CHAPTER 4

THE ZININ REDUCTION OF NITROARENES

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CONTENTS

INTRODUCTION

The Zinin reduction is a method for the reduction of nitroarenes by negative divalent sulfur (sulfide, sulfhydrate, and polysulfides). This versatile reaction can be carried out in standard laboratory equipment and has been used for plant-scale manufacture of aromatic amines when other reduction media are destructive to sensitive compounds or result in undesired side reactions.

The reaction, first used by Zinin in 1842 to prepare aniline from nitrobenzene,[1] has since been of great importance in the preparation of aromatic amines. With the advent of catalytic reduction procedures, Zinin's method has seen less use in the laboratory as a preparative technique. Recently published laboratory texts of organic chemistry often fail to mention this rather simple procedure for the preparation of a host of ordinary or rare amines. Economically, in most instances it has not proved so attractive as the iron reduction method in commercial applications,[2] but it is used with more sensitive compounds that would not be compatible with acid media or would be reduced farther than desired by the iron or catalytic hydrogenation process.

Refinements in technique[3] and a better understanding of the reaction mechanism (see below) should make the method attractive for the preparation of a variety of amines. A closer look at the technology may lead to the development of processes which offer advantages over many current catalytic and iron reduction methods. For instance, a recent article describes a continuous process for reducing 1-nitronaphthalene with aqueous sodium disulfide.[4] Several reactions discussed on pp. 460–464 produce products other than the expected amines and should lead to general preparative methods for materials not readily obtainable by other reduction methods.

MECHANISM

The stoichiometry of the Zinin reduction is illustrated by Zinin's original reduction of nitrobenzene by aqueous ammonium sulfide.

$$4\ C_6H_5NO_2 + 6\ S^{2-} + 7\ H_2O \rightarrow 4\ C_6H_5NH_2 + 3\ S_2O_3^{2-} + 6\ OH^-$$

[1] N. Zinin, *J. Prakt. Chem.*, [1] **27**, 149 (1842).

[2] P. H. Groggins, *Unit Processes in Organic Synthesis*, McGraw-Hill, New York, 1958, pp. 186–190.

[3] H. I. Stryker, U.S. Pat. 3,223,727 (1965) [*C.A.*, **64**, 4051 (1966)].

[4] G. M. Tomokkin and B. I. Kissin, *Khim. Prom.*, **3**, 79 (1960) [*C.A.*, **55**, 469 (1961)].

If the reductant is disulfide, the equation is analogous.

$$C_6H_5NO_2 + S_2^{2-} + H_2O \rightarrow C_6H_5NH_2 + S_2O_3^{2-}$$

Although earlier studies,[5–7] particularly those by Hodgson,[8,9] provide insight into the mechanism, the kinetic work of Hojo and co-workers is the most helpful.[10] They worked mostly with disulfide, which reduced nitrobenzene much more rapidly than did sulfide. The medium they used was aqueous methanol, and the rate increased rapidly with increasing concentration of water. They showed that when sufficient alkali is present to keep the equilibrium

$$S_2^{2-} + H_2O \rightleftarrows HS_2^- + OH^-$$

far on the side of disulfide ion, the rate of reaction is first-order in disulfide ion and first-order in nitroarene. Electron-withdrawing substituents speeded up the reaction considerably; the relative rates fitted the Hammett equation well, with $\rho = -3.55$. Azoxybenzene is reduced very slowly compared to nitrobenzene. These observations suggest that the rate-determining step is attack of disulfide ion on the nitro group. Probably the first product is a nitroso compound, which is rapidly reduced to a hydroxylamine and then an amine.

$$ArNO_2 + S_2^{2-} \rightarrow ArNO \rightarrow ArNHOH \rightarrow ArNH_2$$

These kinetic studies suggest to the experimenter that disulfide ion rather than sulfide ion be used; that as high a concentration of water be used as is consistent with complete or partial solution of the nitroarene in the reaction mixture; that enough excess alkali be used to have almost all the reductant present as sulfide ion or disulfide ion; and that excess reductant be used to ensure a rapid reduction that does not stop at an intermediate stage, thus minimizing condensations of intermediates to give azoxy or azo compounds.

The uniqueness of the Zinin reduction of nitroarenes, as compared to reduction by iron or catalytic hydrogenation, lies in its lower reduction potential and its narrow useful range of electromotive force. This means that functional groups other than nitro are less likely to be reduced. Moreover, selective reduction of one nitro group in a dinitro- or trinitroarene is often possible. Some useful generalizations (pp. 458–459) often enable

[5] H. Goldschmidt and H. Larsen, *Z. Phys. Chem.* (Leipzig), **71**, 437 (1910).
[6] K. Brand, *J. Prakt. Chem.*, [2] **74**, 449 (1906).
[7] I. M. Kogan and A. I. Kizber, *J. Gen. Chem.*, **5**, 1762 (1935).
[8] H. H. Hodgson, *J. Soc. Dyers Colour.*, **59**, 246 (1943).
[9] H. H. Hodgson, *J. Chem. Soc.*, **1944**, 75.
[10] M. Hojo, Y. Takagi and Y. Ogata, *J. Amer. Chem. Soc.*, **82**, 2459 (1960).

one to predict which isomer will be obtained, but the detailed mechanistic knowledge necessary for more comprehensive generalization is lacking. Steric hindrance and the relative reduction potentials of the different nitro groups may be factors. Hodgson has invoked resonance[9] and hyperconjugation[11] to explain relative ease of detachment of oxygen from different nitro groups. Studies on the sulfur-sulfide electrode[12] may be used to explain the limits of the reduction medium.

It is evident that much remains to be learned about the mechanism and that studies using modern techniques and instruments would be desirable.

SCOPE AND LIMITATIONS

While the reaction may be called the sulfide reduction method, the hydrosulfide method, or the polysulfide method, the term Zinin reduction which credits the discoverer is more general in implication and would properly include the many related procedures generated from Zinin's initial research. Generally, the reaction is applied to the reduction of mono- and poly-nitroarenes to the corresponding amines and nitroamines, but has found application in the conversion of some nitroso and azo compounds to amines. It can also be used for the preparation of some hydroxylamines and benzotriazoles starting with the proper nitro compounds (see pp. 461, 462).

Generally the reagents used are ammonium, sodium, or potassium sulfides, hydrosulfides, or polysulfides. Manganous sulfide[13] and ferrous sulfide[14] are also used. An improvement in reductions with alkali sulfides by the addition of selenium has been suggested.[15] The tables show that the method is applicable to practically any type of nitroarene. The presence of a wide variety of substituents on the aromatic nucleus can be tolerated without seriously reducing the effectiveness of the sulfur reagent.

The positions of the substituents play an important role in the progress of the reaction. For example, they affect the ease of reduction of mononitroarenes. In polynitro compounds the relative positions of the groups determine whether reduction gives monoamino or polyamino derivatives and determine the isomer distribution of the monoamino products. One of the advantages of the Zinin reduction is that it often stops at the nitroamine stage to give a particular isomer in high yield. Consideration of the

[11] H. H. Hodgson, *J. Soc. Dyers Colour.*, **62**, 114 (1946).

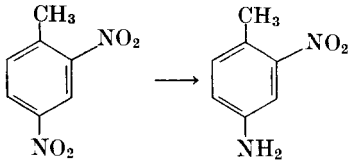
[12] P. L. Allen and A. Hickling, *Chem. Ind.* (London), **1954**, 1558.

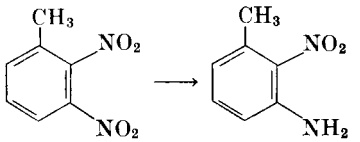
[13] General Aniline and Film Co., U.S. Pat. 1,765,660 (1930) [*C.A.*, **24**, 4051 (1930)].

[14] R. E. Kirk and D. F. Othmer, *Encyclopedia of Chemical Technology*, Vol. I, Interscience Encyclopedia, New York, 1947, p. 701.

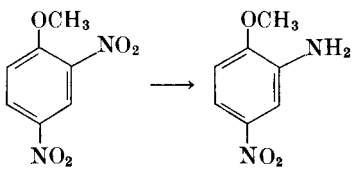
[15] F. Feigl and P. W. West, *Anal. Chem.*, **19**, 351 (1947).

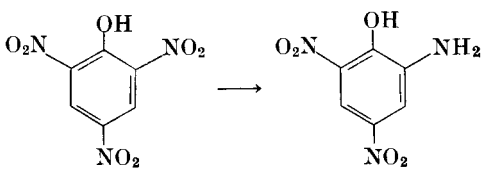
tables suggests some useful generalizations. For example, in substituted dinitro- and trinitro-benzenes (Tables II and III) the least hindered nitro group is preferentially reduced.





No simple generalization can be made about dinitronaphthalenes (Table II). In dinitro- and trinitro-phenols and their ethers (Table IV), a nitro group *ortho* to hydroxy or alkoxy is preferentially reduced.





