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A cyclic *cis*-nitroso dimer, 3,4-dibromo-3,5,5-trimethylpyrazoline 1,2-dioxide was oxidized directly to an open chain 1,3-dinitro compound by a peroxyacid but nitrosyl chloride displaced bromine, added, and oxidized the same compound to 3-chloro-4-nitro-3,5,5-trimethylpyrazoline 1,2-dioxide.

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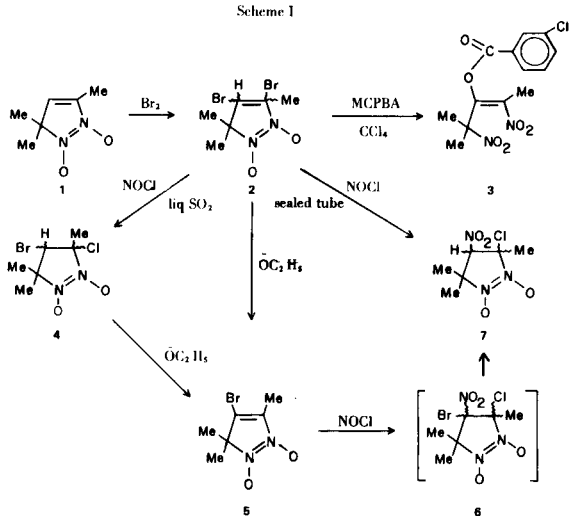
C-Nitroso compounds are commonly pictured as equilibrium mixtures of monomeric (blue) and dimeric (white) forms. Reactions of nitroso compounds are invariably shown as occurring on the monomer. This has never seemed to us a necessary assumption. However, since the equilibrium is generally mobile, it is not an easy assumption to test. In at least one case, **1** (Scheme I), the nitroso compound has been shown by Freeman (1) to be the stable dimeric cyclic *cis* form. We were able to oxidize the dibromo adduct **2** directly to a dinitro product **3** by means of *m*-chloroperbenzoic acid (MCPBA). The transformation of compound **2** into **3** may take the pathway shown in Scheme II. Freeman (1) has oxidized 3,5,5-trimethylpyrazoline without disruption of the five-membered ring by means of perbenzoic acid.

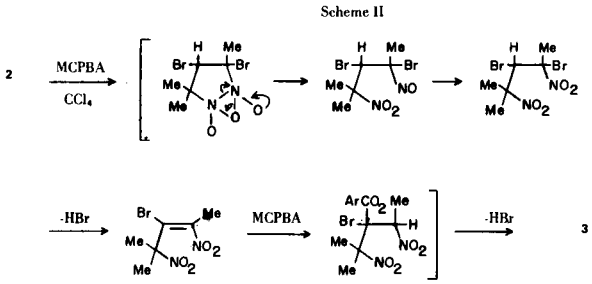
In connection with other work (2) we had first tried the reaction with nitrosyl chloride. In a sealed tube nitrosyl chloride does not oxidize the nitroso groups but instead gives an anomalous product **7**. The structure of **7** was deduced by arriving at the same end product via the pathway **4,5,6,7**.

In liquid sulfur dioxide, nitrosyl chloride replaces the tertiary bromine (3) of **2** to give **4**. Base dehydrohalogenates **2** or **4** to give **5**. Nitrosyl chloride then adds and oxidizes **5** to **6** and finally **6** is hydrolyzed (reduced) in the work-up to **7**. The placement of chlorine at C-3 and the nitro group at C-4 in **7** (and hence **6**) was a

Scheme I



Scheme II



necessity to account for the solubility of **7** in 5% sodium hydroxide. Also the nmr spectra of **4** and **7** do not differ significantly with respect to the methyl protons at C-3. There is early precedent in the case of α-bromonitrocamphor (4) for the hydrolysis of a geminal bromonitro compound to result in a reduction to a nitro compound.

Compound **2** was prepared by a published procedure (5) and the nmr spectrum was reported as that of a single isomer (1). However, we observed an nmr spectrum for **2** which can only be interpreted as due to a mixture of *cis* and *trans* isomers (see Experimental). In carbon tetrachloride as solvent, nitrosyl chloride reacts with only one isomer, but in liquid sulfur dioxide and other polar solvents, the tertiary bromine at C-3 is replaced in both isomers. The stereochemistry at C-3 and C-4 in **2, 4, 6,** and **7** are therefore not specified. The stereochemistry of nitrosyl chloride additions seemed to be well established as a *trans* addition in olefins (6,7) until Meinwald (8) found that in strained double bonds, *cis* additions occurred. Ponder (9) in contrast to Ohno (10) also found that cyclohexene added nitrosyl chloride in a *trans* manner in both polar (liquid sulfur dioxide) and non-polar (carbon tetrachloride) solvents at both -30° and 20°. We did not establish whether compound **5** adds nitrosyl chloride in a *cis* or *trans* manner.

EXPERIMENTAL

Infrared spectra were taken on a Perkin-Elmer Model 257; nmr spectra were taken on a Varian A-60A using TMS as internal standard.

3,4-Dibromo-3,5,5-trimethylpyrazoline 1,2-Dioxide (**2**).

