Theoret. Chim. Acta (Berl.) 49, 13–23 (1978)

THEORETICA CHIMICA ACTA

Alternative Paths in the Ring Opening of Oxadiaziridine: the Diimide N-oxide versus the Oxodiimide Rearrangement

An *ab initio* Study

Renzo Cimiraglia, Maurizio Persico
Istituto di Chimica Fisica dell'Università di Pisa, Via Risorgimento, 35, I-56100 Pisa, Italy

Jacopo Tomasi
Laboratorio di Chimica Quantistica ed Energetica Molecolare del C.N.R., Via Risorgimento, 35, I-56100, Pisa, Italy

The ring opening of the oxadiaziridine by cleavage of the N–N bond has been theoretically investigated by SCF calculations improved with limited CI. The possible competition of this reaction with the better known ones (N–O bond cleavage, inversion of the N atom) is discussed. The chemical implications of the formation of a new type of 1,3-dipole are examined.

Key words: Ring opening reactions – 1,3-Dipoles – Diimide N-oxide interconversion mechanisms

1. Introduction

The photochemical and thermal rearrangement processes of the molecular system oxadiaziridine-diimide N-oxide are of noticeable mechanistic interest because they involve a quite large number of different processes: isomerization around a double bond, interconversions between linear open and cyclic closed forms, isomerizations in the three-membered cycle. Some of these mechanisms have been recognized and experimentally studied in different compounds pertaining to the two series of the azoxycompounds and of the oxadiaziridines [1, 2], and recently we have performed on the parent compounds an *ab initio* investigation [3, 4] concerning the inversional and the rotational mechanism ruling the *cis-trans* conversion of the linear form (see scheme 1 in Fig. 1), the mechanism of the photochemical formation (and of the thermal disruption) of the cycle in four different paths (see scheme 2 of Fig. 1), and finally the *cis-trans* isomerization process of the cyclic form, through an inversional path (see scheme 3 of Fig. 1).

0040–5744/78/0049/0013/$02.20

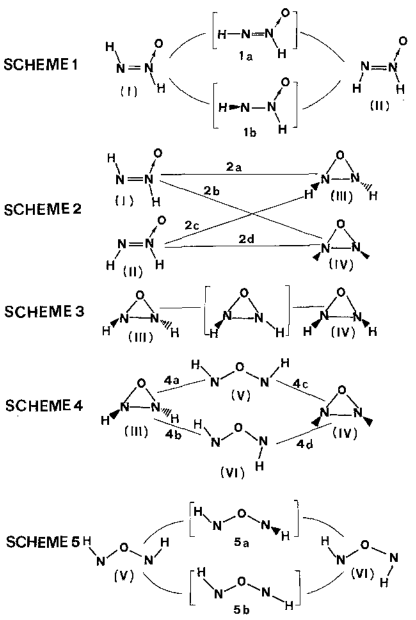

Fig. 1. Diimide N-oxide, oxadiaziridine and oxodiimide and their interconversion mechanisms. Unstable compounds (transition states) have been enclosed in square brackets

In this paper we shall report on other possible transformations of the oxadiaziridine ring, involving a different open isomer, the oxodiimide[1] (structural formulas V and VI in Fig. 1). The oxodiimides, to the best of our knowledge, have never been detected experimentally, but are not devoid of interest because they constitute one of the thus far missing examples of the octet stabilized 1,3-dipoles [5, 6].

We shall examine two different processes; a) the conversion between oxadiaziridines and oxodiimides (scheme 4 of Fig. 1); b) the isomerization process between the (anti,anti)- and (anti,syn)-periplanar forms of HNONH (scheme 5 of Fig. 1). These two processes are in a certain sense symmetric with the processes depicted in schemes 1 and 2 and a parallel examination of all these mechanisms presumably will shed more light on the possible interplay of the different isomers.

2. Computational Procedures and Identification of the Oxodiimide

In analogy with our previous studies we have made use of two basis sets, the STO-3G one [7] and the STO-3G + *sp* one (i.e. a STO-3G basis set supplemented with diffuse *s* and *p* Gaussian functions on the N and O atoms [3]). The STO-3G basis set has been employed to obtain a first guess of the SCF equilibrium geometries, this basis set being more reliable to this purpose than the second one which tends to overestimate the distance between bound atoms (unpublished calculations). In the description of the energy hypersurface we have employed the second basis

---

[1] We shall adopt this name in analogy with the IUPAC name "carbodiimides", attributed to the hypothetical compounds R–N=C=N–R; Huisgen *et al.* [5] refer to this compound as a nitroso imine.

set which was found to give a more balanced description, from the energetic point of view, between open and cyclic structures.