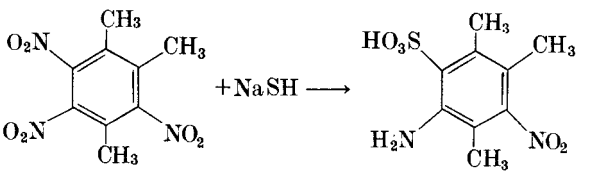
As a convenient laboratory procedure for converting nitroarenes to arylamines, the Zinin reduction is rarely surpassed by any other method. Catalytic hydrogenation requires more expensive equipment, and the techniques are considerably more difficult if one takes into account catalyst preparation, catalyst poisoning hazards, and the risk of reducing other groups. Reduction by iron is not generally a convenient laboratory method, being reserved for large-scale commercial applications. Moreover, it cannot be used for reduction of a single nitro group on a polynitro compound, nor can it be used on substrates harmed by acid media (*e.g.*, some ethers and thioethers). Although there are some exceptions, lithium aluminum hydride and lithium borohydride generally convert nitro compounds to mixtures of azoxy and azo compounds.

Side Reactions

The reduction of a nitroarene does not always give the corresponding arylamine. The reduction may stop at the intermediate hydroxylamine stage, or another group in the molecule may undergo reduction or other reaction. Generally these reactions are unwanted and should be avoided as much as possible. Occasionally the reaction is useful, as in the conversion of *o*-nitroazobenzenes to benzotriazoles or the conversion of *p*-nitrotoluene to *p*-aminobenzaldehyde. The principal side reactions are briefly described below.

Dehalogenation ($ArHal \rightarrow ArH$). Dehalogenations are rare. Only two occurrences were found in the literature: the conversion of 4,5-dichloro-3-iodonitrobenzene to 3,4-dichloroaniline[16] and the reduction of 2-chloro-1,3-dinitrobenzene to *m*-nitroaniline.[17]

Formation of Sulfonic Acid ($ArNO_2 \rightarrow ArSO_3H$). Three examples of the replacement of a nitro group by a sulfonic acid group are known. Each involves a trinitrobenzene with electron-releasing groups. The mechanism of this reaction is not known, but an oxygen exchange from the displaced nitro group to the entering sulfur species probably takes place. A Piria reaction* would be a possible explanation if excessive exposure to oxygen occurred.[3] 1,2,4-Trimethyl-3,5,6-trinitrobenzene is reduced to 1,2,4-trimethyl-5-amino-3-nitrobenzene-6-sulfonic acid in 40% yield.[18]



Similarly, 2,3,5-trinitro-1,4-xylene is converted to 3-amino-5-nitro-1,4-xylene-2-sulfonic acid[19] and 2,5-dimethyl-3,4,6-trinitroanisole to 2,5-dimethyl-4-amino-6-nitroanisole-3-sulfonic acid.[20]

* The formation of aminosulfonic acids from nitroarenes and metal sulfites; R. Piria, *Ann.*, **78**, 31 (1851).

[16] G. Koerner and A. Contardi, *Atti Acad. Lincei*, [5] **22**, 835 (1914); F. Beilstein, *Handbuch der Organischen Chemie*, Vol. XI–XII, 4th Ed., First Supplement, Julius Springer, Berlin (1933), p. 301.

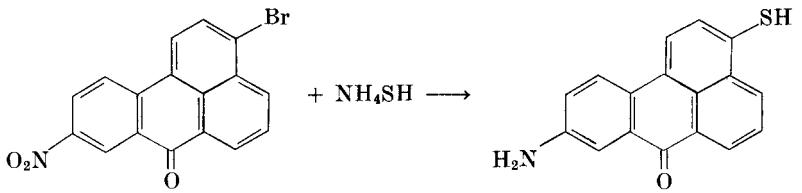
[17] W. Borsche and D. Rantscheff, *Ann.*, **379**, 160 (1911).

[18] J. J. Blanksma, *Rec. Trav. Chim. Pays-Bas*, **34**, 17 (1915).

[19] J. J. Blanksma, *Rec. Trav. Chim. Pays-Bas*, **24**, 49 (1905).

[20] J. J. Blanksma, *Rec. Trav. Chim. Pays-Bas*, **24**, 50 (1905).

Replacement of Halogen by the Mercapto Group (ArHal → ArSH). In the large number of Zinin reactions that have been studied, each involving sulfhydryl, sulfide, or polysulfide reagents, it is surprising that only one example of a halogen atom being replaced by a mercapto group was found: 3-bromo-9-nitro-7H-benz[de]anthracen-7-one was converted to 9-amino-3-mercapto-7H-benz[de]anthracen-7-one.[21] The bromine was activated by conjugation to a carbonyl group, which helps explain this unique replacement.



Hydroxylation (ArH → ArOH). Two examples of hydroxylation were found. In both, the hydroxyl group entered *ortho* to an acid group and a *meta* nitro group was reduced to amino. 3-Nitrobenzoic acid was converted to 3-amino-6-hydroxybenzoic acid.[5] 3-Nitrobenzenesulfonic acid was similarly converted to 3-amino-6-hydroxybenzenesulfonic acid.[22]

Hydroxylamine Formation ($ArNO_2 \rightarrow ArNHOH$). Hydroxylamines are thought to be intermediates in the Zinin reaction, but they have been isolated in only four instances. In none did the authors explain why further reduction did not occur. The reason may be that there was insufficient Zinin reagent to complete the reduction, or complexes resistant to reduction may have formed. Further study of these reactions using modern techniques should be made. The four examples are: dimethyl nitroterephthalate to dimethyl (hydroxyamino)terephthalate;[24] N-(*o*-nitrobenzyl)-*o*-toluamide to N-(*o*-hydroxyaminobenzyl)-*o*-toluamide;[25] N-methyl-3′-nitro-*p*-toluenesulfonanilide to N-methyl-3′-hydroxyamino-*p*-toluenesulfonanilide;[25] and dimethyl 5-nitroisophthalate to dimethyl 5-(hydroxyamino)isophthalate.[23] (Equation on p. 462.)

Thiosulfonic Acid Formation ($ArSO_3 \rightarrow ArSO_2SH$). Thiosulfonic acid derivatives were formed by the reduction of nitrobenzenesulfonic acids in two instances. In both, ammonium sulfide was the reducing agent.

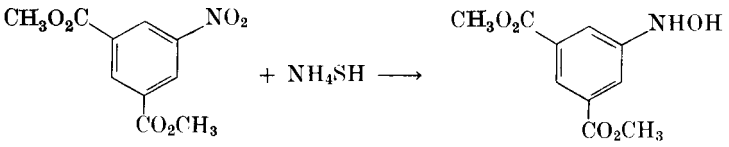
[21] E. Holzapfel, O. Braunsdorf, and P. Nawiasky, Ger. Pat. 443,022 (1927) [*Frdldr.*, **15**, 725 (1928)]. Here and elsewhere *Frdldr.* means P. Friedlaender, *Fortschritte der Teerfarben-fabrikation*, Julius Springer, Berlin.

[22] H. Goldschmidt and H. Larsen, *Z. Phys. Chem.* (Leipzig), **71**, 440 (1910).

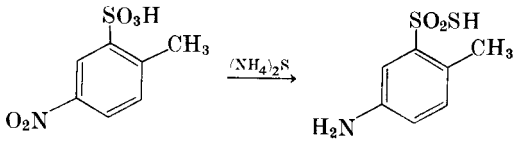
[23] J. B. Cohen and D. McCandlish, *J. Chem. Soc.*, **87**, 1269 (1905).

[24] K. Auwers and E. Frese, *Ann.*, **450**, 302 (1926).

[25] O. Baudisch, H. Gurewitsch, and S. Rothschild, *Ber.*, **49**, 200 (1916).

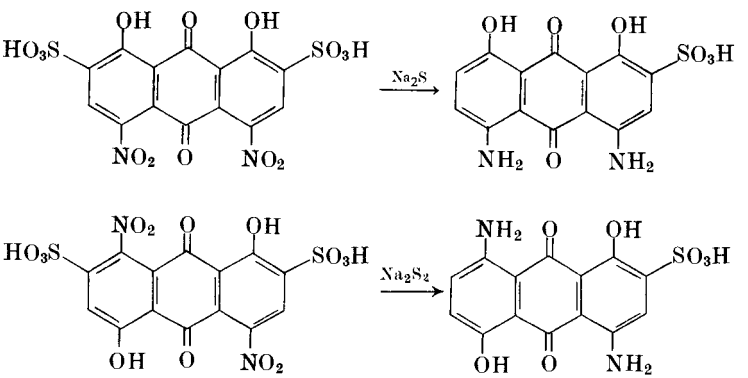


5-Nitro-*o*-toluenesulfonic acid was converted to 5-amino-*o*-toluenethiosulfonic acid.[26] Similarly, 3,5-dinitro-*p*-toluenesulfonic acid gave 3,5-diamino-*p*-toluenethiosulfonic acid.[27]



Reduction of Azido Groups ($ArN_3 \rightarrow ArNH_2$). In the reduction of nitro compounds containing an azido group the azido group is reduced to amino. Examples of this reaction are the reduction of 2-azido-1-nitroanthraquinone to 1,2-diaminoanthraquinone[28] and of 2,6-diazido-1,5-dinitroanthraquinone to 1,2,5,6-tetraaminoanthraquinone.[28]

