Mechanism of the Wolff Rearrangement. V. Semiempirical Molecular Orbital Calculations on α-Diazo Ketones, Oxirenes, and Related Reaction Intermediates

I. G. Csizmadia,[1a] H. E. Gunning,[1b] R. K. Gosavi,[1b] and O. P. Strausz*[1b]

Contribution from the Departments of Chemistry, University of Toronto, Toronto, Ontario, and University of Alberta, Edmonton, Alberta. *Received April 4, 1972*

Abstract: An extended Hückel molecular orbital study has been made on diazoethanone, 3-diazo-2-propanone, 2-diazo-3-propanone, 3-diazo-2-butanone, their decomposition products, the oxirenes, ketenes, and related intermediates. From computed MO and state energies together with symmetry correlations it is concluded that the thermal decomposition of diazo ketones follows the reaction path: $RCOCN_2R' \rightarrow N_2 + RCO\ddot{C}R' \rightarrow {}^{-}|\overline{\underline{O}}CR{=}C^{+}R' \rightarrow O{=}C{=}CRR'$. The oxirene state lies above the transition state of the ketene forming step and can only be reached in photochemical excitation where rearrangement of the zwitterion to oxirene can effectively compete with ketene rearrangement. Therefore, the intervention of oxirene in the photochemical and its absence in the thermal Wolff rearrangement of diazo ketones is attributed to the difference in excess vibrational energy of the ketocarbene or its tautomeric zwitterion, from the two modes of excitation. Oxirene and its simple methyl derivatives are inherently unstable with respect to C–O bond cleavage and they are predicted to exist only as short-lived transients. The decomposition sequences of thermally, photolytically, and chemically activated ketenes are also discussed in relation to the role of oxirene intermediates.

Recent experimental studies on the photochemical behavior of α-diazo ketones, α-diazo esters, and ketenes yielded firm evidence for the long-debated existence of unsaturated epoxides, the family of oxirenes.[2] It is now well established that the photochemical decomposition of these molecules involves the oxirene structure as a short-lived transient. The thermolysis of these molecules, on the other hand, which in most cases leads to the same final products, proceeds *via* a different reaction path bypassing the oxirene structure.

As experimental data accumulated, it became increasingly evident that an unambiguous mechanistic interpretation of the results would not be possible without the aid of detailed quantum mechanical studies. For this reason we have undertaken a semiempirical LCAO–MO study, within the framework of extended Hückel molecular orbital (EHMO) theory,[3] of a number of α-diazo ketones, their decomposition products the ketocarbenes, oxirenes, ketenes, and some of the connecting reaction surfaces.

Results and Discussion

Data on the molecular geometry of diazo ketones and the various intermediates are not available and it was necessary to use estimated values for the geometrical parameters. The Slater-type atomic orbital exponents[4] and Coulomb integral[5] values were taken from the literature.

State energies were calculated for the ground and lower lying excited states of diazoethanone, α-diazopropanone, and α-diazobutanone along with those of their related decomposition products, the carbenes, zwitterions, oxirenes, and ketenes. The data are presented in Figures 1–3. Since the EHMO method does not take configuration interaction into consideration, the calculated energy levels of open-shell species represent average values of singlet- and triplet-state energies. In the following discussion it will be assumed that the singlet–triplet splitting in these molecules is approximately 30 kcal/mol, placed symmetrically above and below the EHMO levels, respectively.

The computed energy differences for the geometrical conformers of the ground-state diazo ketones and the energy barriers for their interconversion are given in Table I in comparison with the experimental data available from the literature.[6] The agreement appears to be satisfactory.

