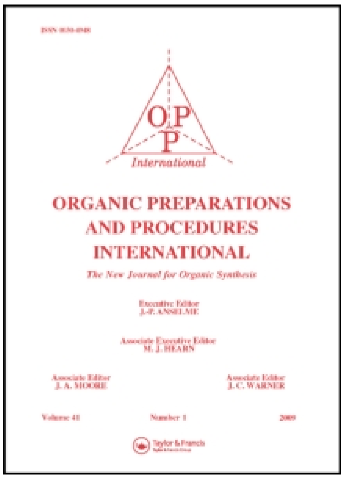

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1,2-DINITROCYCLOHEXENE

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yellow fluffy crystals, mp. 71-72°, lit.[3] 71-72.5°.

Nitromesidine (2) showed the following spectral properties: ^{1}H (CDCl$_3$): δ 2.03 (3 H, s, ring CH$_3$); 2.13 (6 H, s, ring CH$_3$), 3.63 (2 H, s, NH$_2$); 6.73 (1 H, s, ring H); ^{13}C NMR(CDCl$_3$): δ 12.30, 16.52, 17.55 (ring methyls); 112.85, 117.83, 123.84, 130.07, 141.62 (aromatic ring carbons). Mass spectrum (70 ev): m/e 180 (M$^+$, 100%), 163 (55%), 148 (4%), 135 (40%), 118 (48%), 108 (47%), 91 (52%), 77 (25%), 65 (23%); IR (KBr): 3360, 3430 (m N-H str); 1640 (b, N-H bend); 1310 (w, C-N); 1520, 1370 (sh, C-NO$_2$) cm^{-1}.

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1,2-DINITROCYCLOHEXENE

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Previously, only five examples of isolated 1,2-dinitroalkenes had been reported: 1,2-dinitroethene (1a),[1] 2,3-dinitro-2-butene (1b),[2] 3,4-

dinitro-3-hexene,[2] dinitrostilbene (1c),[3] and tetranitroethene.[4,5] Mild to extensive thermal decomposition (25°) has been noted for these 1,2-dinitroalkenes. We now describe the conversion of the oxime of α-nitrocyclohexanone (2)[6] to 1,2-dinitrocyclohexene (5), isolated as an unstable yellow oil which, to our knowledge, is the first example of a 1,2-dinitrocycloalkene.

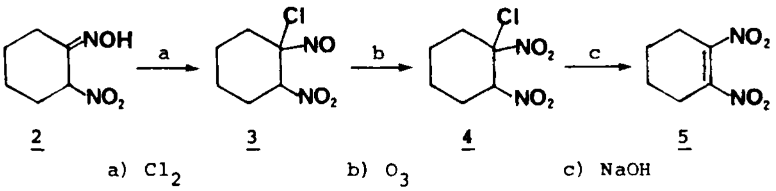
$O_2NC(R) = C(R)NO_2$

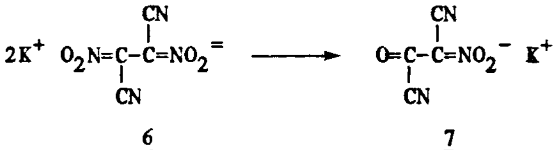
1

a) R = H

b) R = CH_3

c) R = Ph





$$2K^+\ O_2N{=}\underset{CN}{\overset{CN}{C}}{-}C{=}NO_2^{=} \longrightarrow O{=}\underset{CN}{C}{-}\overset{CN}{C}{=}NO_2^-\ K^+$$

6 7

Recently bromine oxidation converted a dimetal salt of each of three 1,2-dinitroalkanes to the corresponding dinitroalkenes 1a-c. A similar preparation of 1,2-dinitrocyclohexene (5) was cited.[7,8] Since experimental details have not been reported for this dehydrogenation of 1,2-dinitrocyclohexane, the olefin (5) was assumed to be unknown (it has not been listed in Chemical Abstracts). Halogen oxidation of a 1,2-dinitronate anion has limited value as an olefin synthesis insofar as halogen addition to an olefinic linkage[1,9] and halogen replacement of a nitro group can also occur.[10] In a recent report, bromine converted the dipotassium salt of α,α'-dinitrosuccinonitrile (6) to the potassium salt of nitroketosuccinonitrile (7).[11] We rejected an investigation of a halogen oxidation of the dinitronate anion of 1,2-dinitrocyclohexane to the olefin (5) to avoid these complications. Moreover a mild alkaline conversion of 1,2-

dinitrocyclohexane at 25° for 6 hrs gave 1-nitrocyclohexene (82%)[12] and apparently did not proceed through the dinitronate anion.

Although chlorine is recommended for the conversion of oxime 2 to the gem-chloronitroso compound 3, tetrabutylammonium hypochlorite[13] also effected the change as evidenced by the development of the deep blue color characteristic of the nitroso compound (3). The latter method was abandoned when an excess of the hypochlorite reagent failed to bring about oxidation to the nitro compound (4). Oxidation of a nitroso compound to the nitro compound (3 → 4) was effected with ozone because the use of m-chloroperbenzoic acid (MCPBA) resulted in considerable difficulty in isolation of the product. Elimination of the elements of hydrogen chloride to give the olefin (5) was brought about in a phase transfer operation with tetrabutylammonium bromide, aqueous sodium hydroxide, and benzene; the competitive alkaline elimination of nitrous acid to give 1-chloro-2-nitrocyclohexene (or isomeric olefins) was not detected.