In contrast to the preceding calculations we have focused our attention on the singlet ground state, for reasons which will be discussed later, and of consequence we have considered it sufficient to limit the improvement of the SCF description to a small CI mixing.

The SCF calculation on the STO-3G basis leads one to recognize that HNONH is a stable molecule, with respect to dissociation into fragments[2] as well as to the ring closure. The molecule is planar and two conformations are possible (V and VI). The geometries, the total energies and the stabilization energies are reported in Tables 1 and 2. It may be remarked that the difference in energy between the two forms is quite small but the elimination of some constraints we have introduced in determining the geometry of VI (which is less important than structure V in the dynamics of this system) could make this form decidedly more stable than the other.

The planarity of the molecule indicates that there are at least three valence structures which play an important role in the description of the ground state wavefunction:

$$\mathrm{HN{=}\overset{+}{O}{-}\overset{-}{N}H} \qquad \mathrm{H\overset{-}{N}{-}\overset{+}{O}{=}NH} \qquad \mathrm{H\dot{N}{-}O{-}\dot{N}H}$$

A B C

A and B are ionic in character, C is diradicalic. In the MO scheme the procedure equivalent to the mixing of structures A, B and C is given by the interaction of two closed-shell configurations, π_+^2 and π_-^2 with a single excitation open-shell configuration $\pi_+\pi_-$; here π_+ and π_- are two molecular orbitals in which the p_π orbitals of the N atoms enter respectively with equal and opposite sign.

In the STO-3G+*sp* calculations we have therefore supplemented the SCF calculations with a 3×3 CI corresponding to these three configurations. The energy lowering of the lowest singlet state is considerable (about 30 kcal/mol, see Table 2); in the singlet ground state of the molecule (V) the relative weights of the configurations π_-^2 and π_+^2 are 0.8677 and 0.1323 (the coefficient of $\pi_+\pi_-$ in this state is zero for symmetry reasons).

Because the energies of the oxadiaziridines (III) and (IV) are only slightly affected by a limited CI (it does not matter what configurations are included in this type of calculation), this procedure decreases probably by too large a factor the difference

---

[2] To give an idea of the energies involved in the dissociation of the oxodiimide, we report the energy of a possible couple of fragments, NH ($^1\Delta$ state) and HNO ($^1A'$ state): the fragments lie about 43 kcal/mol higher in energy than the undissociated molecule, at the SCF-STO-3G level. If one considers the dissociation in NH ($^3\Sigma^-$) and HNO ($^3A''$) (still allowed by the spin conservation rule), it is experimentally known that the energy required is about 18 kcal/mole less than that of the above process.

Table 1. Geometrical parameters of oxadiaziridines and oxodiimides[a]

	$R_{N'O}$	$R_{N''O}$	$R_{N'H'}$	$R_{N''H''}$	$\widehat{N'ON''}$	$\widehat{H'N'O}$	$\widehat{H''N''O}$	α[b]	β[c]
Trans-oxadiaziridine	1.439	1.439	1.058	1.058	61.6°	104.5°	104.5°	82.7°	82.7°
Cis-oxadiaziridine	1.439	1.439	1.061	1.061	61.8°	104.5°	104.5°	78.9°	78.9°
(ap,ap)-oxodiimide	1.320	1.320	1.063	1.063	117.0°	99.6°	99.6°	0°	0°
(ap,sp)-oxodiimide[d]	1.320	1.320	1.063	1.063	119.1°	99.6°	102.7°	0°	0°

[a] Bond lengths in Å.

[b] Dihedral angle between the plane of N'ON'' and that of ON'H'.

[c] Dihedral angle between the plane of N'ON'' and that of ON''H''.

[d] H' indicates the syn periplanar hydrogen atom, H'' the anti periplanar one.

