[CONTRIBUTION FROM THE RESEARCH CENTER, HERCULES POWDER CO.]

The Synthesis of Sodium Ethylenesulfonate from Ethylene

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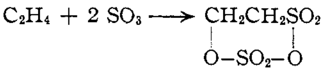
Carbyl sulfate (I) has been prepared in almost quantitative yield by the reaction of sulfur trioxide with excess ethylene in the vapor phase. Treatment of carbyl sulfate with sodium hydroxide has given sodium ethylenesulfonate in 94% yield. In a one-step reaction, in which carbyl sulfate was not isolated, an 89% yield of sodium ethylenesulfonate has been obtained.

Sodium ethylenesulfonate is a readily polymerizable monomer.[1] It was of interest, therefore, to develop a simple, economic synthesis for its preparation. The synthesis of sodium ethylenesulfonate from ethanol has been described,[2] and this paper is concerned with its synthesis from ethylene.

Sodium ethylenesulfonate was prepared by the following series of reactions.



$$C_2H_4 + 2\,SO_3 \longrightarrow \underset{\displaystyle O{-}SO_2{-}O}{CH_2CH_2SO_2} \quad \text{I}$$

$$\text{I} + 2\,NaOH \longrightarrow \underset{\text{II}}{NaO_3SOCH_2CH_2SO_3Na} + H_2O$$

$$\text{II} + NaOH \longrightarrow CH_2{=}CHSO_3Na + Na_2SO_4 + H_2O$$

There are numerous methods described in the literature[3] for the synthesis of carbyl sulfate (I), all based on the reaction of a sulfonating agent (sulfur trioxide, pyrosulfuric acid, chlorosulfonic acid) with ethylene or with a substance which gives ethylene on treatment with the sulfonating agent (ethanol or diethyl ether). Although the original preparation of carbyl sulfate involved a vapor-phase reaction between ethylene and sulfur trioxide,[4] only two subsequent reports[5,6] on this reaction have been found; carbyl sulfate was obtained in unstated yields in both cases. We have now found that carbyl sulfate can be prepared readily in almost quantitative yields by the reaction of sulfur trioxide with excess ethylene in the vapor phase.[7] The apparatus used is shown in Fig. 1 and the procedure is described in the Experimental section.

Carbyl sulfate as prepared by this method was obtained as an amber to brown crystalline solid, smelling strongly of sulfur dioxide. During the reaction a tendency was noted for carbyl sulfate to crystallize on the walls of the steam-heated condenser. This was rather surprising, since the reported melting point of carbyl sulfate is approximately 80°.[4,6] Therefore, a sample was recrystallized from ethylene chloride and found to melt at 107.5–109°. Apparently the previously reported low melting point was caused by contamination with large amounts of sulfur trioxide.

The formation of carbyl sulfate from ethylene and sulfur trioxide is a highly exothermic reaction. From data obtained on the heat of combustion of carbyl sulfate (1240 cal./g.), the heat of formation of carbyl sulfate from ethylene and sulfur trioxide was calculated to be 158 kcal. per mole.[9]

In order to determine the optimum conditions for converting carbyl sulfate into sodium ethylenesulfonate, a series of experiments was carried out in which solutions of sodium ethionate (II) were heated with a 10% excess of sodium hydroxide at various temperatures; the results are shown in Fig. 2. A maximum yield of 88% was obtained at 70° in about two hours; the yields at 60 or 80° were uniformly lower. Although the indicated maximum in the 70° curve is of doubtful significance, it is quite obvious that sodium ethylenesulfonate is not stable to aqueous alkali at 80°, presumably because of base-catalyzed hydration of the double bond.

In actual practice a 94% yield of sodium ethylenesulfonate was obtained by adding carbyl sulfate to a solution of sodium hydroxide at 60°, heating at 70° for two hours, cooling, and neutralizing to *p*H 8. However, in order to avoid handling solid carbyl sulfate, it was found more convenient to prepare sodium ethylenesulfonate by adding carbyl sulfate, as it formed in the reaction, to a caustic solution kept at room temperature, and then heating the solution at 70° for two hours. In this manner an 89% yield of sodium ethylenesulfonate based on sulfur trioxide was obtained.

