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An *ab Initio* Study of the Reactivity of Nitrosoketene with Formaldehyde

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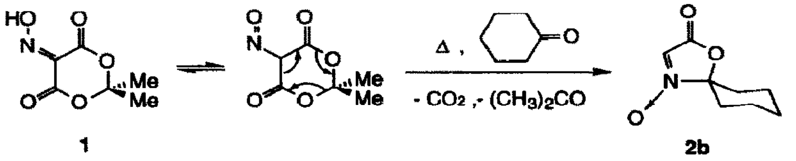
Abstract: *Ab initio* molecular orbital theory (RHF/6-31G*) was used to locate pseudopericyclic transition structures for the cycloaddition of formaldehyde to the *Z* and *E* conformations of nitrosoketene. The [3+2] pathway, with a calculated activation energy of only 3.5 kcal/mol, is predicted to be significantly favored over the [4+2] alternative.

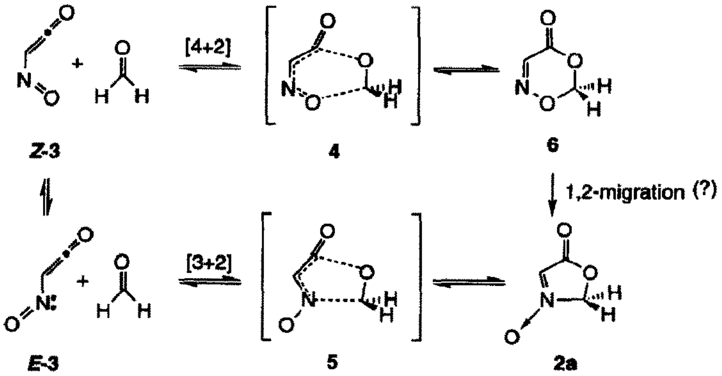
Katagiri *et al.*[1] have recently proposed that nitrosoketene (3) is an intermediate in the thermolysis of hydroxyimino Meldrum's acid (**1**) and synthesized a series of cyclic nitrones (e.g. **2b**) by trapping **3** with ketones, as shown in equation 1. They considered two reactions pathways (scheme 1), a [4+2] cycloaddition followed by a 1,2-migration or a direct [3+2] cycloaddition, although they favored the former. We recognized both cycloadditions as orbital symmetry allowed, pseudopericyclic reactions[2] and were intrigued as to which of these competing reactions might prevail. We report here the results of *ab initio* calculations which indicate that E-nitrosoketene (***E*-3**) undergoes a [3+2] reaction with formaldehyde (a model carbonyl compound) to form the cyclic nitrone **2a** via a five-membered transition structure (TS) **5** rather than the alternative [4+2] cycloaddition via TS **4**.



(1)

Structures of **2a**, ***Z*-3**, ***E*-3**, **4**, **5**, and **6** were fully optimized at the RHF level of theory with the 3-21G and 6-31G* basis sets and were characterized by vibrational frequency calculations.[3] The two different conformations of the nitrosoketene, *viz.* ***Z*-3** and ***E*-3**, were both calculated to be planar. Single point energies were calculated at the MP4(SDQ)/6-31G* (frozen core) level at the RHF/6-31G* optimized geometries and scaled (0.9) zero point energy (ZPE) corrections (RHF/6-31G*) were made.[4,5] Absolute energies are reported in Table 1 and relative energies in Table 2. At the RHF/6-31G* level, ***E*-3** is 1.7 kcal/mol more stable than ***Z*-3**, but at both the MP2/6-31G* and MP4(SDQ)/6-31G* + ZPE levels, the preference for ***E*-3** was only 1.0 kcal/mol. It has previously been suggested that a balance between electrostatic and steric effects determine the conformational preferences of substituted α-oxoketenes.[4] The large energy preference found for ***E*-3** would imply that the electrostatic attraction between the non-bonding electrons on the nitrogen (which nonetheless bears a net positive charge) and the partially positive central carbon (C_2) in the ketene is stronger than the electrostatic attraction between this carbon and the partially negative nitrosyl oxygen O_5 in **Z-3**.

Scheme 1.



Concerted transition structures were located for the [4+2] cycloaddition of formaldehyde to **Z-3** (**4**) and for the [3+2] cycloaddition to **E-4** (**5**) (Figure 1). The geometry of **4** is very similar to that found for the addition of formaldehyde to acetylketene.[2b,6] The forming C_2O_7 bond in **4** is 0.154 Å shorter than the O_5C_8 bond, and the formaldehyde is twisted slightly out of plane. This indicates that the nucleophilic addition of an O_7 lone pair to C_2 leads the reaction, and nucleophilic addition of an O_5 lone pair to the π^* of formaldehyde follows. There is greater asynchronicity in **4** than in the reaction of acetylketene[2b] because of the electronegative nitrogen (N_4) which decreases the nucleophilicity of the attached oxygen (O_5), thus reducing O_5C_8 bond formation in **4**.

