0.02 mol) and triethylamine (2.23 g, 0.022 mol) in diethyl ether (15 ml) at 0 °C. After 3 h of stirring at room temperature, the reaction mixture was washed with dilute hydrochloric acid, and then with water, and dried over magnesium sulfate. The solvent was then removed, and the residue was subjected to distillation *in vacuo*, giving 2-trifluoromethyl-3-phenoxy-1,1,1,4,4,5,5,5-octafluoro-2-pentene (**6**, R=Ph) (4.8 g, 65%); bp 69—71 °C/19 mmHg.

Found: F, 56.3%. Calcd for $C_{12}H_5F_{11}O$: F, 55.9%. IR: 1647 (C=C), 1100—1400 (C-F) cm^{-1}. MS: *m/e* 374 (M^+), 305 (M^+-CF_3), 186 ($305-C_2F_5$), 77 (C_6H_5).

Reaction of Perfluoro-2-methyl-2-pentene (Dimer 1) with Sodium Alkoxides. Into a mixture of the dimer **1** (9.0 g, 0.03 mol) and ethanol (15 ml), an ethanolic solution of sodium ethoxide (Na, 2.3 g, 0.01 mol and EtOH, 30 ml) was added dropwise, in a course of 1 h, while the temperature was kept at −10—0 °C. After stirring at 0 °C and then at room temperature, both times for 0.5 h, the resulting precipitate of sodium fluoride was filtered off, and the filtrate was poured into water. The separated oily matter was washed with water and refluxed for 16 h with a 15% aqueous potassium hydroxide solution in order to complete the elimination of HF from the contaminated addition product. The oily matter was separated, washed with water, and then dried over magnesium sulfate. Vacuum distillation gave a mixture of two isomers (3 : 2) of 1,3,4-triethoxy-2-trifluoromethyl-1,3,4,5,5,5-hexafluoro-1-pentene (**9**, R=Et) (3.6 g, 32%); bp 111—114 °C/16 mmHg.

Found: F, 45.2%. Calcd for $C_{12}H_{15}F_9O_3$: F, 45.2%. IR: 1675 (C=C), 1000—1400 (C=F) cm^{-1}.

A similar reaction with sodium methoxide in methanol gave an oil, bp 94—97 °C/17 mmHg, in a 57% yield. This was also a mixture of two isomers (3 : 1) of 1,3,4-trimethoxy-

2-trifluoromethyl-1,3,4,5,5,5-hexafluoro-1-pentene (**9**, R=Me). In this case, no treatment with an aqueous alkali solution was necessary.

Found: F, 50.7%. Calcd for $C_9H_9F_9O_3$: F, 50.9%. IR: 1675 (C=C), 1100—1400 (C-F) cm^{-1}.

*Reaction of the Dimer **2** with Sodium Ethoxide.* An ethanolic solution of sodium ethoxide (Na, 1.0 g, in EtOH, 20 ml) was vigorously stirred into the dimer **2** (6.0 g, 0.02 mol), the temperature being kept at −10—0 °C. After 30 min of stirring at 0 °C, the reaction mixture was poured into water; the resulting oily matter was separated, washed with water, and then subjected to refluxing with a 15% aqueous potassium hydroxide solution for 16 h. After washing and drying, distillation *in vacuo* gave a mixture of two isomers (3 : 1) of 1,3-diethoxy-2-trifluoromethyl-1,3,4,4,5,5,5-heptafluoro-1-pentene (**10**, R=Et), bp 81—82 °C/20 mmHg, in a yield of 52%.

Found: F, 54.0%. Calcd for $C_{10}H_{10}F_{10}O_2$: F, 54.0%. MS: *m/e* 352 (M^+), 307 ($M^+-OC_2H_5$), 233 ($M^+-C_2F_5$), 205 ($233-C_2H_4$).

The reaction with methanolic sodium methoxide was carried out in a similar manner. A mixture of two isomers of 1,3-dimethoxy-2-trifluoromethyl-1,3,4,4,5,5,5-heptafluoro-1-pentene (**10**, R=Me), bp 66—68 °C/20 mmHg, was obtained in a 51% yield.

Found: F, 59.9%. Calcd for $C_8H_6F_{10}O_2$: F, 58.6%.

*Reaction of the Dimer **2** with Sodium Phenoxide.* Sodium phenoxide (2.55 g, 0.02 mol) was added portionwise to a solution of the dimer **2** (6.0 g, 0.02 mol) in diethyl ether (30 ml), while the temperature was kept between −15 and 5 °C. Stirring was continued at 0 °C for 30 min and then at room temperature for 1 h. The sodium fluoride thus precipitated was removed by filtration, and the filtrate was distilled *in vacuo*. A mixture, bp 59—61 °C/15 mmHg (5.3 g, 70%), of 3-phenoxy-2-trifluoromethyl-1,1,1,4,4,5,5,5-octafluoropentene-2 (**6**, R=Ph) and 3-phenoxy-2-trifluoromethyl-1,1,3,4,4,5,5,5-octafluoro-1-pentene (**11**) (2 : 11) was thus obtained. These components were separated from each other by means of preparative gas chromatography.

(**11**): Found: F, 56.6%. Calcd for $C_{12}H_5F_{11}O$: F, 55.9%. IR: 1725 (C=O), 1100—1400 (C-F) cm^{-1}. MS: *m/e* 374 (M^+), 305 (M^+-CF_3), 281 (M^+-OPh), 255 ($M^+-C_2H_5$).

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