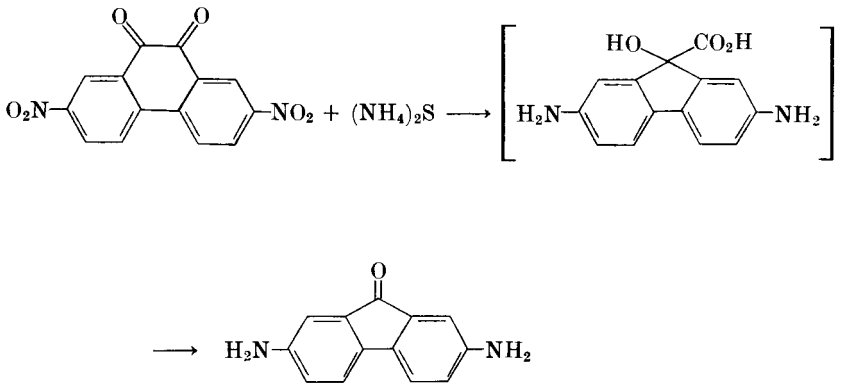
Elimination of a Sulfonic Acid Group ($ArSO_3H \rightarrow ArH$). There are two instances of hydrolysis of a sulfonic acid group from an aromatic ring during a Zinin reduction. Both involve disulfonic acids in which one group is hydrolyzed. The systems are both aqueous, sodium sulfide being utilized in the first reaction and sodium disulfide in the second. 1,8-Dihydroxy-4,5-dinitro-2,7-anthraquinonedisulfonic acid is reduced to



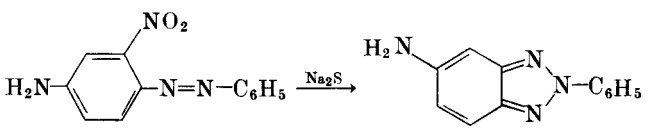
[26] H. Limpricht and A. Hefster, *Ann.*, **221**, 345 (1883).
[27] J. J. Blanksma, *Chem. Weekbl.*, **10**, 136 (1913).
[28] Bayer and Co., Ger. Pat. 337,734 (1921) [*Frdldr.*, **13**, 400 (1921)].

4,5-diamino-1,8-dihydroxy-2-anthraquinonesulfonic acid[29] and 1,5-dihydroxy-4,8-dinitro-2,7-anthraquinonedisulfonic acid to 4,8-diamino-1,5-dihydroxy-2-anthraquinonesulfonic acid.[29]

Decarbonylation (ArCOCOAr → ArCOAr). 2,7-Dinitrophenanthraquinone is converted to 2,7-diaminofluorenone by boiling with aqueous ammonium sulfide.[30] The decarbonylation probably results from a benzilic acid rearrangement followed by loss of carbon dioxide from the intermediate diphenyleneglycolic acid.



Benzotriazole Formation. An elegant method for preparing benzotriazoles is afforded by Zinin reduction of *o*-nitrophenylazo compounds. In the four reported examples, the yields are good. The reactions take place in alcoholic media using either ammonium sulfide or sodium sulfide. The structure required is a nitro group *ortho* to the azo group in a phenylazo compound. For example, 3-nitro-4-phenylazoaniline is converted to 5-amino-2-phenyl-2H-benzotriazole.[31] The other examples are *p*-(*o*-nitrophenylazo)aniline to 2-(*p*-aminophenyl)-2H-benzotriazole,[32] 4-(1-naphthylazo)-3-nitroaniline to 5-amino-2-(1-naphthyl)-2H-benzotriazole,[31] and *p*-(4-amino-2-nitrophenylazo)benzenesulfonic acid to *p*-(5-amino-2H-benzotriazol-2-yl)-benzenesulfonic acid.[32]



[29] Bayer and Co., Ger. Pat. 119,228 (1901) [*Frdldr.*, **6**, 1353 (1901)].
[30] G. Schultz and R. Anschutz, *Ber.*, **10**, 325 (1877).
[31] B. Chakrabarty and K. K. Barat, *J. Indian Chem. Soc.*, **5**, 585 (1928).
[32] B. Chakrabarty and K. K. Barat, *J. Indian Chem. Soc.*, **5**, 558 (1928).

Oxidation of Methyl or Methylene. An unusual reaction was extensively studied by Hodgson wherein *p*-nitrotoluene was reduced with sodium polysulfide in an alcoholic medium to give a 75% yield of *p*-aminobenzaldehyde;[33] detailed directions are given in *Organic Syntheses*.[34] Excess sodium hydroxide leads to a 10% yield with correspondingly higher *p*-toluidine production. In a similar reaction, 4,4'-dinitrodiphenylmethane is converted to a mixture of 4,4'-diaminobenzophenone and 4-amino-4'-nitrobenzophenone.[35]

Zinin Reduction of Compounds without a Nitro Group

A few kinds of compounds other than nitroarenes have been reduced under conditions of the Zinin reduction. Except for reduction of nitrosobenzenes to arylamines, the reductions have found little use. New applications could probably be found.

Reduction of Nitrosoarenes to Arylamines (Table XI). When reduced under the same conditions as the corresponding nitro compounds, nitrosoarenes produce the corresponding amines. Two N-nitrosoanilines have given the corresponding arylhydrazines.

Cleavage of Azo Groups ($ArN{=}NAr \rightarrow ArNH_2$). Two azo compounds substituted with hydroxy and ethoxy groups have been reduced with cleavage of the azo group: *p*-(3-hydroxy-4-methoxyphenylazo)-benzenesulfonic acid to 5-aminoguaicol[36] and *p*-(2-ethoxy-4-hydroxyphenylazo)benzenesulfonic acid to 4-amino-3-ethoxyphenol.[37]

Reduction of Azobenzenes to Hydrazobenzenes. The only example of hydrazobenzene formation from an azo compound, the conversion of 4,4'-dinitroazobenzene to 4,4'-diaminohydrazobenzene by ammonium sulfide in alcoholic solution, is in the 1850 literature and probably should be reinvestigated.[38]

EXPERIMENTAL CONDITIONS AND PROCEDURES

The experimental procedures given by no means cover all the modifications that have been employed during the more than one hundred years

[33] H. H. Hodgson, R. R. Davies, and H. G. Beard, *J. Chem. Soc.*, **1944**, 4.

[34] E. Campaigne, W. M. Budde, and G. F. Schaefer, *Org. Syntheses, Coll. Vol.* **4**, 31 (1963).

[35] L. M. Litvinenko, N. F. Levchenko, and S. U. Tsukerman, *Zh. Obshch. Khim.*, **29**, 1470 (1959) [*C.A.*, **54**, 8721 (1960)].

[36] M. Heidelberger and W. A. Jacobs, *J. Amer. Chem. Soc.*, **41**, 1459 (1919)

[37] M. Heidelberger and W. A. Jacobs, *J. Amer. Chem. Soc.*, **41**, 1467 (1919).

[38] A. Laurent and C. Gehrhardt, *Ann.*, **75**, 74 (1850).

this method has been used. It is hoped that the examples given will furnish the chemist with sufficient information that he may tailor the reagents or conditions to favor the reduction he requires. The large number of references should give ample background for the reduction of the particular type of compound that may be under investigation. In the tables eight reducing methods (based on the reduction system) are catalogued (see p. 467), and three of the methods are exemplified below. The reaction need not be limited to these systems, since other alkali sulfides or polysulfides may prove adequate. While the reaction mechanisms that have been presented indicate the involvement of water in the reaction, it may prove advantageous to use systems containing other solvents with reduced amounts of water.

5-Nitro-*m*-phenylenediamine (Method II).[39] An ammonium sulphide solution is prepared by passing hydrogen sulfide into a solution of 54 ml of concentrated aqueous ammonia and 100 ml of 95% ethyl alcohol. The solution is cooled during the addition, which continues until approximately 10.5 g (0.30 mol) of hydrogen sulfide is absorbed.

3,5-Dinitroaniline (5 g, 0.027 mol) is dissolved in 50 ml of 95% ethyl alcohol in a 150–200 ml flask provided with a reflux condenser and a dropping funnel. The solution is brought to a boil and 41 ml of the ammonium sulfide solution is added dropwise to the refluxing solution over a 3-hr period. The hydrogen sulfide content of the solution is approximately 2.8 g (0.082 mol).

After the addition the mixture is cooled and made strongly acid by the addition of 6 N hydrochloric acid. (Care should be taken to safely neutralize or otherwise remove the toxic hydrogen sulfide that may be evolved during the acidification). The hot reaction mixture is filtered to remove sulfur, and the filtrate is concentrated to about 200 ml. The solution is treated with aqueous ammonia to a blue test on litmus paper and cooled to precipitate 3.35 g (0.022 mol) of 5-nitro-*m*-phenylenediamine. The product is collected by filtration and the filtrate is saved for the recovery of an additional 0.2 g (0.0013 mol) of product by treatment with aqueous sodium carbonate and extraction with ether. The total yield is 85%, mp 140–141°; mp of N,N-diacetyl derivative, 270° (dec).

