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Ab initio Calculations on the Thermal Ring Closure of Acrolein

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The electrocyclic reaction which interconverts acrolein and oxetene is investigated by *ab initio* calculations, using a 4-31G basis set. Like the transition state of the thermal ring closure of cis-butadiene, the transition state of this reaction shows a torsion of about 18° around the central bond, in spite of the absence of H–H repulsion. The resulting oxetene is 43 kcal/mol endothermic with regard to acrolein. The calculated activation energies for ring closure and -opening are 3.4 and 1.0 eV. The conformational result of the ring opening reaction is discussed.

Key words: Acrolein, ring closure of ~ – Oxetene, ring opening of ~

1. Introduction

The thermal ring closure of cis-butadiene to form cyclobutene has a long history of interest, resulting in a number of calculations, the most important of which will be cited here [1a–e]. Van der Lugt [1b] was the first to point out by semi-empirical valence-bond calculations that the allowed (conrotatory) process shows a torsion of 40° around the central bond in the transition state (Fig. 1). Later *ab initio* calculations led to a value of about 20°.

This torsion could have two causes. Primarily, if C_1 and C_4 have to approach each other to form a bond before the methylene-group rotates, which is thought to be the case, the steric repulsion of both inside hydrogen atoms would be very large but for torsion, which allows them to slip one above the other. Secondary, there is a better overlap for the upper lobe of one and the lower lobe of the other carbon π-orbital that are going to be forged together. We wondered about the relative importance of both factors and if this torsion would still occur when the hydrogen-hydrogen repulsion was absent.

Isoelectronic with butadiene is acrolein, $CH_2{=}CH{-}CH{=}O$, missing one of the innerside hydrogen atoms. This compound should be able to perform the same trick as butadiene and undergo ring closure to form oxetene.

2. Calculation

We have performed *ab initio* calculations with the Gaussian-70 program [2][1]. We used the standard extended 4-31G basis set, given by Ditchfield *et al.* [3]. The use of a sufficiently large basis set is necessary, since too restrictive a basis

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[1] We thank Dr. W. J. Hehre for giving us the possibility to use his program before it was released under Q.C.P.E.

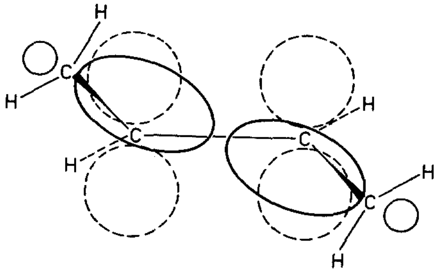

Fig. 1. The transition state for conrotatory ring closure of cis-butadiene

set may lead to even qualitatively incorrect results. The flexibility of our basis set is thought to be sufficient for a valence isomerization and as we expect to be able to estimate the correlation energy differences over the reaction path, the results should be reliable.

A disadvantage in producing a realistic reaction path is the number of variables. The number of degrees of freedom for the complete molecule is given by 3N-6, which for a molecule consisting of 8 atoms totals 18. The 4 first-row atoms can be described by 6 variables: three distances, two angles and one torsion angle. In acrolein R(C1–C2) is short, R(C2–C3) is long and R(C3–O) is short; in oxetene just the opposite is the case. It is not unreasonable to expect that the bond lengths will change their character simultaneously, so that three variables can be described by one parameter: the bond phase γ. It is chosen in such a way that $\gamma = 0$ describes the bond lengths of acrolein and $\gamma = 1$ the bond lengths of oxetene. A justification may be that the intermediates will not without need have a biradical character. This simplification was also used by Hsu *et al.* [1c–e]. Another relation connects the angles of both secondary carbonatoms: these are about 120° in acrolein and about 90° in oxetene. We expect the angles to shrink simultaneously. As the twist energy is quadratically in the twist angle, it will be cheaper in energy to twist two angles a certain amount than one the double amount. The angular decrease now is represented by the second parameter: χ.

The sixth variable is the torsion we would like to investigate; it is given the parameter θ. We now consider the hydrogen atoms. To the methine-hydrogens, which do not play an important role, is given no parameter. The methylene-hydrogens rotate somewhere during the process, and this results in the fourth parameter: ϕ^2. $\phi = 0$ represents the planar acrolein-like system, $\phi = 90$ corresponds to an oxetene-like geometry. The fifth parameter is the methylene flapping angle α which proved to be not unimportant for severely angle-twisted acrolein, due to hydrogen-oxygen repulsion.

