a drop of 10% sodium hydroxide solution had been added. From the solution, filtered and freed from acetone, 84% of the acetal was recovered.

Benzylidene- and ethylidene trimethylene glycols showed a similar behavior.

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Summary

1. Partition experiments between an aldehyde and a mixture of a 1,2- and a 1,3-glycol, in which a small amount of dil. sulfuric acid is used as a catalyst, indicate that at the equilibrium point there is present a larger proportion of the 6- than of the 5-membered cyclic acetal.

2. It would thus appear that in the cases investigated the 6-membered cyclic acetal rings are more stable towards hydrolysis than the 5- and are also the more easily formed. The results found thus run parallel to those obtained by the acetylene-partition method.[3]

3. With an increase in molecular weight of the aldehyde the amount of 6-membered ring formed increases rapidly over that of the 5-membered ring.

4. Partition experiments between a 1,2- or a 1,3-glycol and a mixture of benzaldehyde and a second aldehyde show that the stability of the cyclic acetal from the latter decreases as the molecular weight of the aldehyde increases.

5. The use of dil. sulfuric acid as a catalyst for the synthesis of cyclic acetals has been shown to be capable of wide application.

6. The following new acetals have been synthesized: butylidene ethylene glycol, butylidene trimethylene glycol and benzylidene ethylene glycol.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

SODIUM HYDROXYLAMINE SULFONATE AS A REAGENT FOR THE PREPARATION OF OXIMES

BY WALDO L. SEMON AND V. RICHARD DAMERELL

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Hydroxylamine, the commonly used reagent for the formation of oximes, is usually prepared from sodium hydroxylamine sulfonate. This latter substance can easily be made by the reduction of sodium nitrite with sodium bisulfite and can be used directly for the preparation of oximes. This not only simplifies the process but is of considerable theoretical and practical importance.

Raschig[1] mentioned that salts of hydroxylamine monosulfonate in

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[1] Raschig, *Ann.*, **241**, 187 (1887).

alkaline solution might be used to prepare oximes, but gave no experimental evidence. Divers and Haga[2] showed this statement to be untrue and that salts of hydroxylamine monosulfonate give a non-reactive salt (such as $KONKSO_3K$, with potassium hydroxide) in alkaline solution and that this decomposes rapidly upon standing. Meyer and Tingle[3] claim that potassium hydroxylamine sulfonate can be used in alkaline aqueous alcoholic solution to prepare oximes and cite the work of Kostanecki[4] who prepared only one oxime by this method. In 1923, Semon[5] prepared acetoxime from the sulfonate in acid solution.

Since there seemed to be some doubt as to the general applicability of this reaction for the preparation of oximes, experiments were undertaken to determine the classes of oximes which could be prepared and also the exact conditions most favorable for the reaction.

Sodium hydroxylamine disulfonate in acid solution is rapidly hydrolyzed to the monosulfonate as has been shown by Wagner.[6] Hence, a solution of the disulfonate as prepared by the method of Semon[5] is rapidly hydrolyzed to the monosulfonate, although in accord with the results of Divers and Haga[7] it may be preserved for months at room temperature with inappreciable further hydrolysis to hydroxylamine sulfate. Thus sodium hydroxylamine monosulfonate solution as prepared[8] (750–800 cc. containing one mole of $HONHSO_3Na$) is a stable and cheap reagent for the preparation of oximes.

A consideration of the following three experiments throws considerable light upon the mechanism of the formation of oximes from monosulfonate. (1) If to a solution of monosulfonate which has been heated to 70°, allowed to cool and stand for several hours, acetone and sodium hydroxide be added to neutrality, there is only a slight reaction with the formation of an inappreciable quantity of acetoxime. This shows that monosulfonate is very slowly hydrolyzed to hydroxylamine at the temperature employed, since any hydroxylamine formed would under the conditions, have reacted to give acetoxime. (2) If acetone be added to monosulfonate, excess of sodium hydroxide added and the mixture heated to 70°, there is an evolution of gas and no acetoxime is formed, showing that monosulfonate and acetone do not react in alkaline solution to give acetoxime. (3) If acetone be added to monosulfonate, the mixture warmed to 70°, allowed to cool and stand for several hours, then neutralized with sodium

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[2] Divers and Haga, *J. Chem. Soc.*, **55**, 766 (1889).