Bromine at 25° added slowly to the olefin (5) to give 1,2-dibromo-1,2-dinitrocyclohexane (stereochemistry unknown). The failure to obtain an adduct between (5) and either cyclopentadiene or anthracene was unexpected insofar as both di-[2] and tetranitroethene[4,5] were highly reactive in additions with these dienes.

EXPERIMENTAL SECTION

Instruments included Perkin Elmer 237B and 521 grating IR, Varian A-60, Bruker WP-80 and A.E.I. MS 30 double beam mass spectrometers. Elemental analyses were provided by Micro-Tech Laboratories, Skokie, Illinois.

1-Chloro-1,2-dinitrocyclohexane (4).- A general procedure for the conversion of an oxime to a gem-chloronitroalkane was followed.[14] Through 1.4 g (8.9 mmol) of oxime 2 in 50 ml of methylene chloride cooled to ice-bath temperature, chlorine gas was bubbled in slowly for 5 min. (or until the green chlorine color persisted). Oxygen was then passed into the solution to remove the excess chlorine (the blue color of the nitroso compound was restored) and was followed by a stream of ozone for about 75 min. or until the blue color of the nitroso compound had dissipated. Oxygen was passed through the solution for 10 min. to remove the excess ozone. Removal of the solvent left a light blue oil. Separation by column chromatography [1:9 ethyl acetate/hexanes (250 ml) on silica gel 60 (3 x 18 cm column)] gave a fraction with an R_f = 0.49 from which a clear oil was obtained after solvent removal. Kugelrohr distillation (1 mm, 140-150°) of the oil yielded 0.77 g (42%) of a diastereoisomeric mixture of 1-chloro-1,2-dinitrocyclohexane as oily colorless crystals, mp. 52-70°.

^{1}H NMR ($CDCl_3$): δ 5.4 (t, 1H), 1.4-2.05 (m, 4H), 2.35 (m, 4H); IR (KBr): 3028, 2960, 2878, 1568, 1440, 1450, 1372, 1353, 1334 cm^{-1}.

Anal. Calcd for $C_6H_9ClN_2O_4$: C, 34.53; H, 4.32; N, 13.43; Cl, 17.03

Found: C, 34.57; H, 4.49; N, 13.26; Cl, 16.67

1,2-Dinitrocyclohexene (5).- To 0.4 g (1.92 mmol) of 1-chloro-1,2-dinitrocyclohexane (4) in 6 ml of benzene and containing 0.68 g (2.1 mmol) of tetra-*n*-butylammonium bromide was added 3.84 ml of 0.5 *N* sodium hydroxide diluted to 5 ml; the mixture was stirred for 1.25 hr at room temperature until the aqueous solution was neutral to moist pH paper. The organic phase was separated, washed with 10 ml of water and dried over anhydrous magnesium sulfate. Removal of the solvent left an orange oil. A 5 ml portion of ether was added and the residual tetra-*n*-butylammonium bromide was removed by filtration. The solvent was removed *in vacuo* to give 0.19 g (58%) of the olefin (5) as a light orange oil.

^{1}H NMR ($CDCl_3$): δ 2.5-2.95 (m, 4H), 1.65-2.05 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 145.09 ($C-NO_2$), 26.28, 20.75 ($-CH_2-$); IR (KBr): 2958, 2879, 1534, 1437, 1456, 1350, 1339, 1370, cm^{-1}.

Further attempts at purification by distillation were unsuccessful; flash chromatographic separation from silica gel with mixtures of ethyl acetate and hexane (1:9) gave a light yellow oil.

Anal. Calcd for $C_6H_8N_2O_4$: C, 41.86; H, 4.65; N, 16.27

Found: C, 42.32; H, 4.66; N, 15.73

1,2-Dibromo-1,2-dinitrocyclohexane.- To 0.19 g (1.1 mmol) of freshly prepared 1,2-dinitrocyclohexene (5) in 6 ml of chloroform, was added dropwise a solution of 0.36 g (2.1 mmol) of bromine in 5 ml of chloroform. The solution was allowed to stand at room temperature for 14 days. The solvent and excess bromine were removed and a yellow solid mixture was taken up in 10 ml of methylene chloride. The solution was extracted with 10 ml of water and dried over magnesium sulfate. Solvent removal left a yellow gum. Recrystallization from hexane yielded 0.21 g (58%) of the dibromide as colorless needles, mp. 199-200° (dec., softening at 150° and shrinking at 190°). This material was sublimed twice at 95-100° at 0.5 mm to yield a white powder, mp. 208-210° (dec., softening and slight yellowing at 195°).

^1H NMR ($CDCl_3$): δ 3.0-2.5 (broad m, 4H), 2.1-1.55 (broad m, 4H); ^{13}C NMR ($CDCl_3$): δ 95.63, 92.50, 39.35, 38.96, 22.18; IR (KBr): 2960, 2890, 1567, 1442, 1452, 1350, 1323 cm^{-1}.

Anal. Calcd for $C_6H_8Br_2N_2O_4$: C, 21.70; H, 2.41; N, 8.44

Found: C, 22.00; H, 2.47; N, 8.18

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