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A CONVENIENT SYNTHESIS OF VINYL SULFONE

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The synthesis of vinyl sulfone has previously been described (1, 2). However all of the methods used the sulfone of mustard gas or its bromo analog to obtain the unsaturation by some type of dehydrohalogenation. In connection with other work, we desired a method of synthesis which would be useful for large quantities of material and which would not employ the very toxic mustard gas. Convenient syntheses of vinyl sulfone are described here by dehydration of β-hydroxyethyl sulfone and deacetylation of the corresponding diacetate (3).

Conversion of β-thiodiglycol to the sulfone was effected with 27–35% hydrogen peroxide in the presence of phosphoric acid. If this oxidation is carried out in glacial acetic acid with an excess of hydrogen peroxide, the principal product (80%) is a cyclic product, *p*-oxathiane sulfone, obtained by cyclization with loss of water. The sulfoxide was obtained by oxidation in glacial acetic acid with no excess hydrogen peroxide present according to the procedure of Reichstein and Goldschmidt (4). Dehydration of the β-hydroxyethyl sulfone was effected by dropwise addition to anhydrous phosphoric acid at 280°. Small amounts of *p*-oxathiane sulfone also form in this process. Over 50 lbs. of vinyl sulfone have been prepared by this method.

The diacetate of β-hydroxyethyl sulfone was prepared from the diacetate of thiodiglycol with excess hydrogen peroxide in glacial acetic acid in 76% yield. A small amount of *p*-oxathiane sulfone also was formed in this oxidation. Pyrolysis of the diacetate to give vinyl sulfone was effected by dropwise addition under nitrogen through a vertical tube packed with glass beads at 450–500°.

An improved procedure for the preparation of the dibenzoate of β-hydroxyethyl sulfone is reported. Attempted pyrolysis of the dibenzoate of β-hydroxyethyl sulfone was unsatisfactory.

Alcoholysis with sodium ethoxide in ethanol of both the diacetate and the dibenzoate of the β-hydroxyethyl sulfone gave *p*-oxathiane sulfone as the principal product.

Due to its low vapor pressure, vinyl sulfone is only a mild lachrymator and does not necessarily require a hood. It is a delayed action vesicant but can be removed from the skin with soap and water. The pure material should be washed off within a few minutes after exposure; dilute solutions can be tolerated for 15–30 minutes without harm. The blisters are mildly irritating but heal as readily as a burn.

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[1] This paper comprises portions of theses presented by P. M. Kamath and Irving Tashlick in partial fulfillment of the requirements for the degree of Doctor of Philosophy and the degree of Master of Science respectively in the Graduate School of the Polytechnic Institute of Brooklyn.

EXPERIMENTAL[2]

Preparation of vinyl sulfone from β-hydroxyethyl sulfone. To thiodiglycol containing 2% phosphoric acid was added two equivalents plus 1 to 2% excess of 27–35% hydrogen peroxide slowly with cooling. During the first half of the exothermic reactions, the temperature was held below 70° by means of an ice-bath. The solution then was heated to reflux and the remainder of the peroxide was added slowly. After complete addition, the solution was allowed to reflux for 2 to 4 hours until a starch-iodide peroxide test was negative. The water was then removed under reduced pressure to give nearly a quantitative yield of light brown viscous oil which may crystallize, m.p. 50°. The product may be utilized without further purification in the dehydration step.

The first step of the oxidation is quite exothermic and some care is required in the first additions of peroxide. The subsequent oxidation of the sulfoxide is also exothermic, however, the later reaction requires a temperature of about 100° to initiate the reaction. The solution should not be evaporated until the peroxide is consumed.

In a typical experiment, a 5-l. flask fitted with a dropping-funnel and a distillation head was charged with 700 ml. of 85% phosphoric acid which was first dehydrated by heating to 300° at 20 mm. The melt was cooled to 280° and liquid β-hydroxyethyl sulfone was added dropwise. Dehydration took place immediately and vinyl sulfone and water were distilled and collected as two layers. Fractionation of the organic layer gave a 65–70% yield of vinyl sulfone, b.p. 90–92°/8 mm. The product should be stabilized during storage by the addition of 0.05% picric acid. Some foaming occurs during pyrolysis and the phosphoric acid slowly becomes inactive due to accumulation of carbonization products. About 1 kg. of vinyl sulfone can be obtained in 8 hours. The temperature should be maintained at 270–290° and the addition rate regulated according to the amount of foaming. Toward the end of the experiment, crystals of *p*-oxathiane sulfone (6), m.p. 132°, accumulate in the condenser and their appearance in quantity is an indication that the experiment should be stopped. [m.p. of *p*-oxathiane sulfone, 130°, from prolonged heating of $HOCH_2SO_2CH_2CH_2SO_2H$ as a by-product (5)].