Table I. Relative Energies of α-Diazo Ketone Conformers

	Activation energy		
	Cis → trans	Trans → cis	ΔE, trans–cis
α-Diazoethanone	19.6	20.7	−1.1 (0.4 expl)[6]
3-Diazo-2-propanone	15.1 (15.5 expl)[6]	14.7	0.4 (0.8 expl)[6]
2-Diazo-3-propanone	18.0	18.7	−0.7
2-Diazo-3-butanone	14.4	9.7	−4.7

Recently Piazza and coworkers[7] have determined the dipole moment of 3-diazo-2-propanone as 3.37 D and calculated the dipole moments of the cis and trans conformers as 3.93 D and 1.76 D, respectively. The computed values of the dipole moments from the present calculations, cis 4.03 D and trans 1.73 D, compare favorably with the values of Piazza, *et al.* Similarly the computed dipole moments for ketene and dimethyl-

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(1) (a) University of Toronto; (b) University of Alberta.

(2) J. Fenwick, G. Frater, K. Ogi, and O. P. Strausz, *J. Amer. Chem. Soc.*, **95**, 124 (1973), and references therein.

(3) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

(4) E. Clementi and D. L. Raimondi, *ibid.*, **38**, 2686 (1963).

(5) O. P. Strausz, R. J. Norstrom, D. Salahub, R. K. Gosavi, H. E. Gunning, and I. G. Csizmadia, *J. Amer. Chem. Soc.*, **92**, 6395 (1970), and references therein.

(6) F. Kaplan and G. K. Meloy, *ibid.*, **88**, 950 (1966).

(7) G. Piazza, S. Sorriso, and A. Foffani, *Tetrahedron*, **24**, 4751 (1968).

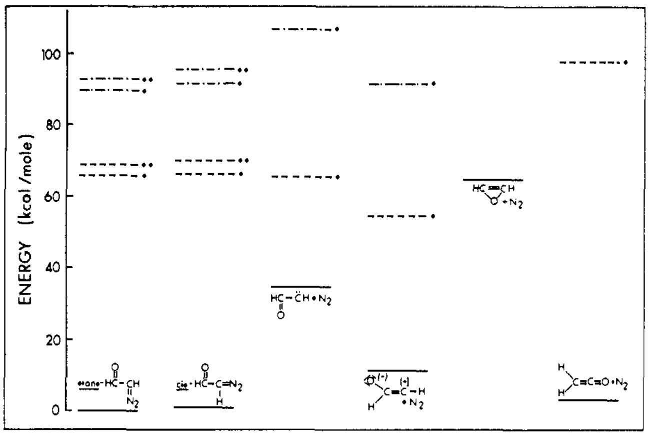

Figure 1. Relative EHMO state energy levels for *trans-* and *cis-*diazoethane, formylmethylene, its isomeric zwitterion, oxirene, and ketene.

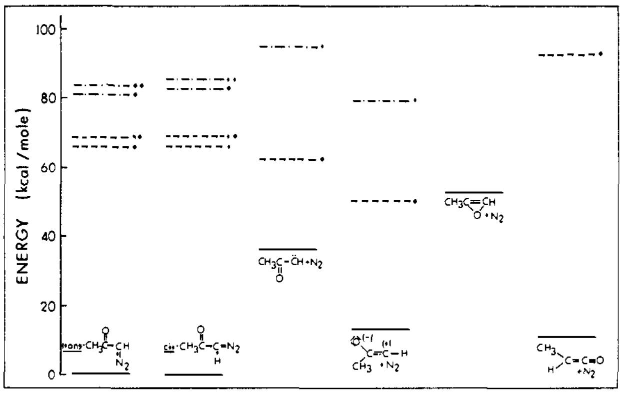

Figure 2. Relative EHMO state energy levels for *trans-* and *cis-*3-diazo-2-propanone, acetylmethylene, its isomeric zwitterion, methyloxirene, and methylketene. The corresponding results for 2-diazo-3-propanone are not indicated.

