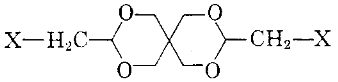
TABLE II

ACETALS OF PENTAERYTHRITOL



	X	M.P.	B.P.	Mm.	Yield, %	Formula	Calcd. C	Calcd. H	Calcd. Cl	Found C	Found H	Found Cl
XIV	*O*-Phenyl	203.5	...	...	39	$C_{21}H_{24}O_6$	67.73	6.45		66.93	6.66	
XV	*O*-Cyclohexyl	40–47	176–200	0.1	50	$C_{21}H_{36}O_6$	65.59	9.43		64.19	9.36	
I	Cl	96–96.5	...	...	35	$C_9H_{14}O_4Cl_2$	42.05	5.49	27.58	42.61	5.17	27.40

mixture was completely soluble in water. No further attempts were made to isolate a reaction product.

Reaction of VI with Ammonia.—A mixture of 82.3 g. (0.5 mole) of the chloroacetal of pentaglycol and 133.2 ml. (2 moles) of concd. ammonium hydroxide in 66.6 ml. of Cellosolve was placed in a sealed iron pipe and heated at 138° for 17 hr. The reaction mixture was then filtered and the filtrate formed two layers. The organic layer was separated and distilled. After a small forerun, a fraction (17.5 g.) was collected at 80–155° (1.3 mm.) which solidified on cooling. On recrystallization from benzene, 15.6 g. (23%) of bis[(5,5-dimethyl-*m*-dioxan-2-yl)methyl]amine, m.p. 60–65°, was obtained. Melting point of an analytical sample was 67–68°.

Anal. Calcd. for $C_{14}H_{27}O_4N$: C, 61.51; H, 9.95; N, 5.12. Found: C, 61.73; H, 10.12; N, 5.11.

Reaction of I with Ammonium Hydroxide.—Reaction of I with ammonia for 8.5 hr. at 140° in a procedure similar to the above, afforded a light-colored gummy material which was soluble in cold dilute hydrochloric acid. The gummy product could not be recrystallized. Attempts to form derivatives by benzoylation and by reaction with picric acid afforded only gummy materials again.

Acknowledgment.—We gratefully acknowledge grants for the support of undergraduate research from the Research Corp., the National Science Foundation, and the Petroleum Research Fund, administered by the American Chemical Society.

Juglone 4-Monooxime, an Isomer of 8-Nitro-1-naphthol

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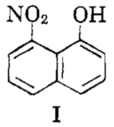
Meldola and Streatfeild[1] were the first to attempt to prepare 8-nitro-1-naphthol (I) by decomposition of the diazonium salt of 8-nitro-1-naphthylamine,



I

but obtained only resinous material. Kozlov and Vorozhtzov[2] repeated this work and obtained a product of m.p. 212° dec., which they considered to be the compound in question. The reaction was later carried out by Luther and Gunzler,[3] and also by Anderson and co-workers[4] and by Bryson,[5] and the product accepted as 8-nitro-1-naphthol.

In the present work, the compound was prepared by the same method for comparison with other products which were suspected of containing this nitronaphthol. From Luther and Gunzler's infrared data, it was seen that the product obtained was identical to theirs. It eventually became apparent, however, that the substance did not have the infrared spectral characteristics nor the chemical properties of a nitronaphthol.

Thus, the spectrum was found to be quite similar to those of a number of naphthaquinone monooximes which had been prepared in this laboratory. Strong nitro bands were missing and three characteristic features of quinone oximes, as indicated by Hadzi,[6] were present: 1. Strong and broad absorption bands centered around 3100 cm.$^{-1}$, with one band appearing at 2830 cm.$^{-1}$. 2. A shoulder at 1655 cm.$^{-1}$, probably due to the C=O stretching mode of the 1,4-monooxime. 3. A strong band at 988 cm.$^{-1}$, ascribed to the N—O bending frequency in quinone oximes. No similar band was found in any of the isomeric nitronaphthols which were examined in this laboratory.

Among various possible structures considered for the compound was that of a 5-hydroxy-1,4-naphthaquinone 4-monooxime (8-hydroxynaphthaquinone 1-oxime) (III), isomeric with 8-nitro-1-naphthol. After further examination, this constitution proved to be compatible with the properties of the substance.

