Orientation of Dinitrogen Trioxide Addition to 2-Methylpropene and Structure of the Addition Product

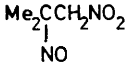
By Josef Pfab

(*Department of Chemistry, Heriot-Watt University, Riccarton, Currie, Edinburgh* EH14 4AS)

Summary The structure of the crystalline addition product of dinitrogen trioxide to 2-methylpropene is established unequivocally as *trans*-2-methyl-2-nitroso-1-nitropropane dimer indicating that the addition proceeds at least partially if not predominantly by a radical mechanism.

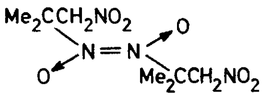
Surprisingly the earlier suggestion[1] that the products of addition of N_2O_3 to alkenes are *vic*-nitroso-nitrites has been revived recently,[2] although the overwhelming majority of evidence available from the literature is in favour of the isomeric *vic*-nitronitroso (pseudonitrosite) structure. An unambiguous assignment of the structure of these adducts is of interest since it establishes the orientation of addition and consequently permits a distinction between an electrophilic and a radical addition mechanism.

Here the results of a re-examination of the structure of the solid 2-methylpropene–N_2O_3 addition product are reported. Using both spectroscopic and chemical techniques the product is shown unequivocally to be 2-methyl-2-nitroso-1-nitropropane (**1a**) and its *trans*-dimer (**1b**). The alternative structures (**2**)—(**4**) and their dimers are excluded.

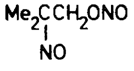


$\underset{\text{NO}}{\text{Me}_2\text{C}}\text{CH}_2\text{NO}_2$

(1a)

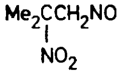


(1b)



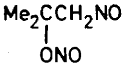
$\underset{\text{NO}}{\text{Me}_2\text{C}}\text{CH}_2\text{ONO}$

(2)



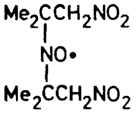
$\underset{\text{NO}_2}{\text{Me}_2\text{C}}\text{CH}_2\text{NO}$

(3)



$\underset{\text{ONO}}{\text{Me}_2\text{C}}\text{CH}_2\text{NO}$

(4)



$\underset{\underset{\text{Me}_2\text{CCH}_2\text{NO}_2}{\text{NO}\cdot}}{\text{Me}_2\text{C}}\text{CH}_2\text{NO}_2$

(5)

When a cold (−70 °C) solution of N_2O_3 in ether–isopentane was added to a solution of an excess of 2-methylpropene in isopentane kept at −20 °C a rapid and exothermic reaction was observed which yielded a white crystalline solid and a blue unstable oil of complex composition. {N.m.r. and g.l.c. analyses indicated three main constituents of the oil [(**1**), 2-methyl-1,2-dinitropropane,† and 2-methyl-1-nitropropan-2-ol‡] and several minor constituents including 2-methyl-1-nitropropene§}. The white solid, of m.p. 83 °C and composition $C_4H_8N_2O_3$, has been isolated previously and has been described as the dimer (**1b**) of (**1a**),[3,4] or the dimers of (**3**)[5] or, more recently, (**4**).[2]

The chemical properties of this compound provide clear evidence, however, that its structure can only be (**1**). Its initially colourless solutions in organic solvents turn blue rapidly at room temperature owing to dissociation. This property is generally typical of only tertiary but not of secondary or primary aliphatic nitroso-compounds for which dissociation is not facilitated by steric hindrance[6] ruling out structures (**3**) and (**4**). Structures (**2**) and (**4**) are also unlikely since solutions in methanol are stable even in the presence of dilute mineral acid and the solvolysis of nitrites in alcohols is known to take place exceptionally easily and rapidly.[7] Neither a nitroso-alcohol nor the methyl nitrite which would be formed are found and the adduct can be isolated unchanged from methanol. Further evidence compatible with (**1**) and (**3**) only is obtained from a study of the oxidation of the adduct. Oxidation of the blue dichloromethane solution by *m*-chloroperbenzoic acid or nitrogen dioxide at room temperature converts the adduct into 2-methyl-1,2-dinitropropane† in 75 and 90% yield, respectively. Finally the thermolysis of the adduct at 95—100 °C was re-investigated since it is reported to provide evidence for (**4**) [or (**3**)] by virtue of oxime formation.[2] The yellow liquid obtained from this decomposition in the melt was found by i.r. and n.m.r. spectroscopy, and g.l.c., to consist of two major products, 2-methyl-1-nitropropene§ and 2-methyl-1,2-dinitropropane† and a minor product, 2-methyl-1-nitropropan-2-ol.‡

None of the three analytical methods used provided any evidence for an oxime¶ and since a terminal nitro-group is present in each of the three products these results again support structure (**1**) rather than (**2**)—(**4**).