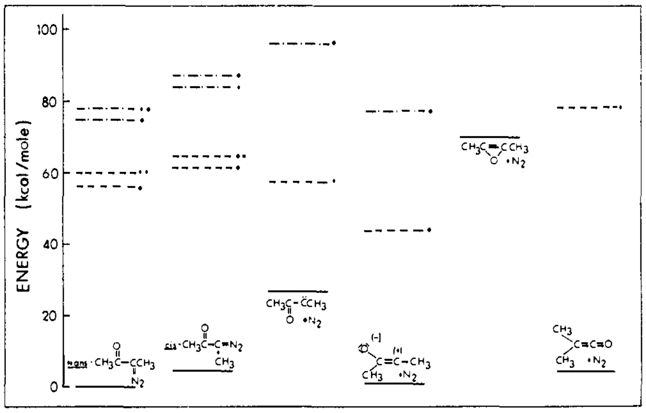

Figure 3. Relative EHMO state energy levels for *trans-* and *cis-*3-diazo-2-butanone, methylacetylmethylene, its isomeric zwitterion, dimethyloxirene, and dimethylketene.

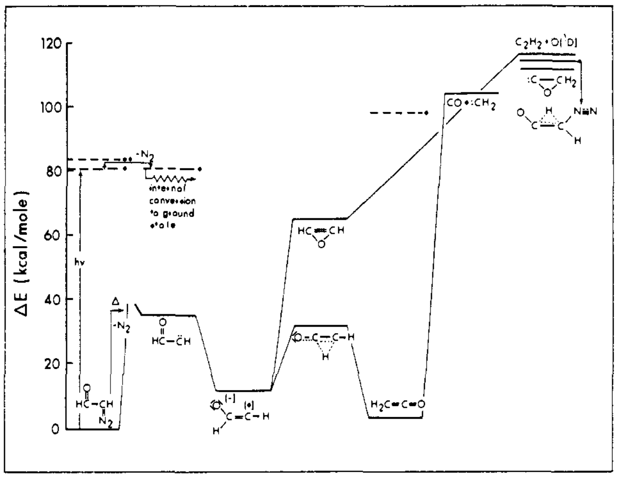

Figure 4. Calculated enthalpy change for the decomposition of diazoethanone.

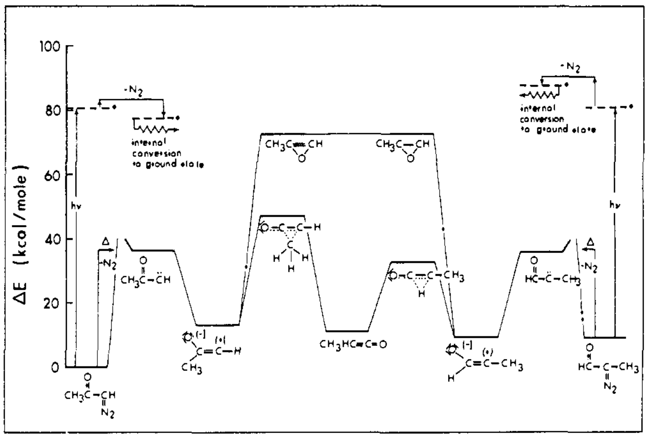

Figure 5. Calculated enthalpy change for the decomposition of α-diazopropanones.

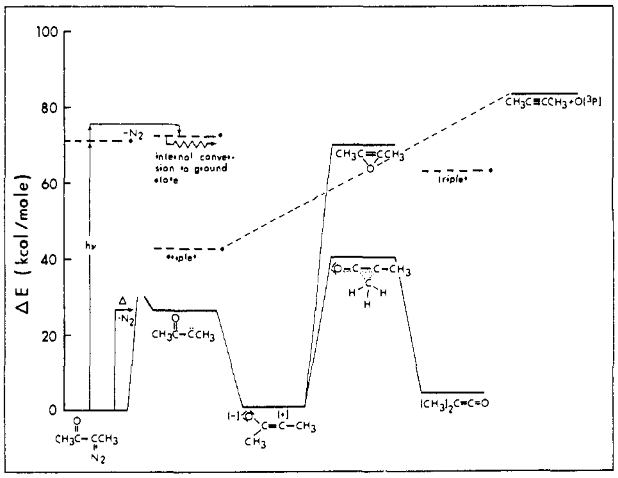

Figure 6. Calculated enthalpy change for the decomposition of 3-diazo-2-butanone.

