

Summary

A number of amino and hydroxy derivatives of the kerosene base 2,3,8-trimethylquinoline have been prepared.

Diazotization of 5-hydroxy-6-amino-2,3,8-trimethylquinoline furnished 2,3,8-trimethylquino-

line-6-diazo-5-oxide which was converted by the action of hydroxylamine to 2,3,8-trimethylquinoline-5,6-quinone dioxime. Such a reaction of *o*-diazo oxides has not been observed before.

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The Treatment of Simple Aliphatic Amines with Nitrous Acid

BY FRANK C. WHITMORE AND R. S. THORPE

It might be assumed that low molecular weight primary aliphatic amines would react easily with nitrous acid to form primary alcohols with liberation of nitrogen according to the equation



This reaction takes place with *n*-butylamine to the extent of 25%.¹ However, very little study has been made of the reaction of the simple amines with nitrous acid. The purpose of the present work was to study the effect of nitrous acid on methylamine, ethylamine and *n*-propylamine under conditions similar to those used in the successful reaction of nitrous acid with *n*-butylamine.¹

In sixteen experiments using methylamine and nitrous acid under a wide variety of conditions neither methyl alcohol nor any other reaction products could be isolated from the reaction mixtures. In every reaction attempted, some methylamine was recovered unchanged. The amount of unreacted amine was never less than 25%, and in some experiments the recovery was greater than 90%. This was in spite of the fact that conditions like those employed with *n*-butylamine¹ were used in several cases. The usual variations of concentrations and temperature were tried. Other solvents than water were used. Even a reaction in the gas phase between methylamine and "nitrogen trioxide" in presence of traces of moisture was attempted.

We believe that the failure to obtain methyl alcohol or any related product from methylamine and nitrous acid is because the nitrite of the amine is more readily hydrolyzed than decomposed.

We were able to confirm the earlier workers by producing small amounts of methyl alcohol from silver nitrite and methylamine hydrochloride.

Ethylamine with nitrous acid gave a 60% yield

of ethyl alcohol. *n*-Propylamine gave 7% *n*-propyl alcohol, 32% isopropyl alcohol and 28% propylene. Traces of ethers were also formed with ethyl and propyl amines.

Experimental

Preparation of Reagents.—Methylamine was prepared by the Hofmann degradation of acetamide with H. T. H. according to the directions of Hauser and Renfrow.² It was necessary to allow several hours for the formation of the *N*-chloroamide before heating to degradation temperature. With this modification it was possible to prepare methylamine and convert it to methylamine hydrochloride, m. p. 230–231°, consistently in 78% yield. For solutions of methylamine in water, free amine gas was bubbled through cold water; the amine strength was determined by titration with standard acid.

Ethylamine was purchased from the Sharples Solvents Corporation as a 33.3% solution in water. Propylamine was prepared by the action of ammonia on *n*-propyl bromide. The propylamine salts were neutralized and the free amines were fractionally distilled. Two fractionations were carried out using a 1.5 × 65 cm. packed column and taking the fraction b. p. 47–49°.

U. S. P. sodium nitrite was used. Silver nitrite was prepared from sodium nitrite and silver nitrate.

Methylamine and Nitrous Acid.—Only a few of the sixteen experiments are given. Methylamine hydrochloride dissolved in water was placed in a 3-liter flask fitted with a mechanical stirrer, dropping funnel and an outlet for gas. At the gas outlet a spiral condenser was arranged and fitted with a receiver cooled with ice. A trap immersed in dry-ice and acetone was used to condense any low boiling material. Alkaline permanganate was used to absorb nitrogen oxides, and finally a graduated carboy was arranged to collect gases. Sodium nitrite solution was introduced through the dropping funnel. Recovery of methylamine was accomplished by finally combining all solutions possibly containing unreacted amine, neutralizing with alkali, distilling the free amine into hydrochloric acid, and evaporating the resulting solution to dryness.

Approximately one-mole amounts of methylamine were mixed with nitrous acid prepared in various concentrations from sodium nitrite and hydrochloric acid. The fact that

(1) Whitmore and Langlois, *THIS JOURNAL*, **54**, 3441 (1932).

(2) Hauser and Renfrow, *J. Chem. Education*, **14**, 542 (1938).

apparently no reaction at all took place was unexpected. The only result obtained was the recovery of large amounts of unreacted amine. No methyl alcohol could be isolated.

The concentrations of reagents were varied—an extreme excess of nitrous acid gave no positive result. Temperature conditions were varied from 0° to boiling temperature. Even gaseous methylamine and nitrous fumes were brought together, but no reaction took place.

By experimentation it was found that as little as 5 cc. of methyl alcohol in 1.5 liters of water could be recovered to the extent of 63% by distilling 500 cc. and then fractionating this distillate through the 1.5 × 65 cm. column. Dimethyl ether, methyl chloride and methyl nitrite, if formed, would be condensed at the temperature of dry-ice and acetone. None was detected.

