methanol or absolute ethanol, crystals of VII separated slowly. Over a period of two weeks 0.121 g. was obtained and shown by chromatography to be pure or almost pure VII. After recrystallization from methanol, from which it separated slowly, and dissolvation at 165–175°, it melted at 221–223° (recorded 225°[16,17]). It resembled naringin and naringenin in giving bright yellow colors with base and strong acid and a purplish-brown with ferric chloride; with ethanol, magnesium and hydrochloric acid it produced a fuschia (red-purple) color like naringin but different from the orange-red of naringenin.

The acetyl derivative of VII was prepared by boiling the 29 mg. of amorphous tan powder isolated from banding on paper for two minutes with excess acetic anhydride and sodium acetate.[24] After several recrystallizations from methanol it did not depress the melting point of V from *A. majus* (see Table IV).

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[24] This acetylation was very unreliable in producing a crystalline product.

LOS ANGELES 24, CALIFORNIA

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS, UNIVERSITY OF MICHIGAN AND TULANE UNIVERSITY]

The Transformation of ψ-*o*-Dinitroso Aromatic Compounds into *o*-Nitroaryl Amines[1]

BY J. H. BOYER,[2] R. F. REINISCH, M. J. DANZIG, G. A. STONER AND F. SAHHAR

RECEIVED APRIL 1, 1955

ψ-*o*-Dinitrosobenzene and 4-methyl-ψ-*o*-dinitrosobenzene were quantitatively transformed by copper in hydrochloric acid into *o*-nitroaniline and a mixture of 3-nitro-4-aminotoluene (39.0%) and 3-amino-4-nitrotoluene (61.0%), respectively. *o*-Benzoquinone dioxime was isomerized by copper in hydrochloric acid, by cuprous chloride and by cupric chloride into *o*-nitroaniline. The treatment of ψ-1,2-dinitrosonaphthalene with copper in hydrochloric acid brought about the formation of nitronaphthylamines in trace amounts and a stable copper chelate. Naphthofurazan was obtained from the chelate. Attempts to oxidize 9,10-phenanthrenequinone dioxime into 9,10-ψ-dinitrosophenanthrene were unsuccessful.

Introduction

An unsymmetrical furoxane structure for the N_2O_2 moiety attached through nitrogen atoms to *o*-positions of an aromatic nucleus has not proved to be satisfactory.[3] Renaming "furoxanes" of this type as ψ-*o*-dinitrosoaromatic compounds and adopting the use of a hybrid structure, *cf.* I, is proposed.[4]

The hybrid structure is in better agreement with the chemical and physical properties of these compounds.[3] It also accounts for the non-existence of certain structural isomers which are predicted from the "furoxane" representation. For example, 4- and 5-methyl-ψ-1,2-dinitrosobenzene are identical.[3a,b] There is no apparent reason why hydroxy or primary amino derivatives of "benzfuroxane" do not exist[5]; however, recognition of tautomeric forms of hydroxy[5a] and amino dinitrosoaromatic compounds affords an understanding of this fact.

Discussion

Copper or nickel metals in acid solution transformed ψ-*o*-dinitrosoaromatic compounds into *o*-nitroarylamines. Recognition of this unique formation of a nitro compound by a reduction procedure followed the observation of the rapid appearance of color around a nickel spatula in a formic acid solution of ψ-*o*-dinitrosobenzene.

The first reduction product of ψ-*o*-dinitrosobenzene is the dioxime of *o*-benzquinone. Curiously enough this represents the only known method for the preparation of this dioxime.[6] It could not, however, be isolated from the reduction with copper in hydrochloric acid. Experiments with known

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[1] The financial support for this work was provided by O. O. R. under contract Nos. DA-20-018-ORD-11814 and DA-01-009-ORD-331. Purchase of the Fisher Elecdropode represents partial use of funds obtained from the Research Corporation. The work was presented in part at the combined Southeast and Southwest Region Meeting, A. C. S., New Orleans, La., December, 1953.

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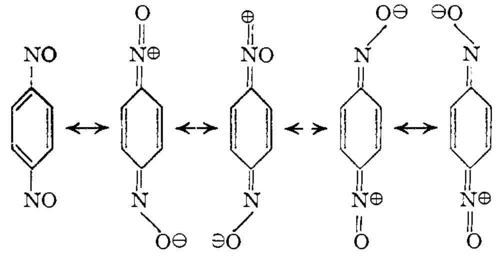
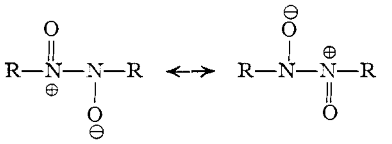
[3] (a) M. O. Forster and M. F. Barker, *J. Chem. Soc.*, **103**, 1918 (1913); (b) D. L. Hammick, W. A. M. Edwardes and E. R. Steiner, *ibid.*, 3308 (1931); J. H. Boyer, D. I. McCane, W. J. McCarville and A. T. Tweedie, THIS JOURNAL, **75**, 5298 (1953).

