acid reaction mixture after distillation in steam to remove nitrobenzene and dilution with water. These attempts were unsuccessful, for though excess nitrous acid was shown to be present, the resulting quinoline contained a considerable amount of aniline. The destruction of aniline was incomplete even with the clear reaction mixture obtained by the method of Cohn and Gustavson.[11]

The author wishes to express his grateful thanks to Dr. J. K. H. Inglis for his kind interest and helpful advice in this investigation.

Summary

1. As neither β-anilinopropionaldehyde nor its acetal or anil could be obtained pure, nothing can be concluded as to the constitution of the Skraup intermediate.

2. Allylaniline can yield small quantities of quinoline by oxidation in solution.

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

NITRIDATION STUDIES. I. INTRODUCTION. II. MERCURIC NITRIDE AND BISMUTH NITRIDE AS NITRIDIZING AGENTS[1]

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I. INTRODUCTION

The term "nitridation" or "nitridation reaction"[2] has been applied to all those reactions which for the ammonia system of compounds are essentially similar to oxidation reactions for the familiar water compounds or for those reactions in which nitrogen plays a part analogous to that played by oxygen in ordinary simple processes of oxidation.

Numerous examples of nitridation reactions are known.[3]

The only agents to be examined to any extent, however, are hydrazoic

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[11] Cohn and Gustavson, THIS JOURNAL, **50**, 2709 (1928).

[1] The material presented in this paper is from a portion of a thesis submitted by Iman Schurman in partial fulfilment of the requirements for the Degree of Master of Science at The Ohio State University.

[2] (a) Browne and Welsh, THIS JOURNAL, **33**, 1728 (1911); Franklin, *J. Phys. Chem.*, **27**, 169 (1923); *cf.* Goldberg, THIS JOURNAL, **34**, 886 (1912). Turrentine [*ibid.*, **34**, 386 (1912)] calls hydrazoic acid a nitridizing agent because many of the reactions of hydrazoic acid are similar to those of nitric acid, an oxidizing agent. (b) Cady and Taft [*Science*, **62**, 403 (1925)] have proposed the terms "electronation" and "delectronation" to be used in place of "reduction" and "oxidation" in the broad sense. Accordingly "nitridation" would be a particular type of "delectronation."

[3] Franklin, *J. Phys. Chem.*, **27**, 169 (1923); THIS JOURNAL, **46**, 2142 (1924); "Reactions in Liquid Ammonia," Columbia University Press, New York, **1927**, p. 16; Bergstrom, THIS JOURNAL, **48**, 2324 (1926); *J. Phys. Chem.*, **32**, 440 (1928); Strain, THIS JOURNAL, **49**, 1558 (1927); **50**, 2220 (1928); **51**, 271 (1929); Chuck, "Dissertation," Stanford University, **1925**; Turrentine, Ref. 2a; Goldberg, Ref. 2a.

acid (ammono nitric acid) and a solution of iodine in liquid ammonia which undoubtedly contains iodo-amine, H_2NI, ammono hypoiodous acid.[4] In addition, certain electrolytic nitridations have been carried out.[5]

The present investigation was undertaken in an endeavor to increase our knowledge concerning nitridation and particularly to discover new nitridizing agents.

II. MERCURIC NITRIDE AND BISMUTH NITRIDE AS NITRIDIZING AGENTS

Mercuric oxide is a substance sometimes used as a mild oxidizing agent.[6] Its ammonia analog, mercuric nitride, should then be a mild nitridizing agent. The explosiveness of mercuric nitride[7] when dry is in harmony with this view. Hydrazobenzene was chosen as a substance to be nitridized because it has been oxidized to azobenzene by means of mercuric oxide[8] and nitridized electrolytically in liquid ammonia solution.[2b]

A preliminary nitridation using a solution of iodine in liquid ammonia showed that hydrazobenzene is easily converted into azobenzene. Mercuric nitride reacts with hydrazobenzene in accordance with the equation

$$3C_6H_5NHHNC_6H_5 + Hg_3N_2 \longrightarrow 3Hg + 3C_6H_5N{=}NC_6H_5 + 2NH_3$$

p-Hydrazotoluene is likewise nitridized to *p*-azotoluene by both iodine and mercuric nitride.

Another nitride showing a considerable degree of instability is bismuth nitride.[9] In preparing this substance Franklin found that it is always contaminated with metallic bismuth as a result of its spontaneous decomposition. In harmony with this behavior of bismuth nitride, the present investigation shows that both hydrazobenzene and *p*-hydrazotoluene are nitridized to the corresponding azo compounds in liquid ammonia solution by bismuth nitride.

