reaction mixture to remove all volatile products which were then trapped in a Dry-Ice cooled receiver.

Fractionation of the liquid in the trap gave 29 g. of starting material I and 15 g. (65%) of VII, b.p. 30.8°/630 mm. n^0_D 1.3236, d^0_4 1.5622, lit.[16] n^{20}_D 1.3145.

The infrared spectrogram of this nitro compound was superimposable on that of the same compound obtained directly in the reaction of tetrafluoroethylene with nitric oxide.

Oxidation of 1-nitro-1,1,2,2-tetrafluoro-2-nitrosoethane (VIII) *to 1,1,2,2-tetrafluoro-1,2-dinitroethane* (IX). About 8.5 g. (0.85 mole) of chromium trioxide, 30 ml. of glacial acetic acid, and 10 ml. of concd. sulfuric acid were placed in a 250-ml. three-neck flask provided with a stirrer, a reflux condenser, and a dropping funnel. The flask and its contents were chilled to about 10° and while stirring 15 g. (0.85 mole) of VIII was added dropwise over a period of 15 min. The mixture was stirred at 10° for 1 hr., and at room temperature for another hour. At the end of this period the mixture was shaken with 200 ml. of ice water in a separatory funnel. The lower layer was drawn off and dried over calcium chloride. Distillation gave traces of starting material, and 10.2 g. (62.4%) of IX, b.p. 52°/630 mm. The infrared spectrogram of this dinitro compound was superimposable on that of the same substance obtained directly from the reaction of tetrafluoroethylene with nitric oxide.

BOULDER, COLO.

[CONTRIBUTION FROM RESEARCH LABORATORY OF UNION CARBIDE CONSUMER PRODUCTS CO., DIVISION OF UNION CARBIDE CORP.]

Electrochemical Synthesis. Reduction of Dinitro-, Iodoxynitro-, and Iodosonitrobenzenes to Azoxy Compounds

M. V. KING

Received January 3, 1961

The electrochemical reduction of some disubstituted nitro-, iodoxy-, and iodosobenzenes is investigated. The identity and yields of the major reduction products are given. It is also shown that, under the conditions used, there is always simultaneous attack of the aromatic ring and side groups.

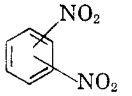
The electrochemical reduction of organic compounds has been studied extensively since 1900 and used where other synthetic methods either failed or proved less specific. The problems of variation of products with conditions such as *p*H, potential, cathode overvoltage, catalysts, and carriers have been extensively explored.[1,2]

One advantage in such reactions is the possibility to control the rate of reaction by controlling the current which is passed through the cell. Another advantage of electrochemical reactions lies in the fact that the product can easily be controlled by the availability of an additional variable, *i.e.*, the potential. Haber and others[3,4,5] have shown in the well known experiments on nitrobenzene that this compound is first reduced to nitrosobenzene, then hydroxylamine and finally to aniline, depending on the electrode potential used in the experiment. A great number of syntheses by either electrochemical reduction or oxidation is given in a review by Swann.[6]

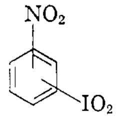
RESULTS AND DISCUSSION

The compounds chosen in this work are disubstituted benzenes which are good oxidizing agents and would, therefore, be expected to reduce fairly easily without complicating side reaction.

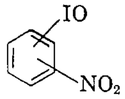
These compounds are given below



Dinitrobenzene



Iodoxynitrobenzene



Iodosonitrobenzene

The *ortho, meta,* and *para* isomers were compared to see if the structure would influence the type of product obtained.

The conditions used were a neutral magnesium bromide (1*M*) solution in water as electrolyte, a zinc plate anode, and a cathode consisting of a graphite cup containing the organic material mixed with acetylene black. The reaction rate was constant since the current was constant (0.5 amp.). The reaction was termed "complete" when the first few hydrogen bubbles became visible at the cathode.

