MNDO-CI Theoretical Study of [2 + 2] Cycloaddition of Cyclopentyne with Ethylene†

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The [2 + 2] cycloaddition reactions of cyclopentyne and acetylene with ethylene have been studied by the MNDO method with a 3 × 3 configuration interaction. Both reactions are predicted to take place stepwise through diradical intermediates. The observed stereospecificity of the cycloadditions of cyclopentyne with olefins is explained on the basis of the extremely short lifetime predicted for the reaction intermediates.

The smallest unsubstituted cycloalkyne which can be easily isolated is cyclo-octyne.[1] Hitherto all attempts to isolate cycloheptyne have failed,[2] but 3,3,7,7-tetramethylcycloheptyne was synthesized in 1971.[3] Cyclohexyne,[2] cyclopentyne,[2] and some other five-membered-ring cycloalkynes (norbornyne,[4] acenaphthyne,[5] and 2,2,5,5-tetramethyl-1-thiacyclopent-3-yne[6]) have been successfully generated and trapped.

Although no experimental proof of the existence of cyclobutyne[2,7] and cyclopropyne is available, multiconfigurational *ab initio* molecular orbital calculations[8] have shown that singlet cyclobutyne is a minimum on the potential energy hypersurface, and that for cyclopropyne only the triplet state fulfils this condition. Cyclopentyne is, in fact, the smallest unsubstituted cycloalkyne for which there is chemical evidence of its transient existence.[2,9–12] An early theoretical study performed by the MINDO/3 procedure suggested that cyclopentyne was a transition state linking two π-complexes. We have subsequently shown[13] that this result was an artefact generated by the monoconfigurational treatment used, and that because of its diradical character, cyclopentyne can only be described accurately by a configuration interaction treatment.

Trapping experiments with cyclopentyne at low temperature have revealed the basic trends of its reactivity: the compound exhibits a strong preference for [2 + 2] cycloadditions with olefins and conjugated dienes.[9–12] These processes have been found to be highly stereospecific, and this fact has implications for the electronic structure of cyclopentyne, and for the mechanism of these cycloadditions. Thus, Fitjer,[11] on the basis of the stereospecificity of the reactions with (*Z*)- and (*E*)-but-2-ene, postulated a singlet ground state with an antisymmetric HOMO for cyclopentyne. On the other hand, Gilbert[12] considered the stereospecificity of the reactions of (*Z*)- and (*E*)-1-methoxypropene as evidence for an antarafacial concerted mechanism.

At this point, a rigorous theoretical study of the cycloadditions of cyclopentyne with olefins was clearly needed in order to ascertain the mechanism and to explain the observed stereochemistry. In this context, we report here a 3 × 3 CI-MNDO study of the [2 + 2] cycloaddition between cyclopentyne and ethylene, to give bicyclo[3.2.0]hept-1(5)-ene (Scheme 1).

A study of the analogous reaction between acetylene and ethylene leading to cyclobutene (Scheme 2), which has never been observed in practice,‡ has also been carried out at the same level with the aim of comparing the two reaction profiles and explaining the differences in reactivity between the two alkynes.

Scheme 1.

Scheme 2.

Theoretical Procedure

The calculations were performed by the standard MNDO[16] semi-empirical SCF-MO method as implemented in the MOPAC[17] program. Since the potential energy surfaces studied involve diradical-like species, the calculations were first carried out using the spin-unrestricted[18] version (UMNDO)[19] of MNDO. However, UMNDO is known to give wavefunctions for singlet diradicals that are highly contaminated by the corresponding low lying triplet states, as shown by the large calculated expected value for the operator S^2 (*ca.* 1.0); this leads to substantial uncertainties in the calculated molecular geometries and energies. To avoid this problem the stationary points located by UMNDO along the minimum-energy reaction paths (MERPs), were then reoptimized by MNDO 3 × 3 configuration interaction (CI), based on molecular orbitals given by the 'half-electron'[20] method (MNDO/HE/CI), as suggested by Salem and Rowland for diradical singlet states.[21] The stationary points were characterized by calculating and diagonalizing the Hessian matrix.[22]

Results and Discussion

The cycloaddition between cyclopentyne and ethylene was studied by the normal reaction co-ordinate method, starting from bicyclo[3.2.0]hept-1(5)-ene (**6**). The possibility of a concerted and synchronous mechanism was first investigated, using a UHF wave function, by constraining C_{2v} symmetry along the MERP. A stationary point corresponding to the

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† *Supplementary data available* (SUP 56466, 8 pp.): co-ordinates of all stationary points on the potential hypersurfaces of the reactions studied. For details of Supplementary Publications see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, 1986, Issue 1.

