

EXPERIMENTAL

Tris(o-methoxymethylphenyl)phosphine, I. Butyllithium (850 cc. of 0.86*M* solution; 0.73 mole) was dropped (2.5 hr.) into a cold (-75°), efficiently stirred solution of *o*-bromobenzyl methyl ether² (141 g., 0.701 mole) in 300 cc. of dry ether under nitrogen. (Carbonation with Dry Ice of a similar reaction mixture permitted the isolation of 62% of *o*-methoxymethylbenzoic acid, m.p. 89–92°, showing that the interchange had proceeded as desired. Recrystallization from hexane raised the melting point to 95–95.5°.)⁶ The addition of 32 g. (0.233 mole) of phosphorus trichloride in 100 cc. of ether over a period of 15 min., warming to room temperature, followed by stirring for 20 hr. and 1 hr. at reflux converted the lithio derivative to the phosphine I. The reaction mixture was hydrolyzed by addition, with supplemental cooling, of 350 cc. of saturated aqueous ammonium chloride. Concentration of combined ether extracts furnished large, colorless crystals of the phosphine; 43.7 g., m.p. 105–106°. Another 8.8 g. of phosphine was collected on further evaporation of the solvent; total yield, 58%. Distillation of the liquid residue yielded 35.7 g. (38%) of *n*-butyl bromide.

An analytical sample was prepared by recrystallization of the phosphine from 95% ethanol; m.p. 105.5–106°.

*Anal.*⁷ Calcd. for $C_{24}H_{27}O_3P$: C, 73.08; H, 6.90. Found: C, 72.79; H, 6.91.

Tris(o-methoxymethylphenyl)phosphine oxide. (a) Oxidation with Iodine. To a solution of 0.82 g. of phosphine I in 15 cc. of ether was added 0.6 g. of iodine in 30 cc. of ethanol and six drops of pyridine. In contrast to the reaction of triphenylphosphine with iodine, which decolorizes immediately, the iodine color in this preparation slowly faded during 20 min. heating on a steam bath. Excess iodine was reduced by a few drops of sodium bisulfite solution, then 10 cc. of water was added to the chilled solution. The precipitate was washed twice with water and dried; 0.70 g. (81%) of crude oxide; m.p. 146.5–147.5°. Two recrystallizations from alcohol raised the melting point to 147–147.5°; weight 0.49 g. (57%).

*Anal.*⁷ Calcd. for $C_{24}H_{27}O_4P$: C, 70.23; H, 6.63. Found: C, 69.87; H, 6.71.

(b) Hydrogen peroxide. Hydrogen peroxide (0.3 g. of 30% solution) with a few cubic centimeters of water was added to a solution of 0.90 g. of phosphine I in 20 cc. of acetone. Most of the acetone was removed *in vacuo*, leaving 0.92 g. (97%) of the phosphine oxide; m.p. 145–146°; 146–147° after recrystallization. It did not depress the melting point of the oxide prepared by iodine oxidation.

Methyl tris(o-methoxymethylphenyl)phosphonium iodide. A mixture consisting of 1.42 g. of the phosphine I, 16.3 g. of methyl iodide, and 0.5 g. of fine copper wire was refluxed on a steam bath for 1 hr.; then excess methyl iodide was distilled. Removal of the copper left 1.93 g. (99%) of white crystals; m.p. 202–202.5°. Reactions carried out in the absence of copper developed a yellow color which was difficult to remove from the crystalline product. Two recrystallizations of the methiodide from ethanol gave 1.55 g. (80%) of product with a slightly higher melting point; 202.5–203°.

*Anal.*⁷ Calcd. for $C_{24}H_{29}O_3PI$: C, 55.98; H, 5.64. Found: C, 56.29; H, 5.53.

Tris(o-chloromethylphenyl)phosphine, II. To 11.5 g. (0.098 mole) of boron trichloride in an ice cooled flask was slowly added 8.90 g. (0.0226 mole) of phosphine I. The mixture was kept cold for 8 hr., then 40 cc. of pentane was added and the mixture allowed to warm to room temperature overnight. The caked solid was washed with water, heated to remove pentane, and washed again with water.

(6) G. R. Clemo and G. A. Swan, *J. Chem. Soc.*, 617 (1946). H. Gilman, G. E. Brown, F. J. Webb, and S. M. Spatz, *J. Am. Chem. Soc.*, 62, 977 (1940), and J. V. Braun, E. Anton, and K. Weissbach, *Ber.*, 63B, 2847 (1930).

(7) Carbon and hydrogen analyses by Miss H. Beck.

