ethanol-water, 64% of white plates; m.p. 206–211°, was obtained.

Anal. Calcd. for $C_{16}H_{15}N_2I$: C, 53.06; H, 4.17. Found: C, 52.80; H, 3.99.

1-(2-Quinolylmethyl)pyridinium iodide methoiodide (IX). Prepared from 1-methylquinaldinium iodide,[14] pyridine, and iodine. Crude yield 30% of orange needles; m.p. 178–180°. Recrystallization from 90% ethanol gave yellow needles; m.p. 183–184° with decomposition.

Anal. Calcd. for $C_{16}H_{16}N_2I_2$: C, 39.21; H, 3.29. Found: C, 38.96; H, 3.27.

1-(4-Quinolylmethyl)pyridinium iodide methoiodide (X). Prepared from N-methyllepidinium iodide,[15] pyridine, and iodine. Crystallization from ethanol gave 53% of greenish yellow plates; m.p. 186–188°. Recrystallization for an analytical sample gave yellow plates darkening at 187–191°, decomposing at 191–193°.

Anal. Calcd. for $C_{16}H_{16}I_2N_2$: C, 39.21; H, 3.29. Found: C, 39.30; H, 3.14.

2-Quinolyl-N-(p-dimethylaminophenyl)nitrone (IV). To a mixture of 3.48 g. (0.01 mole) 1-(2-quinolylmethyl)pyridinium iodide (IIIa) in 5 ml. water and 1.65 g. (0.011 mole) of *N,N*-dimethyl *p*-nitroso aniline in 50 ml. ethanol cooled to 0.5°, 10 ml. of *M* sodium hydroxide was added. The mixture was stirred for 45 min. Filtration gave 1.6 g. (54%) of reddish crystals; m.p. 154–155°. Recrystallization from benzene-hexane gave red needles; m.p. 161–161.5°.

Anal. Calcd. for $C_{18}H_{17}N_3O$: C, 74.4; H, 5.88. Found: C, 74.69; H, 5.74.

2-Quinoline carboxaldehyde-2,4-dinitrophenylhydrazone. A solution of 0.4 g. (0.0014 mole) of 2-quinolyl-*N*-(*p*-dimethylaminophenyl)nitrone (IV) was shaken with 50 cc. of 3*N* HCl. Addition of 2,4-dinitrophenylhydrazine precipitated the 2-quinoline carboxaldehyde derivative as yellow plates; m.p. 245–248°. Recrystallization from ethanol-water gave yellow needles which softened at 245° and melted at 252–254°. Reported m.p. 251–253°.[8]

4-Quinolyl-N-(p-dimethylaminophenyl)nitrone (VI). The procedure was essentially the same as for the preparation of 2-quinolyl-*N*-(*p*-dimethylaminophenyl)nitrone (IV). From 3.4 g. (0.01 mole) 1-(4-quinolylmethyl)pyridinium iodide 1.95 g. (65%) reddish crystals was obtained. Crystallization from benzene-hexane gave 1.42 g. (49%) of red needles; m.p. 179–181°.

Anal. Calcd. for $C_{18}H_{17}N_3O$: C, 74.40; H, 5.88. Found: C, 74.67; H, 5.63.

1-(1-Methyl-2-quinolylidenylmethyl)pyridinium iodide (XI). To 1 g. (0.0025 mole) of 1-(2-quinolylmethyl)pyridinium iodide methoiodide (IX) dissolved in 5 ml. of water, *M* sodium hydroxide was added dropwise until no further precipitate was observed. The red precipitate was collected by filtration. Yield 0.6 g. (82%) of red powder; m.p. 184–190°.

Anal. Calcd. for $C_{16}H_{15}N_2I$: C, 53.05; H, 4.17. Found: C, 52.90; H, 4.14.

