[Contribution from the Department of Chemistry of the University of Washington]

THE PREPARATION OF HYDROXYLAMINE HYDROCHLORIDE AND ACETOXIME

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Hydroxylamine sulfate is a substance which can be readily prepared but for most purposes the hydrochloride is preferable since it is soluble in organic solvents. The method for the preparation of the sulfate was suggested by Raschig,[1] modified by Divers[2] and admirably described by Adams and Kamm.[3] The conversion of the sulfate so prepared into the hydrochloride has previously been rather long and tedious.

In Raschig's method[4] for the preparation of hydroxylamine hydrochloride, sodium bisulfite is added to a cold solution of sodium nitrite and the sodium sulfite which is formed, is removed by passing in an excess of sulfur dioxide. The product is hydrolyzed, sulfate removed by means of barium chloride, filtered and the filtrate evaporated to dryness. The hydroxylamine hydrochloride is separated from the sodium chloride by extraction with absolute alcohol.

The excess of sodium bisulfite which is formed during the removal of the sodium sulfite is liable to react with the sodium hydroxylamine disulfonate to form sodium nitrilo-sulfonate.

$$HON(SO_3Na)_2 + NaHSO_3 \longrightarrow N(SO_3Na)_3 + H_2O. \qquad (1)$$

Hence, it is not surprising that the yield is small (27 to 39% of that calculated on the basis of the sodium nitrite used).

Divers' method is based upon the following series of partial reactions

$$Na_2CO_3 + SO_2 + H_2O \longrightarrow NaHCO_3 + NaHSO_3 \qquad (2)$$

$$2NaNO_2 + 2NaHSO_3 \longrightarrow 2NaOH + 2ONSO_3Na \qquad (3)$$

$$2NaOH + 2SO_2 \longrightarrow 2NaHSO_3 \qquad (4)$$

$$NaHCO_3 + SO_2 \longrightarrow NaHSO_3 + CO_2 \qquad (5)$$

$$2ONSO_3Na + 2NaHSO_3 \longrightarrow 2HON(SO_3Na)_2 \qquad (6)$$

which give when summarized

$$Na_2CO_3 + 2NaNO_2 + 4SO_2 + H_2O \longrightarrow 2HON(SO_3Na)_2 + CO_2. \qquad (7)$$

The next step is the hydrolysis.

$$2HON(SO_3Na)_2 + 4H_2O \longrightarrow (NH_2OH)_2H_2SO_4 + Na_2SO_4 + 2NaHSO_4. \qquad (8)$$

These reactions are carried out by passing sulfur dioxide into a cooled solution (0°) of sodium carbonate and sodium nitrite. When the solution becomes acid it is warmed to 90° and kept at that temperature for 48 hours in order to hydrolyze the sodium hydroxylamine disulfonate. This method is sound in theory and works out well in practice, giving yields of 50 to 80%.

However, Reactions 2 and 5 are markedly exothermal. The heat evolved lowers the efficiency of the cooling. By allowing these reactions to take place previous to

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[1] Raschig, *Ann.*, **241**, 161 (1887).

[2] Divers, *J. Chem. Soc.*, **69**, 1665 (1896).

[3] Adams and Kamm, This Journal, **40,** 1283 (1918).

[4] Biltz and Biltz, "Laboratory Methods of Inorganic Chemistry," trans. Hall and Blanchard, John Wiley and Sons, New York, **1909,** first ed., p. 156.

Reactions 3, 4 and 6 it was found possible to decrease considerably the amount of ice needed for cooling and to cut the time necessary for the reduction in half.

Raschig[1] mentioned that it was possible to prepare oximes directly from sodium hydroxylamine disulfonate. His findings have been confirmed and in this present method the cold solution of sodium hydroxylamine disulfonate is mixed with acetone and warmed to 70° at which temperature the formation of oxime takes place.

$$2HON(SO_3Na)_2 + 2H_2O + 2CH_3COCH_3 \longrightarrow \{(CH_3)_2CNOH\}_2H_2SO_4 + Na_2SO_4 + 2NaHSO_4. \qquad (9)$$

The acetoxime is now in an acid solution and cannot be extracted from it directly. Accordingly, the solution is neutralized with sodium hydroxide, whereupon the acetoxime partially separates as an oily layer. The remainder can easily be distilled with steam.