ketene, 1.81 D and 1.48 D, are in satisfactory agreement with the experimental values of 1.52 D and 1.85 D.[8]

Enthalpy changes were estimated from the computed state energy levels for the various modes of decomposition of the diazo ketones. These are shown graphically in Figures 4–6. The solid lines connecting the relative state energies represent symmetry allowed reaction paths (*vide infra*). It is seen from Figure 4 that the decomposition of diazoethanone to nitrogen and formyl methylene is endoenergetic by ~35 kcal/mol. Since in the transition state the $\cdots N{\equiv}N$ linkage may

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[8] A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman, San Francisco, Calif., 1963.

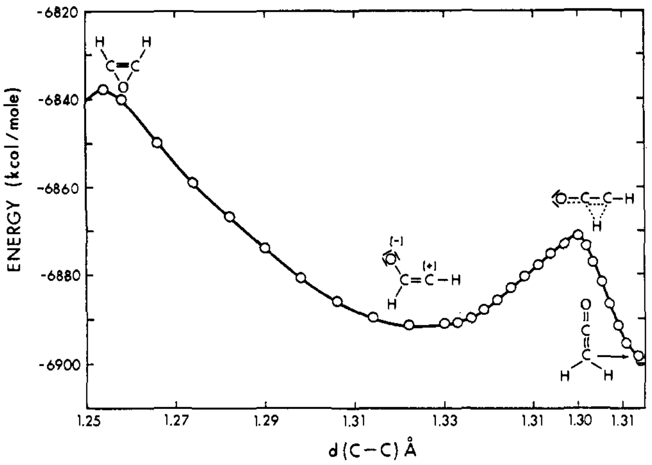


Figure 7. Reaction profile for the transformation oxirene ↔ zwitterion ↔ bridged intermediate ↔ ketene.

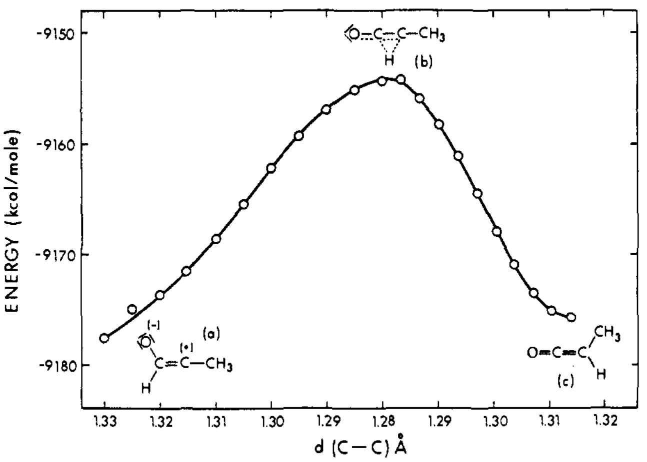


Figure 9. Reaction profile for the zwitterion (a) ↔ cyclic intermediate (b) ↔ methylketene (c) transformations.