Further and even more conclusive evidence for (**1**) was obtained from an investigation of the spectroscopic properties of the adduct. The values for the chemical shifts in the n.m.r. spectra in $CDCl_3$[8] and $(CD_3)_2CO$[2] were confirmed but they cannot discriminate unambiguously between the four structures. However at a concentration of 0·1 M in $CDCl_3$, at *ca.* 38 °C and at equilibrium >98% of the adduct is dissociated to monomer according to the n.m.r. spectrum, supporting the chemical evidence in favour of (**1**). The i.r. spectrum** of the solid dimer shows strong absorptions characteristic of a primary aliphatic nitro group and of a *trans*-azodioxy linkage[10] whilst the characteristic pattern for Me_2CNO_2[9] or absorptions for a nitrite group are absent. Consequently the i.r. spectrum is only compatible with structure (**1b**).

The electronic absorption spectrum in methanol [λ_{max} 663 (ϵ 20·6) and 253 nm (265)] is as expected for a completely dissociated tertiary aliphatic *C*-nitroso-compound.

---

† M.p. 50 °C., lit.,[4] 53 °C; i.r. (KBr): 1560, 1550, 1405, 1385, 1380, 1352, and 1272 cm^{-1}; n.m.r. δ (Me_4Si; CCl_4) 1·75 and 4·95.

‡ I.r. (CCl_4): 3520, 3375, 1560, and 1385 cm^{-1}; n.m.r. δ (Me_4Si; $CDCl_3$) 1·36 (6H), 3·01 (1H), and 4·44 (2H).

§ I.r. (CCl_4): 1525 and 1359 cm^{-1}; n.m.r. δ (Me_4Si; CCl_4) 1·96 (3H, *J* 1·5 Hz), 2·25 (3H, d, *J* 1·5 Hz), and 6·95 (1H, septet, *J* 1·5 Hz).

¶ The n.m.r. spectrum wrongly assigned to an oxime in the literature[2] is due to 2-methyl-1-nitropropene§ since a spectrum identical to the one published[2] was obtained for this compound in $(CD_3)_2CO$.

** I.r. (KBr) 1562, 1382, 1278, 1260, and 1222 cm^{-1}.

The absorption in the u.v. spectrum, although stronger than usual, is attributable to a nitro but not to a nitrite group. Finally an additional unambiguous distinction between (**1**) and (**3**) was achieved by e.s.r. spectroscopy. When a benzene solution of the nitroso-adduct was exposed to visible light, a method known to result in the formation of *sym*-dialkyl nitroxides from nitroso-compounds by photo-dissociation of the C–NO bond, a strong nitroxide spectrum was observed [a_N 14·8 G (triplet), a_H 0·536 G (quintet); g 2·0062]. The e.s.r. parameters measured, particularly the small hyperfine splitting due to four equivalent γ-hydrogen atoms observed at high resolution, provide firm evidence that the species observed is (**5**). The formation of such a nitroxide is only consistent with structure (**1**) for the adduct since (**2**) is eliminated on account of the electronic spectrum.

In summary both chemical as well as spectroscopic techniques confirm that the addition product of N_2O_3 to 2-methylpropene is the dimer of (**1**). Consequently these results support the interpretation that the addition of N_2O_3 to alkenes proceeds by a radical mechanism[5,11] and it appears that suitable conditions have yet to be found where an electrophilic addition mechanism[2] will predominate in additions of N_2O_3 to alkenes.

(*Received*, 1*st August* 1977; *Com.* 799.)

[1] J. Schmidt, *Ber.*, 1902, **35**, 2323.

[2] J. R. Park and D. L. H. Williams, *J.C.S. Perkin II*, 1976, 828.

[3] J. F. Brown, *J. Amer. Chem. Soc.*, 1957, **79**, 2480.

[4] N. Levy, C. W. Scaife, and A. E. Wilder-Smith, *J. Chem. Soc.*, **1948**, **52**.

[5] A. Michael and G. H. Carlson, *J. Org. Chem.*, 1940, **5**, 1.

[6] J. C. Stowell, *J. Org. Chem.*, 1971, **36**, 3055.

[7] G. Bertoni, *Gazzetta*, 1882, **12**, 438.

[8] L. Parts and J. T. Miller, *J. Phys. Chem.*, 1969, **73**, 3088.

[9] J. F. Brown, *J. Amer. Chem. Soc.*, 1955, **77**, 6341.

[10] B. G. Gowenlock, H. Spedding, J. Trotman, and D. H. Whiffen, *J. Chem. Soc.*, 1957, 3927.

[11] L. Jonkman, H. Muller, and J. Kommandeur, *J. Amer. Chem. Soc.*, 1971, **93**, 5833.