The reduction data are given in Table I. In Table II are the initial open circuit potentials, E_{o_i}, of these compounds *versus* the hydrogen electrode, as well as the cell efficiencies. The efficiency is based on the number of coulometric equivalents passed through the cell divided by the number of theoretical equivalents assuming complete reduction of the substituent groups.

In a special instance, to see if the reaction could be stopped to reduce selectively, one of the two substituents, the reduction of *o*-, *m*-, and *p*-iodoxynitrobenzene up to 4 electrons per molecule was

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(1) M. J. Allen, *Organic Electrode Processes*, Reinhold Publishing Corp., New York, N. Y., 1958.

(2) C. J. Brockman, *Electroorganic Chemistry*, John Wiley & Sons, New York, N. Y., 1926.

(3) F. Haber, *Z. Elektrochem.*, **4**, 506 (1898).

(4) F. Haber and C. Schmidt, *Z. Physikal. Chem.*, **32**, 271 (1900).

(5) L. Gattermann, *Ber.*, **29**, 3037, 3040 (1896).

(6) S. Swann, *Trans. Electrochem. Soc.*, **88**, 103 (1945).

TABLE I

Reduction Products of Iodoxynitro, Iodosonitro, and Dinitrobenzenes

Compound	Main Product (% Yield)[a]	Secondary Product (% Yield)	Tarry Residue (% Yield)[b]
o-Dinitrobenzene	*o*-Dinitrobenzene (70)	*o*-Phenylenediamine (10)	12
m-Dinitrobenzene	*m*-Dinitrobenzene (40)	3,3′-Dinitroazoxybenzene (28.4)	12.5
p-Dinitrobenzene	4,4′-Dinitroazoxybenzene (40)	*p*-Dinitrobenzene (35)	5
o-Iodoxynitrobenzene	*o*-Iodonitrobenzene (43%)	2,2′-Diiodoazoxybenzene (36)	16.7
m-Iodoxynitrobenzene	3,3′-Diiodoazoxybenzene (86)	—	3.3
p-Iodoxynitrobenzene	4,4′-Diiodoazoxybenzene (80)	—	18.7
o-Iodosonitrobenzene	*o*-Iodonitrobenzene (32.3)	2,2′-Diiodoazoxybenzene (30)	11.3
m-Iodosonitrobenzene	3,3′-Diiodoazoxybenzene (77)	—	11.6
p-Iodosonitrobenzene	4,4′-Diiodoazoxybenzene (88.5)	—	13.0

[a] By weight. [b] Mole per cent.

TABLE II

Efficiency and Potential Data (*Vs.* N.H.E.) on Dinitro-, Iodoxynitro-, and Iodosonitrobenzenes

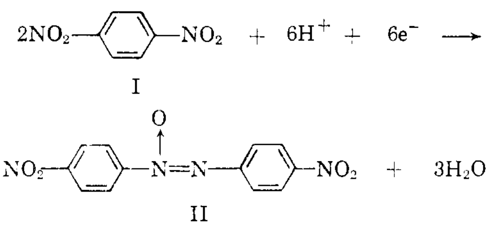
Compound	$E_{0i}{}^{a}$(v)	Theoretical Equivalent	% Efficiency
o-Dinitrobenzene	+0.11	12 electrons	51.8
m-Dinitrobenzene	−0.19	12 electrons	50.4
p-Dinitrobenzene	−0.09	12 electrons	24.7
o-Iodoxynitrobenzene	−0.15	10 electrons	44.6
m-Iodoxynitrobenzene	−0.11	10 electrons	81.0
p-Iodoxynitrobenzene	−0.23	10 electrons	82.0
o-Iodosonitrobenzene	−0.26	8 electrons	61.8
m-Iodosonitrobenzene	−0.10	8 electrons	88.7
p-Iodosonitrobenzene	−0.21	8 electrons	84.5

[a] These represent oxidation potentials using the American sign convention, *i.e.*, Zn is positive and Cu is negative.

