

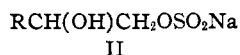
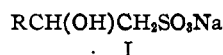
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Addition of Sodium Bisulfite to Alkylene Oxides

BY WALTER M. LAUER AND ARCHIE HILL

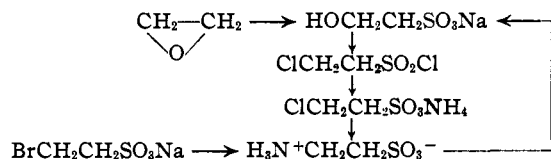
The addition of sodium or potassium bisulfite to an alkylene oxide has generally been assumed¹⁻⁵ to yield the corresponding salt of a β -hydroxy-sulfonic acid, even though the structure of addition compounds of this type has not been rigorously established. The work of Fromm, Kapeller and Taubmann⁶ has introduced an element of doubt, however, since they have reported that the sodium bisulfite addition product obtained from epichlorohydrin, $\text{ClCH}_2\text{CH}-\text{CH}_2$, after boiling with aqueous

sodium hydroxide and subsequent treatment with hydrochloric acid, gave a positive test for sulfur dioxide. They regarded this as evidence for a C-O-S linkage and it therefore became of interest to attempt to decide between the two structures



for the product obtained by the action of sodium bisulfite on an alkylene oxide.

The following series of reactions, which demonstrates the correctness of the β -hydroxysulfonic acid structure (I), was carried out.



The taurine obtained in this manner from the bisulfite addition compound of ethylene oxide was identical with that obtained from sodium β -bromoethanesulfonate by the method of Marvel, Bailey and Sparberg⁷ and the completion of the cycle of transformations by conversion of the taurine to the original addition compound makes a structural rearrangement improbable.

Since the alkali metal salts of β -hydroxysulfonates are water soluble and not infrequently difficult to free of inorganic sulfites, it is conceivable that the presence of sulfur dioxide upon acid

treatment of the addition compound of Fromm, Kapeller and Taubmann can be accounted for in this way.

Experimental

Sodium β -Hydroxyethanesulfonate.—Ethylene oxide was passed into a concentrated solution of sodium bisulfite contained in a 500-cc. three-necked round-bottomed flask fitted with a mechanical stirrer and a reflux condenser. The ethylene oxide was absorbed rapidly with the evolution of heat. The bisulfite addition compound was obtained by evaporating the solution to dryness and extracting the solid residue repeatedly with 95% alcohol. Colorless crystalline sodium β -hydroxyethanesulfonate (m. p. 192–194°) separated from the alcoholic extract in approximately 60% yield.

Anal. Calcd. for $\text{C}_2\text{H}_5\text{O}_4\text{SNa}$: Na, 15.52. Found: Na, 15.68, 15.53.

Acetylation in a manner similar to that used in the case of the bisulfite addition compound of formaldehyde,⁸ followed by crystallization from alcohol, yielded the acetyl derivative.

Anal. Calcd. for $\text{C}_4\text{H}_7\text{O}_5\text{SNa}$: Na, 12.10. Found: Na, 11.82, 11.98.

Potassium β -hydroxyethanesulfonate (m. p. 191–193°) was prepared in a manner similar to that described for the sodium compound. It was easier to obtain in pure form than the sodium salt.

Anal. Calcd. for $\text{C}_2\text{H}_5\text{O}_4\text{SK}$: K, 23.80. Found: K, 23.82, 23.94.

The acetylated product melted at 258–260°.

Anal. Calcd. for $\text{C}_4\text{H}_7\text{O}_5\text{SK}$: K, 18.95. Found: K, 19.08, 18.75.

The myristoyl derivative of the sodium β -hydroxyethanesulfonate, prepared by means of myristoyl chloride, was obtained in the form of a white powder which was rather difficult to purify. A mixture of benzene and water formed an emulsion when shaken with some of this material.

Anal. Calcd. for $\text{C}_{18}\text{H}_{31}\text{O}_5\text{SNa}$: Na, 6.44. Found: Na, 6.76.

β -Chloroethanesulfonyl Chloride.—The directions of Kolbe,⁹ with slight modifications, served for the conversion of either the sodium or potassium β -hydroxysulfonate to β -chloroethanesulfonyl chloride. After the initial vigorous reaction with excess phosphorus pentachloride, the reaction mixture was refluxed gently for two to three hours. The reaction mixture was then poured onto ice. The oily layer was next fractionated; b. p. 13 mm. 86–88° (198–204° at 760 mm.). Twenty grams of the sodium bisulfite addition product and 57 g. of phosphorus pentachloride

(1) Erlenmeyer and Darmstaedter, *Z. Chem.*, 342 (1868).(2) Darmstaedter, *Ann.*, **148**, 125 (1868).(3) Pawschke, *J. prakt. Chem.*, [2] **1**, 86 (1870).(4) Brunel, *Compt. rend.*, **137**, 63 (1903).

(5) German Patent 569,148 (1931).

