[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, TULANE UNIVERSITY]

Aromatic *o*-Dinitroso Compounds. 6,7-Dinitrosoquinoxalines[1]

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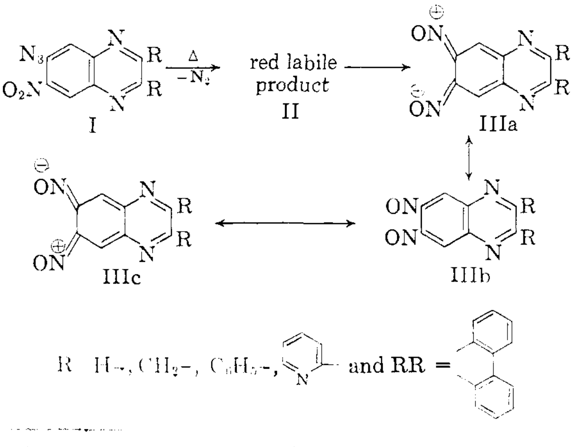
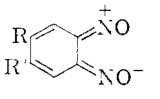
Labile (red) forms (II) of 6,7-dinitrosoquinoxalines are thermally converted into stable (blue-black) forms (III). Each of five colorless or yellow *o*-dinitroso aromatic compounds (IV, V, VI, VII, VIII) has been chromatographically separated into polar and less polar interconvertible, presumably isomeric, species. These examples demonstrate for the first time a separation of symmetrically substituted *o*-dinitrosoaromatic derivatives into two modifications.

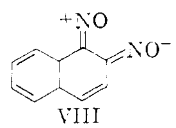
Aromatic *o*-dinitroso derivatives are produced upon pyrolysis of corresponding *o*-nitroazido derivatives. From 6-azido-7-nitroquinoxalines[3] (I) with substituents in the 2,3-positions, pyrolysis in the solid state as a slurry or in solution gives corresponding 6,7-dinitrosoquinoxalines (III); however, without aryl substituents in the heterocyclic ring, dry pyrolysis leads to complete disintegration. In four examples the presence of carbon as a contaminant is indicated by elemental analysis.

By measuring the rate of pyrolysis of *o*-nitrophenyl azide, it was concluded that a cyclic transition state is required for the formation of *o*-dinitrosobenzene.[4] It is now assumed that a cyclic, presumably quinonoid, transition state is also required for the pyrolytic transformation of 6-azido-7-nitroquinoxalines into 6,7-dinitrosoquinoxalines. The color change in all pyrolyses reported here from yellow (starting material) *via* red to blue-black suggests that the transition state from each azide (I) leads to a corresponding labile red product, which changes to a stable blue-black insoluble dinitrosoquinoxaline. Both red and blue-black modifications of dinitrosodiphenylquinoxaline (II, III, R = C_6H_5) have been isolated and analyzed. The red soluble form gives an orange-red benzene solution and is monomolecular in freezing benzene. Each modification is reduced by hydrogen iodide to 2,3-diphenyl-6,7-diaminoquinoxaline. Since aminoquinonoid chromophores may be red or blue and the nitroso chromophore may be blue it is possible that both II and III are quinonoid; however, III may be benzenoid dinitroso derivatives in which contributions from quinonoid species, *e.g.*, IIIa,c, are relatively unimportant.



Isolation of labile and stable modifications of *o*-dinitrosoquinoxalines made it necessary to reinvestigate known dinitrosoaromatic derivatives for the presence of comparable structures. Using paper chromatography, two different modifications for each of *o*-dinitrosobenzene (IV), 4-methyl-1,2-dinitrosobenzene (V), 4-nitro-5-chloro-1,2-dinitrosobenzene (VI), 4-nitro-5-azido-1,2-dinitrosobenzene (VII) and 1,2-dinitrosonaphthalene (VIII) have been detected. In the development of the chromatogram for each compound, the use of polar solvents permits the sample to move as a single species; however, development with non-polar solvents gives rise to two distinct spots in each case. One spot moves with the solvent front, the other stays absorbed at its original position. When the paper strips containing the original spots are heated prior to chromatography, the chromatograms show a strong increase in the intensity of the stationary (bottom) spot whereas the moving (top) spot nearly disappears. On the other hand, chromatography at 0° gives an increase in the intensity of the moving spot and the stationary spot becomes very weak. The stationary and moving spots can be removed individually from the paper with ethanol. Chromatography of solutions of these separated spots again gives stationary and moving spots. The chromatographic separations demonstrate the presence of interconvertible materials with markedly different polar properties. In each case it is assumed that the spot which moves with a non-polar solvent represents a less polar species than that represented by the stationary spot.