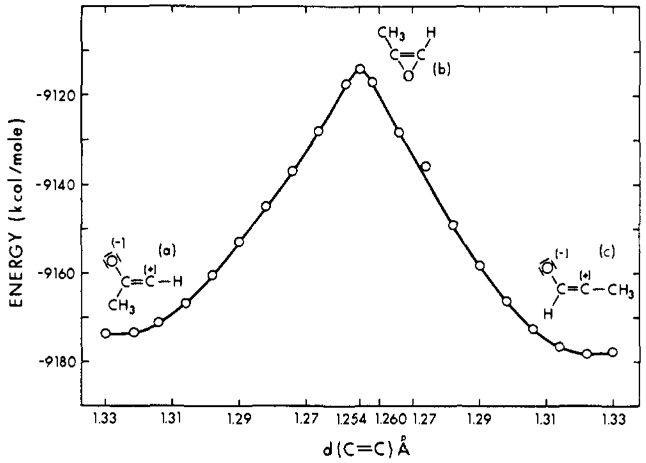


Figure 8. Reaction profile connecting methyloxirene with the two isomeric zwitterions (a and c).

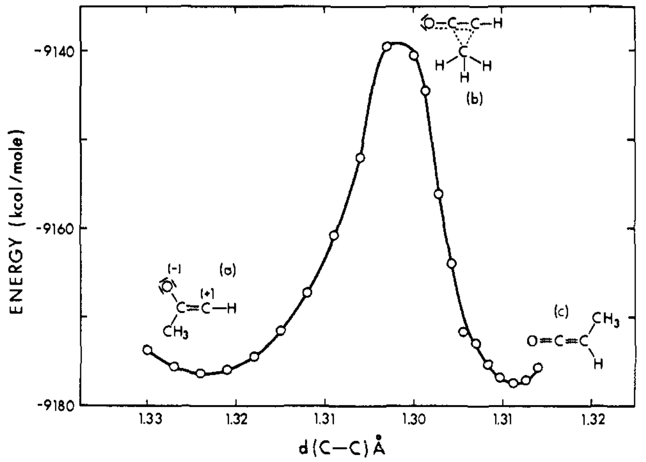
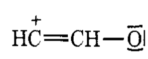


Figure 10. Reaction profile for the zwitterion (a) ↔ cyclic intermediate (b) ↔ methylketene (c) transformations.

be somewhat stretched as compared to the N≡N bond length, the nitrogen may form with some excess vibrational energy, thereby increasing the activation energy of the decomposition above the enthalpy change. On the other hand, the valence isomer of the carbene, the zwitterion **1**, lies at a considerably lower energy, and its intervention in the decomposition could decrease the activation energy. The estimated activation energy, *ca.* 35 kcal/mol, is in line with the well-known low thermal stability of diazo ketones. In any event the intermediate should have sufficient internal energy to pass through the energy barrier represented by the bridged transition state **2**, since rearrangement to



$\overset{+}{\mathrm{HC}}=\mathrm{CH}-\overline{\mathrm{O}}|^{-}$

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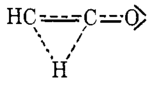


2

ketene is rapid and the carbene cannot be scavenged readily by olefins. Huisgen and coworkers[9] reported, however, the scavenging of the 1,3-zwitterion from the decomposition of a number of diazo ketones in the form of 1,3-addition products. These results are in agreement with the high stability of the zwitterion **1** found in the present study. Nonetheless, it must be pointed out that the EHMO method is noted for its tendency to strongly overemphasize the stability of ionic structures and consequently the distinction between the ketocarbene and zwitterion structure may not be marked.

It is also important to note that the transition state for hydrogen migration, **2**, lies about 3 kcal/mol below the energy of the carbene, and 33 kcal/mol below the oxirene state, thus providing a simple and plausible explanation for the distinct difference in behavior exhibited by the thermal and photochemial systems.

In photoexcitation, decomposition of the diazo ketone occurs from an excited singlet state giving a singlet excited ketocarbene which has sufficient energy for rearrangement to oxirene. Since the process is symmetry forbidden (*vide infra*), it is assumed that the excited singlet state carbene undergoes efficient internal conversion to the ground state and the transformation to oxirene takes place from the vibrationally excited ground state carbene. Thus, the intervention of oxirene in the photochemical Wolff rearrangement of α-diazo ketones and its absence in the thermal decomposition is attributed to the difference in excess vibrational energy in the ketocarbene from the two modes of excitation.

