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The Reaction of Tetranitromethane with Olefins

by

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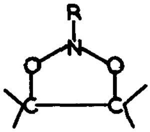
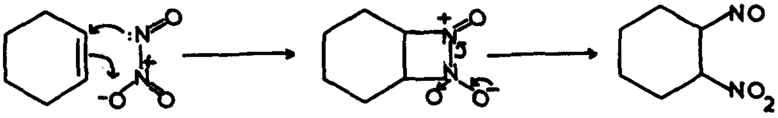
Considerable confusion exists in the literature as to the part played by tetranitromethane (TNM) in its reactions with olefins. Macbeth and his co-workers (1-3) concluded from spectroscopic evidence that an organic nitrite was developed transiently in the reaction, whereas other workers (4-6) have advocated the presence of charge transfer complexes, as in aromatic nitro-compounds. Recently, Lagercrantz et al., (7, 8) have established that with light inducement, free radicals are formed in the reaction of cyclo-hexene with TNM. Again, it has been suggested (9-11) that a chemical bond might be formed, for example, as shown in (I) (12), and in this connection, it is interesting to note that Thun et al., (13) have very recently succeeded in isolating 1,1,4-trimethyl-4-(β, β-dinitrovinyl)-2-tetrazine as its dipolar ion, from the reaction of 1,1, 4, 4-tetramethyl-2-tetrazine and TNM.



(I)

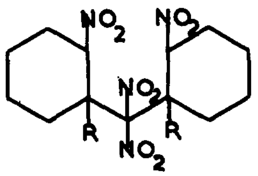
In the present work, the products isolated from the reaction of TNM with olefins are discussed, and an investigation of the colour reactions of TNM with double bonds (14-16) will appear elsewhere. In general it has been found by NMR studies that the olefinic protons at ca. 4.4 τ disappear, and new signals occur at 4.9-6.0 and ca. 7.6 τ, thus indicating that the unsaturation in the molecule is destroyed.

In the case of cyclo-hexene, a water soluble solid was formed in ca. 5% yield, which readily isomerized to 1-nitro-2-nitroso-cyclo-hexane (II) tautomeric with its oxime form. This product may arise from attack of N_2O_3(produced from the decomposition of TNM) in the following way.



(II)

Chromatographic separation of the residual oil gave 2-nitro-cyclo-hexanone, 2-nitroso-cyclo-hexanone, 1,2-dinitro-cyclo-hexane, and (IIIa), each in ca. 15% yield. These results were also substantiated in the case of oct-1-en. Although all the products from chromatographic separation of the crude reaction mixture

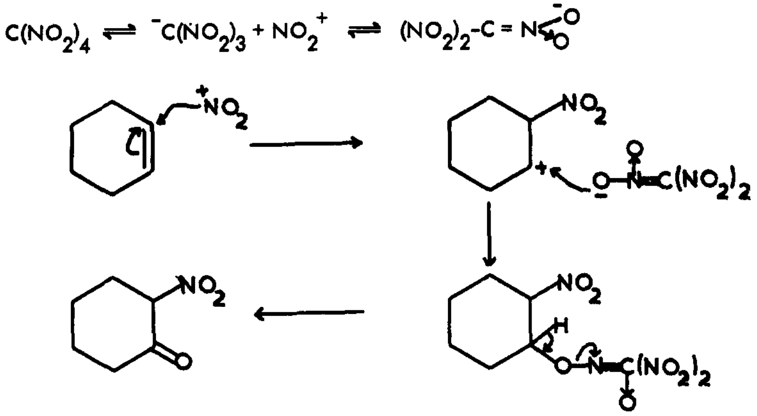


(a) R = H

(b) R = CH_3

(III)

except (IIIa) have previously been isolated from reactions of NO_2 (17), N_2O_4 (18, 19) or HNO_3 (20) with <u>cyclo</u>-hexene, and other simple olefins (21-24), there remains the interesting speculation that the ketonic products might arise <u>via</u> the mechanism indicated in Table 1.

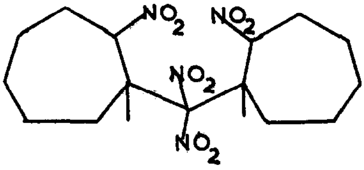


$$C(NO_2)_4 \rightleftharpoons {}^{-}C(NO_2)_3 + NO_2^{+} \rightleftharpoons (NO_2)_2\text{-}C = N\begin{smallmatrix}O^{-}\\O\end{smallmatrix}$$

TABLE 1

In order to test this hypothesis, 1-methyl-<u>cyclo</u>-hexene was treated with TNM, when it was found that only 2-5% of total ketonic products were produced. Therefore it would appear that the above mechanism may be largely responsible for the formation of ketonic products in this instance.

Although small traces of 1,2-dinitro-1-methyl-cyclo-hexane and 1-nitro-1-methyl-2-nitroso-cyclo-hexane were also detected, the major product from this reaction was found to be (IIIb) (60-70%). These results were corroborated by a study with 1-methyl-cyclo-heptene, when a small quantity of ketonic product (3%) was isolated, together with (IV) in 80% yield. The most likely mechanism for the formation of these poly-nitro compounds (III) and (IV), is shown in Table 2, since it is well known that TNM (25) and trinitromethanes (3) readily dissociate. It is furthermore reasonable to assume that the inductive effect of the exo-cyclic methyl group, in these cases, would enhance the



(IV)

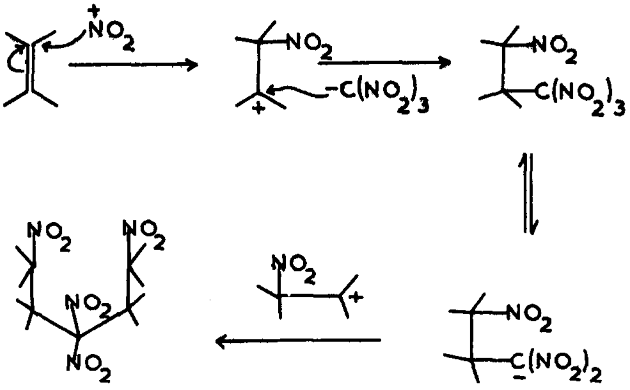
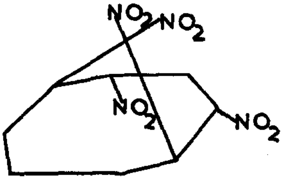


TABLE 2

the polarisation of the double bond leading to the formation of larger yields of (IIIb) and (IV), compared with the simpler cases where no position of preferential attack is indicated.

In order to extend this reaction, TNM was treated with cyclo-octa-1, 5-diene, and cyclo-octatetraene in the hope that internal addition would occur to give products of the type (V). Amorphous orange brown solids were, however, isolated in each case, which from molecular weight determinations proved to be polymers of 2-4 molecules of olefin to 1-2 molecules of TNM. These results are not unexpected, since the stereochemical addition of TNM across a double bond would almost certainly require $-C-(NO_2)_3$ to be equatorially placed.



(V)

The reaction of TNM with 1-methyl-cyclo-heptene was found to be unique in that a small quantity (8%) of an unstable dark blue oil was isolated which proved to be 1-methyl-1-nitroso-2-nitro-cyclo-heptane. This substance can only exist in the nitroso form, as no α-hydrogen atoms are available for tautomerisation.

Furthermore, the reaction of TNM with cyclo-octene, followed an anomalous path in that the major product of the reaction was found to be suberic acid (45%), presumably formed as a result of oxidative cleavage of the double bond, although it would be expected that cyclo-hexene would give rise to adipic acid. No such product was detected in this reaction.

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