For $\theta \neq 0$ and $\phi \neq 0$ the outer methylene hydrogen and the oxygen atom lie both above the plane.

We now have five parameters, representing eight variables. For a matter of convenience we will show where the other ten have gone. All C–H distances are assumed to be 1.090 Å, equal to or near the values of many other calculations and structural data (4 variables).

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[2] In comparison to Hsu *et al.* the definition of ϕ and θ has been interchanged.

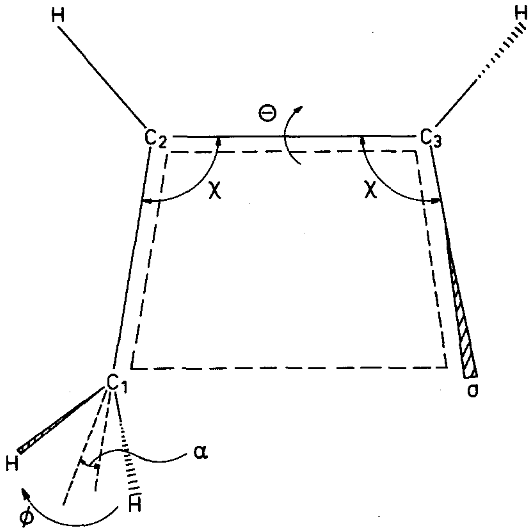

Fig. 2. The parameters used in this calculation. Not shown is the bond phase γ

Each of the methine hydrogens is lying in the plane formed by the carbonatom it is attached to and its both neighbour atoms, and the hydrogen is placed on the outer-bisector of the angle formed by these three atoms (4 variables). This is in accordance with the findings of Hsu *et al.* who originally had the H–C–C angle fixed upon a value of 120° but later found the appreciable effect of optimizing this angle. The carbonatoms apparently have a preferance for a correct hybridisation. The methylene angle is 117° for the sp^2-hybridised C1 of acrolein and 112° for the sp^2-hybridised C1 of oxetene (1 variable). It changes its value simultaneously and monotonically upon methylene rotation. The bisector of the methylene group is lying in the C1–C2–C3 plane (1 variable). Its position upon methylene rotation changes from a certain starting value given by α_0 to an end value in which it is coinciding with the bisector of the C2–C1–O angle, simultaneously and monotonically upon rotation of the methylene group. α_0 was optimized once for every value of χ with $\phi = 0$.

3. Results and Discussion

We investigated the quality of the basis set by energy-optimising the geometry of both acrolein and oxetene. The results are given in Table 1. Resulting bond lengths and -angles are in accordance with chemical intuition and with the structural data of trans-acrolein from Cherniak *et al.* [4].

To the best of our knowledge no structural data have been reported for either oxetene or cis-acrolein. Acrolein exists at room temperature for more than 95 percent in a trans conformation, as reported by Alves *et al.* [5a] and Bair *et al.* [5b]. The most reliable estimate gives trans-acrolein 0.082 eV more stable than cis-acrolein (Cole *et al.* [5c]), although for e.g. 1-amino-acrolein a cis-conformation is preferred (Kvitko *et al.* [5d]).

Table 1

	Acrolein	Parameter	Oxetene
R(C1–C2)	1.337 Å	$=0 \quad \phi \quad =1$	1.539 Å
R(C2–C3)	1.491 Å		1.331 Å
R(C3–O)	1.211 Å		1.422 Å
L C1 C2 C3	121°	$\chi(R)$	89.4°
L C2 C3 O	123.8°		96.7°
R(C–H)	1.09 Å		1.09 Å
(C1C2C3)$*$(H5C1C2)	0°	ϕ	90°
(C1C2C3)$*$(C2C3O)	0°	θ	0°
L H5 C1 H6	117.0°	$fct(\phi)$	112.0°
HCH flapping	− 0.45°	$\alpha = fct(\alpha_0, \phi, \alpha_{90})$	(42.6)°

Table 2

R	γ_{opt}
0	0.0 (def.)
1	−0.009
2	−0.024
3	−0.050
4	−0.107

Conjugation of the double bond is small, but large enough to make cis-acrolein a planar molecule. "Cis"-butadiene is thought to exist in a nonplanar gauche conformation [6a–d]. The calculated ground-state energy for acrolein is −190.47628 a.u., for oxetene −190.40743 a.u. The energy difference of 43.18 kcal/mol is very large compared to the energy difference between cyclobutene and butadiene, which Hsu *et al.* even calculate to be negative in the SCF-phase.