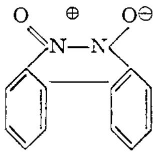
[4] The deficiencies of those structures which represent true nitroso compounds, cyclic dioxime peroxides and those which require a four-membered ring of alternating nitrogen and oxygen atoms have been demonstrated.[3b]

Whereas *m*-dinitrosobenzene is a true nitroso compound, the *p*-isomer is not (T. W. J. Taylor and W. Baker, Sidwick's "Organic Chemistry of Nitrogen," Oxford University Press, London, 1945 (corrected), p. 213). A similar hybrid structure for ψ-*p*-dinitrosobenzene is in agreement with the paucity of information which describes properties of the molecule[3a] (R. Nietzki and F. Kehrmann, *Ber.*, **20**, 613 (1887); see reference 14).



These hybrid structures for ψ-dinitroso aromatic compounds are analogs of C-nitroso dimers (C. P. Fenimore, THIS JOURNAL, **72**, 3226 (1950)) and 2,2-dinitrosobiphenyl (S. D. Ross and I. Kuntz, *ibid.*, **74**, 1297 (1952)).

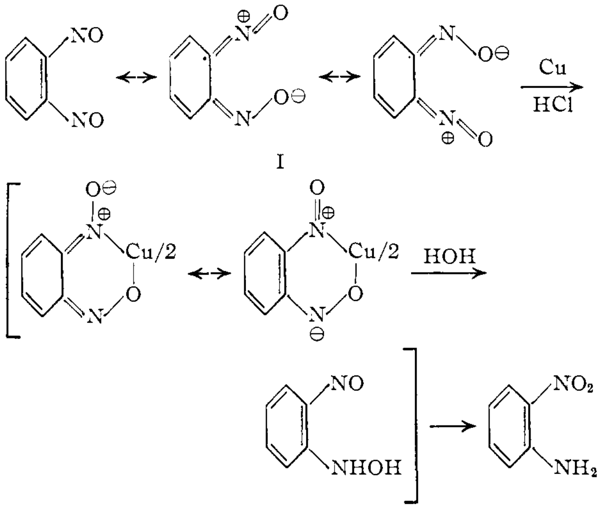




[5] (a) T. Zincke and A. Ossenbeck, *Ann.*, **307**, 1 (1899); (b) private communication from R. J. Gaughran, Picatinny Arsenal; (c) unpublished work with U. Toggweiler.

[6] (a) T. Zincke and P. Schwarz, *Ann.*, **307**, 28 (1899); (b) A. G. Green and F. M. Rowe, *J. Chem. Soc.*, **101**, 2452 (1912).

samples of the dioxime verified that isomerization into *o*-nitroaniline rapidly occurred in the presence of copper in acid solution, cuprous chloride or cupric chloride. Presumably, the isomerization proceeded with the formation of the chelate of the *amphi*-form of the dioxime.[7] Acid catalysis of this chelate as it was obtained directly from I apparently promoted the formation of *o*-nitroso-*β*-phenylhydroxylamine rather than formation of the dioxime or the isomerization into the chelate of the *anti*-dioxime.[8] Internal oxidation–reduction then occurred with the isomerization into *o*-nitroaniline.



I

Facile dehydration of 1,2-dioximes brings about the formation of the corresponding furazane.[7,9] Since benzfurazane did not react with copper in hydrochloric acid, it was not an intermediate in the transformation of *ψ*-*o*-dinitrosobenzene into *o*-nitroaniline.[10] Naphthfurazane, on the other hand, was obtained from *ψ*-1,2-dinitrosonaphthalene. The isolation of trace amounts of nitronaphthylamines indicated that acid catalysis of the copper chelate in this case favored the formation of a stable, presumably *anti*-, copper chelate.[8] Hydrolysis of the chelate by a mixture of sodium and ammonium hydroxides apparently led to the formation of the dioxime since steam distillation of the reaction mixture afforded the separation of naphthfurazane.