‡ Note, however, that simple alkynes react well with non-activated olefins under Lewis acid catalysis.[14] On the other hand, a non-catalytic [2 + 2] cycloaddition, between acetylene and tetrafluoroethylene at 225 °C, has also been reported.[15]

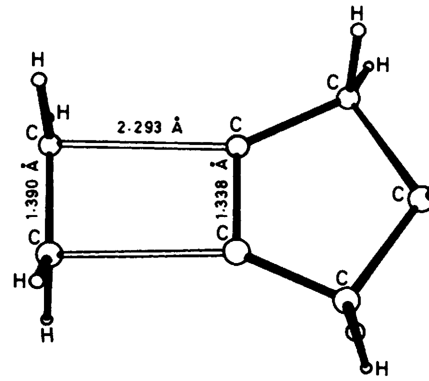

Figure 1. Computer plot of the second-order saddle point corresponding to the synchronous cycloaddition of cyclopentyne with ethylene

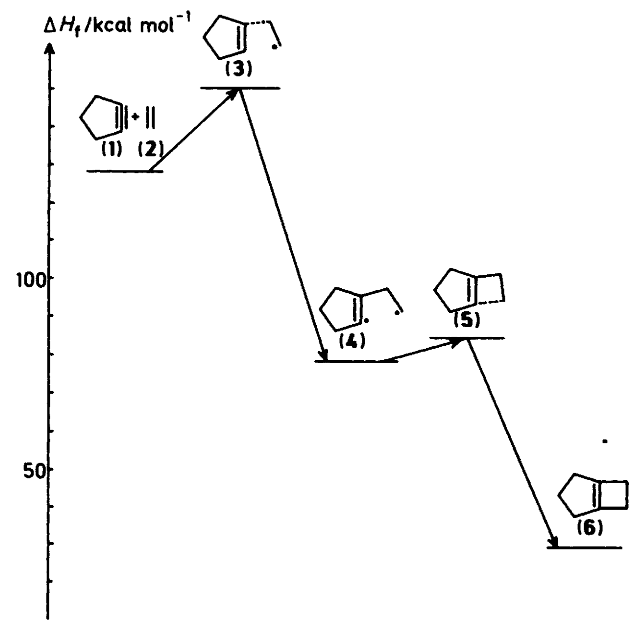

Figure 2. Schematic representation of the minimum-energy reaction path (MERP) for the [2 + 2] cycloaddition of cyclopentyne and ethylene

synchronous formation of bonds C(1)–C(4) C(2)–C(3) was located (Figure 1). However, the calculated Hessian matrix had two negative eigenvalues. The form of one of the corresponding eigenvectors was that expected for the symmetric approach of the two reacting molecules, whereas the form of the other was that corresponding to a breaking of symmetry. Consequently, a non-synchronous reaction path ought to exist, proceeding through a true transition state of lower energy.[23] The reaction was subsequently studied without symmetry constraints (see Figure 2), allowing the location of the highly unsymmetrical transition state (**5**) (Figure 3), where the C(2)–C(3) bond is essentially broken whereas C(1)–C(4) remains practically unchanged. Interestingly, the atomic orbitals containing the unpaired electrons arising from the bond-breaking process lie on the same plane as the four carbon atoms of the cyclobutene ring. The allowance of geometry relaxation in this transition state led to the diradical intermediate (**4**) (Figure 3), which is

