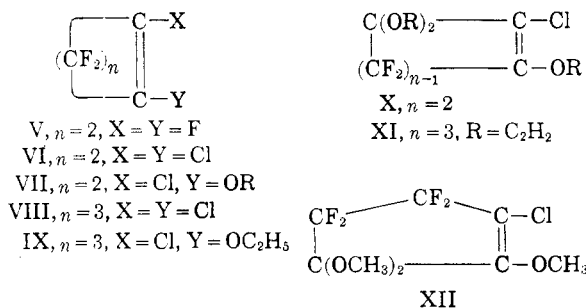
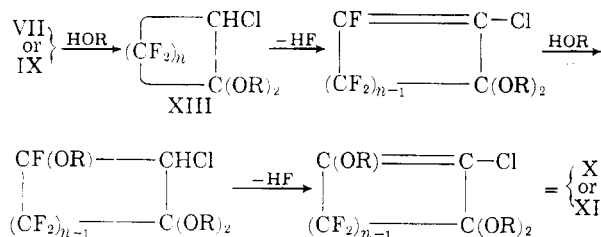


only unsaturated ethers on treatment with alcohols and alkali.



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-

paring highly fluorinated ketones. By the action of dry silver fluoride on the vapors of 1,1,1-tribromo-3,3,3-trifluoropropanone, we have prepared the known 1,1-dibromo-1,3,3,3-tetrafluoropropanone¹ in 81% yield. When the reaction was carried out in dry acetone medium the tribromotrifluoropropanone underwent 84% conversion to approximately equimolar quantities of the dibromotetrafluoropropanone and the hitherto unreported bromopentafluoropropanone. Since 1,1,1-tribromo-3,3,3-trifluoropropanone is readily prepared² by base-catalyzed bromination of commercially available trifluoropropanone, this sequence appears to offer some advantage over less direct routes¹ to bromopolyfluoropropanones. Presumably, it may be extended to the several higher alkyl perfluoroalkyl ketones.³

Bromopentafluoropropanone is a volatile liquid whose vapor fumes in air and is a potent lachrymator. The liquid may be stored in darkness under refrigeration but releases free bromine on standing in light at room temperature. We were unable to isolate any organic product of this decomposition.

EXPERIMENTAL

1,1-Dibromo-1,3,3,3-tetrafluoropropanone. A 100-ml. flask containing 34.9 g. (0.10 mole) of 1,1,1-tribromo-3,3,3-trifluoropropanone² was fitted with a 25 cm. × 1 cm. i.d. Vigreux column, which was loosely packed with dry powdered silver fluoride (about 0.3 mole) and wrapped with heating tape.

Glass tubing connected the top of the column to two Dry Ice-cooled traps in series. The column temperature was held at 125° while the ketone was kept at a gentle reflux (b.p. 147°). The vapors leaving the top of the column remained at 80–82° throughout the reaction. When the pot was nearly empty, the contents of the cold traps were allowed to come to room temperature. The very small quantity of liquid in the second trap vaporized completely below 0°, fuming copiously in the moist air. Distillation of the contents of the first trap yielded 23.3 g. (81%) of 1,1-dibromo-1,3,3,3-tetrafluoropropanone¹ at 81–82°.

Bromopentafluoropropanone. To a vigorously stirred mixture of 50.8 g. (0.40 mole) of silver fluoride and 150 ml. of dry acetone, 34.9 g. (0.10 mole) of 1,1,1-tribromo-3,3,3-trifluoropropanone was added gradually at room temperature. The mixture was then refluxed for 10 hr. After filtration to remove silver salts, the filtrate was distilled through a small fractionating column, yielding 10.5 g. (46%) of bromopentafluoropropanone at 68–72° and 11.0 g. (38%) of dibromotetrafluoropropanone at 81–82°. Redistillation of the lower boiling product gave 10 g. of liquid at 71–72°, colorless when collected, but developing color characteristic of bromine upon standing in light at room temperature. The analytical sample was sealed and protected from light immediately upon distillation.

Anal. Calcd. for C₃OBrF₅: Br, 35.21. Found: Br, 34.92.

Acknowledgment. This work was performed under Contract No. Nonr 1859(01) of the Office of Naval Research.

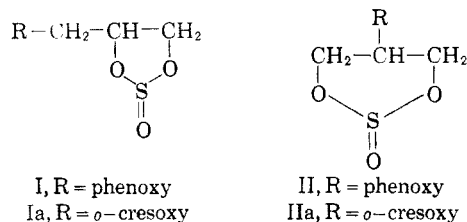
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A Novel Rearrangement of Substituted Cyclic Sulfites

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In the course of the preparation of several cyclic sulfites of pharmacological interest, which will be described in a later publication, it was found that the reaction of 3-chloropropylene sulfite with phenol or *o*-cresol yields two isomeric substances which, for reasons set out in this note, have been identified as the corresponding 1,2 and 1,3 sulfites, I and II.



That the two pairs of isomers obtained from phenol and *o*-cresol are indeed the respective 1,2 and 1,3 sulfites has been proved by analysis, examination of their infrared spectra, and comparison with those of a number of cyclic sulfites as ascertained by other investigators.¹ Peaks which are typical of infrared stretching frequencies of the S=O bond in 1,2 sulfites could be observed at 1220 and 1221 cm.⁻¹ These values agree fairly well with values found by De la Mare and co-workers, and by Szamant and Emerson.¹ The 1,3 sulfites have these bands displaced to 1189 and 1192 cm.⁻¹ respectively. These bands may be attributed to the S=O stretching frequencies which usually appear in this region.² In addition, the 1,3 sulfites have a broad band in the 960 cm.⁻¹ region. (S—O stretching frequency³), which for the 1,2 sulfites is significantly shifted to 950 cm.⁻¹; both bands show similar contours but the 950 cm.⁻¹ band is of lesser intensity. The appearance of several identical absorption bands in both 1,2 and 1,3 sulfites is probably due to incomplete separation of

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(3) K. T. Dishart and R. Levine, *J. Am. Chem. Soc.*, **78**, 2268 (1956), and references therein.

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