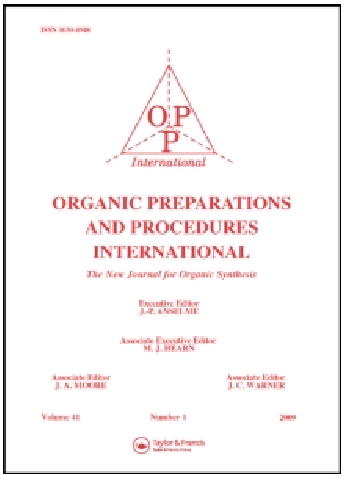

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O-CYANOMETHYLOXIME OF NITROGLYOXYLONITRILE

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its ir and nmr spectra were identical with those of authentic material.

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O-CYANOMETHYLOXIME OF NITROGLYOXYLONITRILE

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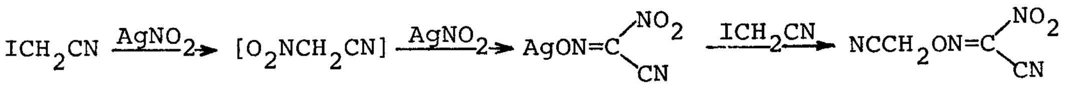
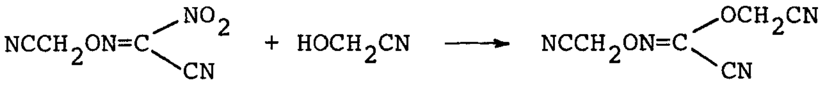
The formation of the O-cyanomethyl ether 3 (a nitrolate ester) of nitroglyoxylonitrile oxime from iodoacetonitrile and silver nitrite (Eq. 1) offers a new preparation of a nitrolate ester independent of an α-nitronitronate ester or anhydride.[1-3]



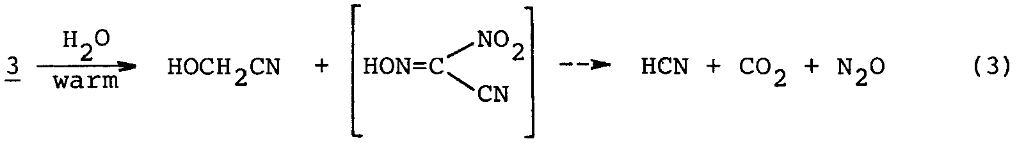
1 2 3 (1)

Nitrosation of unisolated nitroacetonitrile 1[4] followed by alkylation of the nitrolate 2[5] by iodoacetonitrile accounted for the formation of the ether 3. Competitive alkylation at the oxime nitrogen atom is apparently retarded by an electron withdrawal into the cyano and nitro groups.[6] The liquid nitrolate ester 3 (44%) was the only product isolated; its structure assignment was supported by spectroscopy, elemental analysis and chemical reaction (Eq. 2).



3 4 (2)

Warm water transformed 3 into the O-cyanomethyl ether 4 (48%) of cyanomethyl cyanoformate oxime, mp. 73-74°[1] (Eq. 2). Its formation can be accounted for by the replacement of the nitro group by glycolonitrile, a hydrolytic intermediate (Eq. 3). The nitrolic acid 5 was undetected and was presumably converted into hydrogen cyanide, carbon dioxide and nitrous oxide (Eq. 3).[7] The structure assignment for compound 4 was



5 (3)

supported by spectroscopy and elemental analysis

EXPERIMENTAL

Instruments included Perkin Elmer 237B and 521 grating ir, Varian T-60 and Bruker WP-30 nmr and Varian MS-30 spectrometers. Elemental analyses were obtained from Micro-Tech Laboratories, Skokie, Illinois.