Fusco and D'Alo (5) reported the synthesis of 3,4-dibromo-3,5,5-trimethylpyrazoline 1,2-dioxide by the addition of bromine to **1**. Freeman (1) reported a simple nmr spectrum for the cor-

responding dichloro compound: δ 1.45, 1.58 (s, 6), 2.00 (s, 3), 4.67 (s, 1), and said that the dibromo compound had a similar spectrum. We report a more complicated spectrum and suggest that diastereomers are formed; ^{1}H nmr (deuteriochloroform): δ 5.29, 4.41, 2.40, 2.32, 1.81, 1.77, 1.71, 1.65. Peaks at 5.29, 2.40, 1.81 and 1.71 (intensities nearly twice as great as the accompanying diastereomer) are due to one diastereomer and peaks at 4.41, 2.32, 1.77, and 1.65 may be interpreted as due to the other. In carbon tetrachloride, nitrosyl chloride gave a product with peaks at 5.00, 4.38, 2.28, 2.26, 1.78, 1.76, 1.69, and 1.65, suggesting that only the first isomer had undergone substitution at C-3.

2,4-Dinitro-3-*m*-chlorobenzoyloxy-4-methyl-2-pentene (**3**).

Compound **2** (0.50 g.), 1.7 mmoles) and 0.25 g. (1.7 mmoles) of 85% *m*-chloroperoxybenzoic acid were dissolved in 5 ml. of chloroform. The solution was diluted to 50 ml. with carbon tetrachloride and refluxed for 5 hours, cooled, and washed three times with 10% sodium hydroxide solution. The organic layer was then dried over magnesium sulfate. The solvent was evaporated to give a solid in a yellow oil. The impure product was placed on a silica gel column and eluted with a 1:1 mixture of carbon tetrachloride and chloroform. The eluted fraction contained 270 mg. (48%) of white, 2,4-dinitro-3-*m*-chlorobenzoyloxy-4-methyl-2-pentene. The analytical sample was recrystallized twice from carbon tetrachloride, m.p. 126-128°; ir (potassium bromide): cm^{-1} (C-H, 3100 d, 3000 s), (C=O, 1730 s), (NO_2, 1540 s, 1310 s); ^{1}H nmr (deuteriochloroform): δ 7.25-8.00 (m, 4), 1.96 (s, 3), 1.59 (s, 3), 1.50 (s, 3).

Anal. Calcd. for $C_{13}H_{13}ClN_2O_6$: C, 47.50; H, 3.99; N, 8.52. Found: C, 47.33; H, 4.00: N, 8.47.

3-Chloro-4-bromo-3,5,5-trimethylpyrazoline 1,2-Dioxide (**4**).

When 400 mg. (11 mmoles) of compound **2** was treated with nitrosyl chloride in liquid sulfur dioxide, a quantitative yield, 350 mg., of 3-chloro-4-bromo-3,5,5-trimethylpyrazoline 1,2-dioxide was obtained. However, the nmr spectrum suggested that compound **4** is a mixture of stereoisomers; nmr (deuteriochloroform): δ 5.00, 4.50, 2.25, 2.16, 1.78, 1.69, 1.65. We were unable to separate the isomers in the mixture but recrystallization from ethanol gave an analytical sample, m.p. 135-140°.

Anal. Calcd. for $C_{12}H_{10}BrClN_2O_6$: C, 27.99; H, 3.91; H, 10.88. Found: C, 28.09; H, 4.11: N, 10.90.

4-Bromo-3,5,5-trimethylpyrazole 1,2-Dioxide (**5**).

3,4-Dibromo-3,5,5-trimethylpyrazoline 1,2-dioxide (**2**) (400 mg., 11 mmoles) dissolved in 25 ml. of absolute methanol, was treated with a catalytic amount of sodium ethoxide and warmed to 45° for 4 hours. After cooling, water (25 ml.) was added and upon standing 10 hours in the refrigerator, white needle-like crystals precipitated. The isolated precipitate was dried *in vacuo* to give 230 mg. (73%) of 4-bromo-3,5,5-trimethylpyrazole 1,2-dioxide, m.p. 149-150° (lit. (5) m.p. 135°). Because of the discrepancy in melting point the compound was analyzed. The same compound was obtained in 75% yield from compound **4** by similar treatment; (potassium bromide): cm^{-1} (C-H, 3010 s), (C=C, 1660 s), (O-N=N-O, 1483 s); ^{1}H nmr (deuteriochloroform): δ 2.25 (s, 3), 1.55 (s, 6).

Anal. Calcd. for $C_6H_9BrN_2O_2$: C, 32.60; H, 4.10: N, 12.67. Found: C, 32.60; H, 4.05; N, 12.89.

3-Chloro-4-nitro-3,5,5-trimethylpyrazoline 1,2-dioxide (**7**).

Compound **5** (500 mg., 2.26 mmoles) was sealed in a glass tube with an excess of nitrosyl chloride for 24 hours at room temperature. After opening the tube and allowing nitrosyl chloride to distill, the remaining solid was extracted with 95% ethanol. Dropwise addition of water to this solution in the cold gave 355 mg. (71%) of 3-chloro-4-nitro-3,5,5-trimethylpyrazoline 1,2-dioxide. The analytical sample was recrystallized three times from a carbon tetrachloride-chloroform mixture, m.p. 147°. The compound was readily soluble in 5% sodium hydroxide solution. The same product was obtained in lower yield by treating compound 2 directly with nitrosyl chloride in a sealed tube; ir (potassium bromide): cm^{-1} (C-H, 2990 d), (NO_2, 1580, 1320 s), (O-N=N-O, 1485 s); ^{1}H nmr (deuteriochloroform): δ 5.02 (s, 1), 2.19 (s, 3), 1.70 (s, 3), 1.67 (s, 3).

Anal. Calcd. for $C_6H_{10}ClN_3O_4$: C, 32.26; H, 4.51; N, 18.79. Found: C, 32.30; H, 4.45; N, 18.91.

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