N-Methyl-2-quinolone. To 2.5 g. (0.005 mole) 1-(2-quinolylmethyl)pyridinium iodide methoiodide (IX) dissolved in 20 cc. water, 10 ml. of 2*N* potassium hydroxide was added. After the hydrolysis was complete the product was extracted with chloroform. Yield 0.55 g. (68%) of tan material melting at 72–73°. Reported for *N*-methyl-2-quinolone, 73°.[10]

N-Methyl-4-quinolone (XII). A solution of 0.5 g. (0.001 mole) 1-(4-quinolylmethyl)pyridinium iodide methoiodide (X) dissolved in 30 cc. water was treated with 4 ml. of 10*N* sodium hydroxide and the mixture heated on the steam bath for 20 min. Extraction with chloroform followed by evaporation of solvent gave 0.17 g. (100%) of white crystals; m.p. 149°.[10]

Acknowledgment. We wish to thank the American Cyanamid Co. for a research fellowship.

EVANSTON, ILL.

[CONTRIBUTION FROM THE ILLINOIS STATE GEOLOGICAL SURVEY]

A Combined Deamination and Nitro Reduction Method for Nitroanilines[1]

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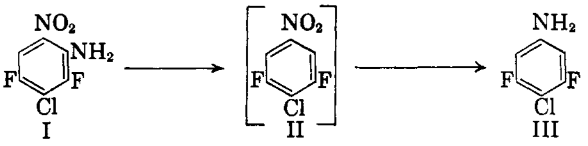
Received June 5, 1958

The hypophosphorous acid–cuprous oxide deamination method on nitroanilines has been modified so that the nitro compounds which are formed are reduced in turn by cuprous oxide to the corresponding amines. Over-all yields of 55–65% are reported for three halogenated nitroanilines.

It was reported previously from this laboratory that in the hypophosphorous acid–cuprous oxide deamination of 2-nitro-3,4,6-trifluoroaniline[2] to 2,3,5-trifluoronitrobenzene, a small amount of 2,3,5-trifluoroaniline was isolated as a by-product. Later other halogenated nitroanilines were observed to give similar results. This indicated that part of the desired nitro compound was reduced to the corresponding amine. At the same time it became apparent that the yield of amine varied considerably between similar experiments. The secondary reaction was investigated. As a result of this study, the deamination process has been modified so that complete reduction of the nitro compound also takes place, and the corresponding amine is isolated as the final product.



As the deamination mixture contains two reducing agents, hypophosphorous acid and cuprous oxide,[3] there is the question whether one agent or the combination of both is chiefly responsible for the

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(1) Published by permission of the Chief of the Illinois State Geological Survey.

(2) G. C. Finger, F. H. Reed, and R. E. Oesterling, *J. Am Chem. Soc.*, **73**, 152 (1951).

(3) Reduction of nitro compounds by copper sponge with sodium hypophosphite has been reported by A. Maihle and M. Murat, *Bull. soc. chim. France*, **7**, 952 (1910).

reduction of a nitro group. The literature[4] is rather mute on the formation of secondary reduction products in the hypophosphorous acid or cuprous oxide catalyzed ethanol deamination procedures. Many nitroanilines are deaminated to the nitro derivatives in high yields by both methods thus inferring that the reducing agents or catalyst have no significant effect on the nitro groups. For a more satisfactory answer, the reducing agents were tested on 4-chloronitrobenzene. To stirred aqueous slurries of sodium hypophosphite, cuprous oxide, and a mixture of both, a solution of 4-chloronitrobenzene dissolved in a large excess of concentrated sulfuric acid was added. The resulting mixtures were heated to about 100° for several hours and then examined for amine formation. Cuprous oxide gave a substantial yield of 4-chloroaniline, whereas sodium hypophosphite gave very little evidence of nitro reduction. Reduction occurred in the sodium hypophosphite–cuprous oxide mixture in proportion to the cuprous oxide content. This explains the variation in amine formation in the earlier deaminations where an arbitrary amount of cuprous oxide was used with only catalysis in mind.

The cuprous oxide reduction of 4-chloronitrobenzene in concentrated sulfuric acid was examined further. With a molar ratio of 3:1 and higher of cuprous oxide to nitro compound, and a heating period of about 4 hr., a yield of 83–90% of steam distilled 4-chloroaniline was obtained. The ratio is as expected on the basis of a simple oxidation-reduction reaction. In practice, however, a ratio of 4:1 or more is recommended. Other nitrobenzenes gave similar results. Due to its convenience, cuprous oxide could be used more frequently for the reduction of nitro compounds.

