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The Conversion of Aldoximes to α-Oximinonitriles, α,α-Dinitronitriles, and 1,1-Dinitroparaffins[1]

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α-Oximinonitriles can be prepared conveniently by dehydrogenation of α-hydroxylaminonitriles which are accessible from aldoximes. The nitration of α-oximinonitriles with 100% nitric acid and ammonium nitrate leads to α,α-dinitronitriles. These in turn can be cleaved to 1,1-dinitroparaffins by action of ammonia.

Aldoximes react with hydrocyanic acid at room temperature to give α-hydroxylaminonitriles (I).[2] On reaction with nitrogen dioxide in chloroform or methylene chloride or with 100% nitric acid and ammonium nitrate these compounds are dehydrogenated and nitrated to α,α-dinitronitriles (II). It is established that the α-oximinonitriles (III)

$$\underset{\text{I}}{\mathrm{RCH(NHOH)C{\equiv}N}} \longrightarrow \underset{\text{II}}{\mathrm{RC(NO_2)_2C{\equiv}N}}$$

are intermediates in the reaction with nitrogen dioxide and that impurities with carbonyl absorption are introduced in this step. α-Hydroxylaminonitriles (I) can be dehydrogenated to III without undesirable by-products by heating with one molar equivalent of *p*-benzoquinone in benzene. This dehydrogenation of I is a general method of preparation for the previously difficultly accessible nitriles III.

The nitration of α-oximinonitriles (III) with nitrogen dioxide or with 100% nitric acid and ammonium nitrate yields the pure α,α-dinitronitriles II.[3] Their structures have been confirmed by infrared absorption spectra and the conversion of II to ammonium salts of 1,1-dinitroparaffins (IV)

$$\mathrm{RC(=NOH)CN}$$

III

$$\mathrm{R\overset{-}{C}(NO_2)_2\overset{+}{N}H_4}$$

IV

by cleavage with ammonia. Previous attempts to prepared α,α-dinitropropionitrile by alkylation of dinitroacetonitrile have failed.[4]

The described reactions represent a new method for the conversion of aldoximes to 1,1-dinitroparaffins. Attempts to apply the reactions to fluorine-containing aldoximes have failed.

EXPERIMENTAL[5]

α-Hydroxylaminonitriles (I). The addition of hydrocyanic acid to aldoximes was carried out according to procedures A and C of Neelakantan and Hartung.[2] It was advantageous in the latter to reverse the order of addition—*i.e.*, adding a concd. aqueous cyanide solution to a stirred and cooled mixture of aldoxime and bisulfite solution. Procedure A gave better yields in all cases and the product was isolated in satisfactory purity when the reaction mixture was filtered

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(1)(a) This work was performed under the auspices of the U. S. Atomic Energy Commission. (b) Presented at the Thirty-first meeting of the Colorado-Wyoming Academy of Science at Boulder, Colorado, May 13, 1960.

(2) L. Neelakantan and W. H. Hartung, *J. Org. Chem.*, 23, 964 (1958) and cited references.

(3) The formation of carbonyl-containing impurities from α-hydroxylaminonitriles (I) and the failure to obtain them from α-oximinonitriles (III) under the same conditions is tentatively ascribed to the formation of intermediate nitrite esters, the elimination of nitrous acid, and hydrolysis of the resultant imines, as follows:

$$\mathrm{RCH(NHONO)CN} \longrightarrow \mathrm{RC({=}NH)CN} \longrightarrow \mathrm{RCOCN}.$$

(4) C-alkylation of dinitroacetonitrile and its salts has been successful only with allyl and *tert*-butyl compounds (C. O. Parker, W. D. Emmons, A. S. Pagano, H. A. Rolewicz, and K. S. McCallum, abstracts of the 136th Meeting of the American Chemical Society, Atlantic City, N. J., September 1959, p. 44P).

(5) All temperatures are corrected. Microanalyses by M. J. Naranjo.

after 24 hr. at 20–25°.[6] The reaction failed with trifluoroacetaldoxime, even under pressure and elevated temperature and in the presence of catalysts such as cuprous cyanide and pyridine.

