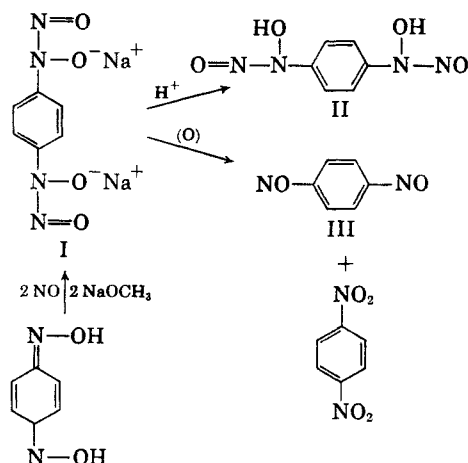


# Communications TO THE EDITOR

## New Reaction of Oximes and Nitric Oxide

Sir:

We wish to report a new reaction of oximes with nitric oxide. When *p*-benzoquinone dioxime was dissolved in a methanolic solution of sodium methoxide, and treated with oxygen-free nitric oxide at pressures ranging from atmospheric to 100 p.s.i., disodium - di - *N* - nitroso - *p* - phenylenedihydroxylamine (I) was obtained in 98% yield. (Anal. Calcd. for  $C_6H_4N_4Na_2O_4$ : C, 29.76; H, 1.66; N, 23.14; Na, 19.4. Found: C, 29.57; H, 1.74; N, 22.88; Na, 19.36; neut. equiv.,  $121 \pm 2$ ).



A positive Liebermann test was obtained from I, or the *aci* form II. Upon mild hypochlorite oxidation of I, *p*-dinitrosobenzene (III) was obtained; use of an excess of oxidizing agent gave only *p*-dinitrosobenzene. Acidic decomposition of II liberated oxides of nitrogen and III; II is considerably unstable and liberates oxides of nitrogen slowly at room temperature.

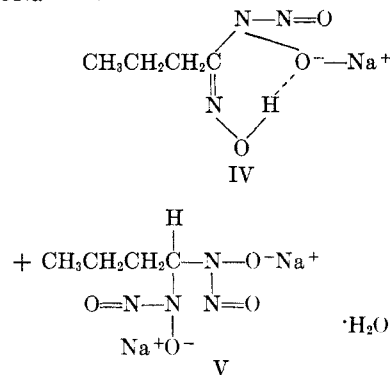
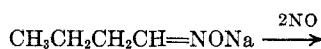
This compound is structurally analogous with *N*-nitrosophenylhydroxylamine (Cupferon), and by using similar methods metal cations may be precipitated. The lead salt was prepared. (Anal. Calcd. for  $C_6H_4O_4Pb$ : Pb, 51.3. Found: Pb, 51.1). Organic basis may be substituted for the metal cation by replacing sodium methoxide. The following examples are cited: piperazino salt (Anal. Calcd. for  $C_{10}H_{16}N_6O_4$ : C, 42.3; H, 5.6; N, 29.6. Found: C, 42.3; H, 5.65; N, 29.5), dipiperidino salt (Anal. Calcd. for  $C_{16}H_{28}N_6O_4$ : C, 52.3; H, 7.66; N, 22.4. Found: C, 52.36; H, 7.63; N, 22.91).

Similar products were obtained from *o*-benzo-

(1) Difficulty was encountered in obtaining accurate analyses because of the explosive character and the light sensitivity of some of these compounds.

quinonedioxime. (Anal. Calcd. for  $C_6H_4Ag_2N_4O_4$ : Ag, 52.9. Found: Ag, 53.3), 9,10-phenanthraquinone-dioxime (Anal. Calcd. for  $C_{14}H_8N_4Na_2O_4$ : Na, 13.5. Found: Na, 13.03), 9,10-anthraquinonedioxime (Anal. Calcd. for  $C_{14}H_8N_4Na_2O_4$ : Na, 13.5. Found: 13.46), thymolquinonedioxime (Anal. Calcd. for  $C_{10}H_{12}Ag_2N_4O_4$ : Ag, 46.1. Found: Ag, 46.0).

Reaction of nitric oxide on sodio-*n*-butyraldioxime in methanol gave *syn*-1-oximino-1-*N*-nitrosohydroxylaminobutane (IV). (Anal. Calcd. for  $C_4H_8N_3NaO_3$ : C, 28.4; H, 4.73; N, 24.9. Found: C, 28.37; H, 4.51; N, 24.4) and smaller amounts of an anti-adduct hydrate (V) (Anal. Calcd. for  $C_4H_{10}N_4O_5$ : C, 20.00; H, 4.17; N, 25.3; Na, 19.17. Found: C, 19.90; H, 4.68; N, 23.9; Na, 19.16). The infrared absorption showed a broad band at  $2340 \text{ cm}^{-1}$  for a bonded OH in IV, and in V absorption occurred at  $3500\text{--}3300 \text{ cm}^{-1}$  (free OH). The remainder of the spectrum is similar.



Using hexane as a solvent in a heterogeneous reaction between the sodium salt of the oxime and nitric oxide, IV was obtained in 88% yield. On acidic decomposition *n*-butyraldioxime was recovered, and basic hydrolysis afforded butyric acid. Analogous products were obtained from isobutyraldioxime (Anal. Calcd. for  $C_4H_8N_3NaO_3$ : C, 28.41; H, 4.73; N, 24.9. Found: C, 27.34; H, 4.62; N, 24.9), benzaldoxime (Anal. Calcd. for  $C_7H_8N_3NaO_3$ : C, 41.4; H, 2.95; N, 20.7; Na, 11.38. Found: C, 41.25; H, 3.07; N, 20.1; Na, 11.03), cinnamaldoxime (Anal. Calcd. for  $C_9H_8N_3NaO_3$ : N, 18.3; Na, 10.04. Found: N, 17.75; Na, 10.11), 2-thiophenaldoxime (Anal. Calcd. for  $C_8H_4N_3NaO_3S$ : C, 28.70; H, 1.93; N, 20.09; Na, 10.99. Found: C, 28.32; H, 2.38; N, 19.99; Na, 10.56), *p*-chlorobenzaldoxime (Anal. Calcd. for  $C_7H_4ClN_3NaO_3$ : C, 35.37; H, 2.12; N, 17.68; Na, 9.67; Cl, 14.95. Found: C, 35.16; H, 1.98; N, 16.72; Na, 9.88; Cl, 15.18).

Extension of the reaction to ketoximes resulted in

