

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.

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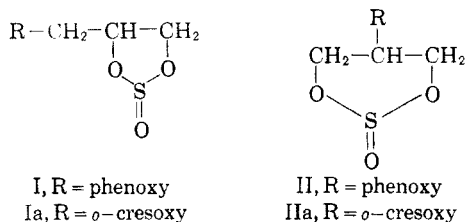
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A Novel Rearrangement of Substituted Cyclic Sulfites

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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

(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.

(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. Bartrop 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 spec-

trum (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.

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Reaction of 2,4-Dinitrophenylhydrazine with Aralkyl Alcohols

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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 stated¹ 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 Braude⁴ further interference may be caused by alcohols containing ethylenic or aromatic substituents conjugated with the carbinol

(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).

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