It was quite evident now that in the deamination of nitroanilines, the resulting nitro compounds could be reduced to the amines in the same operation if sufficient cuprous oxide was present. Due to interest in halogenated nitroanilines, a number of these compounds were submitted to the deamination procedure as modified with excess cuprous oxide. In general, the nitroanilines were diazotized by the nitrosylsulfuric–phosphoric acid procedure.[5,6] The diazonium solutions were added slowly to a water slurry of sodium hypophosphite and cuprous oxide. Subsequent heating at 90–100° for about 4 hr. completed the deamination and nitro reduction. After neutralization with alkali, steam distillation removed the amines. The crude amine yields are based on the amount of nitroaniline used.

Yield data obtained on three nitroanilines are (1) 5-fluoro-2-nitroaniline to 4-fluoroaniline, 55%, (2) 2,6-dichloro-4-nitroaniline to 3,5-dichloroaniline 59%; and (3) 4,6-difluoro-5-chloro-2-nitroaniline to 3,5-difluoro-4-chloroaniline, 64%.

EXPERIMENTAL[7]

As the nitroanilines under investigation were weakly basic amines, they were diazotized by the nitrosylsulfuric–phosphoric acid procedure. In contrast to earlier studies,[2,8] the diazonium solutions were added to the reducing agents thus reversing the order of addition. To complete the deamination and reduction of the nitro group, the reaction was heated on a steam bath. As a routine procedure, a 4-hr. heating period is essential, although in some instances the entire process appeared to be complete in a very short time. The free amine may also be recovered by solvent extraction with the disadvantage that a large volume of solution must be handled.

The method and procedure are illustrated by the preparation of 3,5-difluoro-4-chloroaniline.

3,5-Difluoro-4-chloroaniline (III). A mixture of 119 g. (0.57 mole) of 4,6-difluoro-5-chloro-2-nitroaniline (I),[9] m.p. 96–97°, and 84 ml. of glacial acetic acid was dissolved in 640 ml. of concd. sulfuric acid. Nitrosylsulfuric acid was prepared by adding 46 g. (0.66 mole) of sodium nitrite to 424 ml. of concd. sulfuric acid at 20–25°. To the amine salt at room temperature was added the nitrosylsulfuric acid, and the mixture stirred for 2 hr. The diazotization was completed by addition at 0–10° of sirupy phosphoric acid (85%) and the mixture warmed on a steam bath to 65–70°. After cooling, the diazonium solution was added slowly to an efficiently stirred slurry of 301 g. of sodium hypophosphite,[10] 326 g. of cuprous oxide,[11] and 500 ml. of water in a large flask. Considerable foaming takes place during the addition. The temperature was allowed to rise to 50°. To complete the reaction process, the mixture was heated at 90–100°, usually on a steam bath, for 4 hr. Steam was passed into the mixture to remove unreduced 3,5-difluoro-4-chloronitrobenzene (II),[9] m.p. 41–42°; usually less than one gram was recovered. The reaction mixture was neutralized with strong sodium hydroxide solution, and the amine was removed by steam distillation. Yield of crude amine, 60 g. or 64%. Recrystallization from ethanol gave 3,5-difluoro-4-chloroaniline as white needles, m.p. 78–79°.

Anal. Calcd. for $C_6H_4ClF_2N$: C, 44.07; H, 2.51; Cl, 21.69; N, 8.56. Found: C, 44.12; H, 2.50; Cl, 21.85; N, 8.60.

The acetyl derivative was recrystallized from benzene to give white needles, m.p. 166–166.5°.

Anal. Calcd. for $C_8H_6ClF_2NO$: N, 6.80. Found: N, 6.74.

URBANA, ILL.

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(6) C. Weygand, *Organic Preparations*, Interscience Publishers, Inc., New York, N. Y., 1945, Ch. 2, p. 110.

(7) Analyses by D. R. Dickerson, microanalyst for the Survey.

(8) G. C. Finger, F. H. Reed, and J. L. Finnerty, *J. Am. Chem. Soc.*, **73**, 153 (1951).

(9) G. C. Finger, R. E. Oesterling, and R. H. White, *Abstracts, 130th Meeting*, American Chemical Society, Sept. 1956, Atlantic City, N. J., p. 26-O.

(10) Sodium hypophosphite, NF grade, 98%.

(11) Red cuprous oxide, USN Type 1, 97%.