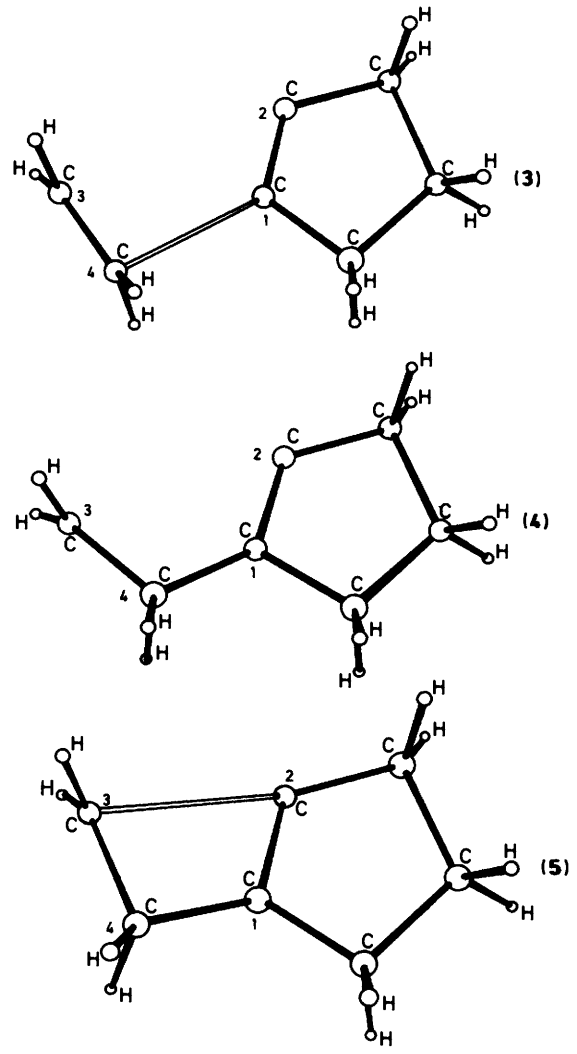

Figure 3. Computer plot for the stationary points (**3**), (**4**), and (**5**) on the MERP for the [2 + 2] cycloaddition of cyclopentyne with ethylene

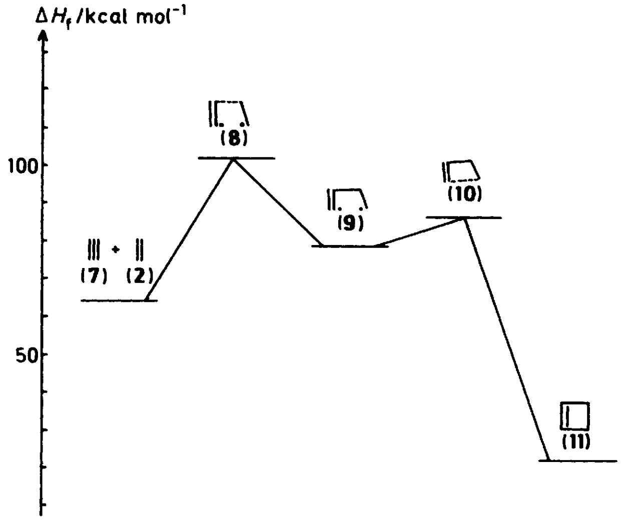

Figure 4. Schematic representation of the MERP for [2 + 2] cycloaddition of acetylene with ethylene

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* 1 kcal = 4.184 kJ.

Table 1. Optimized relevant bond lengths *d* (Å) and angles θ (°), dihedral angles ψ (°), and heats of formation (kcal mol^{-1} at 25 °C) of all stationary points on the MERP for the [2 + 2] cycloaddition of cyclopentyne with ethylene (numbering according to Figure 3)

	d C(1)–C(2)	*d* C(1)–C(4)	*d* C(3)–C(4)	*d* C(2)–C(3)	θ_{214}	θ_{143}	ψ_{2143}	ΔH_f/kcal mol^{-1}
(1)	1.263							121.73
(2)			1.353					6.31
(3)	1.276	2.258	1.342	3.291	131.0	97.4	0.6	149.96
(4)	1.328	1.494	1.490	3.024	131.9	114.6	1.1	78.20
(5)	1.339	1.489	1.507	2.376	116.0	100.9	0.0	84.87
(6)	1.388	1.513	1.586	1.513	93.7	86.2	0.0	22.59