Janny[5] has shown that acetoxime can be hydrolyzed by heating with hydrochloric acid. To secure hydroxylamine hydrochloride, therefore, all that is necessary is to add an excess of hydrochloric acid to the acetoxime, prepared as described, distil the acetone and evaporate the solution to dryness.

$$(CH_3)_2CNOH + H_2O + HCl \longrightarrow (CH_3)_2CO + NH_2OH,HCl. \qquad (10)$$

Preparation of Hydroxylamine Hydrochloride.[6]—A solution of 325 g. of dry soda ash is made in 900 cc. of water and saturated with sulfur dioxide. The hot solution is now cooled in running water and finally in a freezing mixture. This is added slowly (about 20 to 30 minutes) to a solution of 410 g. of technical (95%) sodium nitrite dissolved in 1.5 liters of water to which 1.5 kg. of crushed ice has been added and which is contained in a 5-liter round-bottom Pyrex flask fitted with a mechanical stirrer and an inlet tube for sulfur dioxide. The entire mixture is kept immersed in a freezing mixture (5 parts of ice to 1 of salt) and the temperature maintained always below 0°. The solution becomes strongly alkaline during the addition of the sodium bisulfite. While the solution is still kept cold (below 0°), sulfur dioxide is passed in until the solution becomes acid. The stream of sulfur dioxide must be continued long enough to bleach the brown color which appears in the flask towards the end of the reaction, and the temperature rise which tends to take place at this stage must be carefully guarded against. The acid solution now contains sodium hydroxylamine disulfonate

To the cold reaction mixture 420 cc. of technical acetone is added, and the contents of the flask heated to 70° at which temperature the formation of acetoxime takes place. The flask is now allowed to cool, preferably overnight.

The solution is neutralized with a solution of sodium hydroxide (2 cc. = 1 g. of sodium hydroxide) using litmus as the indicator. The oily layer is separated and treated with 300 cc. of conc. hydrochloric acid. The aqueous layer is distilled until no more acetoxime comes over with the steam. To test the completeness of the distillation, collect 3 cc. of dis-

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[5] Janny, *Ber.*, **16**, 170 (1883).

[6] The author wishes to thank Messrs. C. Z. Draves, John Sullivan and F. A. McMillin for verifying this method.

tillate, add to it 1 cc. of ether, shake, pour off the ether and allow it to evaporate on a watch glass. Crystals of acetoxime will remain on the glass if the distillation is not complete.

Add the distillate and 150 cc. more of hydrochloric acid to the acetoxime previously removed. Distil the acetone (about 60% is usually recovered) and evaporate the residual liquid to dryness on the steam-bath; yield, 210 to 300 g. of crude hydroxylamine hydrochloride or 53 to 77%. The crude product so obtained can be purified by recrystallization from $^1/_2$ its weight of hot water.

Preparation of Acetoxime.—If acetoxime is the desired product, the reduction, formation of the oxime and neutralization are carried out as before. The oily layer is separated and the aqueous layer extracted with two 100cc. portions of benzene. These 3 portions are mixed and the water which separates is added to the liquid which has just been extracted. The benzene solution of acetoxime is distilled, acetoxime passing over at 133–136° (the boiling point of the pure product is 135°); yield, 280 to 320 g.

The liquid which was extracted with benzene can be distilled to secure the acetoxime which invariably remains. This can be treated with hydrochloric acid and evaporated to obtain hydroxylamine hydrochloride as explained above; yield, 50 to 60 g.

Summary

1. A new method for the preparation of hydroxylamine hydrochloride has been described which (a) approximately halves the time necessary for the preparation; (b) is economical of ice; (c) gives a product free from ammonium salts.

2. An easy method is given for the preparation of acetoxime.

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[Contribution from the Chemical Laboratory of the University of Michigan]

TRIPHENYLMETHYL. XXXI. TAUTOMERISM OF ORTHO-HYDROXY-TRIPHENYL CARBINOL; ORTHO-HYDROXY- AND ALKYLOXY-TRIPHENYLMETHYL

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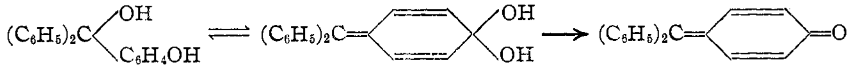
It has been shown in previous papers that *p*-hydroxy-triphenyl carbinol and many of its analogs are prone to tautomerize and, when heated, yield *p*-fuchsones, as for example,



The two tautomeric carbinols have been actually isolated in a number