In contrast, transition structure **5** is planar and the N_4C_8 distance is 0.039 Å shorter than the C_2O_7 distance. Since the N_4C_8 bond (1.470 Å) in **2a** is longer than the C_2O_7 bond (1.353 Å), it is clear that N_4 bonding to C_8 is more significant in the transition structure than C_2O_7 bonding. In this case the in-plane lone pair on N_4 of **E-3** leads the reaction, adding as a nucleophile at C_8 to the π^* of the formaldehyde. As electron density accumulates in the π system of the formaldehyde, it adds as a nucleophile to C_2 of the ketene. The planar transition structure requires that the nucleophilic and electrophilic sites on formaldehyde are coplanar.

The calculated activation energy for forming **2a** via **5** is only 3.5 kcal/mol, which is significantly lower than 8.8 kcal/mol to form **6** via **4**. Three factors contribute to this low barrier. First, the planarity of the TS allows for maximum orbital overlap, in contrast to the non-planar TSs of most pericyclic reactions which result from compromises in the overlap between breaking and forming bonds.[7] Secondly, the lack of a closed loop of interacting orbitals at the pseudopericyclic TS avoids the electron-electron repulsion[2b] inherent in most pericyclic reactions[8] and also means that the number of electrons is irrelevant. Thirdly, the nitrogen at N_4 (**5**), being a better nucleophile than O_5 (**4**), reacts more readily as well.

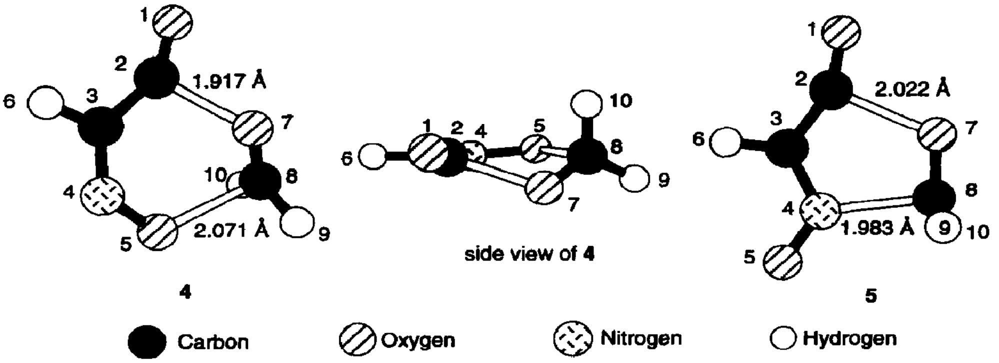


Figure 1. Fully optimized geometries of the transition structures **4** and **5** at the RHF/6-31G* level.

Table 1. Absolute energies (Hartree) of structures optimized at the RHF/6-31G* level.

Structure	RHF/6-31G*[a]	ZPE[b]	MP2/6-31G*[c]	MP4(SDQ)[c]+ ZPE[d]
Z-3	-280.36197	20.9	-281.11527	-253.01745
CH_2O	-113.86633	20.3	-114.17496	-102.76344
4	-394.20137	41.8	-395.27713	-355.76855
6	-394.31018	46.8	-395.36675	-355.85533
E-3	-280.36469	20.9	-281.11685	-253.01911
5	-394.20980	42.2	-395.28946	-355.77698
2a	-394.29655	46.6	-395.37156	-355.85183

[a] At the RHF/6-31G* optimized geometry. [b] Zero-point vibrational energy in kcal/mol. [c] Calculated using the frozen core approximation. [d] Zero-point vibrational energy correction from RHF/6-31G* frequencies and scaled by 0.9.

Table 2. Relative energies (kcal/mol) of structures optimized at the RHF/6-31G* level.

Structure	RHF/6-31G*	MP2/6-31G*[a]	MP4(SDQ)[a]+ ZPE[b]
E-3 + CH_2O	0.0	0.0	0.0
4 (TS)	18.6	9.2	8.8
6	-49.7	-47.0	-45.7
5 (TS)	13.3	1.5	3.5
2a	-41.1	-50.0	-43.5

[a] Calculated using the frozen core approximation at the RHF/6-31G* geometry. [b] Zero-point vibrational energy correlation from RHF/6-31G* frequencies and scaled by 0.9.

A search for a TS related to the postulated 1,2-migration which would connect **6** to **2a** was attempted. Beginning with the optimized structure **2a**, the N_4C_8 bond was lengthened and the rest of the geometry was optimized. However, this optimization moved O_5 away from the ring instead of making the six membered ring. A similar search with the angle O_5-N_4-C_8 constrained also failed to locate a transition structure for the 1,2-migration. These results suggest that the observed ring contraction of 5,6-dihydro-1,2-oxazin-4-ones to 4,5-dihydropyrrol-3-one-1-oxides[9] may occur via a fragmentation/recombination pathway.

In conclusion, the lower barrier for the [3+2] cycloaddition and the absence of a transition structure for the 1,2-migration suggest that the formation of cyclic nitrones such as **2a** occurs directly via the [3+2] reaction mechanism.

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