Metanilic Acid (Method VII).[3] A solution of 49.2 g (1.23 mol) of aqueous 30% sodium hydroxide and 67.4 g (1.14 mol) of sodium hydrosulfide (sodium sulfhydrate) in 211 ml of water is placed in a suitable Pyrex flask equipped with a stirrer, a reflux condenser, and a Glascol

[39] B. Flurscheim, *J. Prakt. Chem.*, [2] **71**, 538 (1905).

heating mantle. To the reducing solution is added 300 g of a 41.7% aqueous solution of the sodium salt of *m*-nitrobenzenesulfonic acid (0.556 mol). The mixture is agitated under reflux for 12 hours and then cooled to room temperature. Sulfur dioxide is passed into the stirred solution until the solution is acidic as indicated by pH test paper or other conventional methods. The resulting suspension is cooled to 20° and the colorless crystals of metanilic acid are removed by filtration. A second crop may be obtained by further cooling of the filtrate. The total yield is 110 g (99%).

The purity of the material is determined by a standard nitrite titration. Positive identification may be obtained by conversion to the sulfonamide derivative (mp 142°)[40] or by comparison of the infrared or ultraviolet spectrum with authentic spectra (*e.g.*, Sadtler Ref. No. 17193 and No. 5427, respectively).[41]

Sodium Picramate (Method IV).[42] Picric acid (10 g, 0.044 mol) is dissolved in 100 ml of methanol by heating the mixture to 55° with agitation. Enough aqueous sodium hydroxide or ammonium hydroxide is added to just neutralize the picric acid, using pH test papers or other conventional methods. The reducing agent (24 g of $Na_2S \cdot 9\ H_2O$, 0.10 mol, and 8.4 g, 0.10 mol, of sodium bicarbonate in 40 ml of water; equivalent to 5.6 g, 0.10 mol, of sodium hydrosulfide) is added evenly to the sodium picrate slurry during 10–15 minutes at 55–60°. The mixture should be tested with ferrous sulfate test paper until a positive black test, indicating the presence of excess sodium hydrosulfide, is obtained. Additional sodium hydrosulfide solution should be added if the test is not obtained. The mixture is cooled to 10°, and 150 ml of chilled water is added. Sodium picramate is filtered from the resulting slurry and washed with chilled salt solution. The yield is 8.37 g as picramic acid (96%).

The purity of the material is obtained by a standard nitrite titration. The melting point of the free acid isolated by acidification from the aqueous solution should be 169°. Further identification may be obtained by comparing the infrared or ultraviolet spectrum with authentic spectra (*e.g.*, Sadtler Ref. No. 5982 or No. 1685, respectively).[41] The authors note that with water alone as solvent a yield of 83% was obtained. With ethanol instead of methanol, the yield was only 55% even though twice the amount of reducing agent was used.

[40] R. L. Shriner and R. C. Fuson, *The Systematic Identification of Organic Compounds*, 2nd Ed., Wiley, New York, 1946, p. 176.

[41] "Sadtler Standard Spectra," Sadtler Research Laboratory, Inc., Philadelphia, Pa.

[42] H. H. Hodgson and E. R. Ward, *J. Chem. Soc.*, **1945**, 663.

TABULAR SURVEY

The tables include reactions reported before January 1973.

Space does not allow a complete description of the reactions listed. Reaction times and conditions are necessarily omitted. The tables do provide a key to the reducing media.

There was very little yield information in the older literature. Any yields reported are given in the tables; the absence of a yield means that none was reported.

The reduction methods are identified under the following designations: Method I, alcoholic ammonium sulfide; Method II, aqueous ammonium sulfide; Method III, alcoholic sodium sulfide; Method IV, aqueous sodium sulfide; Method V, alcoholic sodium polysulfide; Method VI, aqueous sodium polysulfide; Method VII, alcoholic sodium hydrosulfide; Method VIII, aqueous sodium hydrosulfide.

TABLE I. REDUCTION OF MONONITROARENES AND THEIR HALOGEN DERIVATIVES

Number of Carbon Atoms	Nitro Compound	Method	Product (Yield %)	Refs.
C_6	Nitrobenzene	I	Aniline	1
		V	" (71)	77
	1-Chloro-2-nitrobenzene	V	*o*-Chloroaniline	43a
	1-Chloro-3-nitrobenzene	V	*m*-Chloroaniline (70)	78
	1-Bromo-3-nitrobenzene	V	*m*-Bromoaniline (Good)	43a, 52
	1-Bromo-4-nitrobenzene	I	*p*-Bromoaniline	48
	1-Iodo-3-nitrobenzene	I	*m*-Iodoaniline	48
	1-Iodo-4-nitrobenzene	I	*p*-Iodoaniline	48
	1,2-Dichloro-3-iodo-5-nitrobenzene	I	3,4-Dichloroaniline	16
C_7	*o*-Nitrotoluene	V	*o*-Toluidine (65)	43a
	m-Nitrotoluene	V	*m*-Toluidine (60)	43a
	p-Nitrotoluene	I	*p*-Toluidine	44a
		V	*p*-Aminobenzaldehyde (75)	33, 34
	4-Chloro-2-nitrotoluene	V	5-Chloro-*o*-toluidine (100)	49
	2-Chloro-4-nitrotoluene	III	3-Chloro-*p*-toluidine	43a
		V	"	43a, 22, 23, 50
	2-Bromo-4-nitrotoluene	I	3-Bromo-*p*-toluidine (85)	51
		V	"	43a
	2-Iodo-4-nitrotoluene	V	3-Iodo-*p*-toluidine	43a
C_9	*p*-(Isopropyl)nitrobenzene	I	*p*-(Isopropyl)aniline	45, 66
C_{10}	1-Nitronaphthalene	I	1-Naphthylamine	1
		VIII	" (75)	46
	2-Nitronaphthalene	VII	2-Naphthylamine	43b
C_{11}	3-Methyl-1-nitronaphthalene	VII	3-Methyl-1-naphthylamine	44b
	6-Methyl-2-nitronaphthalene	VII	6-Methyl-2-naphthylamine	44b
	7-Methyl-1-nitronaphthalene	VII	7-Methyl-1-naphthylamine	44b
C_{12}	5-Nitroacenaphthene	I	5-Aminoacenaphthene	66
C_{14}	4-Nitrophenanthrene	I	4-Phenanthrylamine	47

Note: References 43–271 are on pp. 477–481.

TABLE II. REDUCTION OF DINITROARENES AND THEIR HALOGEN COMPOUNDS

Number of Carbon Atoms	Nitro Compound	Method	Product (Yield %)	Ref.
C_6	*o*-Dinitrobenzene	I	*o*-Nitroaniline	53, 57
		III	"	43a
		VII	"	88
	m-Dinitrobenzene	H_2S, pyridine	*m*-Nitroaniline (67)	54
		I	"	55
		VII	"	6
	p-Dinitrobenzene	I	*p*-Nitroaniline	56
	2-Chloro-1,3-dinitrobenzene	I	*m*-Nitroaniline	17
	5-Chloro-1,3-dinitrobenzene	I	5-Chloro-3-nitroaniline	23
	4-Chloro-2,6-dinitrotoluene	I	2-Amino-4-chloro-6-nitrotoluene	23
C_7	2,3-Dinitrotoluene	I	2-Nitro-*m*-toluidine (Low)	57, 58
	2,4-Dinitrotoluene	I	3-Nitro-*p*-toluidine	59
		VII	" (80)	62
	3,5-Dinitrotoluene	II	5-Nitro-*m*-toluidine	67
		I	" (86)	61
	2,6-Dinitrotoluene	I	3-Nitro-*o*-toluidine (Good), (96), (80)	63, 64
C_8	1-Ethyl-2,4-dinitrobenzene	II	4-Ethyl-3-nitroaniline (Low)	60
	3,5-Dinitro-*o*-xylene	II	5-Nitro-3,4-xylidine	68
	2,4-Dinitro-*m*-xylene	I	3-Nitro-2,4-xylidine	69
	4,6-Dinitro-*m*-xylene	I	5-Nitro-2,4-xylidine	70
	2,5-Dinitro-*p*-xylene	I	4-Nitro-2,5-xylidine	71
	2,6-Dinitro-*p*-xylene	I	3-Nitro-2,5-xylidine	70
C_9	3,5-Dinitro-1,2,4-trimethylbenzene	I	2,4,5-Trimethyl-3-nitroaniline	72
		III	2-Amino-4-nitro-3,5,6-trimethylbenzenesulfonic acid (40)	73
	3,6-Dinitro-1,2,4-trimethylbenzene	I	2,3,5-Trimethyl-4-nitroaniline	72
	2,6-Dinitromesitylene	I	2,4,6-Trimethyl-3-nitroaniline (40)	89
C_{10}	1,3-Dinitronaphthalene	II	3-Nitro-1-naphthylamine	75
	1,5-Dinitronaphthalene	I	5-Nitro-1-naphthylamine (63)	76, 77
	1,6-Dinitronaphthalene	I	5-Nitro-2-naphthylamine (40)	75
	1,7-Dinitronaphthalene	I	8-Nitro-2-naphthylamine	75
	1,8-Dinitronaphthalene	$(NH_4)_2S$ in $C_6H_5NH_2$	1,8-Diaminonaphthalene (77)	86
	2,3-Dinitronaphthalene	III	3-Nitro-2-naphthylamine	11
C_{11}	1,5-Dinitro-2-methylnaphthalene	I	6-Methyl-5-nitro-1-naphthylamine	79
C_{12}	5-t-Butyl-2,4-dinitro-*m*-xylene	IV	4-t-Butyl-3-nitro-2,6-xylidine	74
	2,4′-Dinitrobiphenyl	I	4-Amino-2′-nitrobiphenyl	84
	4,4′-Dinitrobiphenyl	I	4-Amino-4′-nitrobiphenyl	80
		VIII	Benzidine	81, 82
C_{13}	4,4′-Dinitrodiphenylmethane	V	4,4′-Diaminobenzophenone, 4-amino-4′-nitrobenzophenone	35
C_{14}	2,4-Dinitrostilbene	I, IV	4-Amino-2-nitrostilbene (Good)	17, 83
	4,4′-Dinitrostilbene	IV	4,4′-Diaminostilbene (Good)	17
	4,4′-Dinitro-3,3′-dimethylbiphenyl	VI	4-Amino-3,3′-dimethyl-4′-nitrobiphenyl	85
	Bis-(2-nitro-*p*-tolyl) disulfide	VI	6-(2-Nitro-*p*-tolyldithio)-*m*-toluidine	250