The necessity for chelate formation in the isomerization step was demonstrated by the recovery of the unchanged dioxime of *p*-benzoquinone after exposure to copper in hydrochloric acid. The inaccessible *ψ*-9-10-dinitrosophenanthrene was not studied; however, a stable copper chelate was obtained from the corresponding dioxime.

Neither *syn*- nor *anti*-benzildioxime underwent reaction with copper in hydrochloric acid. Both were oxidized readily to diphenylfuroxane.[11] The furoxane also was found to be unreactive toward copper in hydrochloric acid. Reduction to the *amphi*-dioxime[7] apparently involved simultaneous dehydration with the formation of diphenylfurazane.

In the reduction of 4-methyl-*ψ*-*o*-dinitrosobenzene the formation of a mixture of isomeric nitrotoluidines was expected. Curiously enough the product (II) obtained quantitatively had a very sharp melting point which did not change upon repeated recrystallization from aqueous ethanol or from chloroform. By polarographic and quantitative infrared analysis the composition of the product was established as 61.0% of 3-amino-4-nitrotoluene (III) and 39.0% of 3-nitro-4-aminotoluene (IV).

Experimental[12]

ψ-**Dinitrosoaromatic Compounds.**—*ψ*-*o*-Dinitrosobenzene,[13] m.p. 69–70°; *ψ*-4-methyl-1,2-dinitrosobenzene,[3a] m.p. 96–97°; and *ψ*-1,2-dinitrosonaphthalene,[14] m.p. 126–127°, were prepared by the literature methods.

Furoxanes and *ψ*-dinitroso compounds have been prepared by the oxidation of dioximes with hypochlorite,[15] ferricyanide,[16] dilute nitric acid[16] and nitrogen dioxide.[17] Attempts to oxidize 9-10-phenanthrenequinone dioxime,[18] m.p. 196–200°, to *ψ*-9-10-dinitrosophenanthrene with each of these reagents failed.

Dioximes.—The dioxime of *o*-benzoquinone, m.p. 145–147°, was obtained by the reduction of *ψ*-*o*-dinitrosobenzene with alkaline hydroxylamine.[6a] The dioxime of *p*-benzoquinone, m.p. 240° dec., was prepared from hydroquinone and hydroxylamine.[19] Phenanthrene was oxidized to 9,10-phenanthrenequinone,[20] m.p. 205–207°, and the ketone transformed into the dioxime,[18] m.p. 197–200°.

A solution of 50 g. (0.24 mole) of benzil and 50 g. (0.4 mole) of hydroxylamine hydrochloride in 400 ml. of methanol was refluxed 3 hours. *α*-Benzildioxime separated from the cooled solution and was isolated by filtration. After two recrystallizations from methanol, there was obtained 34.0 g. (59%) of *α*-benzildioxime, m.p. 238–240°.[21] From the combined mother liquors, *β*-benzildioxime, m.p. 205–206°,[21] was obtained in 25% yield upon dilution with ether.

To a solution of 15.0 g. (0.063 mole) of *α*-benzildioxime dissolved in 100 ml. of 10% sodium hydroxide diluted with 200 ml. of water was added 350 ml. of 1.0 *N* sodium hypochlorite. The precipitate which formed was filtered, washed and dried giving 14.5 g. (97.3%) of diphenylfuroxane, m.p. 114–115°, which upon recrystallization had a constant m.p. of 118°, and checked the melting point and mixed

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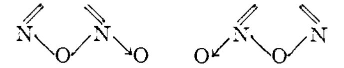
[7] Reduction of 4,5-disubstituted furoxanes leads to the formation of *amphi*-1,2-dioximes (A. Angelli, *Ber.*, **26**, 527 (1893); J. Meisenheimer, H. Lange and W. Lamparter, *Ann.*, **444**, 94 (1925)). Analogical reasoning allows the tentative assignment of *amphi*-configuration to the dioxime of *o*-benzquinone obtained upon reduction of *ψ*-*o*-dinitrosobenzene.

[8] A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice–Hall, Inc., New York, N. Y., 1952, p. 332.

[9] L. Wolff, *Ber.*, **28**, 70 (1892); M. O. Forster, *J. Chem. Soc.*, **83**, 54 (1907).

