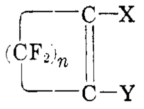
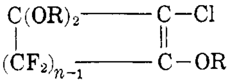
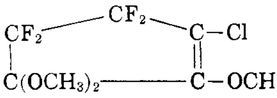
only unsaturated ethers on treatment with alcohols and alkali.



V, $n = 2$, X = Y = F
VI, $n = 2$, X = Y = Cl
VII, $n = 2$, X = Cl, Y = OR
VIII, $n = 3$, X = Y = Cl
IX, $n = 3$, X = Cl, Y = OC_2H_5

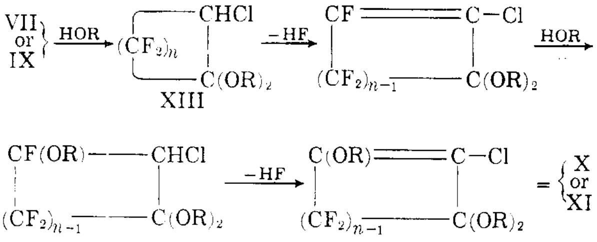


X, $n = 2$
XI, $n = 3$, R = C_2H_2



XII

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 $CaCl_2$ and distilled, yielding 3.40 g. (31%) of clear colorless product at 129–131°.

Anal. Calcd. for $C_8H_4OF_{14}$: F, 69.61. Found: F, 70.42. $n_{\mathrm{D}}^{20} = 1.2992$, $d_{20}^{20} = 1.635$. 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 $C_9H_6OF_{14}$: 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 $NaHSO_3$ and dried over Na_2SO_4. Distillation yielded 3.40 g. (70%) of colorless oil at 202–204°.

Anal. Calcd. for $C_8HOCl_3F_{14}$: Cl, 21.91. Found: Cl, 21.66.

The product was recovered unchanged after successive treatments with (a) 98% H_2SO_4 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 $C_9H_6O_2F_{12}$: 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 $CaCl_2$ 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 $C_7H_5OClF_6$: Cl, 13.92. Found: Cl, 13.97. $n_{\mathrm{D}}^{20} = 1.3774$.

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 $CaCl_2$ and distilled, yielding 5.81 g. (49%) of product at 224–225°.

Anal. Calcd. for $C_{11}H_{15}O_3ClF_4$: Cl, 11.56. Found: Cl, 11.71. $n_{\mathrm{D}}^{20} = 1.4193$.

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

DEPARTMENT OF CHEMISTRY
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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-

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(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).

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-tetrafluoropropanone[1] 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 prepared[2] by base-catalyzed bromination of commercially available trifluoropropanone, this sequence appears to offer some advantage over less direct routes[1] 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-trifluoropropanone[2] 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-tetrafluoropropanone[1] 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 C_3OBrF_5: 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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[1] E. T. McBee, O. R. Pierce, and H. W. Kilbourne, *J. Am. Chem. Soc.*, **75**, 4091 (1953).

[2] E. T. McBee and T. M. Burton, *J. Am. Chem. Soc.*, **74**, 3902 (1952).

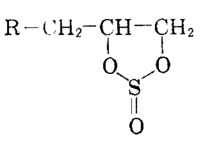
[3] K. T. Dishart and R. Levine, *J. Am. Chem. Soc.*, **78**, 2268 (1956), and references therein.

A Novel Rearrangement of Substituted Cyclic Sulfites

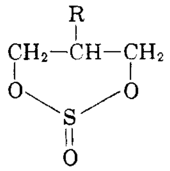
D. BEN-ISHAY

Received June 23, 1958

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.



I, R = phenoxy
Ia, R = *o*-cresoxy



II, R = phenoxy
IIa, R = *o*-cresoxy

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 coworkers, 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 frequency[3]), 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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[1] P. B. D. de la Mare, W. Klyne, D. J. Millen, J. G. Pritchard and D. Watson, *J. Chem. Soc.*, 1812 (1956).

[2] D. Barnard, J. M. Fabian, and H. P. Koch, *J. Chem. Soc.*, 2442 (1949).

