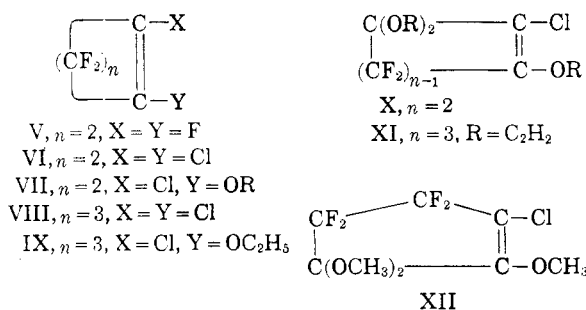
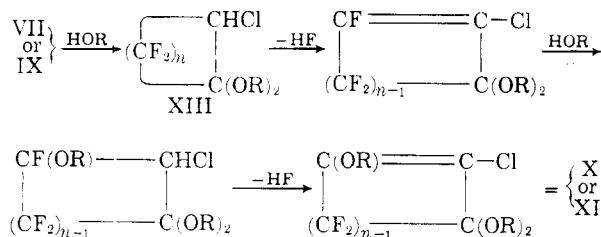


only unsaturated ethers on treatment with alcohols and alkali.



The 1,2-dichlorotetrafluorocyclobutene (VI) gave ethers of structure VII, but with excess alcohol and alkali triethers were formed with the probable structure X.⁷ We have found that the analogous 1,2-dichlorohexafluoro cyclopentene (VIII) behaves in similar fashion with ethanol and alkali to yield the ethyl ether IX. This may be converted with additional ethanol and alkali to the triether, probably XI. In his doctoral thesis,¹¹ Latif reported similar results with VIII and methanol, but claimed structure XII for the triether. Their extreme inertness makes structure-proof of the triethers difficult. Park *et al.*⁷ postulate that their triethers were formed by direct displacement of the "allylic" fluorine atoms of the monoether VII to yield X. Since there is little precedent for "allylic" displacement of fluoride in such highly fluorinated structures, we propose the more plausible mechanism:



Both our monoether (IX) and triether (XI) resisted all efforts to cleave the ether linkages with sulfuric acid, hydriodic acid, or aluminum chloride. They were also inert to chlorine, to bromine and to hydrogen with Adams catalyst at two atmospheres.

EXPERIMENTAL

1-Methoxy-2-hydroperfluoroheptane (I). A solution of sodium methoxide was prepared from 96 g. (3 moles) of methanol and 0.23 g. (0.01 gram atom) of sodium. To this was added dropwise, with stirring and cooling to 5°, 10.0 g. (0.0286 mole) of perfluoro-1-heptene, prepared by pyrolysis of sodium perfluoro-octanoate.¹² The reaction mixture was allowed to come to room temperature under continuous stirring. It was then poured into 200 ml. of cold water. The dense fluoro-organic layer was separated, washed with water, dried over CaCl₂ and distilled, yielding 3.40 g. (31%) of clear colorless product at 129–131°.

(11) L. A. Latif, Ph.D. Thesis, Ohio State University (1952).

(12) J. D. LaZerte, L. J. Hals, T. S. Reid, and G. H. Smith, Jr., *J. Am. Chem. Soc.*, **75**, 4525 (1953).

Anal. Calcd. for C₈H₄O₂F₁₄: F, 69.61. Found: F, 70.42. $n_D^{20} = 1.2992$, $d_4^{20} = 1.635$. M.R. = 43.59. A.R. (F) = 1.30.

1-Ethoxy-2-hydroperfluoroheptane (II). By the same procedure as above, addition of ethanol to perfluoro-1-heptene gave a 46% yield of the ethyl ether (II), b.p. 144–146°.

Anal. Calcd. for C₉H₆O₂F₁₄: F, 67.15. Found: F, 67.05.

1-Trichloromethoxy-2-hydroperfluoroheptane (III). Chlorine gas was bubbled slowly through 2.83 g. (0.0074 mole) of 1-methoxy-2-hydroperfluoroheptane (I) for 8 hr., with continuous illumination from a 300-watt tungsten lamp. The pale yellow reaction mixture was taken up in ether and the solution washed with aqueous NaHSO₃ and dried over Na₂SO₄. Distillation yielded 3.40 g. (70%) of colorless oil at 202–204°.

Anal. Calcd. for C₉H₆OCl₃F₁₄: Cl, 21.91. Found: Cl, 21.66.

The product was recovered unchanged after successive treatments with (a) 98% H₂SO₄ at 100° for 2 hr., (b) ultraviolet irradiation for 7 hr., and (c) di-*t*-butyl peroxide at 100° for 2 hr.

Ethyl 2-hydroperfluoroheptanoate (IV). Four grams (0.01 mole) of 1-ethoxy-2-hydroperfluoroheptane was added to 25 g. of 90% sulfuric acid, and the mixture was heated at 100° for 6 hr. It was then poured into ice water and extracted with ether. The dried ether extract was concentrated and the residue was distilled at reduced pressure, yielding 0.71 g. (19%) of colorless liquid at 66–67° (3 mm.).

Anal. Calcd. for C₉H₈O₂F₁₂: F, 60.94. Found: F, 61.31.

1-Chloro-2-ethoxyhexafluorocyclopentene (IX). To a solution of 9.66 g. (0.17 mole) of potassium hydroxide in 150 ml. of absolute ethanol, 60 g. (0.245 mole) of 1,2-dichlorohexafluorocyclopentene was added gradually while the mixture was stirred and cooled in ice. The mixture was then allowed to come to room temperature, with continued stirring for an additional hour. It was filtered to separate the precipitated potassium chloride, and the filtrate was poured into 700 ml. of ice water. The dense organic layer was separated, dried over CaCl₂ and distilled, yielding 21.9 g. (0.089 mole) of unreacted 1,2-dichlorohexafluorocyclopentene at 90–91° and 29.2 g. (0.115 mole) of product (IX) at 143–144°.

Anal. Calcd. for C₇H₅OClF₆: Cl, 13.92. Found: Cl, 13.97. $n_D^{20} = 1.3774$.

Chlorotriethoxytetrafluorocyclopentene (structure XI postulated). A mixture of 10 g. (0.039 mole) of 1-chloro-2-ethoxyhexafluorocyclopentene (IX), 10 g. (0.17 mole) of potassium hydroxide and 50 ml. of absolute ethanol was refluxed with stirring for 4 hr. The mixture was then filtered and the filtrate poured into 400 ml. of ice water. The dense organic layer was separated, dried over CaCl₂ and distilled, yielding 5.81 g. (49%) of product at 224–225°.

Anal. Calcd. for C₁₁H₁₁O₃ClF₄: Cl, 11.56. Found: Cl, 11.71. $n_D^{20} = 1.4193$.

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Halogen Exchange Reaction of 1,1,1-Tribromo-3,3,3-trifluoropropanone with Silver Fluoride

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To our knowledge, halogen exchange using metal fluorides has not been reported as a method of pre-