Table 2. Total energies of oxadiaziridines and oxodiimides, ground state, in atomic units

	STO-3G SCF	STO-3G+*sp* SCF	3×3 CI	CIPSI	4-31G SCF
Trans-oxadiaziridine	−182.36201	−182.51939	−182.51983	−182.85046	−184.41410
Cis-oxadiaziridine	−182.35053	−182.50432	−182.35062	—	—
(ap,ap)-oxodiimide	−182.26422	−182.45873	−182.51103	−182.82585	−184.36730
(ap,sp)-oxodiimide	−182.26880	−182.45884	−182.50718	—	—

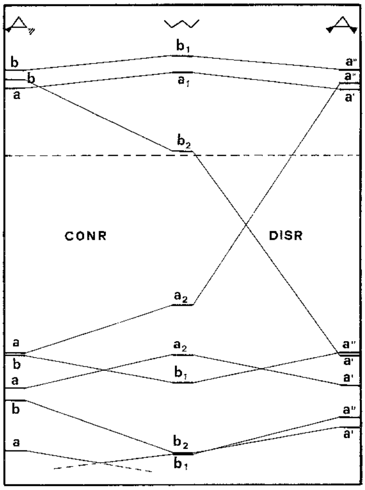

Fig. 2. Molecular orbital correlation diagram for the closure of (ap,ap)-oxodiimide. The molecular orbitals have been labelled with the correct symbols pertaining to the full symmetry groups of each molecule

in energy between open and closed forms with respect to the SCF estimates. As a consequence it is necessary to resort to larger CI calculations to have a better estimate of the difference in energy.

It is difficult to coherently evaluate the gain in energy one might obtain by performing large CI calculations on limited basis set SCF wavefunctions of compounds having such a different electronic structure as in the case of oxodiimides and oxadiaziridines, because contributions due to correlation effects are mixed with contributions arising from the deficiencies of the basis set to reach the HF level. Our best estimate is derived from a CIPSI calculation [8] performed on the STO-3G+*sp* wavefunctions of (V) and (III) which gives, for compound (V) a gain of energy $\Delta E = -0.3671$ a.u. obtained as a sum of a diagonalization energy in a subspace S_0 of 23 determinants ($\Delta E_d = -0.0924$ a.u.) and a perturbation energy made with the contributions of about 180.000 determinants ($\Delta E_p = -0.2747$ a.u.), while for compound III the values are $\Delta E = -0.3311$, $\Delta E_d = -0.0077$ (S_0 includes 3 determinants), $\Delta E_p = -0.3233$ (calculated over 49.000 determinants). In both calculations the parameter η, the threshold below which the coefficients of the configurations are excluded from the CIPSI zero space, has nearly the same value, $\eta = 0.028$. According to these calculations the oxodiimide (VI) is about 17 kcal/mol higher in energy with respect to the *trans* oxadiaziridine (III).

Also the extension of the basis set influences the energy difference. In general the minimal bases favour the cyclic structures; this effect is quite evident at the SCF level and is only partially corrected by CI calculations. Also in the present case, an enlargement of the basis set produces a lowering of the energies of (V) and (VI) larger than that of (III) and (IV). To show this effect of the basis set we have added in Table 2 to the SCF energies obtained with the STO-3G and the STO-3G+*sp* bases also the ones obtained with the 4-31G one.

In Table 3 we have reported the electronic gross charges on the oxygen and on the NH groups, separating the σ and π contributions, as calculated by 3 × 3 CI in the

Table 3. Group charges (electrons) in the oxodiimide, the diimide N-oxide and the oxadiaziridine[a]

		(ap,ap)-oxodiimide	*trans*-diimide N-oxide	*trans*-oxadiaziridine
N'H'[b]	σ	6.7148	6.9010	—
	π	1.2498	1.2433	—
	total	7.9646	8.1443	7.8395
N"H"	σ	6.7148	6.1082	—
	π	1.2498	1.2262	—
	total	7.9646	7.3344	7.8395
O	σ	6.5703	6.9909	—
	π	1.5004	1.5304	—
	total	8.0707	8.5213	8.3209

[a] SCF plus 3 × 3 CI calculations in the STO-3G+*sp* basis set.
[b] In the diimide N-oxide N" is the nitrogen bound to the oxygen atom.

STO-3G+*sp* basis. The results of Table 3 refer to the (ap,ap)-oxodiimide and are compared with those obtained for the diimide N-oxide and the oxadiaziridine. As the valence structures A and B suggest, in both the open forms the central atom is more positive (or less negative) than in the oxadiaziridine.

A last point about the structure and energy of the oxodiimide concerns the relative position of the lower triplet state. At the geometry (V), a CIPSI calculation, analogous to that performed for the singlet state, gives for T_1 an energy of -182.7599 a.u., about 40 kcal/mol higher than S_0. In the most simplified description of the electronic structure of the 1,3-dipoles, the T_1 state is represented by only one valence structure (diradicalic), while the lowest singlets are mixtures of the three structures shown above; thus it seems correct to compute the energy of T_1 as a single rigid excitation, and compare it with the result of the 3 × 3 CI for S_0; in this approximation, T_1 turns out to be about 21 kcal/mol higher in energy than S_0. As we shall observe later on, in the present context we are not interested in mechanisms involving excited states, so we have not reported the energy curves for the triplet.