(6) Fromm, Kapeller and Taubmann, *Ber.*, **61**, 1353 (1928).(7) Marvel, Bailey and Sparberg, *THIS JOURNAL*, **49**, 1833 (1927).(8) Lauer and Langkammerer, *ibid.*, **57**, 2361 (1935).(9) Kolbe, *Ann.*, **122**, 42 (1862); see also ref. 7.

yielded 14 g. of β -chloroethanesulfonyl chloride. Hydrolysis yielded β -chloroethanesulfonic acid.¹⁰

Ammonium β -Chloroethanesulfonate.—The viscous β -chloroethanesulfonic acid was treated with concd. ammonium hydroxide and the solution evaporated to dryness under reduced pressure. The residue was crystallized from alcohol.

Anal. Calcd. for $C_2H_5O_3CINS$: C, 14.86; H, 4.99. Found: C, 15.18; H, 5.25.

Taurine was prepared by heating ammonium β -chloroethanesulfonate for twelve hours in a sealed tube at 105° with an excess of concd. ammonium hydroxide. Upon cooling, taurine separated out. It was recrystallized several times from water and was identical with a sample of taurine prepared by the method of Marvel, Bailey and Sparberg.⁷ Identity was established by means of crystallographic examination.¹¹

Potassium β -Hydroxyethanesulfonate from Taurine.—Acetic acid was added slowly to a hot aqueous solution

(10) Kohler, *Am. Chem. J.*, **20**, 683 (1898).

(11) We are indebted to Dr. E. B. Sandell of the Division of Analytical Chemistry for the crystallographic comparisons reported in this paper.

containing taurine and potassium nitrite. After no further gas evolution, addition of acetic acid was discontinued and the solution was evaporated to dryness. The solid residue was extracted with hot alcohol. The alcohol extract yielded crystalline potassium β -hydroxyethanesulfonate; m. p. $189-191^\circ$.

Anal. Calcd. for $C_2H_5O_4SK$: K, 23.80. Found: K, 23.84.

A crystallographic examination showed this product to be identical with the one obtained by the addition of potassium bisulfite to ethylene oxide. Attempts to convert sodium β -bromoethanesulfonate to sodium β -hydroxyethanesulfonate by means of silver oxide led to products which were unsuited for crystallographic comparison.

Summary

The addition compound obtained by the action of sodium or potassium bisulfite on ethylene oxide has been shown to possess the β -hydroxysulfonic acid structure, a result which was generally accepted, but not demonstrated previously.

MINNEAPOLIS, MINN.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

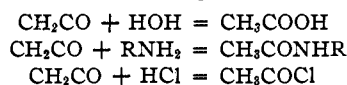
The Reaction of Haloamines with Ketenes

BY GEORGE H. COLEMAN, ROLF L. PETERSON AND GILBERT E. GOHEEN

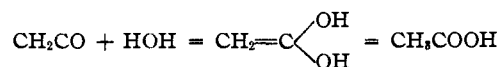
Previous work in this Laboratory has shown that in the addition of nitrogen trichloride to unsaturated compounds¹ a chlorine atom in nitrogen trichloride behaves as though it were electropositive with respect to the NCl_2 group. By analogy it might be assumed that the halogens in other haloamines such as monochloroamine, monobromoamine, dibromoamine and the alkylchloroamines would show a similar behavior. The reactions of these compounds with reducing agents support this assumption. Attempts to bring about addition reactions of some of the haloamines other than nitrogen trichloride with unsaturated hydrocarbons have not been thus far successful. Monochloroamine reacts with Grignard reagents² to form primary amines and ammonia. With many of these reagents the percentage of amine formed is much greater than the percentage of ammonia. Such a result does not seem to be consistent with the assumption that in all reactions the NH_2 group in monochloro-

amine is electronegative with respect to the chlorine.

In the present work a study was made of the reactions of monochloroamine, dibromoamine, nitrogen trichloride and dimethylchloroamine with ketene and diphenylketene. The suitability of ketenes for this work depends on the fact that they are very reactive substances which add diverse molecules in a definite manner, as illustrated in the following well-known examples



The activity of this class of compounds may be due to addition to the carbonyl group first and then rearrangement of the resulting enol form as postulated by Staudinger,³ *e. g.*



Regardless of the mechanism, however, by which the addition takes place, the final product is such that the electropositive portion of the adding molecule is found attached to the carbon farthest

(1) Coleman and co-workers, *THIS JOURNAL*, **48**, 3084 (1923); **49**, 2593 (1927); **50**, 1816 (1928); **50**, 2739 (1928); **50**, 2754 (1928); **51**, 937 (1929).

(2) (a) Coleman and Hauser, *ibid.*, **50**, 1193 (1928); (b) Coleman and Yager, *ibid.*, **51**, 567 (1929); (c) Coleman and Forrester, *ibid.*, **58**, 27 (1936).

(3) Schlenk and Bergmann, "Ausführliches Lehrbuch der organischen Chemie," Franz Deuticke, Vienna, 1932, Vol. I, p. 374.