[3] Meyer and Tingle, "Determination of Radicles in Carbon Compounds," John Wiley and Sons, New York, second ed., **1903**, p. 80.

[4] Kostanecki, *Ber.*, **22**, 1344 (1889).

[5] Semon, THIS JOURNAL, **45**, 189 (1923).

[6] Wagner, *Z. physik. Chem.*, **19**, 678 (1896).

[7] Divers and Haga, *J. Chem. Soc.*, **69**, 1665 (1896).

[8] The solution is hereafter termed "monosulfonate."

hydroxide, acetoxime is formed in a yield of 80% or better. Therefore acetone takes an active part in the hydrolysis of acid monosulfonate. The greatly increased rate of hydrolysis (six hours in place of a week) suggests that an intermediate compound is formed even though this may be subsequently hydrolyzed in the solution. This is a general behavior since similar results have been obtained with aldehydes and other ketones. The mechanism of the reaction of aldehydes and ketones with hydroxylamine sulfonates is being investigated more fully and will be reported shortly.

It is evident, therefore, that in certain cases oximes can be formed in acid solution of monosulfonate. Negative results were obtained, however, with certain carbonyl compounds such as benzil and quinone monoxime. This can be due either to the insolubility of the ketone preventing contact and retarding the rate of formation or to the destruction of the oxime in the acid solution.

The preparation of certain representative oximes is described in the following paragraphs.

Acetoxime.—The preparation of acetoxime from acetone has been described in a previous paper[5] and is entirely analogous to that given here for methylethyl ketoxime.

Methylethyl Ketoxime.—To 800 cc. of 1.29 *M* monosulfonate was added 72 g. of methylethyl ketone. The mixture was heated to 70° and allowed to stand for 12 hours in a flask surrounded by cloths to prevent too rapid cooling. The mixture was neutralized with 12 *N* sodium hydroxide solution and the oxime extracted with benzene. Fractional distillation yielded 65 g. of methylethyl ketoxime boiling at 152–154°; yield, 75%, based on the methylethyl ketone.

Acetophenone Oxime.—To 40 cc. of 1.29 *M* monosulfonate was added a solution of 5.0 g. of acetophenone in 20 cc. of alcohol. The mixture was refluxed on a water-bath for five hours, 25 cc. of 12 *N* sodium hydroxide solution was added and the mixture distilled slowly until all of the alcohol and unchanged acetophenone had been removed. The solution was then neutralized with 18 *N* sulfuric acid and the resulting oxime extracted with ether. The extract was dried with anhydrous sodium sulfate and the ether evaporated. The yield was 4.9 g. of acetophenone oxime melting at 59° or 87%, based upon the acetophenone.

When an alkaline solution, such as that obtained after vaporizing the excess of acetophenone, was allowed to cool, white plates of the sodium salt of acetophenone oxime separated. These crystals were filtered from the concentrated solution; in this manner practically all of the oxime was removed. Upon treatment with dilute acid, they yielded pure acetophenone oxime.

***d*-Camphor Oxime.**—To 50 cc. of 1.24 *M* monosulfonate was added a solution of 7.1 g. of camphor in 50 cc. of alcohol. The mixture was refluxed for eight hours on a water-bath, made alkaline by the addition of 50 cc. of 6 *N* sodium hydroxide and the heating continued for two hours. After twelve hours (overnight), 50 cc. more of 6 *N* sodium hydroxide was added, the mixture warmed to 50° to dissolve the oxime, cooled and filtered from any remaining camphor. The clear filtrate was neutralized with sulfuric acid, whereupon the oxime separated as fine, white crystals. These were filtered off, washed and dried. They weighed 5.2 g. and melted at 110°. After recrystallizing from petroleum ether, the camphor oxime melted at 119°. The yield was 67%, based upon the camphor originally taken.