VIII

IV, R = R' = H

V, R = CH_3; R' = H

VI, R = NO_2; R' = Cl

VII, R = NO_2; R' = N_3

Absorption spectra of three compounds, 1,2-dinitrosobenzene, its 4-methyl derivative and its 4-nitro-5-methyl derivative, were measured at near 0°, room temperature and near 90°. Neither ultraviolet absorption for each in isoöctane nor infrared absorption for each in potassium bromide disks revealed a structure variation with temperature. Each set of absorption data was exactly reproduced at the three temperatures.

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(2) The work described here is abstracted from a part of the thesis of R. S. Buriks submitted to Der Rijks-Universiteit, Leiden, Holland, in partial fulfillment of the requirements for the Ph.D. degree. Now at Peter Stuyvesant College, Willemstad, Curacao, The Netherlands, Antilles.

(3) J. H. Boyer and R. Buriks, THIS JOURNAL, **82**, 2213 (1960).

(4) T. F. Fagley, J. R. Sutter and R. L. Oglukian, *ibid.*, **78**, 5567 (1956).

TABLE I

PYROLYSIS OF 2,3-DISUBSTITUTED-6-AZIDO-7-NITROQUINOXALINES

I, R =	Method	Time, hr.	Temp., °C.	II or III formula	Color	Analyses Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Oxygen, % Calcd.	Oxygen, % Found
C_6H_5	Dry	360	100[a]	$C_{20}H_{12}N_4O_2$	Blue-black	71.99[b]	72.16	3.36[b]	3.70	15.69[b]	15.45	8.96[b]	8.80
C_6H_5	Slurry[c]	4	85	$C_{20}H_{12}N_4O_2$[d]	Red	70.58	69.98	3.55	3.62	16.46	16.64	9.40	9.39
α-C_5H_4N	Dry	360	76[a]	$C_{12}H_{10}N_6O_2$	Red	59.43[e]	59.86	2.77[e]	3.21	29.01[e]	29.01	8.79[e]	9.22
CH_3	Soln.[f]	6–24	100–124	$C_{10}H_8N_4O_2$	Blue-black	58.85[g]	58.58	3.43[g]	3.29	24.00[g]	23.98	13.72[g]	11.62
H	Soln.[f]	6	140	$C_8H_4N_4O_2$	Blue-black	57.45[h]	57.54	1.85[h]	2.47	25.90[h]	25.80	14.80[h]	11.87

[a] At a pressure of 0.10 mm. [b] Insoluble in boiling benzene, ethanol, acetone, methanol and ether. Calcd. for $C_{20}H_{12}N_4O_2$ + 5% C. [c] For 1.0 g. of I, 125 ml. of 20% isopropyl alcohol was used. [d] Recrystallized from ethanol. The product, upon prolonged heating in ethanol or other solvents, changed into unidentified insoluble yellow to dark brown material. The pure dry red crystals slowly become blue-black upon storage above 100°; cryoscopic mol. wt. in benzene: calcd. 340, found 355 (determined by Huffman Microanalytical Laboratories, Wheatridge, Colo). [e] Calcd. for 78% I and 22% II (III). Pyrolysis above 80° gives extensive decomposition. [f] Dry pyrolyses led to explosions: I (R = CH_3) was dissolved in refluxing dioxane or ethylene glycol monomethyl ether; I (R = H) was dissolved in refluxing cyclopentanol. [g] Calcd for $C_{10}H_8N_4O_2$ + 8% C. Another sample upon analysis gave the values: C, 58.22; H, 3.59; N, 23.65; O, 13.06. [h] Calcd. for $C_8H_4N_4O_2$ + 15% C.

Acknowledgment.—We are indebted to Mr. R. T. O'Connor, Southern Regional Research Laboratory, for ultraviolet and infrared absorption data.

Experimental[5]

Pyrolysis Procedures.—A slurry of 3.0 g. (0.008 mole) of 7-azido-8-nitro-1,2,3,4-dibenzphenazine in 100 ml. of 95% ethanol was refluxed with stirring for 24 hours as the original golden yellow crystals of analytically pure starting material slowly changed to purple-red. The filtered product, 2.7 g., was washed with ether and dried. Elemental analysis indicated that it was a 3:2 mixture of starting material and 7,8-dinitroso-1,2,3,4-dibenzphenazine.