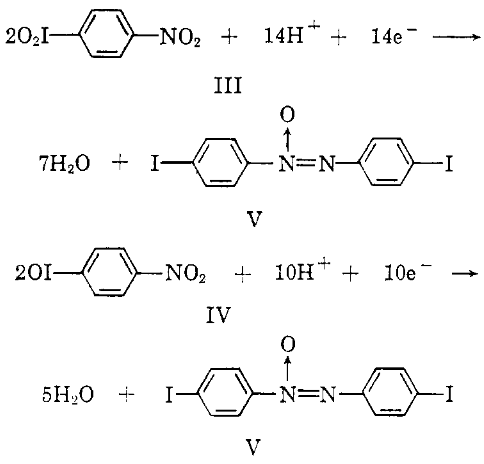
carried out. The main products were: *o*-iodoxynitrobenzene: 70.5% 2,2′-diiodoazoxybenzene; *m*-iodoxynitrobenzene: 75.0% 3,3′-diiodoazoxybenzene; and *p*-iodoxynitrobenzene: 60.0% *p*-iodonitrobenzene. The additional products consisted of tarry residues. The attempt to stop at an intermediate stage was successful only in the case of the *para* compound (probably due to lesser stability of the intermediates in the case of *o*- and *m*-iodoxynitrobenzene).

In all cases, including the 4 electron reductions, the infrared spectra of the tarry residues showed aliphatic carbon-hydrogen bands around 3.40 μ,[7] thus indicating simultaneous attack of the aromatic rings and the side group.

The reduction of *p*-dinitrobenzene (I) to 4,4′-dinitroazoxybenzene (II) can be schematized as follows:



The reduction of *p*-iodoxynitrobenzene (III) and *p*-iodosonitrobenzene (IV) to 4,4′-diiodoazoxybenzene (V) can be shown as



It is evident from the data in Table I that the structure of the parent compounds does affect the end product. In the case of the *ortho* compounds, steric hindrance between the two substituents always causes them to give different products from the *meta* and *para* isomers.

It is also of interest to note that the *o*-dinitrobenzene gives more product due to attack on the ring than on the substituent group.

The fact that the reactions do not go to completion can be attributed to various factors:

(a) In the case of the *ortho* compounds, it is probably mostly a steric factor which favors kinetically side reactions such as hydrogen evolution and/or attack at other positions in the ring.

(b) For the other isomers, it can be attributed to poor contact between the electrolyte and the cathode cake due to improper wetting of the carbon black. It can also be attributed to bad contact between the conducting carbon black and nonconducting organic compound.

(c) The yield of material is also affected by the current density (rate of reaction). The yield of reduced product is inversely proportional to the current density. A reduction of *p*-iodoxynitro-

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(7) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed., J. Wiley & Sons, Inc., New York (1958).

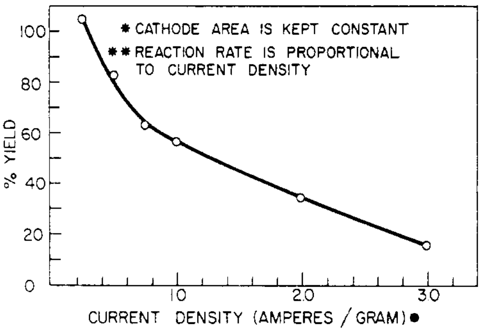


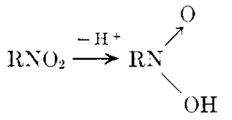
Fig. 1. Reduction of *p*-iodoxynitrobenzene; yield *vs.* rate**

benzene was carried out in the same cell, using the same amount of organic material, but varying the current density. The results are shown in Fig. 1. Similar results were obtained with the other compounds in this paper.