Note: References 43–271 are on pp. 477–481.

TABLE III. Reduction of Trinitroarenes

Number of Carbon Atoms	Trinitro Compound	Method	Product (Yield %)	Ref.
C_6	1,3,5-Trinitrobenzene	V	3,5-Dinitroaniline	90
		I	"	91
		VII	"	43a
C_7	2,4,6-Trinitrotoluene	I	3,5-Dinitro-*p*-toluidine	92
		I	N-(2,4-Dinitro-*o*-tolyl) hydroxylamine	93
C_8	1-Ethyl-2,4,6-trinitrobenzene	I	4-Ethyl-3,5-dinitroaniline	94
	2,4,6-Trinitro-*m*-xylene	I	3,5-Dinitro-2,4-xylidine	95
	2,3,5-Trinitro-*p*-xylene	I	6-Amino-4-nitro-2,5-xylenesulfonic acid	19
C_9	2,4,6-Trinitromesitylene	I	2,4,6-Trimethyl-3,5-dinitroaniline	96
		I	2,4,6-Trimethyl-5-nitro-*m*-phenylenediamine	97
	1,2,4-Trimethyl-3,5,6-trinitrobenzene	I	2-Amino-3,5,6-trimethyl-4-nitrobenzenesulfonic acid (40)	18
C_{11}	3-*t*-Butyl-2,4,6-trinitrotoluene	I	4-*t*-Butyl-3,5-dinitro-*o*-toluidine	99
C_{12}	5-*t*-Butyl-2,4,6-trinitro-*m*-xylene	I	4-*t*-Butyl-3,5-dinitro-2,6-xylidine	98

Note: References 43–271 are on pp. 477–481.

TABLE IV. Reduction of Nitrophenols and Ethers

Number of Carbon Atoms	Nitro Compound	Method	Product (Yield %)	Ref.
C_6	*o*-Nitrophenol	I	*o*-Aminophenol	100
	2,4-Dinitrophenol	I	2-Amino-4-nitrophenol (32)	103
	2-Chloro-4,6-dinitrophenol	I	6-Amino-2-chloro-4-nitrophenol	104
	2-Bromo-4,6-dinitrophenol	I	6-Amino-2-bromo-4-nitrophenol	105
	4-Bromo-2,6-dinitrophenol	II	2-Amino-4-bromo-6-nitrophenol	106
	Picric acid	I	2-Amino-4,6-dinitrophenol (84)	111
		VIII	" (84)	112
		IV	" (96)	40
C_7	*o*-Nitroanisole	I	*o*-Anisidine	18
	p-Nitroanisole	I	*p*-Anisidine	101
	2,4-Dinitroanisole	V	5-Nitro-*o*-anisidine	43a
C_8	2-Methyl-5-nitroanisole	V	4-Methyl-*m*-anisidine	102
	2,4-Dinitrophenetole	I	5-Nitro-*o*-phenetidine	43a
C_9	2,3-Dimethoxy-5,6-dinitrotoluene	I	4,5-Dimethoxy-2-nitro-*m*-toluidine	107
	2,3-Dimethoxy-4,6-dinitrotoluene	VIII	2,3-Dimethoxy-5-nitro-*p*-toluidine (Excellent)	108
	1,2,4-Trimethoxy-5,6-dinitrobenzene	I	3,4,6-(or 3,5,6)-Trimethoxy-2-nitroaniline	109
	2,5-Dimethyl-3,4,6-trinitroanisole	VII	6-Amino-3-methoxy-4-nitro-2,5-xylenesulfonic acid	20
C_{15}	2,4-Dinitro-4′-methoxystilbene	I	4-Amino-4′-methoxy-2-nitrostilbene	110

Note: References 43–271 are on pp. 477–481.

TABLE V. Reduction of Nitroaryl Ketones and Aldehydes

Number of Carbon Atoms	Nitro Compound	Method	Product (Yield %)	Ref.
C_6	*p*-Nitrobenzaldehyde	V	*p*-Aminobenzaldehyde	43a
	5-Bromo-3-nitrobenzaldehyde	V	3-Amino-5-bromobenzaldehyde	113
C_7	4-Nitro-*o*-anisaldehyde	V	4-Amino-*o*-anisaldehyde	102
	4-Nitro-*m*-anisaldehyde	V	4-Amino-*m*-anisaldehyde	114
C_{12}	3,5-Dinitrobenzophenone	I	3-Amino-5-nitrobenzophenone	116
C_{13}	2-Nitrofluorenone	III	2-Aminofluorenone (77)	115
	3-Nitrofluorenone	IV	3-Aminofluorenone	115
	3,5-Dinitro-4-methylbenzophenone	I	3-Amino-4-methyl-5-nitrobenzophenone	117
	2,7-Dinitrofluorenone	V	2,7-Diaminofluorenone	117
	4-Methyl-3,4′,5-trinitrobenzophenone	I	4′,5-Diamino-4-methyl-3-nitrobenzophenone	117
C_{14}	2-Methoxy-7-nitrofluorenone	III	7-Amino-2-methoxyfluorenone	115
	3-Nitro-7H-benz[de]anthracen-7-one	VI	3-Amino-7H-benz[de]anthracen-7-one (83)	121
	3-Bromo-9-nitro-7H-benz[de]-anthracen-7-one	I	9-Amino-3-mercapto-7H-benz[de]-anthracen-7-one, 3,3′-thiobis(9-amino-7H-benz[de]anthracen-7-one	21
C_{15}	N-(4,5-Dimethoxy-2-nitrobenzylidene)aniline	III	N-(2-Amino-4,5-dimethoxybenzylidene)aniline (80)	120
C_{17}	N-(5-Ethoxy-2-nitrobenzylidene)-*p*-phenetidine	III	N-(2-Amino-5-ethoxybenzylidene)-*p*-phenetidine	118
C_{18}	6-*t*-Butyl-2,4-dimethyl-3,3′,5-trinitrobenzophenone	II	3-Amino-6-*t*-butyl-2,4-dimethyl-3′,5-dinitrobenzophenone	118

Note: References 43–271 are on pp. 477–481.

TABLE VI. Reduction of Nitroarene Carboxylic Acids, Esters, and Amid

Number of Carbon Atoms	Nitro Compound	Method	Product (Yield %)	Ref.
C_7	*m*-Nitrobenzoic acid	II	5-Amino-2-hydroxybenzoic acid	5
	2-Chloro-3-nitrobenzoic acid	II	3-Amino-2-chlorobenzoic acid (60)	122
	p-Nitrobenzoic acid	II	*p*-Aminobenzoic acid	123
	p-Nitrobenzamide	II	*p*-Aminobenzamide	125
	3-Nitrosalicylic acid	II	3-Aminosalicylic acid	132
	3,5-Dinitrobenzoic acid	I	3-Amino-5-nitrobenzoic acid	137
		I	3,5-Diaminobenzoic acid	138
	3,5-Dinitrobenzamide	II	3,5-Diaminobenzamide	139
	3,5-Dinitrosalicylic acid	II	3-Amino-5-nitrosalicylic acid	142
C_8	*p*-Nitrophenylacetic acid	II	*p*-Aminophenylacetic acid (84)	129
	3-Nitrophthalic acid	IV	3-Aminophthalic acid	131
	4-Nitrophthalic acid	IV	4-Aminophthalic acid	131
	p-Nitrobenzoylurea	I	*p*-Aminobenzoylurea	134
	5-Bromo-3-nitroanisic acid	II	3-Amino-5-bromoanisic acid	135
C_9	4-Nitrohippuric acid	II	4-Aminohippuric acid (45)	126
	2,4-Dimethyl-6-nitrobenzoic acid	IV	2-Amino-4,6-dimethylbenzoic acid	128
	2,4-Dimethyl-3,5-dinitrobenzoic acid	I	5-Amino-2,4-dimethyl-3-nitrobenzoic acid (95)	140

Note: References 43–271 are on pp. 477–481.