O-Cyanomethyl Ether of Nitroglyoxylonitrile Oxime (3).- Iodoacetonitrile (20.04 g, 0.12 mole) was dissolved in 200 ml of dry ether in a 500 ml three-necked round-bottom flask equipped with a mechanical stirrer and reflux condenser. Silver nitrite (22.95 g, 0.15 mole) was added in one portion. After the mixture was heated at reflux temperature with vigorous stirring for 20 hrs, it was cooled and filtered. The ethereal solution was dried ($MgSO_4$) and concentrated to give oxime 3 as a yellow viscous oil (8.1 g, 44%). The oxime was eluted from a column (4 x 90 cm) of silica gel (100 g) by chloroform to give 6.8 g (37%).

Anal. Calcd for $C_4H_2N_4O_3$: C, 31.18; H, 1.31; N, 36.36.
Found: C, 31.22; H, 1.28; N, 36.08.

IR(CH_2Cl_2): 3005(w, CH_2), 2220(w, CN), 1605(s, C=N), 1570(s, NO_2) and 1340 cm^{-1} (m, NO_2); pmr($CDCl_3$): δ 5.2 (s, not exchangeable with D_2O); ^{13}C nmr($CDCl_3$): δ 125.49(-N=C), 113.01 ($N\underline{C}$-CH_2), 103.24(=C-$\underline{C}$N) and 63.89 ppm (OCH_2), split into a triplet in the coupled spectrum; MS: m/e(70 ev)(%) 154(100)$^{M+}$, 153(40), 152(50), 138(90), 137(50), 127(80), 126(75) and 109 (75).

O-Cyanomethyl Ether of the Oxime of Cyanomethyl Cyanoformate (4).- A mixture of the oxime ether 3 (2 g, 12 mmoles) and water (10 ml) was refluxed (25 hrs), cooled and filtered to give the ether 4 as a light yellow solid, 0.51 g (48%), mp. 73-74°[1] after recrystallization from a mixture of ethyl acetate and hexane.

IR(CH_2Cl_2): 2250(w, CN) and 1615 cm^{-1} (m, C=N); pmr[$(CD_3)_2$-

CO]: δ 5.13 (s, CH_2) and 5.26 (s, CH_2), neither exchangeable with D_2O); ^{13}C nmr [$CDCl_3$ and $(CD_3)_2SO$]: δ 138.28 (N=C), 115.10 (CN), 113.35 (CN), 105.53 (=C-$\underline{C}$N), 60.93 (OCH_2) and 54.42 (OCH_2); MS: m/e (70ev)(%) 164(15) M^+, 138(10), 134(20), 109(5), 107(10), 104(20), 94(90), 84(20), 80(80) and 79(100).

Anal. Calcd for $C_6H_4N_4O_2$: C, 43.91; H, 2.46, N, 34.14.
Found: C, 43.96; H, 2.38; N, 34.04.

Acknowledgement.- Financial support was received from the Office of Naval Research.

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1. R. Scholl [Ber., 29, 2415 (1896)] reported the reaction between iodoacetonitrile and silver nitrite but incorrectly identified compound 3, bp. 160-162° (12 mm), as dicyanomethazonic acid ($O_2NCH(CN)C(CN)=NOH$). He also obtained compound 4, $C_6H_4N_4O_2$, but did not assign a structure. With very minor modifications his directions have been repeated.
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4. Nitroglyoxylonitrile oxime (a nitrolic acid) 5 was obtained from nitroacetonitrile and sodium nitrite [W. Stein-

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A SIMPLE, INEXPENSIVE SYSTEM FOR PERFORMING HIGH PRESSURE REACTIONS

Submitted by
(2/26/82)

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A pressure system capable of maintaining reaction volumes at pressures of 1-8 Kbar was required because previously reported systems[1] have a variety of flaws:

1. They required elaborate pumping apparatus for attaining the required pressure and are therefore, expensive.
2. Large reaction volumes could not be employed.
3. The system utilized a gas-pressurized reaction vessel, thus introducing safety considerations.

We now report a high pressure system which is mechanically simple, inexpensive to build, safe, and which can be used with