On drying 7.5 g. of solid, m.p. 117–131°, was obtained. Recrystallization from ethanol-water gave 4.03 g. of material melting at 132–137°. Subsequent recrystallizations from alcohol and from chloroform raised the melting point to 140–141°.

*Anal.*⁷ Calcd. for $C_{21}H_{18}Cl_3P$: C, 61.86; H, 4.45. Found: C, 62.02; H, 4.33.

This phosphine was converted to its oxide in 94% yield with 30% hydrogen peroxide by the procedure described above; m.p. 178–181°. Recrystallization two times from chloroform-pentane gave the pure oxide, m.p. 185–185.5°, which exhibited the characteristic strong absorption in the infrared at 8.45 μ attributed to P—O bonding.^{8,9}

*Anal.*⁷ Calcd. for $C_{21}H_{18}Cl_3OP$: C, 59.52; H, 4.28. Found: C, 59.56; H, 4.33.

Reaction of II with aluminum chloride. (a) Nitromethane solvent. The chloromethylphenylphosphine II, (0.42 g.) in 15 cc. of nitromethane was added to a solution of 0.55 g. of aluminum chloride in 20 cc. of nitromethane and the mixture was heated on a steam bath for 40 hr. The mixture was poured into dilute hydrochloric acid and nitromethane was removed by steam distillation. On cooling, a brown solid (0.38 g., 87%) was recovered, m.p. 172–175°. Its infrared spectrum was the same as that of the phosphine oxide, IV.

(b) Aluminum chloride. To 1.1 g. of aluminum chloride in 15 cc. of carbon disulfide was slowly added 0.75 g. of II in 15 cc. of carbon disulfide. The solution immediately turned a deep red. After standing at room temperature for 2 hr. it was poured onto ice, hydrochloric acid was added, and the organic layer was separated and washed with water, dried, and warmed to distill the carbon disulfide. Crystals (0.40 g., 53%) of phosphine II, as shown by the infrared spectrum, remained. Recrystallization from ether-pentane yielded 0.30 g. of recovered phosphine, m.p. 135–137°. Some tars insoluble in ether or concentrated hydrochloric acid were also obtained from the reaction mixture.

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(8) L. W. Daasch and D. C. Smith, *Anal. Chem.*, 23, 853 (1951).

(9) Our infrared spectra were taken in a Baird double beam recording spectrophotometer. The sample was dispersed in a plate of potassium bromide.

2-Nitro-9,10- ψ -dinitrosophenanthrene¹

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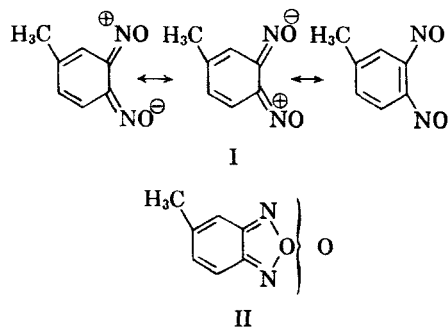
Symmetry requirements for *o*-dinitroso aromatic compounds, e.g. 4-methyl-1,2- ψ -dinitrosobenzene (I), do not allow the structural assignment as isomeric furoxanes, e.g. 5-(6-) methylbenzofuroxane (II), although they have been so described since 1912.^{2,3} Meisenheimer, Lange, and Lamparter demonstrated the unsymmetrical nature of the furoxane ring in a preparation of isomeric furoxanes by an oxidation of corresponding γ -(*amphi*)

(1) Partial support of this work under contract DA-01-009-ORD-428 with the Office of Ordnance Research is gratefully acknowledged.

(2) A. G. Green and F. M. Rowe, *J. Chem. Soc.*, 101, 2452 (1912).

(3) J. H. Boyer, R. F. Reinisch, M. J. Danzig, G. A. Stoner, and F. Sahhar, *J. Am. Chem. Soc.*, 77, 5688 (1955).

dioximes of *p*-methoxy benzil.⁴ Both furoxanes were obtained from *d*-(*anti*) and *β*-(*syn*) dioximes of the unsymmetrical benzil.⁴ This method has now been chosen to establish the symmetry requirements for a mono-substituted derivative of 9,10-dinitroso-phenanthrene.