Also, other types of excitation may be considered to

[9] R. Huisgen, G. Binsch, and L. Ghosez, *Chem. Ber.*, 97, 2628 (1964), and references therein.

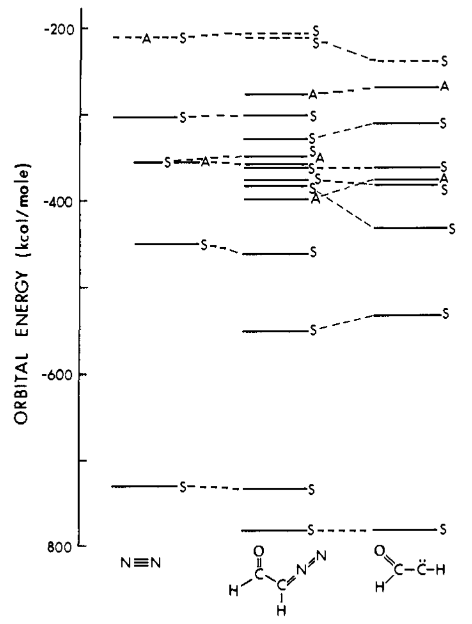


Figure 11. EHMO orbital symmetry correlation diagram for the decomposition of diazoethanone into N_2 + formylmethylene.

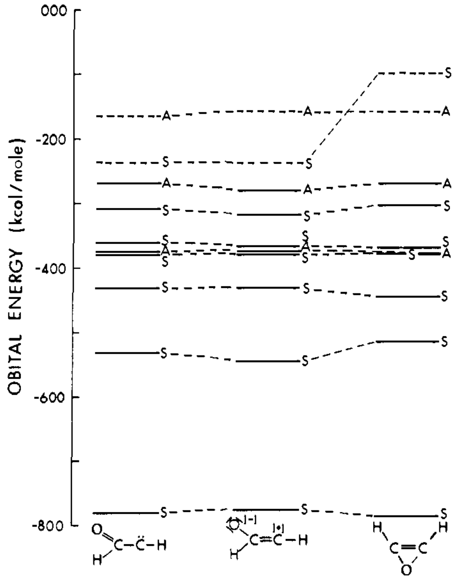


Figure 12. EHMO orbital symmetry correlation diagram for the transformation of formylmethylene to zwitterion and to oxirene.

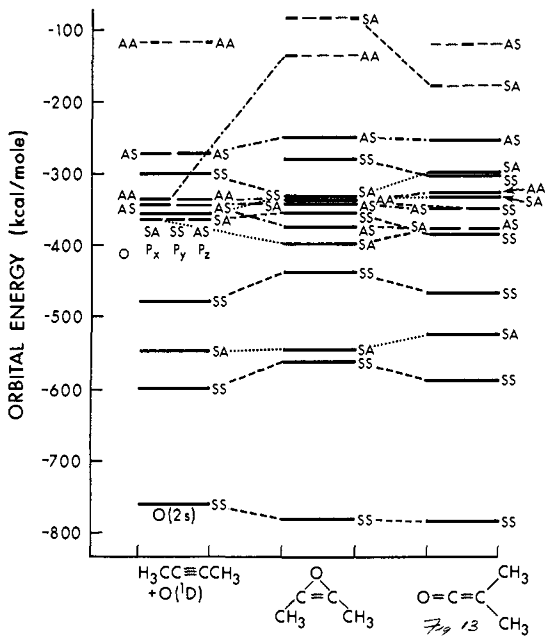


Figure 13. EHMO orbital symmetry correlation diagram for the addition of $O(^1D_2)$ atom to dimethylacetylene.

induce oxirene formation. The addition of $O(^1D_2)$ atoms to acetylene should give oxirene in a single step, spin and orbital symmetry allowed concerted reaction. Oxirene formation from ground state $O(^3P)$ atom addition to acetylene is improbable because this step would violate both spin and orbital symmetry conservation. Chemically activated ketenes from the addition of singlet methylene to carbon monoxide and photoexcited ketenes after internal conversion to the ground state both possess sufficient vibrational energy to form oxirene *via* H migration and ring closure of the resulting zwitterion.