Ordinarily, under the conditions applied here, the organic material has a more negative potential than the hydrogen ion. The reaction at the cathode can occur in two possible ways:

1. Direct transfer of electrons from the cathode to the neutral organic molecules followed by addition of hydrogen ions:

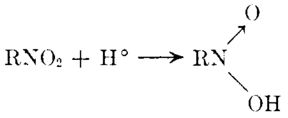
$$RNO_2 + \bar{e} \longrightarrow RNO_2^- \qquad (1)$$



$$RNO_2 \xrightarrow{-H^+} RN(\nearrow O)(\searrow OH) \qquad (2)$$

2. Addition of electrons to hydrogen ions to form a hydrogen atom. This is a free radical which will react rapidly with the compound.

$$H^+ + e^- \longrightarrow H^\circ \qquad (3)$$



$$RNO_2 + H^\circ \longrightarrow RN(\nearrow O)(\searrow OH) \qquad (4)$$

In the first case, the rate of formation of the organic anion (Equation 1) is balanced by the rate of addition of hydrogen ions (Equation 2). In the second case, under thermodynamic equilibrium, the rate of formation of nascent hydrogen (Equation 3) is balanced by the rate of disappearance of nascent hydrogen (Equation 4).

There are, however, two competitive simultaneous reactions—one electrochemical:

$$H^+ + 1e^- \longrightarrow {}^1/_2H_2(g) \qquad (5)$$

the other chemical:

$$2\ H^\circ \longrightarrow H_2 \qquad (6)$$

As one increases the current density and thereby the polarization, one approaches the hydrogen potential and increases the probability of the reaction shown in Equation 5.

At the same time, if the rate of formation of hydrogen atoms is much more rapid than the rate of combination with the organic molecule, then the concentration of highly reactive hydrogen atoms builds up. The probability of collisions and combination between them as shown in Equation 6 is also increased.

These mechanisms explain adequately the appearance of hydrogen gas long before the organic compound has been fully reduced, at high current densities.

In all the compounds mentioned in this paper, each ring substituent is electron-withdrawing and therefore reduces the electron density to some extent at the other substituent position. If this process occurs through resonance delocalization, the potential of the *para* isomer should be more negative than that of the *meta*. If this process occurs by inductive (dipole-dipole) proximity effect, the *meta* isomer should have the more negative potential. The results in Table II indicate as follows:

In the dinitrobenzene series, the *meta* isomer has the more negative potential and the inductive effect must predominate. In the iodosonitro- and iodoxynitrobenzene series, the *para* isomers have the more negative potentials and the resonance effect predominates. It is difficult to include the *ortho* isomers in this discussion, due to the complicating steric effects which would distort the picture.

In comparing the initial open circuit voltages of the disubstituted compounds with those of the monosubstituted compounds: nitrobenzene—0.13 volt; iodosobenzene—0.51 volt; iodoxybenzene—0.63 volt, it appears logical to suggest the following conclusions:

Introduction of another electron-withdrawing group in the nitrobenzene ring does not always give the parent compound a more negative potential. Introduction of an electron-withdrawing group such as the nitro group in the iodoxy- or iodosobenzene ring definitely decreases the negativity of the potentials of the parent compounds. This is probably due to the increase in stability of the iodoxy and iodoso groups toward reduction by additional resonance energy in the new system.

EXPERIMENTAL

Analyses. The halogen and nitrogen analyses were done by Huffman Microanalytical Laboratories (Wheatridge, Colo.).

Materials. o-Dinitrobenzene (Aldrich Chemical Co.), *m*- and *p*-dinitrobenzene (Eastman Chemicals Co.) were recrystallized to a constant melting point.

All the nitroiodosobenzenes were prepared according to a method described by Ortoleva.[8] The nitroiododichloride was first obtained by chlorination of the nitroiodo compound in a petroleum ether (b.p. 60–80°) chloroform mixture; the

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[8] G. Ortoleva, *Chem. Zentralblatt,* I, 722 (1900); *Giornale della Società di Scienze Naturali ed Economiche* **23** [16/2.], Palermo.