For many purposes sodium ethylenesulfonate can be used in an aqueous solution. Extraction with glacial acetic acid was found most convenient for isolating crystalline sodium ethylenesulfonate free from inorganic salts; the product was obtained in a purity of about 85%, since it held acetic acid very strongly. However, on a small scale an analytically pure sample was obtained. The use of 95% alcohol instead of acetic acid was inferior; in agreement with the results of Whitmore and Landau,[10] prolonged heating in alcohol yielded an alcohol-insoluble yellow oil which contaminated the product.

Thus, a solution of sodium ethylenesulfonate can be prepared with a yield of about 90% based on sulfur trioxide by treating sulfur trioxide with excess ethylene and heating the product with aqueous sodium hydroxide. The sodium ethylenesulfonate can be separated from inorganic salts with an ef-

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[1] D. S. Breslow and A. Kutner, *J. Polymer Sci.*, in press.

[2] D. S. Breslow, R. R. Hough and J. T. Fairclough, THIS JOURNAL, **76**, 5361 (1954).

[3] See, for example, C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 130–131; C. Ellis, "The Chemistry of Petroleum Derivatives," Chemical Catalog Co. (Reinhold Publ. Corp.), New York, N. Y., Vol. I, 1934, p. 1032.

[4] V. Regnault, *Ann. chim. phys.*, [2] **65**, 98 (1838); *Ann.*, **25**, 32 (1838).

[5] S. R. Merley and O. Spring, U. S. Patent 1,904,160 (1933).

[6] A. Michael and N. Weiner, THIS JOURNAL, **58**, 294 (1936).

[7] It is reported[8] that carbyl sulfate can be prepared in 90% yield by the reaction of ethylene with sulfur trioxide using liquid sulfur dioxide as a solvent. However, the excess sulfur trioxide which is used consumes a large amount of alkali in the succeeding step and requires the separation of sodium ethylenesulfonate from an excessive quantity of sodium sulfate.

[8] K. Daimler and K. Platz, U. S. Patent 1,913,794 (1933).

[9] We are indebted to Drs. John H. Elliott and Richard Mock of this Laboratory for these figures.

[10] W. F. Whitmore and E. F. Landau, THIS JOURNAL, **68**, 1797 (1946).

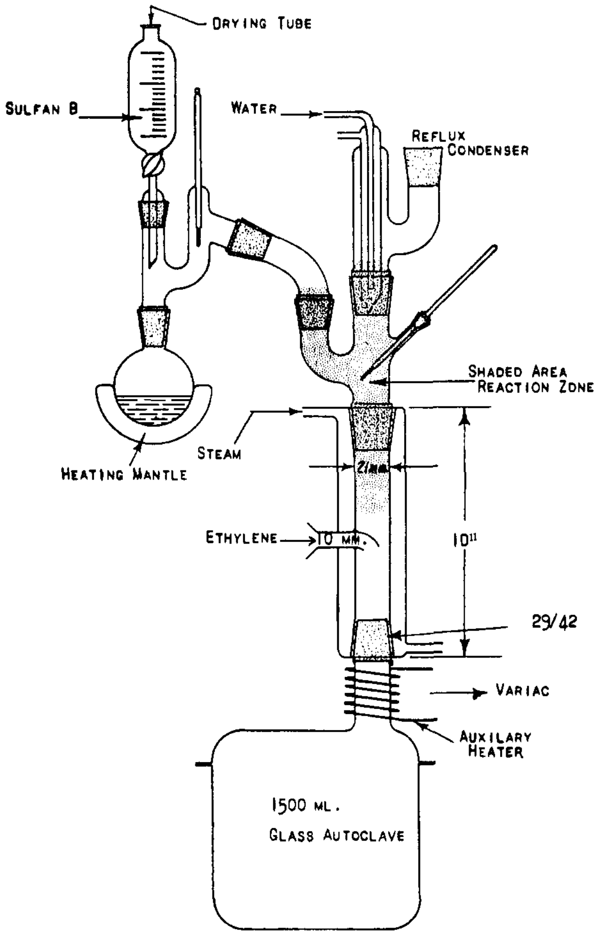

Fig. 1.—Apparatus for the preparation of carbyl sulfate.

ficiency of 85–95% by the use of hot glacial acetic acid. The synthesis of sodium ethylenesulfonate from ethylene is preferred to its synthesis from ethanol; yields are higher and the compound is obtained in a higher state of purity.