Anal. Calcd. for 60% $C_{20}H_{10}N_6O_2$ and 40% $C_{20}H_{10}N_4O_2$: C, 68.83; H, 2.98; N, 19.11; O, 9.17. Found: C, 69.10; H, 2.55; N, 18.89; O, 9.48.

Dry heating of an analytically pure sample of 6-azido-7-nitro-1,2,3,4-dibenzphenazine at 100° in an evacuated drying pistol (100 mm.) for 120 hours gave quantitatively blue-black 7,8-dinitroso-1,2,3,4-dibenzphenazine, m.p. >300°.

Anal. Calcd. for $C_{20}H_{10}N_4O_2$: C, 71.00; H, 2.98; N, 16.55; O, 9.46; Found: C, 70.79; H, 3.07; N, 16.68; O, 9.27.

An unidentified yellow solid is obtained upon heating this product in benzene.

Other pyrolyses are reported in Table I.

Both the red and blue-black forms of 2,3-diphenyl-6,7-dinitrosoquinoxaline were refluxed in isopropyl alcohol with an excess of 48% hydroiodic acid for 24 hours. The mixture was filtered and iodine was removed from the filtrate by adding a saturated solution of sodium bisulfite. Upon adding sodium hydroxide to the orange solution, 2,3-diphenyl-6,7-diaminoquinoxaline separated as yellow microcrystals, m.p. 268–273°. In hot acetic acid the diamine coupled with phenanthrenequinone. The product, m.p. >300°, gave a deep blue color with concentrated sulfuric acid. After several washings with ether it was analyzed.

Anal. Calcd. for $C_{34}H_{20}N_4$: C, 84.29; H, 4.14; N, 11.57. Found: C, 83.74; H, 4.78; N, 11.44.

Paper Chromatographic Separations.—The ascending method was used with Whatman No. 2 filter paper. Position of spots was determined by their fluorescence to ultraviolet light. With a micropipet a small spot, 0.5 to 1.0 cm. in diameter, of a methanol, ethanol or carbon tetrachloride solution of the compound was placed on the paper strip about 4 cm. from the bottom edge. After evaporation of methanol, ethanol or carbon tetrachloride, the strips were lowered into other solvents so that the initial spot remained 3 cm. above the surface of the liquid. After the solvent front had moved up the paper strip 15 to 18 cm. the observations were made.

Polar solvents (butanol, acetic acid, water or aqueous isopropyl alcohol) allowed all compounds tested (IV, V, VI, VII and VIII) to move as single species with the solvent front. The use of non-polar solvents (petroleum ether, carbon tetrachloride or hexane) gave rise to two spots in each case. One moved with the solvent front, the other stayed at its original position.

A third series of experiments indicated a temperature effect upon the behavior of the compounds tested. Preheating the paper strips with the original spot just before chromatographic separation brought about a strong increase in the intensity of the bottom or stationary spot while the top or moving spot nearly disappeared. On the other hand, chromatographic separation at or near 0° gave an increase in the intensity of the top spot while the bottom stationary spot became hardly noticeable.

With each compound, the separated spots were dissolved from the paper into ethanol and individually rechromatographed. In each instance, both top and bottom spots again gave rise to two distinct spots, one stationary and one moving.

Chromatographic experiments on red 2,3-diphenyl-6,7-dinitrosoquinoxaline with non-polar solvents failed due to poor solubility; however, samples of this compound in benzene did separate into two spots, one stationary and one moving, at room temperature.

7-Nitro-1,2,3,4-dibenzphenazine.—A mixture of 4-nitro-1,2-phenylenediamine and 2-nitro-1,4-phenylenediamine, obtained from reducing 2,4-dinitroaniline with sodium sulfide and sulfur in ethanol, was treated with an excess of phenanthrenequinone in hot acetic acid. The product, 7-nitro-1,2,3,4-dibenzphenazine, separated as a yellow solid which recrystallized from chloroform and from nitrobenzene as yellow needles, m.p. 265–268°.[6] This same material, m.p. and mixture m.p. 266–269°, was obtained from diazotized 8-nitrodibenzphenazine in hot acetic acid which also contained some sulfuric acid.

Anal. Calcd. for $C_{20}H_{11}N_3O_2$: C, 73.84; H, 3.38; N, 12.92; O, 9.84. Found: C, 73.22; H, 3.19; N, 13.34; O, 10.00.

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[5] Semi-micro analyses by Alfred Bernhardt, Microanalytisches Laboratorium, Mülheim (Ruhr), Germany. Melting points are uncorrected.

[6] E. Heim, *Ber.*, **21**, 2306 (1888).