TABLE VI. REDUCTION OF NITROARENE CARBOXYLIC ACIDS, ESTERS, AND AMIDES (*Continued*)

Number of Carbon Atoms	Nitro Compound	Method	Product (Yield %)	Ref.
C_{10}	3-Nitro-4-isopropylbenzoic acid	II	3-Amino-4-isopropylbenzoic acid	127
	2-(*p*-Nitrophenyl)butyric acid	II	2-(*p*-Aminophenyl)butyric acid	130
	Dimethyl 5-nitroisophthalate	II	Dimethyl 5-(hydroxyamino)isophthalate	23
	Dimethyl nitroterephthalate	I	Dimethyl (hydroxyamino)terephthalate	24
	N-(*p*-Nitrophenacyl)glycine	I	N-(*p*-Aminophenylacetyl)glycine	133
	2-(2,4-Dinitrophenyl)isobutyric acid	II	2-(4-Amino-2-nitrophenyl)isobutyric acid	141
C_{14}	*o*-Methoxyphenyl *p*-nitrobenzoate	II	*o*-Methoxyphenyl *p*-aminobenzoate	124
	5,5′-Dinitrodiphenic acid	IV	5,5′-Diaminodiphenic acid	143
C_{15}	N-(*o*-Nitrobenzyl)-*o*-toluamide	I	N-(*o*-Hydroxyaminobenzyl-*o*-toluamide (80)	25

Note: References 43–271 are on pp. 477–481.

TABLE VII. REDUCTION OF NITROARENESULFONIC ACIDS

Number of Carbon Atoms	Nitro Compound	Method	Product (Yield %)	Refs.
C_6	*o*-Nitrobenzenesulfonic acid	I	*o*-Aminobenzenesulfonic acid	144
	m-Nitrobenzenesulfonic acid	I	Metanilic acid	145
		VII	"	5
		VII	" (99)	3
		IV	4-Amino-1-phenol-2-sulfonic acid	22, 146
	p-Nitrobenzenesulfonic acid	I	Sulfanilic acid	144
	4-Bromo-3-nitrobenzenesulfonic acid	II	4-Bromometanilic acid	147
	5-Bromo-2-nitrobenzenesulfonic acid	II	2-Amino-5-bromobenzenesulfonic acid	148
	6-Nitro-1-phenol-2,4-disulfonic acid	IV	6-Amino-1-phenol-2,4-disulfonic acid	166
	2-Hydrazino-4-nitrobenzenesulfonic acid	I	2-Hydrazinosulfanilic acid	167
	2,6-Dinitro-1-phenol-4-sulfonic acid	IV	2-Amino-6-nitro-1-phenol-4-sulfonic acid	173
C_7	2-Nitro-*m*-toluenesulfonic acid	I	2-Amino-*m*-toluenesulfonic acid	149
	2-Nitro-*p*-toluenesulfonic acid	I	2-Amino-*p*-toluenesulfonic acid	59
	4-Nitro-*o*-toluenesulfonic acid	I	4-Amino-*o*-toluenesulfonic acid	150
	3(or 5)-Bromo-2-nitro-*p*-toluenesulfonic acid	I	2-Amino-3(or 5)-bromo-*p*-toluenesulfonic acid	151
	5-Nitro-*o*-toluenesulfonic acid	I	5-Amino-*o*-toluenesulfonic acid	59
	5-Nitro-*o*-toluenesulfonic acid	I	5-Amino-*o*-toluenethiosulfonic acid	26
	6-Nitro-*m*-toluenesulfonic acid	I	6-Amino-*m*-toluenesulfonic acid	152
	m-Nitro-α-toluenesulfonic acid	I	*m*-Amino-α-toluenesulfonic acid	156
	2-Nitro-4-sulfobenzoic acid	I	4-Sulfoanthranilic acid	161
		II	" (55)	162
	3-Nitro-4-sulfobenzoic acid	I	3-Amino-4-sulfobenzoic acid	163
	4-Nitrotoluene-2,6-disulfonic acid	I	4-Aminotoluene-2,6-disulfonic acid	164

Note: References 43–271 are on pp. 477–481.

TABLE VII. REDUCTION OF NITROARENESULFONIC ACIDS (*Continued*)

Number of Carbon Atoms	Nitro Compound	Method	Product (Yield %)	Refs.
C_7 (contd.)	3,5-Dinitro-*p*-toluenesulfonic acid	I	3-Amino-5-nitro-*p*-toluenesulfonic acid	168–17
			3,5-Diamino-*p*-toluenethiosulfonic acid	27
	2,4-Dinitro-α-toluenesulfonic acid	II	2(or 4)-Amino-4(or 2)-nitro-α-toluenesulfonic acid	171
C_8	5-Nitro-2,4-xylenesulfonic acid	I	5-Amino-2,4-xylenesulfonic acid	153
C_9	3-Nitro-2,4,6-trimethylbenzenesulfonic acid	II	3-Amino-2,4,6-trimethylbenzenesulfonic acid	155
C_{10}	4-Nitro-1-naphthalenesulfonic acid	I	4-Amino-1-naphthalenesulfonic acid	157
	5-Nitro-1-naphthalenesulfonic acid	I	5-Amino-1-naphthalenesulfonic acid	158
	5-Nitro-2-naphthalenesulfonic acid	I	5-Amino-2-naphthalenesulfonic acid	159
	8-Nitro-2-naphthalenesulfonic acid	I	8-Amino-2-naphthalenesulfonic acid	160
	4-Nitro-2,6-naphthalenedisulfonic acid	I	4-Amino-2,6-naphthalenedisulfonic acid	165
	4-Nitro-2,7-naphthalenedisulfonic acid	I	4-Amino-2,7-naphthalenedisulfonic acid	165
	8-Hydroxy-5,7-dinitro-2-naphthalenesulfonic acid	IV	2-Amino-4-nitro-1-naphthol-7-sulfonic acid	172
	4,5-Dinitro-2,7-naphthalenedisulfonic acid	I	4,5-Diamino-2,7-naphthalenedisulfonic acid	167
C_{11}	5-Isobutyl-3-nitro-*o*-toluenesulfonic acid	I	3-Amino-5-isobutyl-*o*-toluenesulfonic acid	154
C_{14}	4,4′-Dinitro-2,2′-stilbenedisulfonic acid	IV	4-Amino-4′-nitro-2,2′-stilbenedisulfonic acid (80)	174

Note: References 43–271 are on pp. 477–481.

TABLE VIII. REDUCTION OF NITROQUINONES AND DERIVATIVES

Number of Carbon Atoms	Nitro Compound	Method	Product (Yield %)	Ref.
C_{14}	1-Nitroanthraquinone	IV	1-Aminoanthraquinone	175
	2-Chloro-5-nitroanthraquinone	IV	1-Amino-6-chloroanthraquinone (90–95)	176
	8-Nitro-2-anthraquinonesulfonic acid	Lead salt H_2S	8-Amino-2-anthraquinonesulfonic acid	187
	2-Nitrophenanthrenequinone	IV	2-Aminophenanthrenequinone (89)	180
	1-Hydroxy-4-nitroanthraquinone	IV	1-Amino-4-hydroxyanthraquinone	183
	2-Azido-1-nitroanthraquinone	IV	1,2-Diaminoanthraquinone	28
	2,6-Diazido-1,5-dinitroanthraquinone	IV	1,2,5,6-Tetraminoanthraquinone	193
	2-Amino-1-nitroanthraquinone	IV	1,2-Diaminoanthraquinone (88)	211
	1-Amino-4-chloro-2-nitroanthraquinone	IV	1,2-Diamino-4-chloroanthraquinone	212
	1,5-Dinitroanthraquinone	II	1,5-Diaminoanthraquinone (90)	194
	1,6-Dinitroanthraquinone	II	1,6-Diaminoanthraquinone	195

Note: References 43–271 are on pp. 477–481.