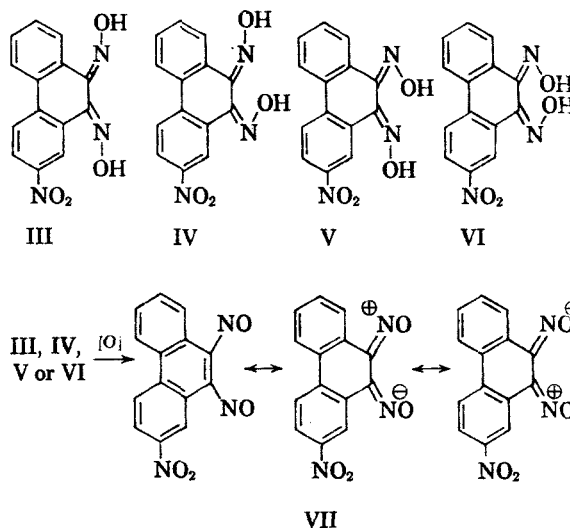
The preparation of 2-nitro-9,10-dinitrosophenanthrene (VII) by dehydrogenating 2-nitrophenanthrenequinone dioxime required mononitration⁵ of phenanthrenequinone and the preparation, separation, and identification of the four isomeric dioximes. The dioximes were prepared from the quinone and hydroxylamine hydrochloride either in refluxing ethanol and pyridine or in ethanol and pyridine (or potassium carbonate) in heated pressure bottles. Structural assignment of the dioximes was based upon chelation tests. In chelation with nickel *bis*-aryl glyoximes with an α -(*anti*) modification give red insoluble precipitates and yellow or yellow-green precipitates are obtained from γ -(*amphi*) modifications.⁶ There is no reaction between nickel salts and β -(*syn*) glyoximes.⁶ Of the four isomers of 2-nitrophenanthrenequinone dioxime, one (m.p. 197°) gives a red insoluble nickel salt and is assumed to be the α -(*anti*) modification (III). Two others (m.p. 172° and 183°) afford yellow-green nickel salts and are therefore assumed to be the expected γ -(*amphi*) forms (IV, V). No attempt was made to differentiate between them. The last one (m.p. 190–191°) fails to form a nickel chelate and is assumed to be the β -(*syn*) isomer (VI).

The product (VII) obtained upon dehydrogenation of each 2-nitrophenanthrenequinone dioxime was not obtained in isomeric modifications. It presumably requires a symmetrical arrangement of the N₂O₂ moiety and is assigned the structure of 2-nitro- ψ -9,10-dinitrosophenanthrene (VII). It was also obtained upon treating phenanthrenequinone dioxime with nitric acid at room temperature.

(4) J. Meisenheimer, H. Lange, and W. Lamparter, *Ann.*, **444**, 94 (1925).

(5) F. M. G. Bavin and M. J. S. Dewar, *J. Chem. Soc.*, 4477 (1955). Indian patent 50,970; *Chem. Abstr.*, **50**, 7870 (1956). S. Kato, M. Maezawa, S. Hirano, and S. Ishigaki, *Yuki Gōsei Kagaku Kyōkai Shi*, **15**, 29 (1957); *Chem. Abstr.*, **51**, 10462 (1957).

(6) A. E. Martell and M. Calvin, *Chemistry of the Metal Chelate Compounds*, Prentice-Hall, New York, 1952, 332.



Reduction of both furoxanes and *o*-dinitrosoaromatic compounds brings about the formation of dioximes. Whereas *amphi*-dioximes are obtained from furoxanes,⁴ the structural modification of the dioximes obtained from *o*-dinitroso aromatic compounds has not previously been determined. In the present case reduction of 2-nitro- ψ -9,10-dinitrosophenanthrene with hydroxylamine in pyridine affords the lower melting *amphi* dioxime of 2-nitrophenanthrenequinone.

EXPERIMENTAL⁷

*Preparation of 2-nitro-9,10-phenanthrenequinone dioximes. Procedure A.*⁸ A mixture of 1.0 g. (0.004 mole) of 2-nitro-9,10-phenanthrenequinone,⁵ 20.0 g. (0.288 mole) of hydroxylamine hydrochloride, 10 ml. of pyridine, and 80 ml. of 95% ethanol was heated at reflux with mechanical stirring for 20 hr. as the color changed from yellow-orange to dark green. After 2 hr. at room temperature, pyridine hydrochloride as long colorless needles was isolated by filtration. Upon adding 150 ml. of water at room temperature to the filtrate a mixture, 1.0 g. (90%), of oximes precipitated and was purified from aqueous methanol. After three precipitations from methanol, a light green powder, one of the γ -(*amphi*) dioximes, 0.77 g. (68%), m.p. 172° (partial dec. at 167°), was collected. Upon the addition of a drop of nickel chloride solution to a sample in 5 ml. of ethanol a characteristic yellow-green precipitate was observed.