[3] J. A. Barltrop and K. J. Morgan, *J. Chem. Soc.*, 4245 (1956).

the isomers, which have boiling points in close proximity. Finally, preparation of the 1,3 sulfites by an independent route from 2-chlorotrimethylene sulfite proves beyond doubt that a rearrangement as postulated above, does take place.

A significant and almost identical difference in the refractive indices for each isomeric pair (0.011 and 0.010) tends to corroborate the formation of these isomeric substances along the lines formulated.

EXPERIMENTAL

3-Chloropropylene sulfite was prepared by the method of De la Mare *et al.*[1] Fractional distillation of the reaction mixture gave 3-chloropropylene sulfite (9.7 g.; 67.3%) b.p. 210°/760 mm., n_D^{25} 1.4807.

Anal. Calcd. for $C_3H_5ClO_3S$: C, 23.0; H, 3.20; Cl, 22.70; S, 20.50. Found: C, 23.5; H, 3.67; Cl, 19.69; S, 22.47.

2-Chloropropane-1,3-diol was prepared by the method of Glattfeld *et al.*[4] The product obtained (60 g.) had b.p. 96–98°/3 mm., n_D^{25} 1.4817.

2-Chlorotrimethylene sulfite was prepared by the method of De la Mare *et al.*[1] Distillation of the reaction mixture under reduced pressure gave, in the temperature range, 70–90°/15 mm. a mixture of *cis-* and *trans*-2-chlorotrimethylene sulfite which was used for reactions with phenol and *o*-cresol without further treatment.

Anal. Calcd. for $C_3H_5ClO_3S$: C, 23.0; H, 3.20; Cl, 22.7; S, 20.5. Found: C, 23.0; H, 3.1; Cl, 22.5; S, 20.3.

Reaction of phenol with 3-chloropropylene sulfite. To absolute ethanol (25 cc.) were added gradually 1.15 g. ($^1/_{20}$ g. atom) of sodium in thin slices so that the mixture boiled steadily; heating was then continued on steam bath and pure redistilled phenol (4.7 g. $^1/_{20}$ mole) added. This was followed by redistilled 3-chloropropylene sulfite (7.9 g.; $^1/_{20}$ mole). After one hour of heating, the mixture was filtered hot and precipitate washed with 3 portions of absolute ethanol. The filtrate and washings were distilled under reduced pressure and the residue under further reduced pressure to yield the following substances:

(*a*) 2-Phenoxy-1,3-propylene sulfite (II) (7.1 g.; 65.7%) white oil, b.p. 77–81°/8 mm., n_D^{25} 1.5130. Infrared spectrum (in chloroform) ν_{max}: 1470(s), 1250(m) (=C—O— grouping), 1189(s) (S=O stretch. vibration), 1071 (m), 1000 (m), 885 (m), 828 (w), 960 (m) (S—O stretch. vibration), 810 (m), 688 (s) cm.$^{-1}$ (s, strong; m, medium; w, weak).

(*b*) 1-Phenoxy-2,3-propylene sulfite (I) (0.9 g.; 8.3%), white oil, b.p. 85–91°/8 mm., n_D^{25} 1.5020. Infrared spectrum (in chloroform) ν_{max}: 1471 (s), 1253 (m) (=C—O— grouping), 1221 (s) (S=O stretch. vibration), 1105 (w), 1080 (w), 1072 (w), 1025 (w), 950 (s) (S—O stretch. vibr.) 885 (w), 841 (m), 810 (m), 688 (s) cm.$^{-1}$

The two fractions gave almost identical analyses.

Anal. Calcd. for $C_9H_{10}O_4S$: C, 50.45; H, 4.7; S, 14.97. Found for II: C, 50.1; H, 4.4; S, 14.7. Found for I: C, 50.1; H, 4.5; S, 14.6.