The effective nuclear charge on a 2p-orbital of oxygen is larger than that on a 2p-orbital of carbon: Slater's rules give 4.55 and 3.25 for them respectively. As a consequence the spatial extension of a 2p(O)-orbital is less than that of a 2p(C)-orbital, resulting in smaller bond lengths for O–X, as is very well known. The smaller value of R(C–O) at the opposite of the double bond results in an extra angle strain at the olefinic carbonatoms which is not fully compensated by the lesser angle strain at the aliphatic carbonatom and the oxygen atom. This could be one of the causes of the large energy difference. Another factor is the larger influence of Valence-Bond ionogenic π-structures in acrolein, making it relative more favorable compared to oxetene and butadiene. This larger influence could as well be the driving force to make cis-acrolein a planar molecule. A last remark: due to Hariharan *et al.* [7] it is known that d-functions, absent in our basis set, preferentially lower the energy of the cyclic structures.

The twist of the angles is an obvious choice for reaction coordinate. It brings together the reacting C1 and O atoms, offering the possibility that methylene rotation and bond phase alteration will begin only at a certain starting value of the reaction coordinate. The reaction coordinate R is running from 0 to 6,

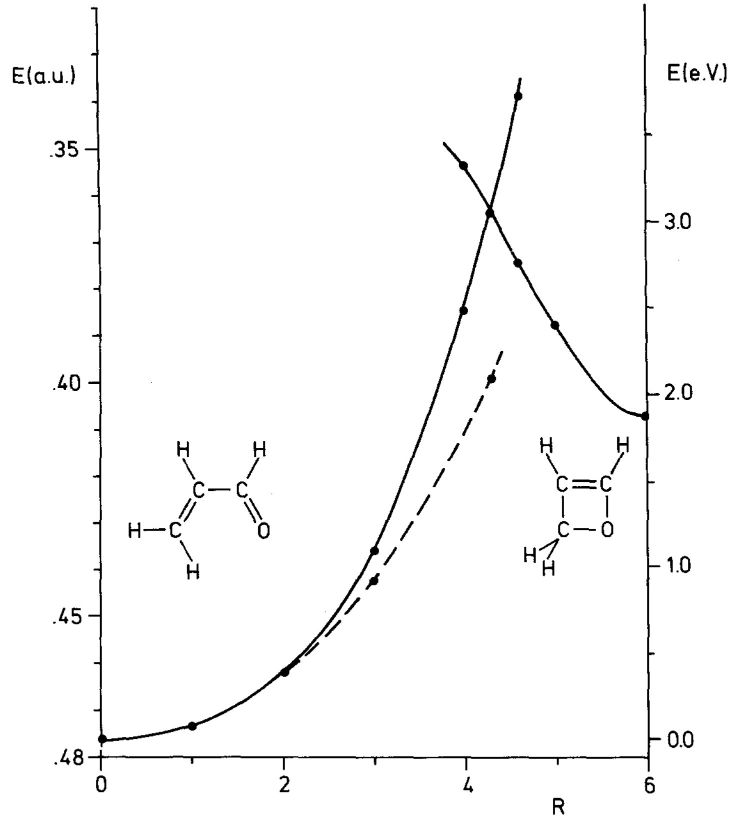

Fig. 3. Energy vs. reactioncoordinate. Curve starting left: acrolein-like molecule. Dotted curve: nonplanar acrolein-like molecule. Curve starting right: oxetene-like molecule

in which $R = 0$ means the angles of the secondary carbonatoms are those found optimal for acrolein (121.0 and 123.8) and $R = 6$ means the corresponding angles are those found optimal for oxetene (89.4 and 96.7). A first exploration of the reaction path shows that up from $R = 2$ the molecule is no longer planar but prefers a gauche- or a trans-conformation. A curious effect can be found for the bond phase in planar acrolein. There seems to be no reason why it should not prepare the alteration by growing smoothly to some value nearer to 0.5. It does not, as is seen in Table 2. The molecule shortens its double and lengthens its single bond. The magnitude of this effect is 0.02 Å, slightly too large to be negligible. It is not impossible that this effect is not shared by all three bonds together but is only undergone by one of them, as there is only one parameter to account for three variables. The energy curves are given in Fig. 3. From $R = 0$ till about $R = 2$ cis-acrolein is planar, only angle twisting occurs here. From $R = 2$ till about $R = 4$ the preferred value of θ is unequal to zero, but if the molecule follows completely the dotted energy curve corresponding to $\theta \neq 0$ trans-acrolein will be formed and the molecule will not be able to undergo ring closure. At or near $R = 4$ θ has to be rather small. Till now the molecule resists to methylene rotation or bondphase alteration. In the region between $R = 4$ and