All three of the *ortho* substituted nitronaphthols (1,2- or 2,1- and 3,2-) have melting points below 130° and a peri (1,8-) isomer, with similar possibilities for chelation or H-bonding likewise might be expected to be less polar and therefore lower melting than other nitronaphthols. The m.p. of 212° dec. given by Kozlov and Vorozhtzov[2] is much higher than would be expected and, indeed, later work by Anderson *et al.*[4] and Bryson[5] give a decomp. point of 242° without melting.

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[1] R. Meldola and F. W. Streatfeild, *J. Chem. Soc.*, **63**, 1056 (1893).

[2] V. V. Kozlov and N. N. Vorozhtzov, *Ber.*, **69B**, 416 (1936).

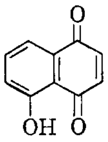
[3] H. Luther and H. Gunzler, *Z. Naturfors.*, **10b**, 445 (1955).

[4] J. R. A. Anderson, A. J. Costoulas, and J. L. Garnett, *Anal. Chim. Acta.*, **20**, 236 (1959).

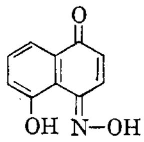
[5] A. Bryson, *Trans. Faraday Soc.*, in press (from ref. 4).

[6] D. Hadzi, *J. Chem. Soc.*, 2725 (1956).

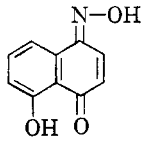
From the suggested structure of a 5-hydroxy-1,4-naphthaquinone 4-oxime, it is evident that this is a derivative of the long known 5-hydroxy-1,4-naphthaquinone or juglone (II). It might be considered possible, therefore, that the compound would be convertible into, or formed from, juglone.



II



III

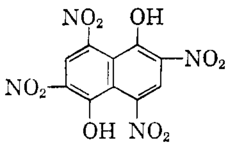


IV

In an effort to test this, compound III was steam distilled from dilute sulfuric acid, hoping to hydrolyze the oxime and volatilize any juglone. The latter was isolated from the distillate in greater than 80% yield, and the infrared spectrum matched that of authentic juglone. It is difficult to see how this compound could be derived from a nitronaphthol.

The monooxime III does not seem to be listed in the literature, though the isomeric monooxime (IV) has been claimed to be the product from juglone and hydroxylamine.[7] The orientation IV might have been expected, since the oxime III would be the product of reaction at a more hindered carbonyl, and in addition, this carbonyl would be less reactive because of H-bonding to the peri-hydroxyl group.

The action of nitric acid under mild conditions on some naphthaquinone oximes results in derivatives of 2,4-dinitro-1-naphthol (Martius Yellow), formed by a combined oxidation and nitration.[8] If this reaction succeeded with the quinone oxime III, it might be supposed that the product would be the 2,4,6,8-tetranitro-1,5-dihydroxynaphthalene



V

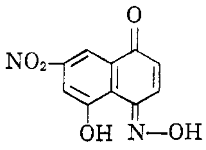
(V) of Thomson, Race, and Rowe.[9] When this was tried with the suspected hydroxyquinone oxime III, it gave a better yield of the tetranitro compound V than was obtained from 1,5-dihydroxynaphthalene by nitration.[9] The infrared spectra of the tetranitro compounds prepared by the two methods were identical. The improved yields with the hydroxyquinone oxime as starting material may be explained by the fact that it is less sensitive to oxidative destruction by nitric acid and also because it is already partly substituted in the desired direction.

8-Nitro-1-naphthol, under the conditions of the nitration, should form 2,4,8 trinitro-1-naphthol. By comparison with authentic material,[8] it was seen that no trace of the infrared peaks of this trinitronaphthol was present in the spectrum of the nitration product of III.

As to the mode of formation of the juglone 4-oxime, it is apparently the result of an internal oxidation-reduction, but a mechanism for its production cannot be discerned at this time.

Further efforts were made to prepare 8-nitro-1-naphthol from the 8-nitro-1-diazonium salts. Attempts to employ the method of Hodgson and Foster[10] involving decomposition of the diazonium zinc chloride complex in acetic anhydride led to intractable tars instead of a nitronaphthyl acetate. No nitronaphthol could be obtained on alkaline hydrolysis of the product. Likewise, the adaptation of Smith and Haller[11] using the diazonium fluoroborate in acetic acid gave a similar result.

In an extension of this work, the diazotization and decomposition of 3,8-dinitro-1-naphthylamine[12] was carried out to determine if 3,8-dinitro-1-naphthol could be formed. However, the properties of the product were best explained by the nitrojuglone oxime formulation, VI. The infrared spectrum of the material shows two strong absorption bands at 985 cm.$^{-1}$ and 995 cm.$^{-1}$,[6] and a strong band at 1640 cm.$^{-1}$ these wave-numbers probably corresponding to the similar values shown by III. In its property of decomposing at a high temperature with partial fusion, VI also resembles the juglone monooxime. This reaction seems to provide an additional example of the formation of a hydroxyquinone oxime from a nitrodiazonium salt.