Reaction of o-cresol with 3-chloropropylene sulfite. Same procedure as for phenol, but 5.5 g. ($^1/_{20}$ mole) of *o*-cresol. The following isomers were obtained:

(*a*) 2-*o*- Cresoxy-1,3-propylene sulfite (IIa) (7.3 g.; 63.4) white oil, b.p. 99–101°/30 mm., n_D^{25} 1.5199. Infrared spectrum (in chloroform) ν_{max}: 1465 (m), 1385 (w), 1330 (m), 1300 (m), 1250 (s) (=C—O— grouping), 1192 (s) (S=O stretch. vibration), 1169 (s), 1104 (s), 1040 (m), 960 (m) (S—O stretch. vibr.), 844 (s).

(*b*) 1-*o*-Cresoxy-2,3-propylene sulfite (Ia), (1.1 g.; 9.6) white oil, b.p. 106–107°/30 mm., n_D^{25} 1.5099. Infrared spectrum (in chloroform) ν_{max}: 1385 (w), 1300 (m), 1250 (s) (=C—O— grouping), 1220 (s), (S=O stretch. vibr.), 1168 (s), 1104 (s), 1040 (m), 950 (s) (S—O stretch. vibr.) 844 (s).

Calcd. for $C_{10}H_{12}O_4S$: C, 52.61; H, 5.3; S, 14.04. Found for IIa: C, 52.5; H, 5.1; S, 13.8. Found for Ia: C, 52.58; H, 5.1; S, 13.85.

Reaction of phenol with 2-chlorotrimethylene sulfite. The procedure was the same as was used for phenol with 3-chloropropylene sulfite. Distillation under reduced pressure yielded 2-phenoxy-1,3-propylene sulfite (II) (8.2 g.; 75.9) white oil of b.p. 81–82°/9 mm., n_D^{25} 1.5131.

Reaction of o-cresol with 2-chlorotrimethylene sulfite. Same procedure as for *o*-cresol with 3-chloropropylene sulfite. Distillation under reduced pressure yielded 2-*o*-cresoxy-1,3-propylene sulfite (IIa) (8.7 g.; 75.6) white oil of b.p. 101–102°/30 mm., n_D^{25} 1.5197.

Examination of both compounds (II and IIa) as synthesized by independent route from 2-chlorotrimethylene sulfite, in the infrared spectrum showed identical contours of the absorption bands particularly in the 1180–1250 cm.$^{-1}$ region.

The infrared absorption spectra were obtained by means of a Perkin-Elmer Model 12c, double beam spectrophotometer, fitted with a sodium chloride prism.

Acknowledgment. I am indebted to Professor H. Heiman for making laboratory space available to me at the Department for Industrial Chemistry of the Israel Institute of Technology, Haifa, and to the Chemistry Department for the infrared spectra. I am grateful to Dr. S. Fruman of this department for helpful discussion.

KIRIAT MOTZKIN, ISRAEL

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[4] J. W. E. Glattfeld, G. Leavell, G. E. Spieth, and D. Hutton, *J. Am. Chem. Soc.*, **53**, 3169 (1931).

Reaction of 2,4-Dinitrophenylhydrazine with Aralkyl Alcohols

SAUL PATAI AND SHELOMO DAYAGI

Received June 24, 1958

The reaction of 2,4-dinitrophenylhydrazine (D-NP) with aldehydes and ketones is generally accepted as being a specific test for the presence of the carbonyl function in organic molecules.[1–3] It is also stated[1] that interfering materials are mainly those that oxidize the hydrazine to form tars, and substances that hydrolyze in the conditions of the reaction to give an aldehyde or a ketone, which may then react with the reagents.

According to Braude[4] further interference may be caused by alcohols containing ethylenic or aromatic substituents conjugated with the carbinol

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[1] S. Siggia, *Quantitative Organic Analysis via Functional Groups*, 2nd ed., John Wiley & Sons, New York, 1954, p. 31.

[2] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, 4th ed., John Wiley & Sons, New York, 1956, p. 97.

[3] K. G. Stone, *Determination of Organic Compounds*, McGraw-Hill Book Co., New York, 1956, p. 73.

[4] E. A. Braude and W. F. Forbes, *J. Chem. Soc.*, 1762 (1951).