Whenever an hydrazo compound was added to either of the nitride precipitates, the solution above the insoluble nitride became dark red. Such behavior undoubtedly indicates either that mercuric and bismuth nitrides—although very insoluble in liquid ammonia—are, nevertheless, sufficiently soluble to give a weakly basic solution, or that the potassium amide had not been entirely removed from these nitride precipitates although the

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[4] For the reaction between iodine and ammonia see Mellor, "A Comprehensive Treatise," etc., Longmans, Greene and Co., New York, **1928**, Vol. VIII, p. 605–611; *cf.* also Bergstrom, *J. Phys. Chem.*, **30**, 12 (1926).

[5] Browne, Holmes and King, THIS JOURNAL, **41**, 1769 (1919); Cady and Taft, *J. Phys. Chem.*, **29**, 1070 (1925).

[6] Gautier, *Ann. chim. phys.*, [4] **17**, 228 (1869).

[7] Franklin, THIS JOURNAL, **27**, 820 (1905); *Z. anorg. Chem.*, **46**, 1 (1905).

[8] Perkin and Kipping, "Organic Chemistry," J. B. Lippincott Co., Philadelphia, **1922**, p. 425. This reference seems to be the only one in the literature on the reaction of hydrazobenzene and mercuric oxide. *Cf.* the similar preparation of phenyl azomethane from the corresponding hydrazine [Fischer, *Ber.*, **29**, 794 (1896)].

[9] Franklin, Ref. 7, p. 847.

number of washings should have been sufficient to remove it. White and Knight[10] observed a similar coloration when a solution of hydrazobenzene or azobenzene was treated with a sodium solution and attributed their results to the formation of a salt, $C_6H_5N(Na)\text{-}N(Na)C_6H_5$. When a solution of hydrazobenzene or *p*-hydrazotoluene is treated with a solution of potassium amide, a brown coloration develops. Cady and Taft observed a similar coloration with sodium amide and hydrazobenzene. The present investigation has shown that this reaction with the alkali metal amides is a reversible one so that the hydrazo compounds, like triphenylmethane,[11] serve as very sensitive indicators of the Ostwald type in liquid ammonia. In pure liquid ammonia or in the presence of an ammonium salt (an acid) the hydrazo compounds yield a light brownish-yellow solution, while in the presence of soluble bases, even at very low concentrations, the deep red-brown color of the alkali metal salt appears. Even potassium hydroxide, whose solubility in ammonia is exceedingly low, imparts a distinct brown color to the solution of hydrazobenzene. Sodium peroxide is also sufficiently soluble in liquid ammonia to give a similar coloration.[2b]

Hexamethylenetetramine, amylene, styrene and azoxybenzene in liquid ammonia show no reaction with mercuric nitride over the space of one week.

Experimental

In carrying out the reactions described in this paper the familiar methods used by Franklin and his co-workers[12] have been employed. In one leg of a two-legged reaction tube was placed a convenient amount of purified and dried mercuric iodide or bismuth iodide; in the other, an excess of potassium, contained in a short length of glass tubing, together with a spiral of iron wire. On distilling ammonia into the reaction tube both the iodide and the potassium dissolved. In the presence of the iron wire catalyst the potassium was rapidly converted, usually in a half hour, into the soluble potassium amide.

After partially opening the stopcock for a moment to release the pressure of the evolved hydrogen, the solution of potassium amide was poured into the leg containing the iodide—an excess of potassium amide was necessary to prevent the formation of ammono-basic salts. The nitride precipitated and settled rapidly.

$$3HgI_2 + 6KNH_2 \longrightarrow Hg_3N_2 + 4NH_3 + 6KI$$

$$BiI_3 + 3KNH_2 \longrightarrow BiN + 2NH_3 + 3KI$$

These precipitates were washed by decantation with fresh ammonia about

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[10] White and Knight, This Journal, **45**, 1782 (1923).

[11] Kraus and Rosen, *ibid.*, **47**, 2743 (1925).

[12] Franklin, *ibid.*, **27**, 831 (1905); **29**, 1275 (1907); **35**, 1460 (1913); *J. Phys. Chem.*, **15**, 510 (1911); **16**, 694 (1912); Fitzgerald, This Journal, **29**, 1694 (1907); Bohart, *J. Phys. Chem.*, **19**, 539 (1915).

five times, to free them of potassium iodide and potassium amide. The solvent was next distilled into the leg containing the precipitated nitride. This leg was then cooled in a bath of liquid ammonia which was open to the atmosphere and the leg containing the washings was opened and cleaned. Finally the hydrazo compound was added and this leg resealed. After the seal had cooled, the other leg of the tube was removed from the liquid ammonia and allowed to warm to room temperature. The hydrazo compound was dissolved in ammonia and the solution poured over the nitride. The final reaction product was obtained by allowing all of the ammonia to evaporate from the tube, or by distilling the solvent into the opposite leg and cooling this leg in an open bath of ammonia. In either case the end of the tube was scratched with a file and broken off by means of a piece of hot glass.