[10] Both physical and chemical properties reveal the lack of similarity between benzfurazane and *ψ*-*o*-dinitrosobenzene. Strong infrared absorption at 1630–1600 cm.$^{-1}$ attributed to the >C=N— group was characteristic of the latter compound but not of benzfurazane (J. H. Boyer, D. I. McCane, W. J. McCarville and A. T. Tweedie, This Journal, **75**, 5298 (1953); R. J. Gaughran, J. P. Picard and J. V. R. Kaufman, *ibid.*, **76**, 2233 (1954)). *ψ*-*o*-Dinitrosobenzene is much more sensitive to nitration (P. Drost, *Ann.*, **307**, 49 (1899)) to oxidation (unpublished work with R. F. Reinisch), and to reduction by hydroiodic acid (unpublished work).[3a]

[11] Insofar as the structural isomers of the type



are known to occur the furoxane structure is correct.[7]

[12] Microanalyses by the Micro Tech Laboratories, Skokie, Ill. Melting points are corrected. Infrared analyses by Mr. J. E. Baudean, Perkin–Elmer Corporation, New Orleans, La.

[13] P. A. S. Smith and J. H. Boyer, *Org. Syntheses*, **31**, 14 (1951).

[14] A. G. Green and F. M. Rowe, *J. Chem. Soc.*, **111**, 612 (1917).

[15] G. Ponzio, *Gazz., chim. ital.*, **36**, II, 103 (1906); *Chem. Zentr.*, **77**, I, 1700 (1906).

[16] T. Zincke and P. Schwarz, *Ann.*, **307**, 40 (1899).

[17] R. Scholl, *Ber.*, **23**, 2499 (1890).

[18] J. Schmidt and J. Soll, *ibid.*, **40**, 2454 (1907).

[19] R. Nietzki and F. Kehrmann, *ibid.*, **20**, 613 (1887).

[20] R. P. Linstead and P. Levine, This Journal, **64**, 2022 (1942).

[21] K. Auwers and V. Meyer, *Ber.*, **21**, 794 (1888).

melting point with samples prepared by the hypochlorite oxidation of β-benzildioxime and the nitrous acid oxidation of α-benzildioxime.[22] Attempts to reduce diphenylfuroxane with zinc and acetic acid to γ-benzildioxime[7] were apparently successful; however, simultaneous dehydration to the anhydride, diphenylfurazane, m.p. 98° (lit.[23] m.p. 94°), also occurred.

Table I

Polarographic Data on the Isomeric Nitrotoluidines (III, IV)

Solution	1	2	3	4	5
m*M* III	0.1000	0.075	0.050	0.025	0
m*M* IV	0	.025	.050	.075	.1000
$-E_{1/2}$, v. (*vs.* S.-C.E.)	.754	.764	.771	.780	.785

Table II

Infrared Absorption Data at 1280 Cm.$^{-1}$ (7.79μ) for the Isomeric Nitrotoluidines (III, IV)

A. Prepared Mixtures

Sample	1	2	3	4	5
III, mg./2 ml.	0	25.5	57.0	75.9	107.7
IV, mg./2 ml.	43.6	50.0	50.0	50.0	50.0
Absorbance	0.093	0.208	0.324	0.420	0.549

B. Samples of Mixture (III)

Sample	6[a]	7[a]	8[b]	9[c]
Concn. mg./2 ml.	99.8	100.8	101.9	102.7
Absorbance	0.257	0.258	0.275	0.280
III,[d] %	37.1	37.7	40.2	40.8
IV, %	62.9	62.3	59.8	59.2

[a] Samples from separate reductions, recrystallized from chloroform. [b] Reduction product, m.p. 77.0–78.0° after one recrystallization from aqueous ethanol. [c] Reduction product m.p. 76.8–77.2°, not purified. [d] Data obtained from calibration curve prepared from the standard solutions (Samples 1–5) by plotting absorbance *vs.* concentration.

Table III

Reactions Induced by Copper or Copper Salts

Temperature maintained at 100° for 6 hr.

Cu metal or salt, g.	Compound	Wt., g.	HCl 12 *N*, ml.	Product	Yield, %
Cu, 1.0	*o*-Benzoquinonedioxime	1.00	1.0	*o*-Nitro aniline	77
Cu, 0.03	*o*-Benzoquinonedioxime	1.00	1.0	*o*-Nitro aniline	71
Cu, 0.20	*o*-Benzoquinonedioxime	1.00	1 drop	*o*-Nitro aniline	Trace
Cu_2Cl_2, 1.00	*o*-Benzoquinonedioxime	1.00	1.0	*o*-Nitro aniline	49.5
$CuCl_2$, 1.00	*o*-Benzoquinonedioxime	1.00	1.0	*o*-Nitro aniline	40.3
	o-Benzoquinonedioxime	1.00	1.0	Uniden. material	
Cu, 1.00	*p*-Benzoquinonedioxime	1.00	1.0	Starting material	
Cu, 1.50	9,10-Phenanthraquinonedioxime	1.50	1.5	Cu complex	
Cu, 1.00	Diphenylfuroxane	1.00	1.0	Starting material	
Cu, 1.00	α-Benzildioxime	1.00	1.0	Starting material	
Cu, 0.50	β-Benzildioxime	0.50	0.50	Starting material	