In both stable conformers of oxodiimides the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) are of π_- and π_+ type (according to the notation stated above). For molecules of this kind the Woodward and Hoffmann rules predict a thermally allowed closure through a conrotatory path, the disrotatory closure being forbidden. The MO correlation energy diagrams for the two closure paths of the oxodiimide (V) are shown in Fig. 7. The symmetry considerations of the W.-H. rules are strictly applicable only to (VI) which has a symmetry element in common with the *trans*-oxadiaziridine (a C_2 axis) and with the *cis* oxadiaziridine (a mirror plane), but the similarity in the electronic structure of the two conformers of the oxodiimide molecule allows one to extend the same predictions to the ring closure mechanisms of (VI). It may be remarked that according to these predictions interconversion is easier between III and V (path 4a in Fig. 1) and between IV and VI (path 4d in the same figure); since a mechanism connecting the two forms of the oxadiaziridine molecule via a unique conformer of the oxodiimide is formally forbidden, it is of some interest to examine whether one of the interconversion mechanisms between V and VI, of rotational and inversional type (see scheme 5 in Fig. 1) is possible.

We have estimated the barriers present along the paths 4a, 4b, 4c, and 4d by means of 3 × 3 CI calculations performed on the basis of STO-3G+*sp* SCF calculations. Along the reaction coordinate connecting cyclic and linear structures, we have linearly varied the following geometrical parameters: a) the N–O and the N–H bond lengths, b) the $\widehat{\mathrm{NON}}$ bond angle, c) the $\widehat{\mathrm{ONH}}$ bond angles, and d) a conrotatory (or disrotatory) angle for each H atom, defined as the dihedral angle between the planes identified by the NON and ONH groups of nuclei.

An exploratory examination of the two-dimensional sheet of the potential energy hypersurface corresponding to the geometrical parameters b and d (the $\widehat{\mathrm{NON}}$ bond angle and the rotational angle of the NH groups) indicates that the position of the barrier on the paths 4a and 4c is not too far from that obtained by introducing the constraint of linear and simultaneous variation of these two parameters. For example, starting from V there is a valley towards III corresponding to a conrotatory motion at a fixed $\widehat{\mathrm{NON}}$ angle which however bends approximately in the middle of the permitted range of variation of the rotational angle and reaches the saddle point at approximately the same position obtained with the above mentioned constraints.

The results are shown in Fig. 3a, b. It appears that the W.-H. predictions are respected.

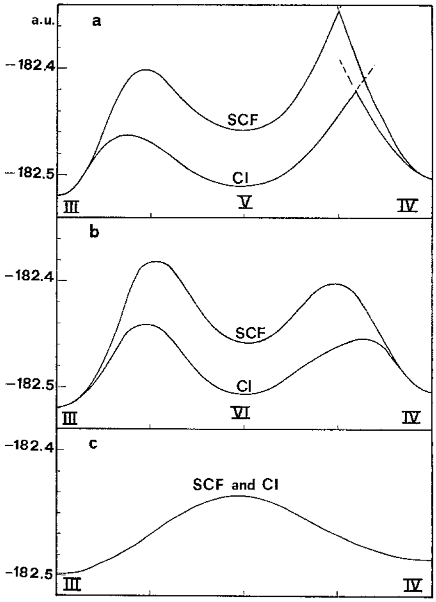

Fig. 3. Energy curves for different paths from *trans*-oxadiaziridine to *cis*-oxadiaziridine.

a) paths 4a and 4c (*trans*-oxadiaziridine → (ap,ap)-oxodiimide → *cis*-oxadiaziridine).
b) paths 4b and 4c (*trans*-oxadiaziridine → (ap,sp)-oxodiimide → *cis*-oxadiaziridine).
c) path 3 (inversion of the oxadiaziridine)

The shape of the curve corresponding to the disrotatory path 4c in Fig. 3a deserves a few words of comment. If one classifies the orbitals of (IV) and (V) according to the only symmetry element maintained in this conversion process (i.e. the reflection plane) the electronic configurations of the two molecules can be written:

cis-oxadiaziridine	(IV)	$\ldots 6a^2\ 3b^2\ 7a^2\ 8a^2\ 4b^2$
(ap,ap)-oxodiimide	(V)	$\ldots 3b^2\ 6a^2\ 4b^2\ 7a^2\ 5b^2$

Clearly the orbitals determined by the SCF process at intermediate geometries will be different in the two cases, because the ratios of occupied/virtual manifolds in the a and b subspaces are different. A limited CI can eliminate this drawback and the energy curve assumes the shape shown in Fig. 3a. Experience on analogous cases suggests that more accurate treatments can lower the height of such a barrier at least by 10 kcal/mol.