TABLE VIII. REDUCTION OF NITROQUINONES AND DERIVATIVES (*Continued*)

Number of Carbon Atoms	Nitro Compound	Method	Product (Yield %)	Refs.
C_{14} (contd.)	2,7-Dinitrophenanthrenequinone	VIII	2-Amino-7-nitrophenanthrenequinone	199
		I	2,7-Diaminofluorenone	30
	1,5-Dinitro-2,6-dihydroxyanthraquinone	III	1,5-Diamino-2,6-dihydroxyanthraquinone	202
	1,8-Dinitro-5,7,12,14-pentacenetetrone	VIII	1,8-Diamino-5,7,12,14-pentacenetetrone (95)	197
	1,2,4,5,6,8-Hexahydroxy-3,7-dinitroanthraquinone	IV	3,7-Diamino-1,2,4,5,6,8-hexahydroxyanthraquinone	203
	7-Bromo-1,8-dihydroxy-4,5-dinitro-2-anthraquinonesulfonic acid	IV	4,5-Diamino-7-bromo-1,8-dihydroxy-2-anthraquinonesulfonic acid	204
	6-Bromo-1,5-dihydroxy-4,8-dinitro-2-anthraquinonesulfonic acid	IV	4,8-Diamino-6-bromo-1,5-dihydroxy-2-anthraquinonesulfonic acid	204
	1,8-Dihydroxy-4,5-dinitro-2,7-anthraquinonedisulfonic acid	IV	4,5-Diamino-1,8-dihydroxy-2-anthraquinonesulfonic acid	29
	1,5-Dihydroxy-4,8-dinitro-2,6-anthraquinonedisulfonic acid	VIII	4,8-Diamino-1,5-dihydroxy-2,6-anthraquinonedisulfonic acid (100)	206
	1,5-Dihydroxy-4,8-dinitro-2,7-anthraquinonedisulfonic acid	IV	4,8-Diamino-1,5-dihydroxy-2-anthraquinonesulfonic acid	29
	2,6-Dihydroxy-1,5-dinitro-3,7-anthraquinonedisulfonic acid	VIII	1,5-Diamino-2,6-dihydroxy-3,7-anthraquinonedisulfonic acid	207
C_{15}	2-Methyl-1-nitroanthraquinone	IV	1-Amino-2-methylanthraquinone (97)	177
	2-Methoxy-1-nitroanthraquinone	IV	1-Amino-2-methoxyanthraquinone	181
	1-Nitro-2-anthraquinonecarboxamide	II	1-Amino-2-anthraquinonecarboxamide	184
	1-Amino-2-methyl-4-nitroanthraquinone	IV	1,4-Diamino-2-methylanthraquinone	212
	1-Hydroxy-3-methyl-2-nitroanthraquinone	IV	2-Amino-1-hydroxy-3-methylanthraquinone	182
	1-Nitro-2-anthraquinonecarboxylic acid	IV	1-Amino-2-anthraquinonecarboxylic acid	184
	5-Nitro-1-anthraquinonesulfonic acid	II	5-Amino-1-anthraquinonesulfonic acid	185
	8-Nitro-1-anthraquinonesulfonic acid	II	8-Amino-1-anthraquinonesulfonic acid	185
	5-Nitro-2-anthraquinonesulfonic acid	VI	5-Amino-2-anthraquinonesulfonic acid	186
	2-Methyl-1,5-dinitroanthraquinone	IV	1,5-Diamino-2-methylanthraquinone (100)	196
	2-Methyl-1,8-dinitroanthraquinone	IV	1,8-Diamino-2-methylanthraquinone (95)	196
	1-Hydroxy-3-methyl-2,4-dinitroanthraquinone	IV	2,4-Diamino-1-hydroxy-3-methylanthraquinone	201
C_{16}	2-Amino-3-nitrofluorenone	III	2,3-Diaminofluorenone	117
	1,2-Dimethoxy-3-nitroanthraquinone	IV	3-Amino-1,2-dimethoxyanthraquinone (100)	188
	1,2-Dimethoxy-4-nitroanthraquinone	II	4-Amino-1,2-dimethoxyanthraquinone (67)	189
	1,3-Dimethyl-2,4-dinitroanthraquinone	IV	1,3-Dimethyl-2,4-diaminoanthraquinone	179
C_{18}	4-Nitrobenz[a]anthracen-7,12-dione	IV	4-Aminobenz[a]anthracen-7,12-dione	190
	3-Methoxy-2-nitro-7-H-benz[de]anthracen-7-one	III	2-Amino-3-methoxy-7-H-benz[de]anthracen-7-one	191
C_{22}	4,10-Dinitrodibenzo[de,jk]pyrene-6,12-dione	IV	4,10-Diaminodibenzo[de,jk]-pyrene-6,12-dione	200

Note: References 43–271 are on pp. 477–481.

TABLE IX. Reduction of Nitroarylamines

Number of Carbon Atoms	Nitro Compound	Method	Product (Yield %)	Ref.
C_6	*o*-Nitroaniline	IV	*o*-Phenylenediamine	208
	2,4-Dinitroaniline	VII	4-Nitro-*o*-phenylenediamine (80)	216
	2,6-Dinitroaniline	I	3-Nitro-*o*-phenylenediamine	119
	3,5-Dinitroaniline	II	5-Nitro-*m*-phenylenediamine (86)	39
C_7	4,6-Dinitro-*o*-toluidine	I	2,3-Diamino-5-nitrotoluene	217
	4,6-Dinitro-*o*-anisidine	II	3-Methoxy-5-nitro-*o*-phenylenediamine	226
	4-Amino-3,5-dinitrobenzoic acid	I	3,4-Diamino-5-nitrobenzoic acid	227
	N-Methyl-2,4-dinitroaniline	VIII	N^1-Methyl-4-nitro-*o*-phenylenediamine (60)	239
	2-Anilino-3,5-dinitrobenzoic acid	II	2-Anilino-2,5-diaminobenzoic acid	246
C_8	2′-Nitro-*p*-acetotoluidide	I	2′-Amino-*p*-acetotoluidide	209
	3,5-Dinitro-2,4-xylidine	I	2,4-Dimethyl-5-nitro-*m*-phenylenediamine	218
	4,6-Dinitro-2,5-xylidine	III	3,6-Dimethyl-4-nitro-*o*-phenylenediamine (81)	219
	N-Ethyl-2,4-dinitroaniline	II	N^1-Ethyl-4-nitro-*o*-phenylenediamine	234
	2,5-Dinitro-N-methyl-*p*-toluidine	I	2-Amino-5-nitro-N^4-methyl-*p*-toluidine	229
	3,5-Dinitro-N-methyl-*p*-toluidine	I	3-Amino-5-nitro-N^4-methyl-*p*-toluidine	235
C_9	2,4,6-Trimethyl-3,5-dinitroaniline	I	2,4,6-Trimethyl-5-nitro-*m*-phenylenediamine	222
C_{10}	2,3,5,6-Tetramethyl-4-nitroaniline	I	2,3,5,6-Tetramethyl-*p*-phenylenediamine	210
	4-Amino-7-nitro-1-naphthalenesulfonic acid	I	4,7-Diamino-1-naphthalenesulfonic acid	215
	4-*t*-Butyl-2,6-dinitroaniline	I	4-*t*-Butyl-6-nitro-*o*-phenylenediamine	220
C_{11}	4-*t*-Amyl-2,6-dinitroaniline	I	4-*t*-Amyl-6-nitro-*o*-phenylenediamine	221
C_{12}	3,5-Dinitro-*o*-phenylenediamine	I	5-Nitro-1,2,3-benzenetriamine	214
	3,4′-Dinitrobiphenylamine	I	3-Nitrobenzidine	223
	2,4-Dinitrodiphenylamine	I	2-Amino-4-nitrodiphenylamine	224
	2,4′-Dinitrodiphenylamine	I	2-Amino-4′-nitrodiphenylamine	236
	4,4′-Dinitrodiphenylamine	IV	4-Amino-4′-nitrodiphenylamine	237
	2′-Chloro-2,4-dinitrodiphenylamine	V	2-Amino-4-nitro-2′-chlorodiphenylamine	238
	4-Amino-2′,4′-dinitrodiphenylamine	I	2,2′-Diamino-4′-nitrodiphenylamine	242
C_{13}	2-Amino-3-nitro-9-fluorenone	III	2,3-Diamino-9-fluorenone	117
	2-Methyl-2′,4′-dinitrodiphenylamine	III	2-Methyl-2′-amino-4′-nitrodiphenylamine	228
	4-Methyl-2′,4′-dinitrodiphenylamine	I	4-Methyl-2′-amino-4′-nitrodiphenylamine	224
	N-Methyl-2,4-dinitrodiphenylamine	III	N-Methyl-2-amino-4-nitrodiphenylamine	240
	4-Anilino-3,5-dinitrobenzoic acid	VI	3-Amino-4-anilino-5-nitrobenzoic acid (93)	245
	N-Methyl-2,2′,4,4′-tetranitrodiphenylamine	I	N-Methyl-2-amino-2′,4,4′-trinitrodiphenylamine	251

Note: References 43–271 are on pp. 477–481.