TABLE III[a]

INFRARED SPECTRA OF A—IODOSONITROBENZENES, B—IODOXYNITROBENZENES, C—DIIODOAZOXYBENZENES

A			B			C		
ortho	*meta*	*para*	*ortho*	*meta*	*para*	2,2′-	3,3′-	4,4′-
3.25	3.25	3.25	3.28	3.25	3.25	6.85s	6.45	6.35s
6.25s	6.25	6.25s	6.15sh	6.25	6.15sh	6.95sh	6.55sh	6.40sh
6.35	6.30sh	6.35s	6.27	6.30sh	6.22s	7.45s	6.65sh	6.45sh
6.55s	6.50s	6.40sh	6.40	6.50s	6.50s	7.95	6.80s	6.80s
6.90	6.90	6.50s	6.53s	6.60sh	6.60sh	9.60	6.85sh	6.85sh
7.48s	7.02	6.75sh	6.60sh	6.90sh	6.70sh	9.85	6.93	6.95sh
7.60s	7.40s	6.80	6.90	7.05	6.80	10.80	7.05sh	7.20
8.60	7.63sh	6.85sh	7.40sh	7.40s	7.20	13.10sh	7.15sh	7.55
8.77	7.85	6.95	7.48s	7.90	7.35s	13.35s	7.75	7.65
9.05	9.90sh	7.10	7.60s	9.20	7.45sh	14.05	7.90	7.77
9.77	10.02	7.18	7.85sh	9.55	7.65	14.60	9.60	8.85sh
11.67	11.25	7.40s	8.77	10.02	7.85sh		10.15	9.50
12.65s	11.57s	7.45s	9.05	11.25	9.10		11.00sh	9.95sh
12.83s	12.45	7.65	11.65	11.60	9.60		11.45	10.00s
13.10sh	12.85sh	7.85sh	12.50s	12.45	9.95		11.85sh	11.00
13.73s	13.05s	8.50	12.60s	13.05s	11.75s		12.70sh	11.10s
13.90sh	13.40s	9.05	12.95s	13.50sh	11.90s		12.85s	14.05
14.30–14.40s	13.75s	9.10sh	13.20s	13.75s	12.10sh		13.95	14.28
14.75–15.00sh	13.95sh	9.50	13.45s	13.95s	12.95–13.03s		14.45	
	14.10s	9.60sh	13.55sh	13.25s	13.35s		14.95s	
		9.90s	13.65sh		13.60s			
		9.95sh	14.35		13.80–13.90s			
		11.75s	14.95sh		14.20			
		11.95s			14.95–15.00			
		12.50sh						
		13.00s						
		13.15sh						
		13.35sh						
		13.60s						
		13.85sh						
		14.25						
		14.90						

[a] s = strong absorption < 50% transmittance; sh = shoulder; λ in microns—accuracy ± 0.03 μ.

dichloride was then hydrolyzed in a 1/1 pyridine-water mixture to give the iodoso compound. Since the iodoso compounds could not be recrystallized without decomposition,[9] they were purified by trituration with cold water and with ether. The powders thus obtained were dried *in vacuo* and analyzed.

Anal. Calcd. for $C_6H_4(IO)(NO_2)$: I, 47.9. Found: *o*-iodosonitrobenzene, 47.3; *m*-iodosonitrobenzene, 48.2; *p*-iodosonitrobenzene, 47.5. These compounds had never been prepared completely pure and these values corroborate the best values found in the literature.[9]

Iodoxybenzene was synthesized according to Formo and Johnson[10] and iodimetric analysis indicated 99-99.9% purity. The iodoxynitrobenzenes were obtained from the corresponding iodonitrobenzenes in the same manner.[10] They were recrystallized from hot water. Iodimetric analysis was not possible as in the case of iodoxybenzene because the compounds decomposed too slowly. A catalytic combustion gave the following results.