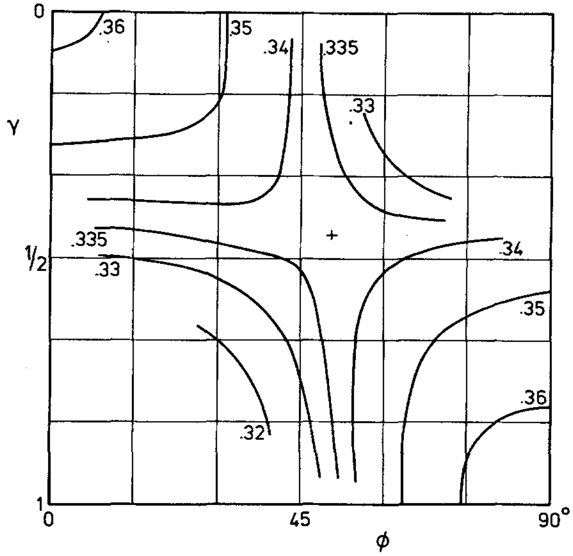

Fig. 4. Energy levels for $R=4.3$ and $\theta=0$

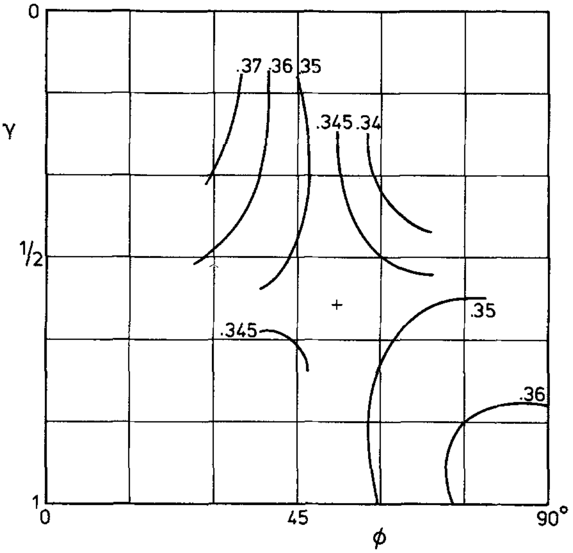

Fig. 5. Energy levels for $R=4.3$ and optimal θ

$R=4.5$ the potential energy curves for strained acrolein and strained oxetene cross, and in this region we must find the transition state. The crossing is characterized by a quick change of ϕ and γ, and possibly of θ. As the least-energy curves are rather steep, it is not likely that the value of R changes much here. From $R=4.5$ till $R=6$ the newly formed oxetene molecule relaxes to its equilibrium geometry.

Table 3. The geometry of the calculated transition state with begin- and final state of the molecule

	Acrolein	Trans. state	Oxetene
R(C1–C2)	1.337 Å	1.45 Å	1.539 Å
R(C2–C3)	1.491 Å	1.41 Å	1.331 Å
R(C3–O)	1.211 Å	1.33 Å	1.422 Å
$\angle$ C1 C2 C3	121.0°	98°	89.4°
$\angle$ C2 C3 O	123.8°	104°	96.7°
ϕ	0°	50°	90°
θ	0° (180°)	18°	0°

Starting at the crossing-point of the curves: $R=4.3$ and keeping $\theta=0$ we calculated a potential surface for γ and ϕ (Fig. 4). As is clear from this picture γ and ϕ change their values together, the molecule passes the transition state approximatively via the diagonal. The saddle point at this surface, marked by a plus-sign (+) is the transition state. The calculated activation energy for the complete reaction is 3.79 eV for ring closure and 1.92 eV for ring opening. If we optimize θ for every value of γ and ϕ, keeping R to its old value of 4.3 still, we calculate the potential surface given in Fig. 5. Still the molecule crosses this region along the diagonal of the picture, but the position of the transition state has changed and the height of it has decreased to 3.50 and 1.63 eV respectively. The left upper part of the surface benefits more from the release of the θ-constraint as θ tends to be fairly large for smaller values of γ and ϕ.

