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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 C₆H₄N₄Na₂O₄: C, 29.76; H, 1.66; N, 23.14; Na, 19.4. Found: C, 29.57; H, 1.74; N, 22.88; Na, 19.36¹; neut. equiv., 121 ± 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*-dinitrobenzene. 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 C₆H₄O₄Pb: 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 C₁₀H₁₆-N₆O₄: C, 42.3; H, 5.6; N, 29.6. Found: C, 42.3; H, 5.65; N, 29.5), dipiperidino salt (*Anal.* Calcd. for C₁₆H₂₈N₆O₄: 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-

quinonedioxime. (Anal. Calcd. for C₆H₄Ag₂N₄O₄: Ag, 52.9. Found: Ag, 53.3), 9,10-phenanthraquinonedioxime (Anal. Calcd. for C₁₄H₈N₄Na₂O₄: Na, 13.5. Found: Na, 13.03), 9,10-anthraquinonedioxime (Anal. Calcd. for C₁₄H₈N₄Na₂O₄: Na, 13.5. Found: 13.46), thymolquinonedioxime (Anal. Calcd. for C₁₀H₁₂Ag₂N₄O₄: Ag, 46.1. Found: Ag, 46.0).

Reaction of nitric oxide on sodio-*n*-butyraldoxime in methanol gave syn-1-oximino-1-N-nitrosohydroxylaminobutane (IV). (Anal. Calcd. for C₄H₈N₃-NaO₃: C, 28.4; H, 4.73; N, 24.9. Found: C, 28.37; H, 4.51; N, 24.4) and smaller amounts of an antiadduct hydrate (V) (Anal. Calcd. for C₄H₁₀N₄O₅: 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 cm.⁻¹ for a bonded OH in IV, and in V absorption occurred at 3500–3300 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-butyraldoxime was recovered, and basic hydrolysis afforded butyric acid. Analogous products were obtained from isobutyraldoxime (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 C₇H₆N₃NaO₃: C, 41.4; H, 2.95; N, 20.7; Na 11.38. Found: C, 41.35; H, 3.07; N, 20.1; Na, 11.03), cinnamaldoxime (Anal. Calcd. for C₉H₈N₃NaO₃: N, 18.3; Na, 10.04. Found: N, 17.75; Na, 10.11), 2-thiophenaldoxime (Anal. Caled. for C₅H₄N₃NaO₃S: 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. Caled. for C7H4ClN3NaO3: 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

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

the absorption of two moles of nitric oxide; however, the products obtained are unstable.

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Alkoxide-Catalyzed Rearrangements of Benzoyltriphenylsilane

Sir:

It has been reported that benzoyltriphenylsilane (I) decomposes in dilute aqueous sodium hydroxide solution at room temperature to triphenylsilanol and benzaldehyde.¹ An even more interesting reaction occurs when the ketone is treated with sodium ethoxide. The major product isolated is benzhydryloxyethoxydiphenylsilane (IV), obtained in 61% yield along with small quantities of benzhydrol and diphenyldiethoxysilane, shown to be formed by subsequent reaction of ethoxide ion with IV.

Evidently nucleophilic attack by ethoxide ion on silicon results in the displacement of a phenyl group from silicon to the carbonyl-carbon atom, the formation of a bond between silicon and the carbonyl-oxygen, and the cleavage of the silicon carbonyl—carbon bond. The result of these 1,2-rearrangements, probably proceeding *via* anion II, is the carbanion III, leading to the final product by reaction with the solvent. A similar result was obtained using sodium methoxide.

$$C_{2}H_{5}O - C_{6}H_{5} \rightarrow C_$$



The reaction may be presumed to occur in two steps, both of which have been observed before. The migration of an aryl group from silicon to an *alpha* carbon has been reported by Eaborn and Jeffrey² under similar conditions, and bond formation between silicon and an oxygen atom once removed is observed in the rearrangement of α -silylcarbinols to their isomeric ethers.³ The distinctive feature of the present reaction is the occurrence of two successive rearrangements. Further work is in progress.

Treatment of 5.0 g. (0.0137 mole) of benzoyltriphenylsilane in 50 ml. of benzene with the sodium ethoxide from approximately 0.1 g. of sodium in 25 ml. of ethanol for 6 hr. at room temperature, during which time the yellow color faded, followed by hydrolysis in dilute acid led to the isolation of a total of 3.24 g. (61%) of benzyhydroxyethoxydiphenylsilane (IV), m.p. 77–78.5° from ethanol (Anal. Calcd. for $C_{27}H_{26}O_2Si$: C, 79.0: H, 6.38. Found: C, 78.8: H, 6.38). The mother liquors on distillation at 126°/1 mm. gave partially crystalline material from which was isolated 0.20 g. (8%) of benzhydrol, m.p. 67-68°, and 0.3 g. (8%) of di. phenyldiethoxysilane, b.p. $130^{\circ}/2 \text{ mm.}$, $n_{\rm D}^{20}$ 1.5303-The infrared spectra of all compounds were consistent with the proposed structures: the latter two compounds were compared with authentic samples.

Treatment of IV in ethanol with hot dilute aqueous sodium hydroxide for 1 hr. gave 73% diphenylsilanediol, m.p. 163–166°, and 68% benzhydrol, m.p. 66–68°, both identified by infrared spectra and mixed melting point. Treatment of IV with one equivalent of sodium ethoxide over 22 hr. at room temperature gave 90% benzhydrol, m.p. 66–68°, a trace of diphenylsilanediol, and 30% of diphenyldiethoxysilane, b.p. $131^{\circ}/2$ mm., $n_{\rm D}^{20}$ 1.5281.

Similar treatment of I with sodium methoxide gave 20% of benzhydryloxymethoxydiphenylsilane, m.p. 45–47.5° from methanol. Anal. Calcd. for $C_{25}H_{24}O_2Si: C, 78.8: H, 6.06.$ Found: C, 78.8: H, 6.03. In addition benzhydrol (31%) and diphenyldimethoxysilane (15%), b.p. 108°/0.5 mm., n_D^{20} 1.550 were obtained, and were identified by comparison with authentic samples. All compounds had infrared spectra consistent with the proposed structures.

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