Diacetate of β-hydroxyethyl sulfone. The diacetate of β-thiodiglycol was prepared from β-thiodiglycol and acetic anhydride according to the procedure of Clayton and Reid (6). The time of reflux was six hours, 96%, b.p. 150–154°/18 mm., n_D^{23} 1.4729 [b.p. 155–156°/20 mm., n_D^{25} 1.4720, from mustard gas and sodium acetate, authors state good yield (7)]. The diacetate was oxidized according to modification of a general oxidation procedure of Pomerantz and Connor who oxidized α-(alkylthio)amides (8). The diacetate of β-thiodiglycol, 250 g. (1.21 moles), was oxidized in 1800 ml. of a 50–50 mixture of glacial acetic acid and acetic anhydride with 390 g. of 30% hydrogen peroxide. The hydrogen peroxide was added slowly with stirring maintaining the temperature at 0°. The reaction mixture then was allowed to come to room temperature and stand for a few days. The temperature of the reaction usually rose during the first few hours of standing. The solvent was removed under a vacuum and the residue was oxidized with 90 g. of 30% hydrogen peroxide in 600 ml. of acetic anhydride. In this second addition, care should be taken that the hydrogen peroxide decomposes on each addition. This may be accomplished by allowing the temperature to rise from 0° to 20°. If an excess of undecomposed peroxide is present, a violent decomposition can result. After removal of the solvent, 190 g. (65%) of the diacetate of β-hydroxyethyl sulfone was collected by distillation under nitrogen, b.p. 202–203°/3 mm., n_D^{25} 1.4654. An analytical sample was redistilled, b.p. 188.5°/1.5 mm., n_D^{30} 1.4651.

Anal.[3] Calc'd for $C_8H_{14}O_6S$: C, 40.33; H, 5.92.

Found: C, 40.38; H, 6.13.

A small amount of solid *p*-oxathiane sulfone, m.p. 132° (5), distilled over initially.

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[2] All melting points are corrected.

[3] Analyses by Drs. Weiler and Straus, Oxford, England; H. S. Clark, Urbana, Illinois.

When the oxidation was carried out with potassium permanganate in aqueous acetic acid, a 62% yield of *p*-oxathiane sulfone was obtained. The powdered potassium permanganate was added in small quantities at such a rate that the temperature did not exceed 30°. The reaction mixture was stirred for 3 hours and allowed to stand for an additional 24 hours and was worked up by addition of sodium bisulfate to destroy any excess potassium permanganate followed by concentrated sulfuric acid to dissolve the manganese dioxide. The solution was then extracted with ether and the solid obtained was recrystallized from alcohol, m.p. 132°.

β-Hydroxyethyl sulfoxide. The sulfoxide was prepared by the procedure of Reichstein and Goldschmidt (4), 66%, m.p. 112° [68%, m.p. 112°, no analysis reported (4)]. An analytical sample was recrystallized from ethanol, m.p. 112°.

Anal. Calc'd for $C_4H_{10}O_3S$: C, 34.77; H, 7.29.
Found: C, 35.06; H, 7.12.

Oxidation of β-thiodiglycol in acetic acid and excess hydrogen peroxide. β-Thiodiglycol, 24.4 g. (0.2 mole) was dissolved in 200 ml. of a 50–50 mixture of glacial acetic acid and acetic anhydride and to this was added slowly with cooling (as described for the diacetate of β-thiodiglycol), 64 g. (0.56 mole) of 30% hydrogen peroxide. Removal of the solvent gave a residue which was recrystallized from an ethanol-acetone mixture to obtain 24.5 g. (90%) of long flaky plates of *p*-oxathiane sulfone, m.p. 132°.