Reaction M-15.—This reaction with methylamine was attempted with conditions similar to those used by Whitmore and Langlois¹ with butylamine and nitrous acid. In 440 cc. of water, 67.2 g. (1.0 mole) of methylamine hydrochloride was dissolved. The amine was neutralized with hydrochloric acid, and through the dropping funnel 96.0 g. (1.4 moles) of sodium nitrite, dissolved in 500 cc. of water was introduced. The reaction mixture was kept cold to prevent the decomposition of nitrous acid. When no reaction was apparent in the cold, heat was applied. Gas evolution took place. The reaction mixture was then distilled to give 350 cc. of condensate. This was acidified with dilute hydrochloric acid and fractionated using the 1.5 × 65 cm. column. With total refluxing for one hour, the head temperature was 97° indicating that no methyl alcohol was present.

The material collected in the trap at low temperature was negligible. In the carboys 15.0 liters of gas (732 mm., 24°) was collected. Gas analysis by absorption methods indicated that a small amount of nitrogen was present, but the greater part of this gas was nitric oxide.

Reaction M-11.—Silver nitrite was used in this experiment. In 800 cc. of water 254 g. (1.65 moles) of silver nitrite was suspended with vigorous agitation. A water solution of 101.5 g. (1.5 moles) of methylamine hydrochloride was introduced through the dropping funnel. Silver chloride precipitated immediately. Even in the cold, considerable gas was liberated. During the reaction 7 cc. of yellow-colored material collected in the trap at dry-ice temperature; this was combined with the condensate that was distilled from the reaction mixture. The mixture was heated under the column. After equilibrium was reached at total reflux the head temperature was 63°. On distillation 4.4 g. of material, b. p. 63–64°, n_D^{20} 1.3399, was obtained. With further refluxing with closed take-off a second small fraction, b. p. 63–64°, was obtained. These fractions contained methyl alcohol as proved by the preparation of the 3,5-dinitrobenzoate, m. p. and mixed m. p. 106.5°. Recovered unreacted methylamine amounted to 32% of the amount used.

Reaction M-14.—Excess nitrous acid would be expected to prevent the hydrolysis of methylamine nitrite and so favor its decomposition to give methanol.

The gases evolved when 10 moles of nitrite was used with methylamine were passed through 50% potassium hydroxide solution. No indication of nitromethane was obtained. No trace of methyl alcohol was found when

the condensate was fractionated. The recovery of unreacted methylamine was 39%.

Ethylamine and Nitrous Acid.—Positive results were obtained in the first reaction attempted, the reaction taking place almost spontaneously.

A total of 6 moles of ethylamine was treated with nitrous acid from 18 moles of sodium nitrite in 2-mole batches. The products were worked up and combined for analysis. For each 2-mole batch, 270 g. of the 33.3% solution of ethylamine in water was placed in the reaction flask, diluted to 1 liter, and neutralized with hydrochloric acid. Then 415 g. (6.0 moles) of sodium nitrite dissolved in 800 cc. of water was introduced with vigorous agitation. No immediate reaction took place but, when heated slightly, the reaction started and proceeded spontaneously. Gas evolution continued for approximately one and one-half hours with moderate heating. Finally the reaction mixture was distilled.

Approximately 300 cc. of material was distilled from each 2-mole batch. This distillate was acidified with dilute hydrochloric acid and redistilled, the distillate being reserved for the analysis of products, and the residual liquid for the recovery of unreacted amine. Approximately 8 cc. of material was condensed in the trap at dry-ice temperature from each 2-mole batch; this was water soluble and was combined with the alcoholic reaction products. The alcoholic layer was salted out from the water in the distillate from each 2-mole reaction and combined with that from the other batches. It was dried with anhydrous potassium carbonate and carefully fractionated. A trap immersed in dry-ice and acetone was arranged at the outlet to condense any low boiling material which might be present. The fractions obtained were: 1, b. p. 33–36°, 1.04 g., odor of ethyl ether; 2, 77–78°, 143.9, identified as ethanol; 3, 78–98°, 2.5; no residue.

Ethyl alcohol was identified by means of the 3,5-dinitrobenzoate derivative, m. p. and mixed 93°.

Recovery of unreacted ethylamine was accomplished as the hydrobromide. The recovery was 129.5 g. (1.03 moles) of ethylamine hydrobromide. On the basis of unrecovered ethylamine (4.97 moles), the yield of ethyl alcohol, considered as 95% alcohol, is 61%.

No ethyl chloride was found, only a trace of diethyl ether was noted and no trace of ethylene was found.

Propylamine and Nitrous Acid.—A total of 3 moles of *n*-propylamine was treated with nitrous acid from 9 moles of sodium nitrite in three batches, with procedure and reaction conditions the same as were used for ethylamine. Absolute alcohol was used instead of sulfuric acid to absorb propene.

A positive reaction was indicated as soon as the nitrite was introduced into the solution of propylamine neutralized with hydrochloric acid. Gas evolution was vigorous. The products were worked up as in the ethylamine reaction, unreacted propylamine being recovered as the hydrochloride.