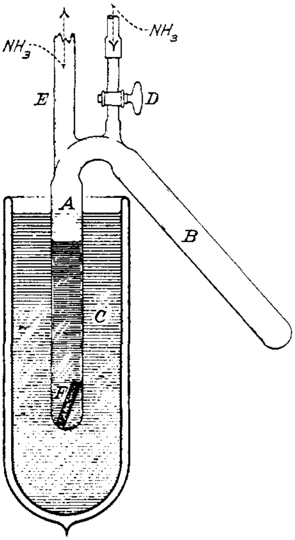

Fig. 1.

The azo compounds were purified by recrystallization either from ligroin or liquid ammonia. Azobenzene and *p*-azotoluene are only slightly soluble in liquid ammonia at the temperature of an open bath of the liquid (about −40°).

For those experiments in which iodine was used as the nitridizing agent, a two-legged reaction tube fitted with an addition tube was employed (Fig. 1). The tube was sealed up with the hydrazo compound in leg A. After distilling ammonia into the tube, leg A was cooled in an open bath of liquid ammonia, C. With a stream of gaseous ammonia entering at D, the end of the addition tube, E, was cracked off with a bit of hot glass. Short pieces of glass tubing packed with the desired weight of iodine were next dropped into the leg A and tube E resealed.[13] After the tube had been removed from the cooling bath and allowed to warm to room temperature, the iodine slowly dissolved and reacted with the solution.[14]

The hydrazobenzene and *p*-hydrazotoluene used in this research were prepared by reducing the corresponding azo compound with zinc dust in a hot alcoholic alkaline solution[15] and recrystallizing from alcohol; m. p. of hydrazobenzene, 129°; *p*-hydrazotoluene, 124°. The values listed in the "International Critical Tables" are 131 and 126°, respectively.

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[13] Such a modification of the usual procedure is necessary because iodine liquefies in a stream of gaseous ammonia and forms a dangerously explosive mixture.

[14] This is the technique employed by Strain (Ref. 3), although not described fully by him.

[15] Gattermann, "Practical Methods of Organic Chemistry," translated by Schober and Babasinian, 3d English ed. from 11th German ed., 1928, p. 228.

Hydrazobenzene and Iodine.—To a solution of 0.2 g. of hydrazobenzene in liquid ammonia was added an excess of iodine. After all of the iodine had dissolved (three hours), the solution was cooled in an open-bath of liquid ammonia. The lowering of the temperature caused the separation of orange crystals (m. p. 68°). A mixture of equal quantities of these crystals and azobenzene (m. p. 68°) melted at 68°.

***p*-Hydrazotoluene and Iodine.**—To an ammonia solution containing 0.14 g. of *p*-hydrazotoluene was added an excess of iodine. Overnight all of the iodine had disappeared and orange crystals had separated out. After washing three times with fresh ammonia, these crystals melted at 144°; when mixed with *p*-azotoluene, melting at 144°, the mixture melted at 144°.

Hydrazobenzene and Mercuric Nitride.—To the mercuric nitride prepared from 1.22 g. of the iodide was added 0.18 g. of hydrazobenzene in ammonia solution. At the end of two days, small globules of metallic mercury were visible in the bottom of the reaction tube. The ammonia-soluble product upon recrystallization from ligroin melted at 67.5°. An equal mixture of these crystals and azobenzene, melting at 68°, melted at 67.5°.

***p*-Hydrazotoluene and Mercuric Nitride.**—Two and one-tenth g. of mercuric iodide was converted to the nitride and treated with an ammonia solution containing 0.22 g. of *p*-hydrazotoluene. At the end of two days finely divided mercury as well as a precipitate of *p*-azotoluene was visible in the tube. The latter product after extraction with ammonia and recrystallization from ligroin gave orange-yellow crystals which melted at 143°. A mixture of equal quantities of these crystals and those of *p*-azotoluene (m. p. 144°) melted at 143.5°.

Hydrazobenzone and Bismuth Nitride.—To the bismuth nitride obtained from 1.32 g. of the iodide was added a solution containing 0.51 g. of hydrazobenzene. The mixture was allowed to stand for two days. The reaction product recrystallized from ligroin gave 0.483 g. of red crystals which melted at 67°; yield, 95%. A mixture of these crystals and an equal quantity of azobenzene melted at 67°.

Hydrazotoluene and Bismuth Nitride.—One and three-tenths grams of bismuth iodide and an excess of potassium were sealed in opposite legs of a reaction tube and ammonia distilled into the leg containing the iodide. During the subsequent distillation of ammonia from this leg into that containing the potassium small yellow needle crystals were observed in the iodide leg. Such a behavior indicates the probable existence of a moderately soluble ammono-basic iodide of bismuth.[16] The solution of *p*-hydrazotoluene remained in contact with the nitride for two days. On recrystallizing the reaction product from ligroin, orange-yellow crystals were obtained which melted at 143°; a mixed melting point with *p*-azotoluene gave 143.5°.