Dibenzoate of β-hydroxyethyl sulfone obtained by direct oxidation of the sulfide. This sulfone was prepared by oxidation of the dibenzoate of β-thiodiglycol with hydrogen peroxide in a similar manner to that described for the corresponding diacetate sulfone. From 66 g. (0.2 mole) of the dibenzoate of β-thiodiglycol, 200 ml. of a 1:1 mixture of glacial acetic acid and acetic anhydride, and 65 g. (0.58 mole) of 30% hydrogen peroxide, there was obtained a 92% yield of product, after recrystallization of the residue from alcohol, m.p. 94–95°. Fromm and Kohn (9) reported m.p. 95° for material prepared by the oxidation of the dibenzoate of β-hydroxyethyl sulfoxide with potassium dichromate and sulfuric acid (78%) (9).

Saponification of the diacetate and the dibenzoate of β-hydroxyethyl sulfone. The saponification of both the diacetate and the dibenzoate of β-hydroxyethyl sulfone was carried out according to the procedure of Hickinbottom (10).

From 23.8 g. (0.1 mole) of the diacetate, there was obtained 13 g. (96%) of *p*-oxathiane sulfone after recrystallization from ethanol, m.p. 132°. From 33 g. (0.1 mole) of the dibenzoate, there was obtained 11 g. (81%), m.p. 132°, mixture m.p. 132°.

Pyrolysis of the diacetate of β-hydroxyethyl sulfone. The pyrolysis was carried out in a vertical cracking apparatus similar to that described in reference (11). A 20-mm. Pyrex tube, 28-mm. long was packed with 6-mm. glass beads 12 in. in length. This tube was inserted into a muffle furnace in a vertical position, 13 in. of the tube being enclosed. An iron-constantin thermocouple encased in a glass tube was inserted about 5 in. from the top between the wall of the pyrolysis tube and the muffle furnace. An inlet tube and dropping-funnel were inserted at the top of the column and a positive pressure of nitrogen was maintained by introducing dry nitrogen at the top of the column. A 250-ml. flask cooled in an ice-bath was attached to the bottom of the pyrolysis tube and this flask was attached to a trap cooled with Dry Ice. A four to five inch vacuum was applied to the system through the described trap. The cracking tube was flushed with 10 ml. of glacial acetic acid before each experiment to test the apparatus. The column was heated to a temperature of *ca.* 515° and the sulfone diacetate (to which was added 0.5% of *p-tert*-butylcatechol) was introduced at a rate of 60 drops per minute. The products collected in the cooled receiver and were distilled under nitrogen. After removal of acetic acid, the fraction boiling at 105–108°/14 mm. was collected. The yields of vinyl sulfone are 40 to 45%. A fraction was redistilled for analysis, b.p. 107.6°/14.5 mm., n_D^{27} 1.4730 [b.p. 118–121°/20 mm., from the sulfone of mustard gas (2)].

Anal. Calc'd for $C_4H_6O_2S$: C, 40.66; H, 5.11.
Found: C, 40.41; H, 5.14.

SUMMARY

Convenient syntheses of vinyl sulfone by dehydration of β-hydroxyethyl sulfone and deacetylation of the corresponding diacetate are reported.

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REFERENCES

(1) ALEXANDER AND McCOMBIE, *J. Chem. Soc.*, 1913 (1931).
(2) KRETOV, *J. Russ. Phys.-Chem. Soc.*, **62**, 1 (1930).
(3) SCHOENE, U. S. Patent No. 2,474,808, July 5, 1949.
(4) REICHSTEIN AND GOLDSCHMIDT, *Helv. Chim. Acta*, **19**, 301 (1936).
(5) BAUMAN AND WALTER, *Ber.*, **26**, 1124 (1893).
(6) CLAYTON AND REID, *J. Am. Chem. Soc.*, **64**, 908 (1942).
(7) HELFRISCH AND REID, *J. Am. Chem. Soc.*, **42**, 1208 (1920).
(8) POMERANTZ AND CONNOR, *J. Am. Chem. Soc.*, **61**, 3386 (1939).
(9) FROMM AND KOHN, *Ber.*, **54**, 320 (1921).
(10) HICKINBOTTOM, *Reactions of Organic Chemistry*, Longmans, Green & Company. London, 1948, p. 267.
(11) OVERBERGER, FISCHMAN, ROBERTS, AROND, AND LAL, *J. Am. Chem. Soc.*, **73**, 2540 (1951).