Experimental[11]

Reagents.—The sulfur trioxide was a stabilized liquid (Sulfan B, Allied Chemical and Dye Corporation, General Chemical Division). Technical ethylene (Matheson Co.), which analyzed 93% ethylene, was used.

Carbyl Sulfate.—The apparatus used is shown in Fig. 1. The jacket of the reactor was heated with steam and the small heating coil was used to prevent clogging of the inlet to the glass receiver. The small distilling flask was heated by a heating mantle, and 934 g. of Sulfan B was added dropwise to the flask over a period of five hours, the level of liquid in the flask being kept constant. Ethylene was passed in at the rate of 650 ml. per minute; too rapid a rate resulted in loss of carbyl sulfate as a fog in the exit gas. The temperature in the reaction zone varied from 150–165°, depending on the rate of addition of the reactants. Carbyl sulfate formed as a pale yellow liquid, and collected in the receiver as a brown, crystalline solid. No difficulty was encountered if the reaction was carried out rapidly enough to prevent crystallization of carbyl sulfate in the reactor. A residue of 12.6 g. remained in the distilling flask and 1046 g. of carbyl sulfate was obtained, a 96.5% yield based on sulfur trioxide.

Carbyl sulfate was removed from the receiver by heating the walls of the receiver with a free flame until the product melted away from the wall. It was broken up into large lumps and stored in a tight container, since it is a deliquescent solid. The material obtained in this fashion smelled strongly of sulfur dioxide. A sample was recrystallized twice from ethylene chloride; carbyl sulfate was obtained as white needles, m.p. 107.5–109°.

Anal. Calcd. for $C_2H_4O_6S_2$: neut. equiv., 94.1. Found: neut. equiv., 94.0.

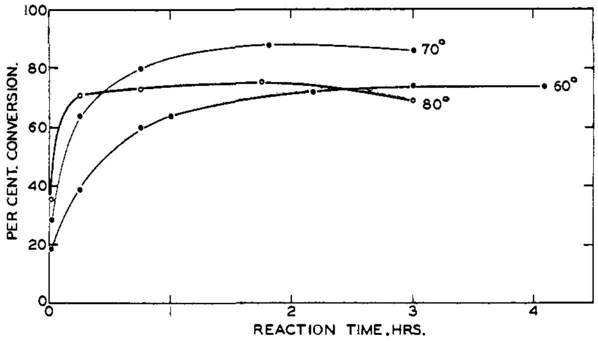

Fig. 2.—Effect of temperature on conversion of sodium ethionate to sodium ethylenesulfonate using 10% excess alkali.

Rate of Conversion of Sodium Ethionate to Sodium Ethylenesulfonate.—A stock solution of ethionic acid was prepared by dissolving 1034 g. of carbyl sulfate in 1800 ml. of cold water; the carbyl sulfate dissolved very slowly. A 100-ml. sample of this solution was neutralized with sodium carbonate at 0–10°. The resulting solution was placed in a 250-ml., three-necked flask equipped with a mechanical stirrer and a reflux condenser, the flask was heated in a constant temperature bath, and the calculated quantity of sodium hydroxide in a known amount of water was added. Ten-milliliter samples were removed periodically, immediately chilled, and titrated to *p*H 8. The resulting solutions were made up to 25 ml. and sodium ethylenesulfonate was determined by quantitative hydrogenation using a palladium–charcoal catalyst. The results obtained are shown in Fig. 2.

Sodium Ethylenesulfonate.—To a solution of 628 g. (15.7 moles) of sodium hydroxide in 4 l. of water was added 918 g. (4.9 moles) of carbyl sulfate in the form of small lumps; the temperature was kept at 60° by cooling. The reaction was heated for two hours at 70°, cooled, and neutralized to *p*H 8 with sulfuric acid. Quantitative hydrogenation showed the presence of 595 g. of sodium ethylenesulfonate, a yield of 94% based on carbyl sulfate.

