

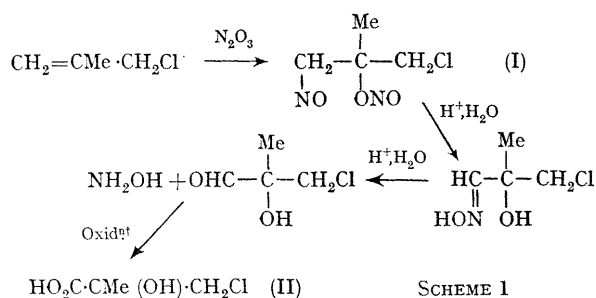
The Reaction of Dinitrogen Trioxide with Olefins

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Summary The products of reaction of dinitrogen trioxide with two olefins are assigned as nitroso-nitrites on the evidence from hydrolysis products.

THERE is considerable discrepancy in the literature regarding the orientation and mechanism of addition of dinitrogen trioxide to olefins. Most workers have regarded the products as nitroso-nitro-compounds,^{1,2} arising by attack of the nitronium ion NO_2^+ followed by reaction with the hyp-nitrite ion NO^- . The possibility that such products are nitroso-nitrites has also been discussed³ and Schechter,⁴ on the basis of unusual product orientations, has suggested a free-radical mechanism. In the light of studies on diazotisation⁵ where, under certain conditions dinitrogen trioxide is the electrophilic reagent transferring NO^+ to the amine, and from the structure of dinitrogen trioxide,⁶ it seems reasonable to expect addition in the sense $\text{NO}^+ \text{NO}_2^-$.



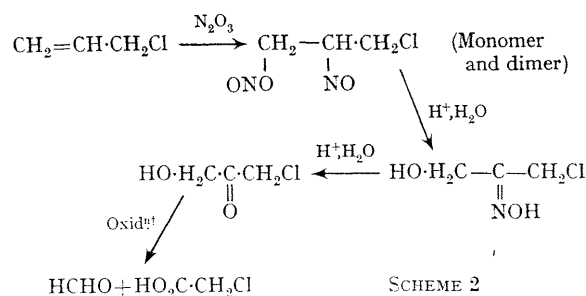
SCHEME 1

† α -Hydroxy-aldehydes are easily oxidised to the corresponding acids (J. De Boer and J. C. Van Velzen, *Rec. Trav. chim.*, 1967, **86**, 107).

We have prepared the product of addition of dinitrogen trioxide to 3-chloro-2-methylpropene, first reported by Kooyman.² It was obtained as a blue oil from (a) liquid N_2O_3 and no solvent, (b) N_2O_3 in ether, and (c) sodium nitrite and acid in water. The structure and orientation of

the product (I) was deduced from its acid hydrolysis products (15% sulphuric acid at *ca.* 65° for two days). Both nitrous acid and hydroxylamine were detected in the reaction mixture and 3-chloro-2-hydroxy-2-methylpropionic acid (II) was isolated in good yield. The identity of (II) was established by analysis of the acid and its S-benzylthiuronium salt and by comparison with an authentic sample prepared from hypochlorous acid and methacrylic acid.⁷ The results are consistent with a 1-nitroso-2-nitrite structure for (I) which undergoes hydrolysis according to Scheme 1. It is difficult to envisage how (II) can be formed from (I) by acid hydrolysis if (I) is a 1-nitro-2-nitroso-compound as suggested by Kooyman.² The splitting pattern shown in the mass spectrum of (I) is also consistent with its formulation as a nitroso-nitrite.

Reaction of dinitrogen trioxide with allyl chloride gave a white solid (probably a dimer) together with a green oil. Both gave chloroacetic acid upon acid hydrolysis and appear to be the 2-nitroso-1-nitrite, *i.e.* with "anti-Markovnikoff" orientation as is mainly the case with the product from hypochlorous acid and allyl chloride.⁷ Scheme 2 is a plausible sequence for the hydrolysis.



SCHEME 2

Two groups of workers⁹ have used an analogous hydrolysis procedure to establish the identity of the products from

dinitrogen tetroxide and olefins as nitroso-nitrates. 3- the product from this olefin also gave the carboxylic acid (II). Chloro-2-methylpropene was among the olefins studied and

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