Anal. Calcd. for C₁₄H₉N₂O₄: C, 59.37; H, 3.20; N, 14.84; O, 22.60. Found: C, 59.49; H, 3.12; N, 14.88; O, 22.51.

From the combined filtrates a flaky light yellow solid precipitated during 24 hr. and was isolated and dried 10 hr. in the vacuum oven at 60°. A solution in ethanol gave a red precipitate, characteristic of an α -(*anti*) dioxime, with a nickel salt. The m.p. was 188–203° with decomposition, while charring occurred some 4° lower.

A mixture of 6.0 g. (0.023 mole) of 2-nitro-9,10-phenanthrenequinone, 120.0 g. (1.727 mole) of hydroxylamine hydrochloride, 80 ml. of pyridine, and 20 ml. of 95% ethanol was heated at reflux with mechanical stirring for 12 hr. as the color of the reaction mixture changed from light to dark green. After overnight standing, the solution was diluted with 1.5 liters of distilled water and a flaky yellow-

(7) Analyses by Alfred Bernhardt, Microanalytisches Laboratorium, Muheim (Ruhr), Germany.

(8) W. E. Bachmann and C. H. Boatner, *J. Am. Chem. Soc.*, **58**, 2097 (1936).

green precipitate of a mixture of oximes was filtered, 5.99 g. (92%), m.p. 150–195°. The crude material was extracted with 600 ml. of boiling water and then with 500 ml. of boiling methanol. The light green methanol solution was filtered while still hot from an orange-green precipitate. Upon dilution with 200 ml. of water, 0.94 g. (13%), m.p. 172° (dec.) of a γ -(*amphi*) dioxime separated as a yellow powder (see above). The orange-green precipitate dissolved in 400 ml. of hot methanol over a period of 12 hr. A negligible amount of foreign material was removed by filtration and the filtrate, diluted with 100 ml. of distilled water was stored overnight at room temperature. The other γ -(*amphi*) dioxime as a flaky yellow powder, 2.22 g. (33%), m.p. 183–185° (charring at 180°) was reprecipitated from methanol and an analytical sample was dried in the vacuum oven for 12 hr. at 80–95°. A pale green precipitate was observed upon adding a drop of nickel chloride solution to an ethanol solution of this dioxime.

Anal. Calcd. for $C_{14}H_9N_3O_4$: C, 59.37; H, 3.20; N, 14.84. Found: C, 59.39; H, 3.38; N, 14.75.

*Procedure B.*⁹ In a pressure bottle, 1.0 g. (0.004 mole) of 2-nitro-9,10-phenanthrenequinone was mixed with 10.0 g. (0.144 mole) of hydroxylamine hydrochloride, 4 ml. of pyridine, and 80 ml. of 95% ethanol. The bottle was sealed, and placed in boiling water for 4 hr. It was then cooled in a Dry Ice and acetone bath and carefully opened. Pyridine hydrochloride was removed by filtration, the filtrate was diluted with distilled water, a yellow flaky precipitate, m.p. 195–198°, 0.95 g. (85%), was removed, dissolved in 300 ml. of hot methanol and reprecipitated by the addition of 80 ml. of distilled water to the cold solution. A yellow-orange powder, after three additional reprecipitations from methanol, gave an analytical sample, m.p. 194.5–195.8° of the α -(*anti*) dioxime. In hot ethanol this dioxime reacted with one drop of a nickel salt solution with the formation of a red precipitate.

Anal. Calcd. for $C_{14}H_9N_3O_4$: C, 59.37; H, 3.20; N, 14.84. Found: C, 59.29; H, 3.29; N, 14.66.

In a pressure bottle 2.0 g. (0.008 mole) of 2-nitro-9,10-phenanthrenequinone was mixed with 20.0 g. (0.288 mole) of hydroxylamine hydrochloride in 80 ml. of 95% ethanol and 5.0 g. of potassium carbonate. The bottle was sealed and placed in boiling water for 22 hr. during which time the color of the reaction mixtures became yellow-orange. The pressure bottle was cooled in the refrigerator for a day at 15°, opened, and the precipitate was extracted twice with ether. The ether extracts were combined and evaporated over a steam bath to dryness. The residue was dissolved in 80 ml. of 95% ethanol and the solution was stored for one week in the refrigerator. A flaky pale green solid precipitated, 0.8 g. (35%), m.p. 188–189° (dec.). After three precipitations from methanol, the solid, m.p. 190–191° (dec.), gave no precipitate upon being treated with a solution of nickel chloride.

Anal. Calcd. for $C_{14}H_9N_3O_4$: C, 59.37; H, 3.20; N, 14.84. Found: C, 61.19; H, 2.87; N, 15.05.