The neutralized solution was evaporated to dryness on a steam-bath *in vacuo*. The resulting solid was added to 3 l. of glacial acetic acid at 100°, the mixture was filtered hot, and the insoluble material was extracted once more with hot glacial acetic acid. The combined filtrates were evaporated almost to dryness on a steam-bath *in vacuo*. The residue was washed with ether and dried *in vacuo* at 65°. Sodium ethylenesulfonate was obtained as an almost white, crystalline solid, with a purity of 85%; it held acetic acid tenaciously. The recovery was only 78%, but in most cases it was 85–95% complete.

The same procedure on a small scale gave an analytically pure sample after drying to constant weight *in vacuo* at room temperature and then at 80° for two hours.

Anal. Calcd. for $C_2H_3O_3SNa$: H_2 absorption, 1.55; C, 18.46; H, 2.32. Found: H_2 absorption, 1.58, 1.60; C. 18.28, 18.40; H, 2.64, 2.69.

The S-benzylthiouronium salt was prepared, m.p. 144–145° (reported[10] m.p. 145–146°).

Direct Preparation of Sodium Ethylenesulfonate.—The apparatus consisted of a one-liter, three-necked flask equipped with a stirrer, thermometer and outlet tube. In the third neck was placed a 16-inch bulb condenser surmounted by the top of a gas-washing bottle which had the inner tube cut off just below the standard taper joint. Sulfur trioxide was distilled into the system through the inner tube, using the apparatus shown in Fig. 1, and ethylene was passed in through the outer tube. The condenser was heated by steam and the receiving flask was cooled by running water.

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[11] Analyses were performed by the Analytical Division of the Hercules Research Center.

In the flask was placed a 25% sodium hydroxide solution prepared from 126 g. (3.1 moles) of sodium hydroxide and 375 ml. of water. Ethylene was passed in at the top of the condenser at a rate of 460 ml. per minute and 160 g. (2 moles) of sulfur trioxide was distilled into the top of the condenser in about 90 minutes; approximately 1.9 moles of ethylene was used. Carbyl sulfate dripped into the solution as it formed, the temperature of the solution being kept at 25–30°. After all the carbyl sulfate had been added, the solution was heated at 65–70° for two hours, cooled, neutralized to *p*H 8 with 10% sulfuric acid, chilled, and the precipitated sodium sulfate filtered off. The precipitate was washed with two 100-ml. portions of ice-water, the combined filtrates weighing 942 g. This solution analyzed for 12.3% sodium ethylenesulfonate, equivalent to 116 g. or a yield of 89% based on sulfur trioxide.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF CALIFORNIA]

The Acetolysis of *cis*- and *trans*-9-Decalylcarbinyl *p*-Toluenesulfonates

BY WILLIAM G. DAUBEN AND JOHN B. ROGAN[1]

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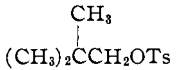
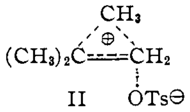
The acetolysis of *cis*- and *trans*-9-decalylcarbinyl *p*-toluenesulfonates has been studied. The rate of reaction of each isomer is the same, the rate being 5 times more rapid than that of neopentyl tosylate. The products of the acetolysis were olefins of the 5,4,0-undecene series showing that the 1,9-bond of the decalin system had migrated. The mechanistic consequences of this type of migration as compared to the 9,10-bond migration found in *trans*-9-decalylhydroperoxide are discussed.

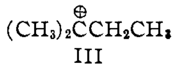
The Wagner–Meerwein rearrangement of neopentyl-type systems (I) to *t*-amyl systems (III) under solvolytic conditions has been the subject of many investigations.[2] Of particular interest is the fact that the formolysis of neopentyl tosylate[3] is as rapid as that of ethyl tosylate despite the appreciable nucleophilic contribution at the rear by solvent in the latter case.[4] This rate of the neopentyl system has been attributed to the anchimeric assistance of the neighboring methyl group,[3] and, accordingly, the transition state would have a bridged-ion structure (II). Compounds of the type IV represent a neopentyl system wherein the migrating group is an integral part of a fused ring system.