INFRARED ABSORPTION BANDS IN POTASSIUM BROMIDE

α-Hydroxylamino-nitriles	λ(OH, NH)	λ(NH)	λ(CN)	λ(NO) μ
Propio	3.04s 3.11s	6.17[a]	4.47m	9.92m
Butyro	3.09s 3.19s	—	4.47m	9.91m
Valero	3.10s 3.20s	—	4.47m	9.88m

[a] Absorption in the N—H deformation region was very weak and could be observed only after dilution of the sample and regrinding.

α-Oximinonitriles (III). α-Hydroxylaminonitriles (0.1 mole) suspended in benzene (500 ml.) were treated with *p*-benzoquinone (0.1 mole) in small portions with shaking. After completed addition, each reaction mixture was refluxed from a steam bath. Quinhydrone crystals deposited rapidly and were gradually replaced with hydroquinone during 3–5 hr. The mixture was cooled, filtered, and evaporated under reduced pressure. The residue was taken up in carbon tetrachloride or carbon tetrachloride–benzene mixtures, depending on solubilities, and filtered again, giving 99–100% yields of hydroquinone. The combined filtrates were evaporated under reduced pressure and distilled from molecular stills.[7] The pure α-oximinonitriles were obtained as colorless oils in yields of 41–64%.

α-Oximinopropionitrile boiled at 35° (0.9 mm.), n_D^{25} 1.4542.

Anal. Calcd. for $C_3H_4N_2O$: C, 42.86; H, 4.79; N, 33.33. Found: C, 42.44, 42.71; H, 4.93, 4.73; N, 33.20.

α-Oximinobutyronitrile[8] boiled at 42° (1 mm.), n_D^{25} 1.4528.

Anal. Calcd. for $C_4H_6N_2O$: C, 48.97; H, 6.16; N, 28.57. Found: C, 49.01, 48.55; H, 6.18, 5.85; N, 28.65, 28.74.

α-Oximinovaleronitrile boiled at 32° (0.03 mm.), n_D^{25} 1.4531.

Anal. Calcd. for $C_5H_8N_2O$: C, 53.51; H, 7.19; N, 24.99. Found: C, 53.59, 53.37; H, 7.40, 7.59; N, 25.07, 24.74.

INFRARED ABSORPTION BANDS—LIQUID FILMS

α-Oximino-nitrile	$\lambda_{(OH)}$	$\lambda_{(C\equiv N)}$	$\lambda_{(C=N)}$	$\lambda_{(N-O)}$, μ
Propio	3.03s	4.47m	6.16m	9.65s
Butyro	3.03s	4.47m	6.16m	9.95s
Valero	3.03s	4.47m	6.19m	10.02s

α,α-Dinitronitriles (II). (a) α-Hydroxylaminonitrile was added slowly with stirring to an equimolar mixture of 100% nitric acid and ammonium nitrate at 20°. The mixture was stirred for 1 hr. at 20° and poured on ice, extracted with methylene chloride, dried, and distilled.

(b) A 2% solution of α-hydroxylaminonitrile in methylene chloride was treated with a slow stream of nitrogen dioxide at 25° until the green solution turned yellow. Evaporation of this solution under reduced pressure gave a good yield of oil with the infrared spectrum of the α-oximinonitrile but containing also a carbonyl band at 5.80 μ. Continued reaction of this oil with nitrogen dioxide in methylene chloride gave oils with the characteristic spectra for the α,α-dinitro compound.

The α,α-dinitro nitriles obtained in these ways were colorless oils with characteristic absorption bands at 4.44 μ (C≡N), 6.26 μ (*asym*-NO_2) and 7.71 μ (*sym*-NO_2). They could be distilled from molecular stills but retained impurities with carbonyl absorption at 5.80 μ, which could not be separated by chromatographic adsorption on silica gel. The crude nitriles were therefore cleaved with ammonia and identified as ammonium salts of the 1,1-dinitroparaffins.

(c) α-Oximinonitrile was added with stirring at 10–20° to a ten-fold excess of an equimolar mixture of 100% nitric acid and ammonium nitrate. A transient blue color was noted immediately after each addition and is believed to be due to the intermediates $RC(NO)(NO_2)C\equiv N$. At 20° the blue color faded within a few seconds, while at 10° it was stable for several minutes. After completed addition, during which nitrogen dioxide was evolved, the mixtures were stirred at 20° for 1 hr., poured on ice, extracted with methylene chloride, dried, and distilled. The residue oils were distilled twice from molecular stills.[7]

α,α-Dinitropropionitrile, b.p. 45° (7 mm.), n_D^{25} 1.4390 was obtained in 8% yield. On cooling to 0° it solidified to a low-melting solid.

