Reaction of Nitrosocyclohexene with Maleic Anhydride

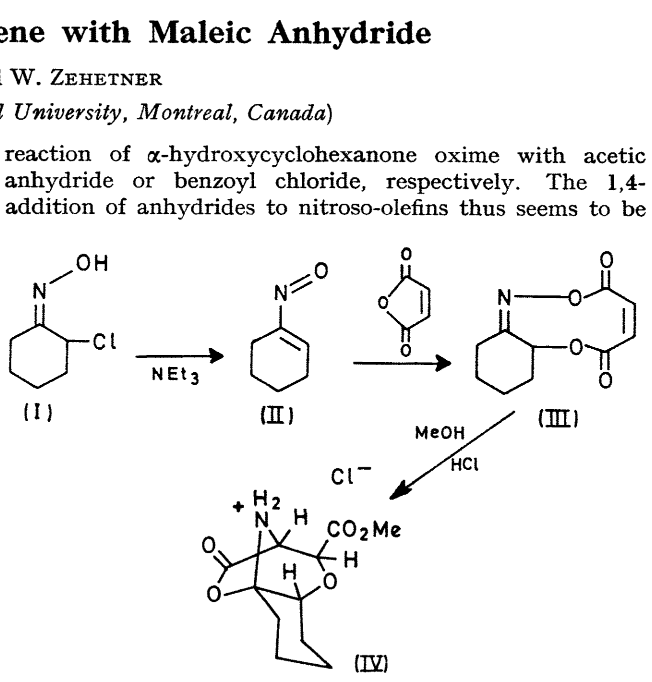
By G. JUST* and W. ZEHETNER

(*Department of Chemistry, McGill University, Montreal, Canada*)

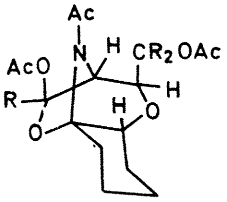
Summary The reaction of nitrosocyclohexene (II) with maleic anhydride did not yield the expected Diels–Alder adduct, but gave the adduct (III), which, when treated with methanolic hydrogen chloride, yielded the dioxa-azaoctanone (IV).

WE report the results of our investigation into the use of nitroso-olefins as dienes in Diels–Alder reactions. Nitroso-olefin (II) is almost instantaneously generated by reaction of α-chlorocyclohexanone oxime (I) with triethylamine in benzene at room temperature,[1] the only by-product being triethylammonium chloride. The intensely blue solution decolourizes over a period of several hours, giving a poly-(oximino-ether).[2]

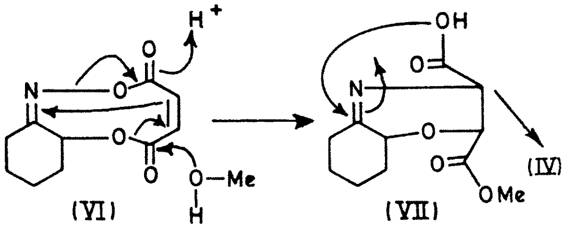
The reaction of (II) with dienophiles has not been previously reported. The closest analogy in the literature has been the successful Diels–Alder reaction of diazo-olefins (–C=C–N=N–) with dienophiles.[3] When maleic anhydride is added to the freshly prepared solution of (II), the colour fades within 10 min. A very slow crystallization from methanol or chloroform permits the isolation in small yield of the 1 : 1 adduct (III), m.p. 205—208° (decomp.), ν 1760, 1725 cm^{-1}, δ 6·20 (2H, s) and 5·35 p.p.m. (1H, m), the composition of which was confirmed by microanalysis. This appears to be an unprecedented method for the formation of a nine-membered ring. Similarly, the addition of acetic anhydride or benzoic anhydride to a solution of (II) yielded the diacetate or dibenzoate of α-hydroxycyclohexanone oxime. These structures were confirmed by the reaction of α-hydroxycyclohexanone oxime with acetic anhydride or benzoyl chloride, respectively. The 1,4-addition of anhydrides to nitroso-olefins thus seems to be quite general. However, no identifiable products could be recovered from the reaction of nitrosocyclohexene with dimethylacetylenedicarboxylate or tetracyanoethylene.



When adduct (III) was dissolved in 0·5N-methanolic HCl and allowed to stand overnight, a quantitative yield of compound (IV), m.p. 180° (decomp.), was obtained by precipitation with chloroform. This type of rearrangement seems to be without precedent in the literature. (IV) could also be obtained in 30—50% yield based on maleic anhydride, when the intermediate (III) was not isolated. Heating of (IV) to *ca.* 100°, led to the evolution of HCl. Analytical data indicated the molecular formula $C_{11}H_{16}NO_5Cl$; this was confirmed by mass spectrometry, which gave a molecular-ion peak at 241·094 ($C_{11}H_{15}NO_5$), verifying that the elements of HCl were easily lost. Neutralization of (IV) with 1 equiv. of NaOH gave the free base of (IV), the spectral data of which were very similar to those of (IV) except for n.m.r. and i.r. bands characteristic of a secondary amine. On treatment with acetic anhydride and pyridine, (IV) gave the *N*-acetyl derivative with m.p. 175—177°, δ 2·18 p.p.m., ν 1640 cm^{-1}, the remainder of its spectra being similar to those of (IV).



(V) a; R = H
b; R = D



The i.r., n.m.r. (C_5D_5N), and mass spectra of (IV) showed the presence of a methoxycarbonyl group, ν 1750 cm^{-1}, δ 3·75 p.p.m. (3H, s), *m/e* 182·082 ($C_9H_{12}NO_3$); a lactone group, ν 1780 cm^{-1}, *m/e* 138·067 ($C_8H_{12}NO$); an ammonium group, ν 2300—2400 cm^{-1}; a low field triplet at δ 4·80 p.p.m., ($-CH_2-CH-O$); and an AB quartet centred at δ 5·09 and 3·98 p.p.m., *J* 7 Hz. Spin-decoupling showed that the two protons were adjacent. When the reaction was repeated, using $(CDCO)_2O$, the n.m.r. spectrum of (IV) was unchanged except for the disappearance of the AB quartet. Pyrolysis of (IV) gave cyclohexenone, identified by g.l.c.–mass spectrometry, indicating that an intact cyclohexane ring was present in (IV). Reduction of (IV) with $LiAlH_4$ and $LiAlD_4$, followed by acetylation, gave compounds (Va) and (Vb), respectively. Comparison of the n.m.r. spectra of (Va) and (Vb) confirmed the structure suggested for (IV).

The rearrangement of (III) to (IV) probably proceeds as shown in (VI). Molecular models show the proximity of the olefinic bond to the incipient cation at nitrogen, making possible this unusual rearrangement. Reaction of carboxylic acid (VII) with the protonated imine would then give (IV).

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