Anal. Calcd. for $C_6H_4(IO_2)(NO_2)$: I, 45.16. Found: *o*-iodoxynitrobenzene, 44.9, 44.5; *m*-iodoxynitrobenzene, 44.2; *p*-iodoxynitrobenzene, 44.1. The iodoxy- and iodosonitrobenzenes have no melting points. They decompose explosively between 210 and 230°.

Apparatus. The reduction of these compounds was carried out in a cell designed by J. S. Dereska.[11] The cathode, a graphite cup, 10.2 cm. in diameter, had an area of 81.5 cm.^{2} which, at 500 ma, gave a geometric current density of 6.14 ma/cm.^{2} The cathode and a zinc plate anode were connected to a d.c. power supply (0–10 amp, 0–50 volts, <0.3% ripple at full current). The electrolyte, 700 ml. of 1*M* magnesium bromide, had a *p*H which stayed fairly constant throughout the run at 6.5 to 7.0. A.S.C.E. electrode was used to check the initial open circuit potentials. These potentials were measured with a Brown recording potentiometer (type 153 Electronik recorder).

Reduction. One gram of organic compound was mixed with 2 g. of acetylene black and moistened with enough magnesium bromide (1 *M*) to form a cake which was spread evenly on the graphite cup. A thin sheet of "Dynel," maintained by a plastic ring, held it in place. The run was carried out until the first few hydrogen bubbles became visible at the cathode. The resistance of the cell was usually about 1 ohm.

Products. Usually the products of two or three runs were combined and placed in a Soxhlet cup. The products were then separated from the carbon by continuous extraction with ether. Recovery of material was from 80 to 100%. The ether extract was then evaporated to dryness and the products were chromatographed on alumina (Fisher A-540, 80 to 200 mesh). The eluent at the start was petroleum ether which was gradually changed to chloroform, then to methanol until all fractions had come down. The various fractions were then submitted to a preliminary identification by their infrared spectra and recrystallized. Usually only one or two major products (*cf.* Table I) were obtained, the other fractions consisting either of tarry polymeric aromatic material or degradation tars containing aliphatic C—H bands.

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(9) I. Masson and W. E. Hauby, *J. Chem. Soc.*, 1699 (1908).

(10) H. W. Formo and J. R. Johnson, *Org. Syntheses*, **Coll. Vol. III**, 486 (1955).

(11) Research Laboratory, Union Carbide Consumer Products Co., Division of Union Carbide Corp.

The products were identified by mixed melting points with independently synthesized authentic samples: 3,3′-dinitroazoxybenzene, m.p. 142–144°[12]; 4,4′-dinitroazoxybenzene, m.p. 190–193°[13]; 3,3′-diiodoazoxybenzene, m.p. 110–113°[14]; 4,4′-diiodoazoxybenzene, m.p. 198–200°.[15] 2,2′-diiodoazoxybenzene, m.p. 140–142°, is a new compound.

Anal. Calcd. for $C_{12}H_8N_2OI_2$: N, 6.23. Found: N, 6.26, 6.13.

This compound was obtained only by electrochemical methods. All attempts at independent syntheses failed.

The synthesis of the authentic samples was carried out according to the references given above.

Infrared spectra were obtained with a double beam Perkin-Elmer Spectrometer Model 21. (Potassium bromide technique)—The absorption maxima are given in Table III.

Acknowledgment. The author wishes to thank Dr. S. Senderoff of Parma Research Laboratory, Union Carbide Corp., for helpful suggestions and discussions.

PARMA 30, OHIO

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[12] H. Hofer and F. Jacob, *Ber.*, **41**, 3195 (1908).

[13] E. Bamberger and R. Hubner, *Ber.*, **35**, 3808 (1903).

[14] S. Gabriel, *Ber.*, **9**, 1409 (1876).

[15] H. Klenzer and R. Pitschke, *Ber.*, **18**, 2552 (1885).

[CONTRIBUTION FROM THE HUGH LORD LABORATORY, LORD MANUFACTURING CO.]