Anal. Calcd. for $C_3H_3N_3O_4$: C, 24.84; H, 2.08; N, 28.96. Found: C, 25.09, 25.17; H, 2.18, 2.38; N, 28.90.

α,α-Dinitrobutyronitrile boiled at 40° (2 mm.), n_D^{25} 1.4372, yield 12%, $\lambda_{max}^{CH_3OH}$ 277 mμ (log ε 2.01).

Anal. Calcd. for $C_4H_5N_3O_4$: C, 30.19; H, 3.17; N, 26.41. Found: C, 30.13, 30.44; H, 3.27, 3.30; N, 26.61, 26.30.

α,α-Dinitrovaleronitrile, b.p. 45° (2 mm.), had n_D^{25} 1.4377, yield 22%.

Anal. Calcd. for $C_5H_7N_3O_4$: C, 34.70; H, 4.07; N, 24.28. Found: C, 34.40, 35.10; H, 4.06, 4.23; N, 24.21.

INFRARED ABSORPTION BANDS—LIQUID FILMS

α,α-Dinitro-nitrile	$\lambda_{(C\equiv N)}$	$\lambda_{(as-NO_2)}$	$\lambda_{(sym-NO_2)}$, μ
Propio	4.43m	6.25s	7.67m
Butyro	4.44m	6.26s	7.70m
Valero	4.44m	6.26s	7.70m

1,1-Dinitroparaffin ammonium salts. A 1–2% solution of α,α-dinitronitrile in dichloromethane or chloroform was cooled to 0° and saturated with anhydrous ammonia. The mixture was allowed to stand for 1 hr. and evaporated under reduced pressure. Crystallization of the crude residue from methanol containing anhydrous ammonia gave pure yellow ammonium salts in yields of around 10%. The mother liquors contained much unchanged starting material and the optimum conditions for the cleavage reaction were not determined.

INFRARED ABSORPTION BANDS OF AMMONIUM SALTS[a,b]

1,1-Dinitro-paraffin	λ, μ	λ, μ	λ, μ
Ethane	6.75m	8.11s	8.90s
Propane	6.77m	8.25s	8.95s
Butane	6.81m	8.32s	8.88s
Pentane	6.78m	8.38s	8.99s

[a] 0.1–0.5% in potassium bromide.

[b] Three bands in the region recorded have been observed also in hydrazinium and potassium salts of 1,1-dinitroparaffins in this Laboratory and are attributed to absorption of the anion.

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(6) Longer reaction times caused the product to be more difficult to purify by crystallization from ether-petroleum ether (b.p. 30–60°).

(7) H. E. Ungnade, *Anal. Chem.*, **31**, 1126 (1959).

(8) T. K. Walker [*J. Chem. Soc.*, **125**, 1625 (1925)] prepared a compound believed to be α-oximinobutyronitrile by nitrosation of ethyl α-cyanobutyrate with ethyl nitrite and potassium ethoxide in ether.

(a) *1,1-Dinitroethane ammonium salt,* m.p. 116° dec., lit., m.p. 90–93° dec.,[9] 127–128°.[10]

Anal. Calcd. for $C_2H_7N_3O_4$: C, 17.53; H, 5.14. Found: C, 17.53; H, 5.07.

(b) *1,1-Dinitropropane ammonium salt,* m.p. 117° dec.

Anal. Calcd. for $C_3H_9N_3O_4$: C, 23.84; H, 6.00; N, 27.81. Found: C, 23.38, 23.97; H, 5.25, 5.53; N, 27.68, 27.18.

(c) *1,1-Dinitrobutane ammonium salt,* m.p. 128° dec.

Anal. Calcd. for $C_4H_{11}N_3O_4$: C, 29.09; H, 6.71; N, 25.45. Found: C, 29.30, 29.47; H, 7.03, 6.71; N, 25.67.

(d) *1,1-Dinitropentane ammonium salt,*[11] m.p. 131–132° dec.

Anal. Calcd. for $C_5H_{13}N_3O_4$: C, 33.52; H, 7.31; N, 23.46. Found: C, 33.30; H, 7.51; N, 23.66.