$(CH_3)_2\overset{CH_3}{C}CH_2OTs$

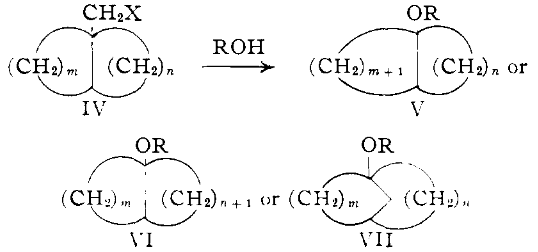
I


$(CH_3)_2\overset{\oplus}{C}\text{---}CH_2$ with bridging CH_3, $OTs^{\ominus}$

II


$(CH_3)_2\overset{\oplus}{C}CH_2CH_3$

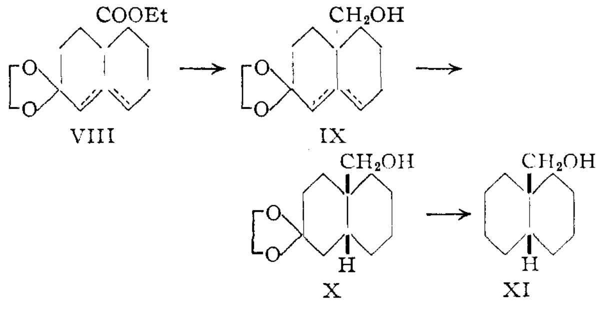
III



The products expected from IV on rearrangement would be of three types (V, VI, VII) depending upon which bond migrated. In view of the spacial requirements demanded in a bridge-ion transition state of type II, the size of the rings and the stereochemistry of the ring juncture as well as the usual migratory appitudes of alkyl groups would be expected to play a role in the rearrangement of compounds of type IV. In order to obtain some preliminary information with regard to the effect of these structural features on the rate and products of reaction, attention has been directed, first, to the decalin ring system (IV, $m = n = 4$) since only two products could be formed.

Synthesis.—The preparation and stereochemical assignment of *trans*-9-decalylcarbinyl tosylate has been described previously.[5–7] In attempts to obtain an entry into the *cis* series, various methods were evaluated and will be discussed below. While this work was being conducted, Idelson, Kronenthal and Becker[8] announced a synthesis of the *cis*-9-decalylcarbinol (XI) and more recently the experimental details of some similar experiments have been reported by Minckler, Hussey and Baker.[9] Their procedures with certain modifications were used to prepare the *cis* isomer.

Lithium aluminum hydride reduction of 2,2-ethylenedioxy - 10 - carbethoxy - Δ⁸ - octalin (VIII) yielded a mixture of products from which a pure crystalline carbinol (IX) was separated. Hydrogenation of the pure ketal IX in ethanol over 5% palladium-on-charcoal yielded 10-(*cis*-2,2-ethyl-



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[1] United States Rubber Co. Predoctoral Fellow in Chemistry, 1954–1955.

[2] A. Streitwieser, *Chem. Revs.*, **56**, 571 (1956).

[3] S. Winstein and H. Marshall, THIS JOURNAL, **74**, 1120 (1952).

[4] A. Streitwieser, *ibid.*, **77**, 1117 (1955).

[5] W. G. Dauben, J. B. Rogan and E. J. Blanz, Jr., *ibid.*, **76**, 6384 (1954).

[6] W. G. Dauben, R. C. Tweit and R. L. MacLean, *ibid.*, **77**, 48 (1955).

[7] A. S. Hussey, H. P. Liao and R. H. Baker, *ibid.*, **75**, 4727 (1953).

[8] M. Idelson, R. L. Kronenthal and E. I. Becker, Abstracts of the 127th Meeting of the American Chemical Society, Cincinnati, Ohio, March 29 to April 7, 1955, p. 49N.

[9] L. S. Minckler, A. S. Hussey and R. H. Baker, THIS JOURNAL, **78**, 1009 (1956).