Potential surfaces like this have been constructed for $R=4.0$ and $R=4.6$, too. The characteristics of these are the same as for $R=4.3$. Energies of the lower rightside are higher resp. deeper than for $R=4.3$ and energies of the upper leftside are deeper resp. higher than for $R=4.3$, changing the position of the transition state to the right and down on the diagram for $R=4.0$ and to the left and up for $R=4.6$. The energy values for the transition states that are found this way are higher than for $R=4.3$, but they offer the opportunity to estimate carefully the position of the final transition state, which is found to be near $R=4.4$. The geometry of the calculated transition state is given in Table 3. θ has a value unequal to zero. It means that in this case the orbital overlap factor is decisive for the nonplanarity of the transition state.

The activation barriers are too high: 3.42 and 1.55 eV for ring-closure and -opening.

Another way in which the orbital overlap factor draws attention to its importance is visualized in Fig. 6 in which the optimal value for θ is set out for γ and ϕ at $R=4.3$. θ proves to be almost independent of the bond phase γ but very sensitive to the value of the methylene rotation ϕ. When starting from stretched oxetene the methylene group has been rotated a small amount, the formyl group rotates out of the molecular plane and searches for a position to give the oxygen atom an optimal interaction with the methylene orbital.

The effect of configuration interaction is known from the study of Hsu *et al.* [1e]. They found an energy gain of 0.8 eV for the transition state relative to the cyclic structure and an energy gain of 0.3 eV relative to the olefinic structure in the C.I.-phase. We can apply their Fig. 6 to our molecule. The geometry of our

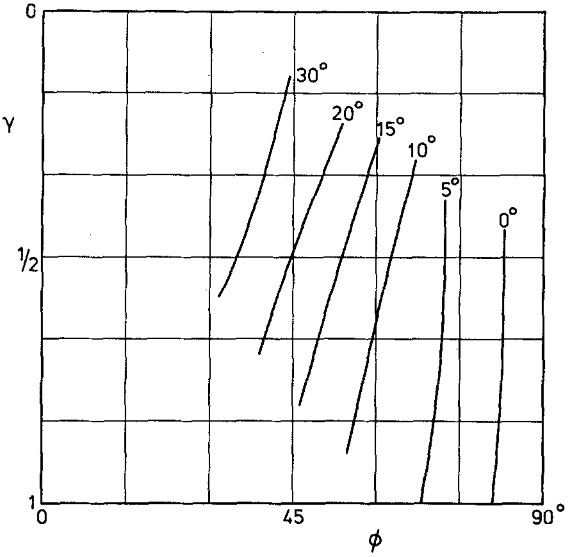

Fig. 6. Optimal values of θ as function of γ and ϕ at $R = 4.3$

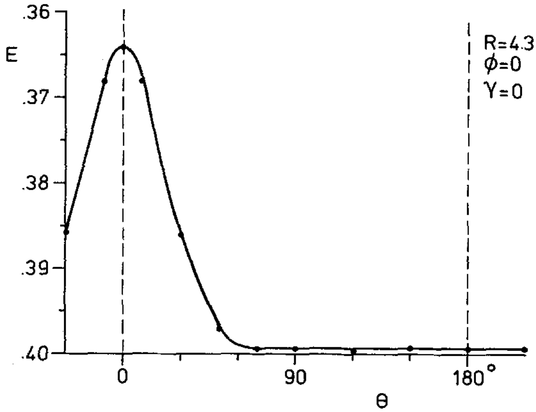

Fig. 7. Energy vs. rotation around the central bond for acrolein near the transition state

transition state is much more cyclic, so relative to oxetene we expect a lowering in the activation energy of roughly 0.5 eV, giving a value for the activation barrier of about 1.0 eV for ring opening. The effect of C.I. upon the activation barrier of ring closure is negligible. It is of importance to note that the configuration interaction describes the same effect in Hsu's study and in ours[3]

Concerning the process of ring opening one question remains unanswered yet: what is the conformation of the end product?

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[3] Hsu *et al.* calculated an activation energy for the thermal valence isomerization of cyclobutene of 2.1 eV, the experimental value is 1.4 eV.