Infrared absorption spectra were determined with a Perkin-Elmer Model 21 spectrophotometer.

LOS ALAMOS, N. M.

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[9] T. S. Belew, C. E. Grabiel, and L. B. Clapp, *J. Am. Chem. Soc.*, **77**, 1110 (1955).

[10] M. F. Hawthorne, *J. Am. Chem. Soc.*, **78**, 4980 (1956).

[11] This salt was prepared from the dinitroparaffin and ammonia in chloroform.

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The Beckmann Rearrangement of Fenchone Oxime

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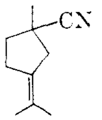
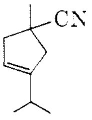
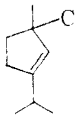
The Beckmann rearrangement of fenchone oxime has been carried out under a variety of conditions to give apparently exclusive formation of products arising from scission of the bridgehead bond. It would appear that both the normal and anomalous products are derived from the concerted *anti*-migration process generally accepted as the initial step in the Beckmann rearrangement, and that the stability of the incipient carbonium ion adjacent to the oximino function is of importance only in determining the relative amounts of the two products.

The literature of the Beckmann rearrangement contains numerous examples of a competitive reaction in which an unsaturated nitrile rather than the usual amide is produced by treatment of a ketoxime with a strong acid.[1–3] Notable among compounds undergoing this anomalous reaction are the oximes of bicyclic ketones having bridgeheads adjacent to the oximino functions. The oximes of camphor,[4] verbanone,[5] and various norcamphane derivatives[6,7] give, under conditions commonly employed for the Beckmann rearrangement, mixed products to which the competitive reaction contributed appreciably. The rearrangement of fenchone oxime (I) is of particular interest in this connection, for despite the ditertiary structure of the oxime, both the normal and anomalous rearrangements proceeded exclusively *via* scission of the bridgehead bond.

Treatment of the sharp melting oxime with *p*-toluenesulfonyl chloride and pyridine, phosphorus pentachloride, or sulfuric acid lead in all cases to the formation of a single lactam which was isomeric with the oxime and a liquid which from its infrared spectrum was obviously an unsaturated nitrile (—C≡N stretching 4.50 μ, C=C stretching 6.03 μ, vinyl C—H stretching 3.32 μ).[8] The inference from infrared data of the presence of a single vinyl hydrogen in this nitrile was confirmed by the ratio of vinyl to total hydrogen as determined by proton magnetic resonance, thus eliminating the possibility that the product might be the isopropylidenecyclopentanonitrile, VI, or any of the three isomeric structures possessing two vinyl hydrogens.


VI


VII


VIIa

From further consideration of the proton resonance data which are summarized in Table I, it appears that the unsaturated nitrile must have the

TABLE I

PROTON RESONANCE DATA

Group	Cps. from H_2O at 56.4 Mc.	Chemical Shift Observed	Chemical Shift Accepted[9]
$-\overset{\vert}{\underset{\underset{CH_3}{\vert}}{C}}-CH_3$	214	3.8	4.1 ± 0.6
$=\overset{\vert}{\underset{\vert}{C}}-CH_3$	183	3.2	3.3 ± 0.5
$=\overset{\vert}{C}-CH_2-$	148	—	—
$-\overset{\vert}{\underset{\vert}{C}}-H$	127	—	—
$=\overset{\vert}{\underset{\vert}{C}}-H$	−23	−0.4	−0.6 ± 0.7

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[1] A. H. Blatt, *Chem. Revs.*, **12**, 215 (1933).

[2] B. Jones, *Chem. Revs.*, **35**, 335 (1944).

[3] L. G. Donaruma and W. Z. Heldt, *Org. Reactions*, (in press).

[4] J. Bredt and W. Holz, *J. prakt. Chem.*, **95**, 133 (1917).

[5] H. Wienhaus and P. Schumm, *Ann.*, **439**, 38 (1924).

[6] M. Gates and S. P. Malchick, *J. Am. Chem. Soc.*, **79**, 5546 (1957).

[7] H. K. Hall, Jr., *J. Am. Chem. Soc.*, **82**, 1209 (1960).

[8] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Methuen and Co., Ltd., London, 1956.

[9] J. D. Roberts, *Nuclear Magnetic Resonance*, McGraw-Hill, New York, 1959, p. 23.