Table 2. Optimized relevant bond lengths *d* (Å) and angles θ (°), dihedral angles ψ (°), and heats of formation (kcal mol^{-1} at 25 °C) of all stationary points on the MERP for the [2 + 2] cycloaddition of acetylene with ethylene (numbering according to Figure 5)

	d C(1)–C(2)	*d* C(1)–C(4)	*d* C(3)–C(4)	*d* C(2)–C(3)	θ_{214}	θ_{143}	ψ_{2143}	ΔH_f/kcal mol^{-1}
(7)	1.195							57.75
(8)	1.223	1.956	1.387	3.415	112.9	106.4	102.6	102.14
(9)	1.296	1.517	1.479	3.487	125.6	113.4	111.2	79.21
(10)	1.316	1.496	1.506	2.391	113.6	103.6	0.0	86.99
(11)	1.374	1.525	1.568	1.525	93.6	86.3	0.0	23.02

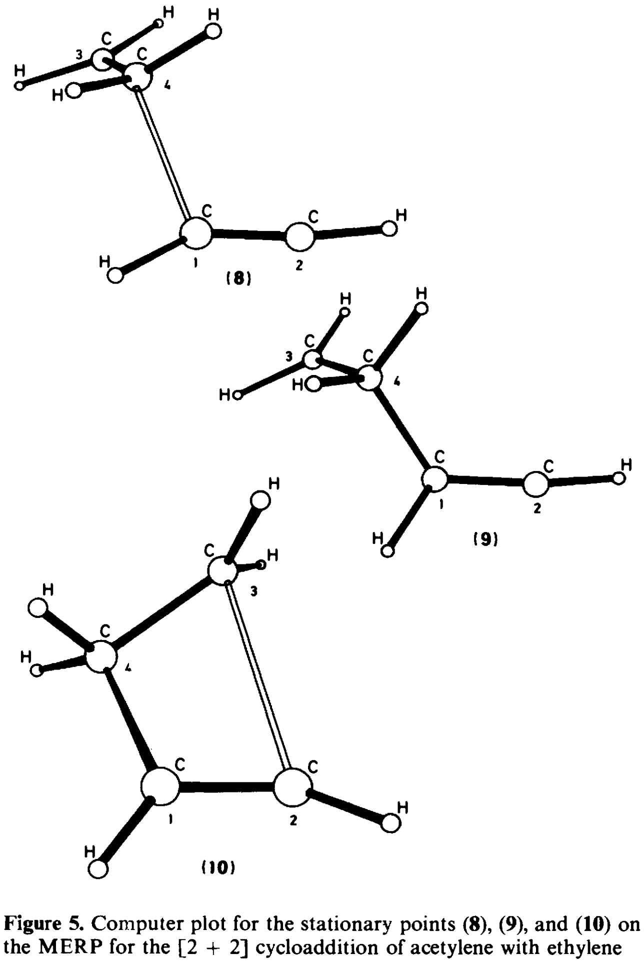

Figure 5. Computer plot for the stationary points (**8**), (**9**), and (**10**) on the MERP for the [2 + 2] cycloaddition of acetylene with ethylene

only 6.7 kcal mol^{-1}* lower in energy and maintains the planarity of the aformentioned atoms. Further elongation of the remaining C–C bond allowed the location of a second transition state (**3**) (Figure 3), connecting intermediate (**4**) with the fragment molecules cyclopentyne (**1**) and ethylene (**2**). The calculated heats of formation and relevant geometric parameters of all the stationary points on the hypersurface are given in Table 1.

The reaction between acetylene (**7**) and ethylene (**2**) leading to cyclobutene (**11**) was studied in a similar way (see Figure 4); the result in this case also was the location of a diradical intermediate (**9**) and of two transition states (**8**) and (**10**) connecting it with the fragment molecules and with cyclobutene, respectively (see Figure 5). The heats of formation and relevant geometric parameters for all the stationary points of this minimum-energy reaction path are given in Table 2.