It has been suggested[6] that the thermal Wolff rearrangement of diazo ketones to ketene follows a single-step, concerted path with the extrusion of nitrogen. We calculate the activation energy of such a step as being prohibitively high, *ca.* 114 kcal/mol, and consider this mechanism extremely unlikely even in photochemical excitation.

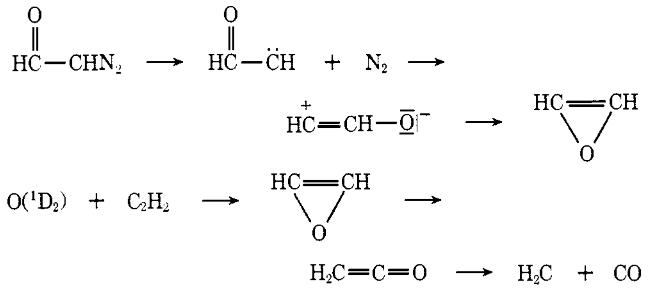
We have calculated the reaction profile for the transformation of the zwitterion **1** to oxirene and ketene *via* the bridged intermediate **2** by the appropriate geometrical changes. The results, reproduced in Figure 7, are illuminating. The zwitterion transforms smoothly in either direction in an orbital symmetry allowed process. The transition state in the ketene-forming step is indeed the bridged structure **2**, and the transition state in the oxirene forming step is the oxirene structure itself. In other words, the oxirene structure is inherently unstable owing to the ring strain, and ring opening by C–O bond cleavage requires no activation. Thus, oxirene and its simple methyl or alkyl derivatives appear to have only transient existence as a high velocity point along the reaction coordinate and not as isolable structures. A definite statement on this question, however, should be postponed until completion of *ab initio* studies presently in progress. Similar reaction profiles connecting the isomeric zwitterions

$$CH_3\overset{+}{C}{=}CH{-}\overline{\underline{O}}|^- \text{ and } H\overset{+}{C}{=}CCH_3{-}\overline{\underline{O}}|^-$$

with the oxirene state and with the ketene *via* the bridged transition states are displayed in Figures 8–10. The introduction of a methyl group does not alter the situation and ring opening by C–O bond cleavage still occurs without an activation energy.

The enthalpy data for the reactions of the two isomeric diazopropanones (Figure 5) and diazobutanone (Figure 6) are all close analogs of those derived for the reactions of diazoethanone. Here we see that as expected, the activation energy for methyl migration is somewhat higher than for hydrogen migration but still the transition state lies below or only slightly above the energy of the carbene and consequently isomerization to the ketene is a feasible process in thermal systems.

The symmetry correlations for the various processes discussed above were examined using the computed orbital energy levels. The diazo ketones and the carbene and zwitterion intermediates have poor symmetry properties; the only symmetry element present is the plane of the NCCO or CCO skeleton of the molecule. Symmetry correlation diagrams have been constructed for the



transformations, some of which are shown in Figures 11 and 12. All these processes are allowed and follow the lowest energy pathways. Interestingly the addition of $O(^1D_2)$ atoms to dimethylacetylene is forbidden (Figure 13), but the symmetry relations for the other processes are unaffected by methylation.