To facilitate a comparison with an alternative path connecting the *trans* and the *cis* form of oxadiaziridine we report in Fig. 3a the energy profile for the path connecting (III) and (IV) via a semiplanar form of oxadiaziridine (path 3 of Fig. 1). It may be remarked that the 3 × 3 CI calculations do not alter significantly the SCF curve: for the cyclic semiplanar transition form the considerations made above about the relatively low effect of a limited CI treatment in improving the energy of the oxadiaziridines still hold. The interested reader can find in a preceding paper [3] an appreciation of the same barrier made with a larger CI.

The last interconversion processes we have examined regard the mutual interconversion of the two forms of the oxodiimide molecule. Scheme 5 of Fig. 1 collects two different mechanisms. Our calculations are rather crude because we have kept fixed all the parameters, with the obvious exception of the rotational angle of a NH group around the N–O bond in the first case (path 5a) and of the angle $\widehat{ONH}$ corresponding to an inversion at the N atom (path 5b). The corresponding curves are reported in Fig. 4. The height of the rotational barrier indicates that in the oxodiimide the N–O bond has a noticeable character of double bond (the population analysis, and the direct inspection of the molecular orbital charge

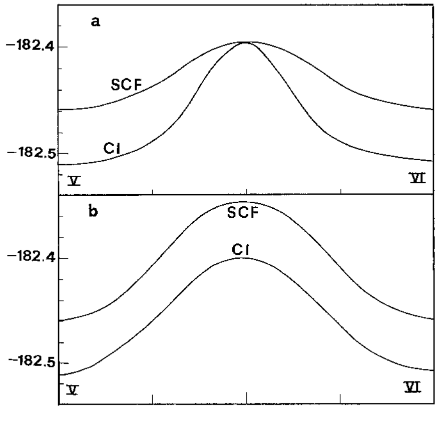

Fig. 4. Energy curves for the conversion between anti,anti and anti,syn periplanar oxodiimide.
a) path 5a (rotation).
b) path 5b (inversion)

distributions confirm this feature) and consequently such rotational mechanism can be compared with the corresponding isomerization processes of the diimide and the diimide N-oxide molecules where the rotation produces the disruption of a formal double bond. In both cases it was found [4, 9] that the elongation of the bond interested in the rotation produces a notable lowering of the barrier. Apart from the geometrical factors, it may be remarked that the rotational intermediate is quite insensitive to the 3 × 3 CI processes. An analogous situation has also been found for the rotational intermediate of the diimide N-oxide, and in that case a larger CI calculation lowered the barrier by about 20–25 kcal/mol.

The energy curves for the inversional mechanism 5b are shown in Fig. 4. The SCF barrier and the 3 × 3 CI one are nearly the same, and both are higher than that calculated by SCF for the rotation about the double bond. Owing to the above considerations about the effect of our limited CI on the rotational barrier, we think that really this barrier is lower than the inversional one.

3. Concluding remarks

We present in Fig. 5 an overall view of the interconversion paths of the system diimide-N-oxide-oxadiaziridine-oxodiimide with the values of the thermal barriers taken from this paper and the preceding ones.

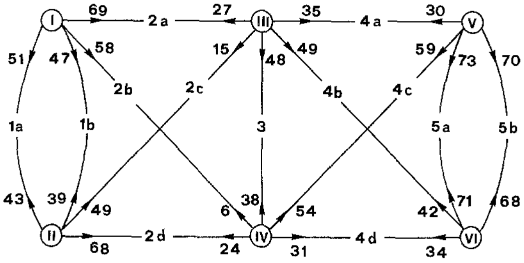

Fig. 5. Overall scheme of the thermal isomerizations in the system: diimide N-oxide, oxadiaziridine, oxodiimide. The energy barriers in both directions of each reaction have been reported in kcal/mol

The numerical values reported in this figure must be used with some caution because they are not obtained to the same degree of accuracy. The main reason for the differences in accuracy is due to the degree of optimization of the geometries corresponding to the barriers, which is higher in the left portion of the diagram concerning the conversion mechanisms between diimide N-oxide and oxadiaziridine.[3] In fact the experience gained in the examination of the diimide N-oxide-oxadiaziridine system indicates that an optimization of all the geometrical para-