Dimethylglyoxime[9] from Biacetyl Monoxime.—To 77.5 cc. of 1.29 *M* monosulfonate was added 10.1 g. of biacetyl monoxime. The mixture was heated on a water-bath to 80° and allowed to cool and stand for 12 hours. Dimethylglyoxime separated from the acid solution in small, white crystals that were filtered off, washed and dried; yield, 11.0 g., or 95%, based upon biacetyl monoxime; m. p., 240°.

***n*-Butyraldoxime from *n*-Butyraldehyde.**—To 400 cc. of 1.29 *M* monosulfonate was added 36 g. of *n*-butyraldehyde, boiling at 70–75°. The mixture was heated to 70° and allowed to stand for 12 hours in a flask surrounded by cloths to prevent too rapid cooling. The mixture was then neutralized with 12 *N* sodium hydroxide and the oxime extracted with ether. Fractional distillation yielded 30 g. of *n*-butyraldoxime boiling at 150° to 155°; yield, 69%, based upon the butyraldehyde.

β-Benzaldoxime Hydrochloride.—To 400 cc. of 1.29 *M* monosulfonate was added 53 g. of benzaldehyde. The mixture was heated to 70° and allowed to stand for 12 hours in a flask surrounded by cloths to prevent too rapid cooling. Concd. sodium hydroxide was added in quantity sufficient to neutralize the acid and dissolve the oxime. The solution was filtered, nearly neutralized with hydrochloric acid, and carbon dioxide was passed in to acid reaction. The oxime was extracted with ether, the extract dried with anhydrous sodium sulfate, and dry hydrogen chloride passed in to complete precipitation of the oxime, as β-benzaldoxime hydrochloride. β-Benzaldoxime prepared from the hydrochloride by the method of Beckmann[10] melted at 127°; yield, 61 g. of β-benzaldoxime hydrochloride, or 78%, based on benzaldehyde.

β-Furfuraldoxime Hydrochloride.—To 430 cc. of 1.29 *M* monosulfonate was added 52 g. of furfural. The mixture was heated to 70° and allowed to stand for 12 hours in a flask surrounded by cloths to prevent too rapid cooling. Concd. sodium hydroxide solution was added in quantity sufficient to neutralize the acid and dissolve the oxime. The solution was filtered, nearly neutralized with hydrochloric acid, and carbon dioxide passed in to acid reaction. The oxime was extracted with ether, the extract dried with anhydrous sodium sulfate, and dry hydrogen chloride passed in to complete precipitation of the oxime as β-furfuraldoxime hydrochloride; yield, 60 g., or 75%, based on furfural.

β-Furfuraldoxime was prepared by covering the hydrochloride with ether, adding excess of a concentrated solution of sodium carbonate, separating and drying the ethereal extract with anhydrous sodium sulfate. Rapid evaporation of the ether left the β-furfuraldoxime in crystals melting at 89°.

Summary

1. The formation of oximes in acid solution, directly from sodium hydroxylamine monosulfonate, has been shown to be a general reaction.

2. Methods have been described for preparing the following oximes in good yield directly from the monosulfonate: methylethyl ketoxime, acetophenone oxime, *d*-camphor oxime, dimethylglyoxime, *n*-butyraldoxime, β-benzaldoxime hydrochloride and β-furfuraldoxime hydrochloride.

SEATTLE, WASHINGTON

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[9] A method is now being perfected for the large scale preparation of dimethylglyoxime using this reaction.

[10] Beckmann, *Ber.*, **23,** 1685 (1890).