In conclusion it should also be mentioned that the present calculations on the four ketocarbenes, $HCO\ddot{C}H$, $CH_3CO\ddot{C}H$, $HCO\ddot{C}CH_3$, and $CH_3CO\ddot{C}CH_3$, and their zwitterion valence isomers, indicate a singlet ground state for these species. This prediction is based on Hoffmann's empirical rule[5,10] that when the optimum σ^2 configuration has an EHMO energy less than about 1.5 eV below the σp configuration at the same $>C:$ angle, then the ground state is likely to be the triplet. From the data in Figures 1–3 it is seen that the first excited states of the species in question are all higher than the ground state, by at least 1.4 eV; this is consonant with accumulated laboratory experience on ketocarbenes concordantly pointing to the existence of a singlet ground state. Further *ab initio* MO studies are in progress.

Acknowledgments. We thank the National Research Council of Canada for financial support.

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(10) R. Hoffmann, G. D. Zeiss, and G. W. V. Dine, *J. Amer. Chem. Soc.*, **90**, 1485 (1968).

Photochemistry of Nonconjugated Bichromophoric Systems.[1] Intramolecular Photocycloaddition of *N*,*N*′-Alkylenedimaleimides in Solution

J. Put[2] and F. C. De Schryver*[3]

Contribution from the Department of Chemistry, Universiteit te Leuven Celestijnenlaan 200 F, B-3030 Heverlee, Belgium.

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Abstract: The photochemical behavior of a series of *N*,*N*′-alkylenedimaleimides in solution is studied. Upon excitation, an intramolecular cycloaddition or an intermolecular polyaddition can occur. For compounds with chain lengths ranging from three to six methylene units, almost quantitative cyclomerization to a tetracycloadduct was observed. The quantum efficiencies vary from 0.42 for *N*,*N*′-hexamethylenedimaleimide to 0.62 for *N*,*N*′-trimethylenedimaleimide in dichloromethane. The absorption spectra of the bifunctional compounds are very similar to that of the monofunctional *N*-butylmaleimide; only a very slight hypochromism for the bichromophores with a shorter chain length is observed. No fluorescence, neither from the bifunctional nor from the monofunctional derivatives, could be detected. While the dimerization of *N*-butylmaleimide is found to proceed through the triplet excited state, the intramolecular cycloaddition occurs from the singlet state. It is proposed that the reaction proceeds through an excited state complex, formed upon excitation of one of the maleimide rings. Rate constants for exciplex formation are calculated and found to be of the order of $10^9\ sec^{-1}$, which is in the same range as the rate constants for intramolecular excimer formation, determined in other systems. It is suggested that the possibility of intramolecular exciplex formation is limited ultimately by the probability to obtain a favorable conformation, within the lifetime of the singlet excited state. The process is reversible and the equilibrium is shifted to the complex only if it is stabilized sufficiently, bond formation being the extreme.

During the last years, much attention has been paid to nonconjugated bichromophoric systems, since the photochemical properties of a chromophore may change appreciably, when two such groups are incorporated in the same molecule. In the bichromophoric molecule, processes may occur which do not take place, or only to a limited extent, in a solution of the monofunctional derivatives, even at high concentrations. The same possibility exists in polychromophoric systems. Bifunctional molecules are therefore good model compounds for the study of the photochemical behavior of macromolecules. The complicated photochemistry of biological polymers such as RNA and DNA could be explained to a certain extent, by the study of bichromophoric models.[4]

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(1) For previous papers in this series, see (a) F. C. De Schryver and J. Put, *Angew. Chem., Int. Ed. Engl.*, **8**, 213 (1969); (b) L. Leenders and F. C. De Schryver, *ibid.*, **10**, 338 (1971).

(2) (a) Nationaal Fonds voor Wetenschappelijk Onderzoek, predoctoral fellow, 1968–1972; (b) abstracted from the doctoral dissertation of J. Put, University of Leuven, Jan 1972; presented in part at the 6th International Photochemistry Conference in Bordeaux, Sept 1971.

(3) Address inquiries to this author.

(4) For a recent review of this photochemistry, see A. A. Lamola and J. Eisinger in "Excited States of Proteins and Nucleic Acids," R. F. Steiner and Y. Weinryb, Ed., Plenum Press, New York, N. Y., 1971.