TABLE IX. REDUCTION OF NITROARYLAMINES (*Continued*)

Number of Carbon Atoms	Nitro Compound	Method	Product (Yield %)	Ref.
C_{14}	2-Amino-1-nitroanthraquinone	IV	1,2-Diaminoanthraquinone (88)	211
	1-Amino-4-chloro-2-nitroanthraquinone	IV	1,2-Diamino-4-chloroanthraquinone	212
	1-Amino-2,4-dinitroanthraquinone	I	1,2,4-Triaminoanthraquinone	225
	3-Nitro-4-*p*-toluidinobenzoic acid	VI	3-Amino-4-*p*-toluidinobenzoic acid (33)	230
	4′-(2,4-Dinitroanilino) acetanilide	I	4′-(2-Amino-4-nitroanilino) acetanilide	241
	2′,6′-Dinitro-*p*-toluobenzamide	II	2′-Amino-6′-nitro-*p*-toluobenzamide	247
C_{15}	1-Amino-2-methyl-4-nitroanthraquinone	IV	1,4-Diamino-2-methylanthraquinone	212
C_{16}	1-Amino-2-ethoxy-4-nitroanthraquinone	IV	1,4-Diamino-2-ethoxyanthraquinone	213
	N-(2,4-Dinitrophenyl)-1-naphthylamine	I	N-(2-Amino-4-nitrophenyl)-1-naphthylamine (60)	243
	N-(2,4-Dinitrophenyl)-2-naphthylamine	IV	N-(2-Amino-4-nitrophenyl)-2-naphthylamine	244
C_{17}	4-(1-Naphthylamino)-3-nitrobenzoic acid	I	3-Amino-4-(1-naphthylamino)-benzoic acid	231
C_{18}	N-Methyl-3′-nitro-*p*-toluenesulfonanilide	III	N-Methyl-3′-hydroxyamino-*p*-toluenesulfonanilide	25
	N-(2,4-Dinitrophenyl)-2-diphenylamine	III	N-(2-Amino-4-nitrophenyl)-2-diphenylamine	252
C_{21}	2-(1-Anthraquinonylamino)-5-nitrobenzoic acid	III	5-Amino-2-(1-anthraquinonylamino)benzoic acid	232
	1-Benzamido-4-nitroanthraquinone	II	1-Benzamido-4-aminoanthraquinone	248
C_{28}	1,5-Dibenzamido-4,8-dinitroanthraquinone	II	1,5-Dibenzamido-4,8-diaminoanthraquinone	249

Note: References 43–271 are on pp. 477–481.

TABLE X. REDUCTION OF NITROARYL AZO COMPOUNDS

Number of Carbon Atoms	Nitro Compound	Method	Product (Yield %)	Ref.
C_{12}	3-Nitroazobenzene	V	*m*-Phenylazoaniline (90)	253
	4-Nitroazobenzene	V	*p*-Phenylazoaniline (90)	253
	p-(*p*-Nitrophenylazo)phenol	I	*p*-(*p*-Aminophenylazo)phenol	255
	4-(*p*-Nitrophenylazo)resorcinol	II	4-(*p*-Aminophenylazo)resorcinol	256
	4-(*p*-Nitrophenylazo)benzenesulfonic acid	II	4-(*p*-Aminophenylazo)benzenesulfonic acid	257
	3-Nitro-4-phenylazoaniline	I	5-Amino-2-phenyl-2H-benzotriazole	31
	p-(*o*-Nitrophenylazo)aniline	I	2-(*p*-Aminophenyl)-2H-benzotriazole	32
	p-(*p*-Nitrophenylazo)aniline	I	4,4′-Diaminoazobenzene	261
		III	4,4′-[Azobis(*p*-phenyleneazo)]-dianiline	262
	4-(*p*-Nitrophenylazo)-*m*-phenylenediamine	IV	4-(*p*-Aminophenylazo)-*m*-phenylenediamine	265

Note: References 43–271 are on pp. 477–481.

TABLE X. REDUCTION OF NITROARYL AZO COMPOUNDS (*Continued*)

Number of Carbon Atoms	Nitro Compound	Method	Product (Yield %)	Ref.
C_{12} (contd.)	*p*-(4-Amino-2-nitrophenylazo)-benzenesulfonic acid	I	*p*-(5-Amino-2H-benzotriazol-2-yl)-benzenesulfonic acid (Good)	32
	4,4′-Dinitroazobenzene	I	4,4′-Diaminohydrazobenzene	38
	4,4′-Azobis-(2-nitrophenol)	I	4,4′-Azobis-(2-aminophenol) (30)	270
	3,3′-Azobis-(6-nitrobenzene-sulfonic acid)	II	3,3′-Azobis-(6-aminobenzene-sulfonic acid)	269
C_{13}	5-(*p*-Nitrophenylazo)salicylic acid	II	5-(*p*-Aminophenylazo)salicylic acid	256
C_{14}	N,N-Dimethyl-*p*-(*o*-nitrophenylazo)aniline	V	*p*-(*o*-Aminophenylazo)-N,N-dimethylaniline	254
	4-(*p*-Nitrophenylazo)-2,5-xylidine	IV	4-(*p*-Aminophenylazo)-2,5-xylidine	258
C_{16}	4-(*p*-Nitrophenylazo)-1-naphthol	II	4-(*p*-Aminophenylazo)-1-naphthol	256
	2-(*p*-Nitrophenylazo)-1-naphthol	I	2-(*p*-Aminophenylazo)-1-naphthol	256
	4-(*p*-Nitrophenylazo)-1-naphthylamine	II	4-(*p*-Aminophenylazo)-1-naphthylamine	263
	4-(1-Naphthylazo)-3-nitroaniline	I	5-Amino-2-(1-naphthyl)-2H-benzotriazole (Good)	31
	4-(2-Naphthylazo)-3-nitroaniline	I	5-Amino-2-(2-naphthyl)-2H-benzotriazole (Good)	260
	2,3-Dimethyl-4′-(*p*-nitrophenylazo)acetanilide	IV	4-(*p*-Aminophenylazo)-2′,3′-dimethylacetanilide	266
	4-Amino-5-hydroxy-6-(*p*-nitrophenylazo)-1-naphthalenesulfonic acid	VI	4-Amino-6-(*p*-aminophenylazo)-5-hydroxy-1-naphthalenesulfonic acid	267
	4,5-Dihydroxy-3-(*p*-nitrophenylazo)-2,7-naphthalenedisulfonic acid	VI	3-(*p*-Aminophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid	268
	N-(2,4-Dinitrophenyl)-1-*m*-tolylazo-2-naphthylamine	V	N-(2-Amino-4-nitrophenyl)-1-*m*-tolylazo-2-naphthylamine	271
	7-Amino-1-hydroxy-2-(*p*-nitrophenylazo)-3,6-naphthalenedisulfonic acid	IV	7-Amino-2-(*p*-aminophenylazo)-1-hydroxy-3,6-naphthalenedisulfonic acid	260
C_{17}	1-(2-Methoxy-4-nitrophenylazo)-2-naphthol	I	1-(4-Amino-2-methoxyphenylazo)-2-naphthol	255
C_{18}	N-Ethyl-4-(*p*-nitrophenylazo)-1-naphthylamine	IV	4-(*p*-Aminophenylazo)-N-ethyl-1-naphthylamine	264
	2,4-Dinitro-2′-phenylazodiphenylamine	V	2-Amino-4-nitro-2′-phenylazodiphenylamine	271
	2,4-Dinitro-4′-phenylazodiphenylamine	V	2-Amino-4-nitro-4′-phenylazodiphenylamine	271
C_{20}	2,4-Dinitro-2′-methyl-4′-*o*-tolylazodiphenylamine	V	2-Amino-4-nitro-2′-methyl-4′-*o*-tolylazodiphenylamine	271
	2,4-Dinitro-4′-methyl-2-*p*-tolylazodiphenylamine	V	2-Amino-4-nitro-4′-methyl-2-*p*-tolylazodiphenylamine	271
C_{22}	N-(2,4-Dinitrophenyl)-1-phenylazo-2-naphthylamine	V	N-(2-Amino-4-nitrophenyl)-1-phenylazo-2-naphthylamine	271
	N^1-[(*p*-2-Naphthylamino)phenyl]-2,4-dinitro-*m*-phenylenediamine	V	N^1-[(*p*-Naphthylamino)phenyl]-4-nitro-1,2,3-benzenetriamine	271
C_{23}	N-(2,4-Dinitrophenyl)-1-*p*-tolylazo-2-naphthylamine	V	N-(2-Amino-4-nitrophenyl)-1-*p*-tolylazo-2-naphthylamine	271
	N-(2,4-Dinitrophenyl)-4-*p*-tolylazo-1-naphthylamine	V	N-(2-Amino-4-nitrophenyl)-4-*p*-tolylazo-1-naphthylamine	271

Note: References 43–271 are on pp. 477–481.

TABLE XI. REDUCTION OF NITROSOARENES AND N-NITROSOANILINES

Number of Carbon Atoms	Nitroso Compound	Method	Product (Yield %)	Ref.
C_7	3-(Methylthio)-4-nitrosophenol	II	4-Amino-3-(methylthio)phenol	233
	N-Methyl-*o*-nitro-N-nitrosoaniline	I	*o*-(1-Methylhydrazino)aniline	205
C_8	N-Ethyl-*o*-nitro-N-nitrosoaniline	I	*o*-(1-Ethylhydrazino)aniline	205
	4-(N-Methyl-N-nitrosoamino)-2-nitrotoluene	I	5-(N-Methyl-N-nitrosoamino)-*o*-toluidine (60)	192
C_{10}	2-Nitroso-1-naphthylamine	II	1,2-Naphthalenediamine	193
C_{12}	2,6-Diallyl-4-nitrosophenol	II	4-Amino-2,6-diallylphenol	259

Note: References 43–271 are on pp. 477–481.

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