VI

It may be noted that another reference exists in the literature describing the synthesis of 8-nitro-1-naphthol, namely that of Bell,[13] who claims its preparation in poor yield by the nitration of the *m*-nitrobenzenesulfonate ester of α-naphthol, followed by hydrolysis. Preliminary attempts to repeat this work have not succeeded.

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[7] H. Goldstein and P. Grandjean, *Helv. Chim. Acta.*, **26**, 181 (1943).

[8] C. Graebe and A. Oeser, *Ann.*, **335**, 145 (1904).

[9] R. H. Thomson, E. Race, and F. M. Rowe, *J. Chem. Soc.*, 350 (1947).

[10] H. H. Hodgson and C. K. Foster, *J. Chem. Soc.*, 747 (1942).

[11] L. E. Smith and H. L. Haller, *J. Am. Chem. Soc.*, **61**, 143 (1939).

[12] E. R. Ward, T. M. Coulson, and J. G. Hawkins, *J. Chem. Soc.*, 4541 (1954).

[13] F. Bell, *J. Chem. Soc.*, 286 (1933).

Experimental

Infrared spectra were obtained on a Perkin-Elmer Model 21 Spectrophotometer, using a sodium chloride prism. The samples were examined as potassium bromide discs.

The hydroxyquinone oxime III was prepared as described by Kozlov and Vorozhtzov,[2] any excess of nitrous acid being destroyed by urea before boiling. As to the decomp. point, the higher value favored by Bryson[5] seems to describe better the behavior of the compound on heating. The Russian workers gave adequate analytical values for III and also its lead salt. In the present work, the molecular weight was obtained by the Osmometer method to be sure the substance was not dimeric.

Mol. wt. Calcd. for $C_{10}H_7NO_3$: 189. Found: 190.

Hydrolysis of III.—A mixture of 150 mg. (0.79 mmole) of the juglone 4-oxime and 200 ml. of 2.5 *N* sulfuric acid was steam distilled for 6 hr. The yellow distillate was extracted twice with ether and the extracts dried and evaporated. A residue of 112 mg. of crystalline material was left. Yield: 81.1%. The spectrum of this product was identical to that of authentic juglone. It also formed the characteristic violet solutions in alkalies. Juglone for comparison was obtained by the method of Fieser and Dunn,[14] from 1,5-dihydroxynaphthalene.

Nitration of III.—A suspension of 0.25 g. (1.32 mmoles) of the hydroxy quinone oxime in 15 ml. of acetic acid was heated to boiling and cooled to 40–50°. A good part of the material crystallized at this temperature, and 5 ml. of 70% nitric acid was added slowly with stirring. The temperature was kept below 50°. After 15 min. at 40–50°, the mixture was cooled, diluted with 6 volumes of water, and left 1 hr. The tetranitro compound was filtered, washed with water, and dried. Yield 285 mg. or 63%. This product becomes red with alkali without solution as described by Thomson *et al.*[9] Comparison of infrared spectra with the authentic product showed identity.

To prepare a comparison sample of the tetranitro compound V, Thomson's work was repeated.[9] A poor yield of yellow-orange crystalline powder was produced which decomp. above 250°.

Authentic 2,4,8-trinitro-1-naphthol was prepared by the procedure of Graebe and Oeser.[8]

Preparation of VI.—This was carried out substantially as for III,[2] except that 40% sulfuric acid was used for the diazotization because of the weaker basicity and more sparing solubility of 3,8-dinitro-1-naphthylamine. Urea was added before boiling. The product was obtained as a yellowish crystalline powder in about 37% yield. The mixture of 3,5- and 3,8-dinitro-1-naphthylamines was prepared from 3-nitro-1-naphthylamine as described by Ward and coworkers,[12] and separated as they direct.[15]

The nitroquinone oxime VI was purified by recrystallization from aqueous methanol. On heating, it darkens above 180°, with softening at 225°, and forms a black smear above 250°.

Anal. Calcd. for $C_{10}H_5N_2O_5$: N, 11.966. Found: N, 11.99.

Acknowledgment.—The authors express thanks to Mrs. Dobbie Roisen for infrared spectra, and to W. M. Padgett II and Dr. J. Hyman for suggestions during the work.