Comparison of the energy profiles of the two reactions (Figures 2 and 4) shows that, according to the MNDO-CI treatment, both processes may be described in a similar way, *i.e.* as two-step reactions the first step of which is rate-determining, and the intermediates of which can be converted into products through small energy barriers. However, some important differences exist that deserve special comment.

In the first place, the activation energy for the first step of the reaction of acetylene is almost twice the corresponding energy for cyclopentyne (38.1 *vs.* 21.9 kcal mol^{-1}). This fact can be easily explained by the fact that the bond of cyclopentyne which is involved in the reaction is already partially broken in the isolated molecule, as indicated by the C–C bond distance (1.263 Å) and the diradical character predicted for cyclopentyne. The practical consequence is that the new bond between cyclopentyne and ethylene begins to form as soon as the reacting molecules approach within bonding distance; this leads to an early transition state at a C–C distance of 2.258 Å. For the corresponding reaction of acetylene with ethylene, a normal bond must be broken when the molecules interact in order to allow the creation of the new bond. Consequently, the reacting molecules must be much closer to each other before the bonding interaction energetically compensates for the bond-breaking process, as shown by the short C–C distance (1.956 Å) in the corresponding transition state.

It is worth noting that the calculated activation energies are consistent with the experimental conditions required to bring about [2 + 2] cycloadditions of cyclopentyne and acetylene with olefins. Thus, the reactions of cyclopentyne with (*Z*)- and (*E*)-but-2-ene,[11] buta-1,3-diene,[11] 2,3-dihydrofuran,[9] and (*Z*)-1-methoxypropene[12] all proceed quickly below 0 °C; on the other hand (although the comparison between tetrafluoroethylene and ethylene can be somewhat crude) it has been reported that acetylene undergoes a non-catalytic [2 + 2] cycloaddition

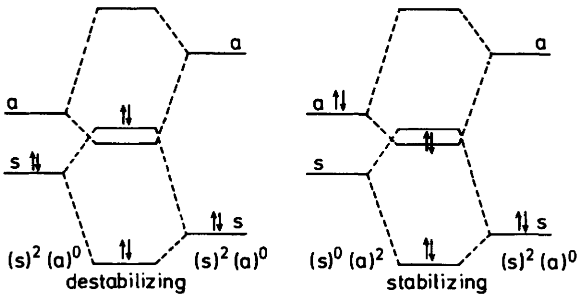

Figure 6. Qualitative PMO diagrams for a planar two-centre/two-centre interaction between a 2π system and the extreme configurations contributing to the description of a species with diradical character

with tetrafluoroethylene[16] when heated to 225 °C; this indicates a large activation energy.

The second important difference between the two reactions lies in the energy changes along the reaction paths, which determine the shape of the corresponding energy profiles. Thus, the release of angular strain in cyclopentyne during cycloaddition is not only reflected in the corresponding ΔH° reaction (-98.6 kcal mol^{-1} for cyclopentyne + ethylene *vs.* -41.4 kcal mol^{-1} for acetylene + ethylene) but also in the unusually low energy level of the diradical intermediate (**4**) relative to the reactant molecules leading to it [ΔH° 15.15 kcal mol^{-1} for (**7**) + (**2**) $\longrightarrow$ (**9**) and -49.15 kcal mol^{-1} for (**1**) + (**2**) $\longrightarrow$ (**4**)].