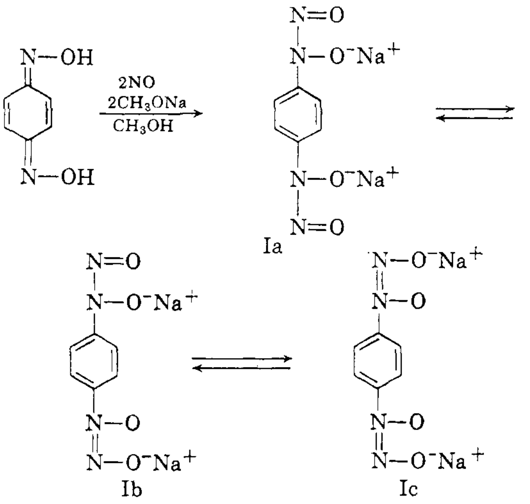
A New Reaction of Oximes and Nitric Oxide

MORRIS J. DANZIG,[1] ROCK F. MARTEL, AND SALVATORE R. RICCITIELLO

Received September 19, 1960

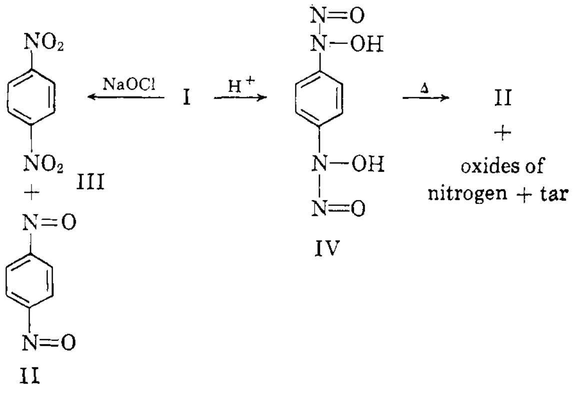
It was found that oxygen-free nitric oxide reacts with certain salts of quinone dioximes to form salts of di-*N* nitrosoaryldihydroxylamines, and with aldoximes to give *syn*-1-oximino-1-*N*-nitrosohydroxylamino types of compounds.

The preparation of *N*-nitroso compounds has usually been limited to the nitrosation reaction. In a recent communication we reported that when a methanolic solution of disodium-*p*-benzoquinone dioxime was treated with oxygen-free nitric oxide, two moles of the gas were absorbed to produce disodium-*N,N′*-dinitroso-*p*-phenylenedihydroxylamine.[2] Structures Ia, b, c represent the tautomeric forms possible. Organic, as well as inorganic, salts may be prepared by an appropriate substitution of the proper base. Transition and heavy metals may be precipitated by using techniques analogous to that for Cupferron (ammonium-*N*-nitrosophenylhydroxylamine).



Upon acidic decomposition there were obtained oxides of nitrogen, *p*-dinitrosobenzene (II) and some resinous materials. The formation of tar is in keeping with the similar decomposition of Cupferron.[3]

The acid form of IV was prepared by careful acidification of I; and upon mild heating, II and tars were obtained. Oxidation of I with sodium hypochlorite also affords II and some *p*-dinitrobenzene (III). When an excess of oxidant was used, only III was obtained. Extension of this reaction to other quinone dioximes and salts with different metals are listed in Table I; in all cases analogous products were obtained.



Methylation of *N*-nitrosophenylhydroxylamine salts produces two isomers[4,5] designated as α and β.

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[1] Present address: American Viscose Corp., Research and Development Division, Marcus Hook, Pa.

[2] M. J. Danzig, R. F. Martel, and S. R. Riccitiello, *J. Org. Chem.*, **25**, 1071 (1960).

[3] E. Bamberger, *Ber.*, **27**, 1554 (1894).

[4] R. Behrend and E. Konig, *Ann.*, **263**, 218 (1891).

[5] R. Lindez, *Ann.*, **275**, 133 (1893).