Preparation of 3-Amino-4-nitrotoluene (III).—Commercially available 3-nitro-4-aminotoluene (IV), m.p. 116–117°, was oxidized with Caro acid to 3-nitro-4-nitrosotoluene,[24] 147–150°, and the latter was oxidized further to 3,4-dinitrotoluene, m.p. 57–58°,[25] using fuming nitric acid. Into a solution of 2.0 g. (0.011 mole) of the dinitrotoluene in 100 ml. of ethylene glycol, in a 3-necked flask fitted with a reflux condenser, thermometer and gas bubbling tube which reached to within 1 cm. of the bottom of the flask, ammonia gas was introduced at a rapid rate as the mixture refluxed at 170–180° for 23 hours. Upon pouring the hot solution onto 150 g. of crushed ice, 3-amino-4-nitrotoluene separated as orange prisms, m.p. 108–109°,[26] after recrystallization from aqueous ethanol; wt. 1.27 g. (76.4%).

Solutions which contained a total concentration of 0.1000 m*M* of mixtures of the isomeric nitrotoluidines (III, IV) were prepared for polarographic analysis. The supporting electrolyte was 0.1 *N* potassium chloride and 0.01% gelatin served as the maximum suppressor. Half-wave potentials were measured against the saturated calomel electrode at 25.0 ± 0.10° using the Fisher Elecdropode. The polarographic data are recorded in Table I.

Reactions with Copper in Hydrochloric Acid.—A solution of 0.020 mole of a ψ-*o*-dinitrosoaromatic compound in 75 ml. of 95% ethanol was treated with 0.030 mole of copper powder and 4 ml. of 37% hydrochloric acid. The mixture was stirred at reflux temperature for 20 hours. After cooling and concentrating by evaporation, copper and copper salts were separated by filtration. The filtrate was treated with 25 ml. of 25% sodium hydroxide at 70–80° for 2 hours. After separating copper hydroxide by filtration the filtrate was placed in a refrigerator overnight. The separation of yellow-orange prisms accounted for quantitative yields of *o*-nitroaniline, m.p. 69–70°, from ψ-*o*-dinitrosobenzene and of a mixture II, m.p. 78–79°, of 3-amino-4-nitrotoluene (III) and 3-nitro-4-aminotoluene (IV) from 4-methyl-ψ-1,2-dinitrosobenzene. The mixture (apparently a eutectic mixture) was recrystallized with no change in m.p. from ethanol and from chloroform; addition of small portions of either pure isomer (III, IV) brought about higher and broader m.p. ranges.

Anal. Calcd. for $C_7H_8N_2O_2$: C, 55.26; H, 5.30; N, 18.41. Found: C, 55.52; H, 5.27; N, 17.15; 17.36; $-E^{1}/_{2}$ (*vs.* S.C.E.) 0.770 v. at 25.0 ± 0.10°.

For an infrared study of the mixture II and of the two pure isomers (III, IV) approximately 4% chloroform solutions were prepared, and their infrared spectra recorded from 2 to 15 μ. The spectra for III and IV were identical except for intense absorption at 1280 cm.$^{-1}$ (7.79 μ) by 3-nitro-4-aminotoluene which was completely absent in the analysis of 4-nitro-3-aminotoluene. The absorbance at this wave length for mixtures of the two isomers is recorded in Table II (samples 1–5). A plot of absorbance *vs.* concentration provided a calibration curve for the standard solutions. The constitution of four samples (6–9) of the mixture II then was determined from the calibration curve. This gave an average ratio of 39.0% 3-nitro-4-aminotoluene (IV) and 61.0% 3-amino-4-nitrotoluene (III).

Results from a series of experiments in which various dioximes and diphenylfurazane were treated with copper in hydrochloric acid or with copper salts are recorded in Table III.

New Orleans, Louisiana

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(22) E. Beckmann, *Ber.*, **22**, 1591 (1889).

(23) K. Auwers and V. Meyer, *ibid.*, **21**, 810 (1888); **22**, 716 (1889).

(24) W. D. Langley, *Org. Syntheses*, **22**, 47 (1942).

(25) H. J. Page and B. R. Heasman, *J. Chem. Soc.*, **123**, 3241 (1923).

(26) J. Kenner and M. Parken, *ibid.*, **117**, 8529 (1920).