Finally, a third difference between the reactions relates to the stereochemical course of the cycloadditions. Thus, whereas the initial interaction between acetylene and ethylene takes place with the two molecules arranged almost perpendicular to each other, and this arrangement is maintained even in the corresponding reaction intermediate, the approach between cyclopentyne and ethylene occurs along the whole reaction path with a synperiplanar arrangement of the four interacting atoms. This different behaviour can be rationalized on the basis of the following arguments. The reaction between acetylene and ethylene is a typical example of a [2 + 2] cycloaddition, completely comparable to the extensively studied thermal cycloaddition between two ethylene molecules. According to the Woodward-Hoffman rules,[24] these processes can take place in a concerted way only through a supra-antara geometric approach, but high level *ab initio* molecular orbital calculations on the thermal cyclodimerization of ethylene have shown that this approach involves a very high energy transition state.[25] The reaction must take place, therefore, stepwise, *via* a diradical intermediate. Two different geometric approaches, antiperiplanar and synclinal, seem to be possible but, in any case, the two carbon atoms not directly implicated in the first step of the reaction tend to separate, in order to avoid their mutual destabilizing interaction. In the case of the [2 + 2] cycloaddition of cyclopentyne with ethylene, the planar approach predicted by the calculation can be ultimately ascribed to the diradical character of cyclopentyne. We have represented qualitatively in Figure 6 the PMO diagrams for a planar two-centre/two-centre interaction between a 2π system and both extreme configurations (or molecules having them) contributing to the description of a species with diradical character. As the weight of the (s)^0(a)^2 configuration in the CI wavefunction (*i.e.* the diradical character) increases, the possibility of a stabilizing interaction between molecular orbitals of the same symmetry arises and the net interaction becomes less destabilizing. A limited diradical character can be enough to account for a synperiplanar approach of the reacting molecules, but this does not necessarily have, in principle, any implication for the stepwise or concerted nature of the overall reaction.

The observed stereospecificity of the cycloadditions of cyclopentyne with olefins can be accounted for by the results of our 3 × 3 CI-MNDO study. On the other hand, the calculated reaction profile predicts that the diradical intermediate (**4**), which arises from a very exothermic reaction and must be formed in a high vibrational state, will be extremely short-lived and easily converted into the cycloadduct (**6**) through dissipation of vibrational energy. In any case, the existence of stereospecificity in the cycloadditions of cyclopentyne with particular olefins would rely on a favourable ratio between the rate of cyclization of the intermediate (**4**) and the rate of rotation around the C(1)—C(4) single bond, which would lead to stereorandomization.

Although 3 × 3 CI-MNDO predicts a low activation energy for the cyclization of (**4**), it is difficult to establish a quantitative comparison between the aforementioned processes at this level of theory, since it is known that MNDO, as a result of the overestimation of repulsions between atoms separated by 1.5—2.5 times the length of a normal bond between them, tends to overestimate energetic barriers for bond-breaking and bond-forming processes,[26] whereas energetic barriers for rotation around single bonds are underestimated.*

Conclusions

We have presented in this paper a detailed study at the 3 × 3 CI-MNDO level of the [2 + 2] cycloaddition reaction between cyclopentyne and ethylene. The analogous reaction between acetylene and ethylene has also been studied at the same level in order to provide a reference model. Both reactions are predicted to take place stepwise through a diradical intermediate. Examination of the synchronous concerted supra-supra approach for the reaction of cyclopentyne with ethylene showed that no transition structure exists.

The stereospecificity of the cycloadditions of cyclopentyne with olefins could be, in principle, explained in three different ways: (i) through a concerted supra-antara geometric approach, as pointed out by Gilbert,[12] (ii) through the involvement of an antisymmetric singlet ground state as suggested by Fitjer,[11] and (iii) through a stepwise process involving a very short-lived diradical intermediate.

For geometrical reasons, the [$_\pi2_s$ + $_\pi2_a$] concerted approach appears highly improbable, and very recent MC-SCF *ab initio* calculations on the thermal cyclodimerization of ethylene have shown that such approach is energetically inaccessible. On the other hand, although our calculations predict a symmetrical HOMO for cyclopentyne, the low energy of the antisymmetric LUMO, which is responsible for the diradical character exhibited by this molecule, makes it necessary to take this orbital into account in the calculation of the wavefunction. The fixed synperiplanar conformation maintained along the reaction path can probably be attributed to this fact. However, the preferred explanation for the stereospecificity of the [2 + 2] cycloadditions of cyclopentyne must be, according to our results, the extremely short lifetime predicted for the diradical intermediate which exists on the 3 × 3 CI-MNDO hypersurface.

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* For instance, MNDO predicts a rotation barrier in ethane of 1.0 kcal mol^{-1}, much lower than the experimental value[27] of 2.9 kcal mol^{-1}.

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