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1,3-DIPOLAR CYCLOADDITIONS OF MESITONITRILE OXIDE WITH SUBSTITUTED CYCLOBUTENEDIONES

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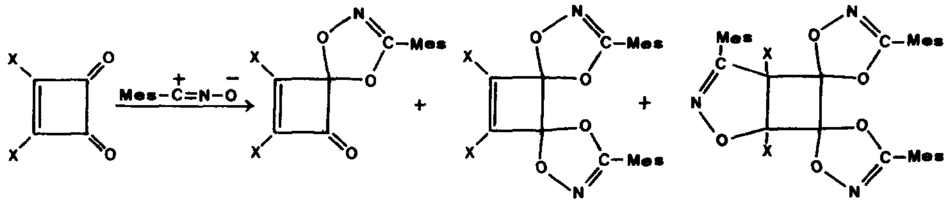
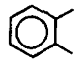
The chemistry of cyclobutenediones has been extensively investigated[2] by many workers, but in contrary very little are known of their behavior as dipolarophiles and on this respect is mentioned the reaction of diazomethane with diphenylcyclobutenedione studied by Ried et al[3]. On the other hand reactions between nitrile oxides and other quinones have been studied previously[4].

The main purpose of this work is to study the periselectivity in 1,3-dipolar cycloaddition of cyclobutenediones with nitrile oxides, to compare the reactivity of C=C and C=O bonds and to correlate the experimental results with those predicted from MO theory.

The cyclobutenediones (Ia-d), despite of their weak dipolarophilic character towards benzonitrile oxide, gave after long heating (30-40 hrs) with excess of the stable mesitonitrile oxide mono- (II), bis- (III) and tri-adducts (IV), as indicated in the following scheme:



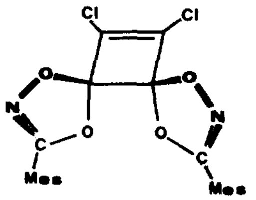
I(a-d) **II(a,b,d)** **III(b,c,d)** **IV(a,b)**

a: X = $-C_6H_5$ **b**: X = $-CH_3$ **c**: X = $-Cl$ **d**: X,X =  **Mes** = 2,4,6-$(CH_3)_3$-C_6H_2-

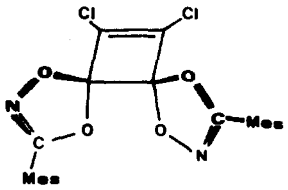
IIa: m.p. 132-133° (25%); IIb: m.p. 69-71° (8%); IId: m.p. 84-86° (18%); IIIb: m.p. 174-176° (7%); IIIc: m.p. 116-117° (18%) and 175-176° (4%), two stereoisomers; IIId: m.p. 144-145° (6%); IVa: m. p. 233-235° (3%); IVb: m.p. 194-196° (8%). All the reaction products were separated on column chromatography and had correct spectroscopic data (IR,NMR,MS) in agreement to proposed structures.

From the reaction products it is evident that the 1,3-dipole preferentially attacks the carbonyl than the ethylene double bond, despite of the usual low reactivity of C=O bonds towards 1,3-dipoles. It is of interest to note that the compound Ic gave two isomeric bis-spiro-dioxazoles (IIIc) and (IIIc′). The product with lower m.p. was assigned as "syn" (IIIc), whereas the other one as "anti" (IIIc′). Both isomers have in general the same chemical and spectroscopical properties and their structure is under further consideration.

The low reactivity of the ethylene double bond of the cyclobutene ring can be explained considering cross conjugating resonance structures[5], a fact which is supported from X-ray data. Thus squaric acid[6] and dichlorocyclobutenedione[7] show a very long ethylene bond length, r C=C



(IIIc)



(IIIc')

being equal to $\sim$ 1,41 Å, whereas r C=C in 1-methyl-cyclobutene is only 1,34 Å [8].

On the other hand the periselectivity as well as the regioselectivity in 1,3-cycloadditions can be predicted[9] on the basis of the type of the frontier orbitals (orbital coefficients - energy level) of dipolarophile and 1,3-dipole. Considering a LUMO(dipole) - HOMO(dipolarophile) interaction, like in the case of tropone[10] and as highest occupied π orbital of dipolarophile the $1a_2$ (C_{2v} group), it is easily concluded that the addition will occur only on the carbonyl group with the formation of 1,3,4-dioxazoles, since only these atoms have orbital coefficients with the same sign with those of LUMO(dipole). If, however, the $2b_1(\pi)$ is the highest occupied orbital as in the case of dimethylene-cyclobutene[11], fact which has also been shown by CNDO/2 calculations on the unsubstituted compound (eigenvalue -11,5 eV), then two peri-isomers should be expected by addition of the dipole on ethylene and on the carbonyl double bonds, in agreement with the experimental results. In this case the peri-selectivity is depended on the magnitudes of orbital coefficients on C=C and C=O atoms. It is of interest to note that the same peri-isomers should be formed, assuming a HOMO(dipole) - LUMO(dipolarophile-$2a_2$ π^*) interaction.Since the energies of the orbitals ($1a_2$, $2b_1$) are in general similar and they are remarkably influenced by the substituents and since data obtained from semiempirical calculations are not completely reliable, accurate experimental values of frontier energies for each compound are required to decide which orbitals are controlling the reaction.

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