---

[3] It should not be forgotten what has been repeated several times in the text, namely that the use of a limited CI in the right portion of the diagram of Fig. 5 can have produced some spurious effects on the relative height of some barriers, and that the limitation of the basis set influences to some extent the ratio of the energies of the closed and open forms. In effect the three factors, quality of the basis set, accuracy of the procedure to get the wavefunction and degree of optimization of the geometries are closely connected, and a completely coherent and reliable description of all the molecular processes of the system here considered should require quite exacting calculations.

meters for the transition states leading to the oxodiimides should lower substantially the corresponding barriers.

Keeping in mind these considerations, one may try to comment on the results. Let us consider for example a *trans* oxadiaziridine, a stable compound which can be obtained photochemically from the corresponding azoxy compound [1, 2]. Provided that it has sufficient internal energy there are three thermal isomerization channels with non-negligible probability. The first two correspond to the cleavage of a N–O bond with formation of *cis* or *trans* diimide N-oxide. The third leads to the formation of the (ap,ap)-oxodiimide (V). It was already remarked that the barrier reported in Fig. 5 (35 kcal/mol) is surely overestimated; it may be added that substitution of the hydrogens with electron-withdrawing groups like $-CH_2OR$, –C(O)–OR, $-CH_2-O-C(O)R$, $-CH_2X$ should stabilize the 1,3-dipole, which carries negative charges on the N atoms (see Table 3); this kind of substituent should also lower the barrier.

What about the fate of (V) after its formation from the oxadiaziridine? We have already said that structure (V) corresponds to a hole in the energy hypersurface, but the barriers with respect to dissociation in fragments are not high; and an increase of its internal energy probably will produce only quite limited amounts of (VI) or of (IV). The only net outcome of this mechanism can be the formation of a new stable compound via the reaction with some reactant, for example a dipolarophile.

The idea that it could be possible to obtain RN–O–NR compounds starting from azoxycompounds was first advanced by Greene and Hecht [1]: the tests they made with dipolarophiles as reagents did not give any evidence for the presence of 1,3-dipoles. However, it must be remarked that these authors, being only interested to prove whether the structure of their photoproduct was like (III) or like (V), only made a limited set of tests at room temperature. There is the possibility that at a somewhat higher temperature or with suitable substituents the channel from *trans* oxadiaziridine to the (ap,ap)-oxodiimide may be open.

Returning now again to the scheme of Fig. 5, it appears that the possibility of obtaining an oxodiimide via the *cis* form of an oxadiaziridine (IV) is smaller. The *cis* oxadiaziridines are unstable products (to the best of our knowledge not a single one has been yet separated) and their main possibility of existence is as transient forms in the photoreactions of the azoxy compounds.

We have not considered in this paper the possible photochemical behaviour of the oxodiimides. A photochemical preparation of such compounds, both in singlet or triplet states, is of scarce practical interest because the oxadiaziridines normally absorb in the vacuum-UV. A study of the photochemical fate of HN–O–NH is surely of remarkable mechanistic interest, but it is probable that the main channel will lead to dissociations, and this argument lies decidedly apart in our present investigation scheme which is centred on the intramolecular conversion mechanisms.

References

1. Greene, F. D., Hecht., S. S.: J. Org. Chem. **35**, 2482 (1970)
2. Taylor, K. G., Isaac, S. R., Swigert, J. L.: J. Org. Chem. **41**, 1146 (1976)
3. Cimiraglia, R., Persico, M., Tomasi, J.: J. Phys. Chem. **81**, 1876 (1977)
4. Cimiraglia, R., Persico, M., Tomasi, J.: Chem. Phys. **24**, 251 (1977)
5. Huisgen, R., Grashey, R., Sauer, J., in: The chemistry of alkenes, S. Patai, Ed., p. 739. London: Interscience (1964)
6. Huisgen, R.: J. Org. Chem. **33**, 2291 (1968)
7. Hehre, W. J., Stewart, R. F., Pople, J. A.: J. Chem. Phys. **51**, 2657 (1969)
8. Huron, B., Malrieu, J. P., Rancurel, P.: J. Chem. Phys. **58**, 5745 (1973)
9. Cimiraglia, R., Riera, J., Tomasi, J.: Theoret. Chim. Acta (Berl.) **46**, 223 (1977)

Received October 4, 1977