Hydrazobenzene as an Indicator.—In the legs of a three-legged reaction tube were sealed 0.5 g. of ammonium nitrate, a small amount of hydrazobenzene and 0.3 g. of potassium, respectively. After the conversion of the potassium to the amide, a drop of this solution was added to the yellow solution of hydrazobenzene. Immediately a reddish-brown color developed. Upon the careful addition of a drop of ammonium nitrate, the hydrazobenzene solution resumed its original yellow color. With the same sample of indicator, this process of discharging the color induced by bases was repeated several times.

Small amounts of hydrazobenzene and potassium hydroxide were sealed in a one-legged reaction tube and ammonia was distilled onto the mixture. The solution was colored dark brown.

***p*-Hydrazotoluene as an Indicator.**—A three-legged tube similar to the one de-

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[16] Franklin and Cady [This Journal, **26**, 512 (1904)] report a similar ammono-basic bismuth nitrate.

scribed above was charged with ammonium chloride, *p*-hydrazotoluene and potassium amide. The same induction and discharge of color were observed as in the case above.

Summary

1. Mercuric nitride and bismuth nitride have been shown to have the properties of nitridizing agents.

2. Hydrazobenzene and *p*-hydrazotoluene have been nitridized to the corresponding azo compounds in liquid ammonia solution using iodine, mercuric nitride and bismuth nitride.

3. Because of the formation of highly colored salts, both hydrazobenzene and hydrazotoluene may be used as sensitive acid-base indicators in liquid ammonia solutions.

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[Contribution from the Laboratory of Organic Chemistry of the University of Wisconsin]

THE MONOPHENYL ETHERS OF GLYCERIC ACID

By C. Frederick Koelsch

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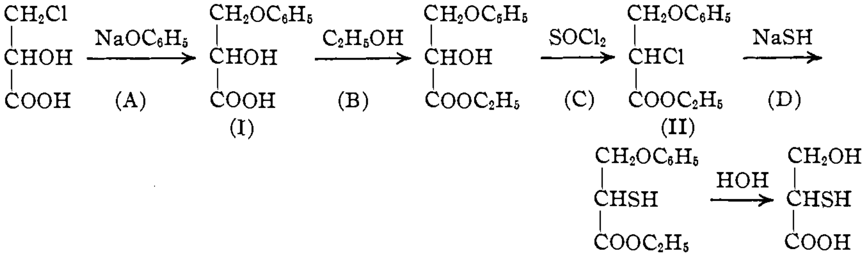
Investigations on the oxidation of β-thioglyceric acid, whose preparation was described in a previous paper,[1] showed the desirability of extending the study there outlined to the still unknown α-thioglyceric acid. It was considered feasible to attempt the preparation of this compound through the following reactions:



$$\begin{array}{l} CH_2Cl \\ | \\ CHOH \\ | \\ COOH \end{array} \xrightarrow[\text{(A)}]{NaOC_6H_5} \underset{\text{(I)}}{\begin{array}{l} CH_2OC_6H_5 \\ | \\ CHOH \\ | \\ COOH \end{array}} \xrightarrow[\text{(B)}]{C_2H_5OH} \begin{array}{l} CH_2OC_6H_5 \\ | \\ CHOH \\ | \\ COOC_2H_5 \end{array} \xrightarrow[\text{(C)}]{SOCl_2} \underset{\text{(II)}}{\begin{array}{l} CH_2OC_6H_5 \\ | \\ CHCl \\ | \\ COOC_2H_5 \end{array}} \xrightarrow[\text{(D)}]{NaSH}$$

$$\begin{array}{l} CH_2OC_6H_5 \\ | \\ CHSH \\ | \\ COOC_2H_5 \end{array} \xrightarrow{HOH} \begin{array}{l} CH_2OH \\ | \\ CHSH \\ | \\ COOH \end{array}$$

Reactions A, B and C were carried out successfully. Reaction D did not proceed as indicated; when ethyl α-chloro-β-phenoxypropionate (II) was treated with sodium hydrosulfide, a practically quantitative yield of phenol was obtained. The remainder of the reaction mixture was a black tar, the constituents of which are as yet unidentified. A study of this reaction is in progress.

This paper deals with the substances obtained in Reaction A. The reaction between β-chlorolactic acid and sodium phenoxide gave a satisfactory yield of β-phenoxylactic acid (I), but when the reaction mixture was worked over, it was found that this was not the sole product. Along

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[1] Koelsch, This Journal, **52**, 1105 (1930).