Oxidation of 2-nitro-9,10-phenanthrenequinone dioxime. Procedure A. To 0.50 g. (0.002 mole) of each of the four isomeric 2-nitro-9,10-phenanthrenequinone dioximes, in 75 ml. of 50% ethanol, chlorine was added over a period of 10 min., during which time the temperature was held at 55–60°. As a colorless precipitate formed, the solution turned from dark red to pale yellow. The mixture was chilled and filtered. A colorless amorphous precipitate, m.p. 211–212°, was recrystallized from aqueous pyridine and washed with hot methanol, 0.45 g. (91%). An analytical sample, m.p. and mixture m.p. 211–212°, was dried in the vacuum oven for 12 hr. at 150°.

Anal. Calcd. for $C_{14}H_7O_5N_3$: C, 59.79; H, 2.50; N, 14.94. Found: C, 59.96; H, 2.48; N, 14.92.

Procedure B. With stirring 0.5 g. (0.002 mole) of each of the four isomeric 2-nitro-9,10-phenanthrenequinone dioximes, was dissolved in 100 ml. of 69% nitric acid. The solution was poured into 400 ml. of ice cold water. A colorless precipitate was collected as a powder, 0.39 g. (70%), m.p. 210–213°. The crude product was dissolved in 20 ml. of hot pyridine and the hot solution was filtered. The filtrate was chilled and diluted with 20–30 ml. of distilled water. A colorless precipitate, m.p. 211–212°, after two reprecipitations with pyridine, gave an analytical sample, m.p. and mixture m.p. 211–212°.

Anal. Calcd. for $C_{14}H_7N_3O_4$: C, 59.79; H, 2.50; N, 14.94. Found: C, 59.48; H, 2.40; N, 14.11.

Nitration and oxidation of 9,10-phenanthrenequinone dioxime. With stirring 0.50 g. (0.002 mole) of 9,10-phenanthrenequinone dioxime, m.p. 199–200°, was added to 80 ml. of 69% nitric acid at room temperature. A pale brown flaky solid formed immediately and was dissolved in 100 ml. of boiling ethanol. The solution was filtered while still hot, chilled in a Dry Ice and acetone bath, and diluted with distilled water. A colorless precipitate of 2-nitro-9,10- ψ -dinitrosophenanthrene, 0.36 g. (62%), m.p. and mixture m.p. 211–212°, was collected.

Reduction of 2-nitro-9,10-dinitrosophenanthrene. To 0.40 g. (0.002 mole) of 2-nitro-9,10-dinitrosophenanthrene in 50 ml. of hot 95% ethanol and 5 ml. of pyridine, 10.0 g. (0.144 mole) of hydroxylamine hydrochloride was added. After heating at reflux temperature for 1 hr., the solution was poured into 300 ml. of distilled water at 0°. A yellow-green precipitate, 0.30 g. (72%), m.p. 172–174° (dec.), of a γ -(*amphi*) 2-nitro-9,10-phenanthrenequinone dioxime was collected.

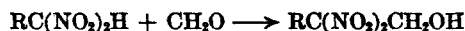
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3,3-Dinitro-1-alkanols

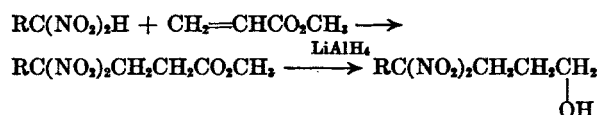
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Of the aliphatic *gem*-dinitro-1-alkanols, the 2,2-dinitro-1-alkanols are readily prepared by the Henry reaction of 1,1-dinitroalkanes and formaldehyde.^{1–3} The 4,4-dinitro-1-alkanols are pre-



pared by the selective reduction of Michael adducts to 1,1-dinitroalkanes:^{4,5}



This paper reports the synthesis of the hitherto unknown 3,3-dinitro-1-alkanols.

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- (2) H. Feuer, G. B. Bachman, and J. P. Kispersky, *J. Am. Chem. Soc.*, **73**, 1360 (1951).
- (3) M. B. Frankel and K. Klager, *J. Am. Chem. Soc.*, **79**, 2953 (1957).
- (4) H. Shechter, D. Ley, and L. Zeldin, *J. Am. Chem. Soc.*, **74**, 3664 (1952).
- (5) H. Feuer and T. J. Kucera, *J. Am. Chem. Soc.*, **77**, 5740 (1955).

(9) E. Mosettig and J. W. Krueger, *J. Am. Chem. Soc.*, **58**, 1311 (1936).