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[14] L. F. Fieser and J. T. Dunn, *J. Am. Chem. Soc.*, **59**, 1018 (1937).

[15] The diazo decomposition reaction on 3,5-dinitro-1-naphthylamine provides a compound which is probably authentic 3,5-dinitro-1-naphthol.

The Mannich Condensation of 3-Amino-1,2-propanediol with 2,2-Dinitropropanol and the Nitration of the Product

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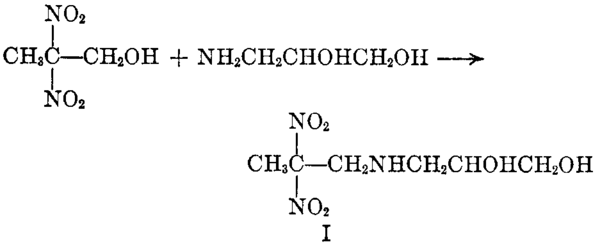
The Mannich condensation of 2,2-dinitro-1-alkanols and some reactions of the products have been reported.[1–4] In the present work, the nitration of the condensate of 3-amino-1,2-propanediol and 2,2-dinitropropanol has yielded a novel product.

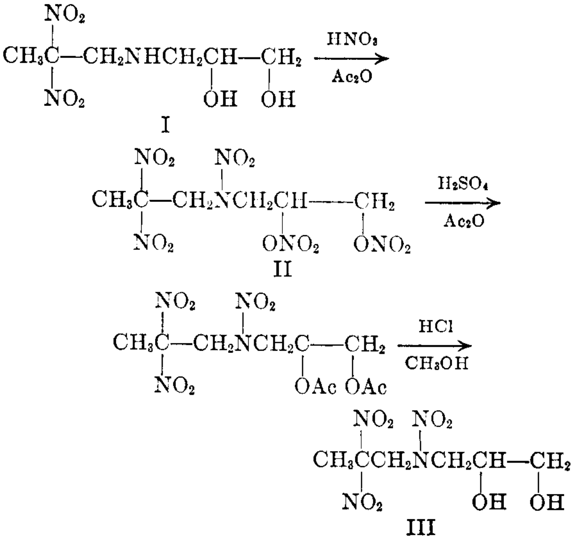
Heating an aqueous suspension of 2,2-dinitropropanol with a solution of 3-amino-1,2-propanediol to 50° gave a dark water-insoluble oil, presumably 6,6-dinitro-4-aza-1,2-heptanediol (I). However, since this material could not be purified without decomposition, the crude product was used directly in the subsequent reactions.



$$\underset{NO_2}{\overset{NO_2}{CH_3C}}—CH_2OH + NH_2CH_2CHOHCH_2OH \longrightarrow \underset{NO_2}{\overset{NO_2}{CH_3C}}—CH_2NHCH_2CHOHCH_2OH$$

I

The nitration of I, which was expected to yield 1,2-dinitroxy-4,6,6-trinitro-4-azaheptane (II), was carried out at 0° in acetic anhydride. An oil was isolated which was sensitive to impact. This oil



$$\underset{NO_2}{\overset{NO_2}{CH_3C}}—CH_2NHCH_2\underset{OH}{CH}—\underset{OH}{CH_2} \xrightarrow[Ac_2O]{HNO_3}$$

I

$$\underset{NO_2}{\overset{NO_2}{CH_3C}}—CH_2\overset{NO_2}{N}CH_2\underset{ONO_2}{CH}—\underset{ONO_2}{CH_2} \xrightarrow[Ac_2O]{H_2SO_4}$$

II

$$\underset{NO_2}{\overset{NO_2}{CH_3C}}—CH_2\overset{NO_2}{N}CH_2\underset{OAc}{C}—\underset{OAc}{CH_2} \xrightarrow[CH_3OH]{HCl}$$

$$\underset{NO_2}{\overset{NO_2}{CH_3C}}CH_2\overset{NO_2}{N}CH_2\underset{OH}{CH}—\underset{OH}{CH_2}$$

III

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[1] H. Feuer, G. B. Bachman, and W. May, *J. Am. Chem. Soc.*, **76**, 5124 (1954).

[2] K. Klager, *J. Org. Chem.*, **23**, 1519 (1958).

[3] M. B. Frankel and K. Klager, *J. Am. Chem. Soc.*, **79**, 2953 (1957).

[4] H. Feuer and W. A. Swarts, U. S. 2,981,750 (April 25, 1961).