Fractionation through a 15-plate packed column of the alcoholic layer salted out from the water solution distilled from the reaction mixture gave fractions: 1, b. p. 36–40°, 0.3 g.; 2, 40–79°, 0.9; 3, 79–81°, n_D^{20} 1.3770, 5.2; 4, 81–82°, 1.3748, 33.1; 5, 82–83°, 1.3750, 10.4; 6, 82–83°, 1.3752, 11.3; 7, 83–88°, 1.3780, 4.5; 8, 88–91°, 1.3819,

12.3; 9, 91-96°, 1.3838, 3.4; 10, 96-98°, 1.3847, 12.7; no residue.

Isopropyl alcohol, cuts 4-6, and *n*-propyl alcohol, cut 10, were identified by means of the 3,5-dinitrobenzoates; the m. p. and mixed m. p. for isopropyl derivative 120-122°; for the *n*-propyl derivative, 73°.

It was thought that cuts 8 and 9 might contain di-*n*-propyl ether, but no identification was accomplished.

The alcohol solution used to absorb propene was diluted with warm water and 34.0 g. of propene was collected. Identification of propene was made by passing the gas into sulfuric acid, diluting and distilling out isopropyl alcohol which was identified by the 3,5-dinitrobenzoate, m. p. 120-122°.

Recovery of unreacted propylamine amounted to only 0.16 mole. On the basis of 2.84 moles of unrecovered amine, the per cent. yields in the reaction were: *n*-

propyl alcohol, 7.4; isopropyl alcohol, 32.0; propene, 28.4.

Summary

1. Neither methyl alcohol nor any other reaction products could be isolated from sixteen attempted reactions of monomethylamine with nitrous acid. Methylamine nitrite merely hydrolyzes into its components instead of decomposing into nitrogen and other products as do the nitrites of the higher amines.

2. Ethylamine and *n*-propylamine react with nitrous acid to yield ethanol, 1-propanol, 2-propanol and propene.

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The Polymerization of Olefins. III.¹ The Polymeric Olefins from Methylisopropylcarbinol

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Drake, Kline and Rose³ studied the decenes obtained when methylisopropylcarbinol is treated with 75% sulfuric acid at 80°. They proved the presence of 3,4,5,5-tetramethyl-2-hexene (I) and 3,5,5-trimethyl-2-heptene (II); their search failed to reveal any other decenes. The first decene is an unexpected product. The fact that it was found in such a large amount, about 50% of the decenes present, in addition to its unusual nature, made further study of this reaction desirable. Moreover, a product involving a similar 1:3-shift of a methyl group had been found in this Laboratory.¹

We have now repeated and confirmed entirely the results of the above workers. Moreover, we have obtained excellent separation of the two decenes by the use of a fractionating column of 85 theoretical plates. Drake and his co-workers studied only the decene fractions; we have in addition studied all products of the reaction.

The action of 75% sulfuric acid on methylisopropylcarbinol results in the following yields: trimethylethylene, 1%; 3-methyl-2-pentene, 3%; methyl isopropyl ketone, 1%; diisobutylenes, 1%; 2,3,4,4-tetramethyl-1-pentene, 2%; other nonenes, 1%; 3,4,5,5-tetramethyl-2-hexene (I),

45%; 3,5,5-trimethyl-2-heptene (II), 35%; higher polymers, 5%. The small amount of total intermediate materials, 5%, indicates the sharpness of the separation.

Trimethylethylene is a normal product of the dehydration of methylisopropylcarbinol. The presence of 3-methyl-2-pentene in appreciable amount is of interest. 3,4,5,5-Tetramethyl-2-hexene contains the grouping R_3C-C-C^* , where the asterisk indicates deficiency of an electron pair. According to the findings of Whitmore and Stahly⁴ this grouping is relatively easy to depolymerize. The products of the splitting process would be 3-methyl-2-pentene and isobutylene. The first is found and the second is polymerized with itself to yield the diisobutylenes and copolymerized with trimethylethylene to yield 2,3,4,4-tetramethyl-1-pentene. The other nonenes found, 3,5,5-trimethyl-2-hexene and 2,3,4,4-tetramethyl-2-pentene, are also formed by the copolymerization process.

The presence of methyl isopropyl ketone is easily understood when it is noted that sulfur dioxide, indicating oxidation by the sulfuric acid, was always observed during the polymerization reaction.

3,5,5-Trimethyl-2-heptene (II) is formed by the union of a *t*-amyl fragment to 1,1-methylethyl-

(1) For paper II of this series see THIS JOURNAL, 63, 756 (1941).

(2) Eastman Kodak Co. Research Fellow in Chemistry, 1939-1940.

(3) Drake, Kline and Rose, THIS JOURNAL, 56, 2076 (1934).

(4) Whitmore and Stahly, *ibid.*, 55, 4153 (1933).