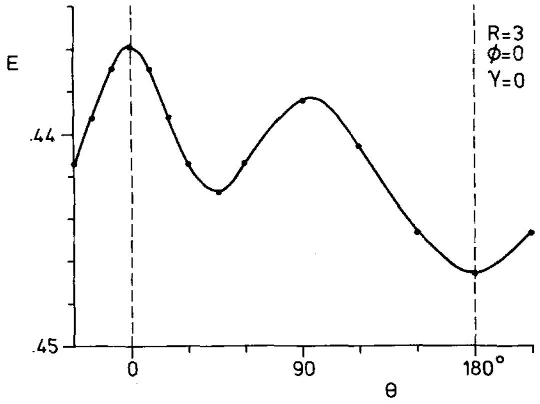

Fig. 8. Energy vs. rotation around the central bond for severely strained acrolein. In relation to Fig. 7 the energy scale has been stretched by a factor 2.5

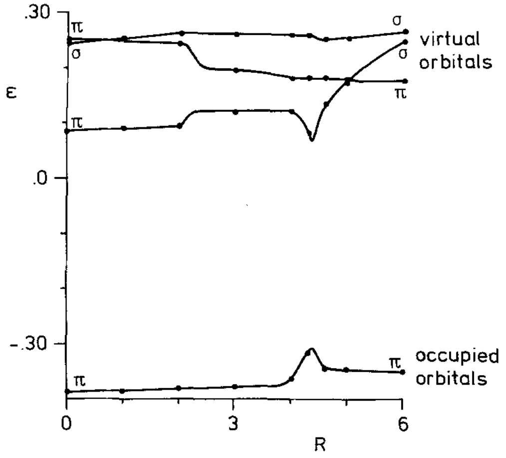

Fig. 9. The orbital energies during the reaction. The subscripts σ and π refer to the symmetry of the orbitals. From $R = 2$ till $R = 4.5$ the molecule has C_1 symmetry

At the transition state θ must be about 18°. For acrolein the energy goes quickly down here for larger θ (see Fig. 7).

For $R = 3$ there exists an energy minimum corresponding to a gauche-like structure (Fig. 8). It is possible that the molecule, if it enters this well, will be able to cross the barrier to yield trans-acrolein; this could particularly be the case in the gas phase. Regarding this aspect of the process Hsu *et al.* state that cis-butadiene will as least occur as an intermediate in the ring opening reaction of cyclobutene, resulting as the end product of the rotational phase of the process. Our reaction shows two differences: the site of the transition state has shifted to the cyclic structure, making a longer part of the traject acrolein-like; and the activation barrier for $R \simeq 3$ to yield trans-acrolein amounts only 3 kcal/mol whereas Hsu *et al.* calculate 11 kcal/mol for the activation barrier near the transition state for their reaction.

Figure 9 shows the behaviour of the orbital energies. Both left- and right-side directed reactions are characterized by a mixing in of the second (or possibly the third) virtual orbital.

In reference to the butadiene reaction there is one difference we have not mentioned yet. Butadiene and cyclobutene have C_{2v}-symmetry, while acrolein and oxetene have only C_s-symmetry. The difference, i.e. the C_2-axis is preserved during the thermal conrotatory butadiene reaction as the methylene groups are thought to rotate simultaneously. The absence of this axis in the acrolein reaction is seen to be irrelevant to the reaction features.

Oxetenes exist and are stable. They are thought to be an intermediate in some reactions [8b, 8c] and tetramethyloxetene was prepared for the first time by Friedrichs and Schuster [8a] who were able to prove its structure. Our activation barrier for ringopening is possibly slightly too high in regard of the thermal instability of the parent molecule, as indicated by Friedrichs *et al.* [8c].

4. Conclusion

Like the cyclobutene reaction the ringopening of oxetene to form acrolein is found to occur in three more or less different steps. The transition state shows a torsion around the central bond despite of the fact that there is no longer a hydrogen-hydrogen repulsion, which can be held responsible for it; this torsion is thus seen to be an orbital effect. The activation barrier is found to be 1.0 eV. For ring closure of acrolein the activation barrier is calculated to be about 3.4 eV. For planar acrolein we found a negative bond phase upon angle twisting. During the second step of the reaction the change in bond phase and the methylene rotation occur simultaneously, while the torsion is dependant exclusively on the methylene rotation. The absence of a C_2-axis in this reaction compared to the ring opening of cyclobutene is found to be of no importance whatsoever.

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