proach is sterically more favorable if the bulky substituent on the olefin points away from the ketene hydrogen. This would explain retention of the olefin geometrical configuration and the preference for *syn*-cycloadduct formation as well as the observed order of reactivity of the olefins. The vicinal position of the substituents of unsymmetrical olefins, 2-methylpropene and vinyl ethyl ether, to the ethoxy group is a consequence of the electrophilic nature of the attack of ketene and has been well documented for related ketene cycloadditions.[1,7] It is known that electrophilic reagents, for example, triplet oxygen atoms,[8] attack preferentially on the terminal position. Thus bond formation between the middle carbon atom of the ketene and the terminal carbon atom of the olefin is preferred over other possibilities. This would require that the olefin reactivity should follow the electron-donating ability of the olefin. However, as pointed out above, overriding steric effects appear to obscure the electronic trend.

Finally the synthetic utility of the reaction should be emphasized: it offers unusually selective routes toward the synthesis of cyclobutanones.

Further studies are in progress in this laboratory.

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

(7) R. Huisgen and P. Otto, *J. Amer. Chem. Soc.*, **90**, 5342 (1968). W. T. Brady and O. H. Waters, *J. Org. Chem.*, **32**, 3703 (1967).

(8) R. J. Cvetanovic, *Advan. Photochem.*, **1**, 115 (1963).

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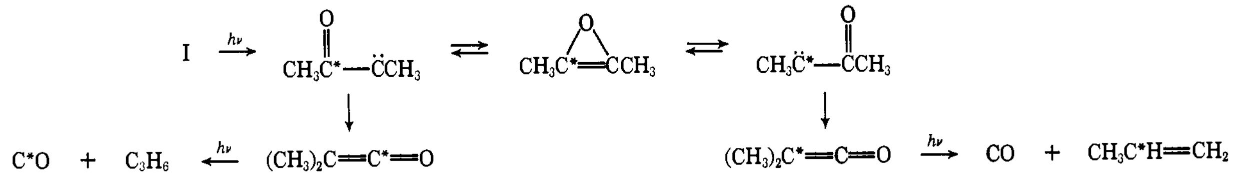
Mechanism of the Wolff Rearrangement. II

Sir:

Although the Wolff rearrangement (WR) has been the subject of numerous mechanistic investigations,[1] a satisfactory rationalization of this reaction has not yet been achieved. Earlier contentions that the WR of diazo ketones proceeds exclusively *via* the migration of the substituent attached to the carbonyl carbon have been shown to be untenable for the vapor-phase photolysis of $CH_3COCN_2CH_3$ (I) and CH_3COCHN_2 (II). Carbon-13 labeling experiments with these molecules indicated the involvement of the oxirene structure in the mechanism, according to Scheme I.[2]

Scheme I



In the past few years it has been established that α-diazo esters also undergo photochemical WR in alcoholic solution[3] and in the vapor phase,[4] and in a more recent communication their WR has been described in olefinic solvents[5] as well.

We wish to report here some recent experimental and computational results which appear to shed additional light on the nature of this important reaction.

We have photolyzed ^{13}C-labeled methyl (III) and ethyl diazoacetate (IV) in the gas phase, at room temperature and at ~ 1-Torr pressure with a medium-pressure mercury arc in a Pyrex vessel. The basic mechanism of the decomposition is adequately represented by Scheme II. Product yields from a typical experiment are compiled in Table I. High-resolution mass spectrometric analysis of the carbon monoxide and ethylene products, after correcting for incomplete labeling in the starting material, yielded C^*O 68.5%, CO 31.5%, $C^*H_2CH_2$ 6.8%, and C_2H_4 93.2%. This gives, for the relative importance of step a to step b, a value of 2.2.

A similar scheme applies to the photolysis of the methyl ester except that the secondary carbene, $CH_3O\ddot{C}H$, tends to release additional CO. Isotopic analysis of the carbon monoxide product, after correcting for incomplete labeling in the starting material, gave 68% for the yield of C^*O. Using a detailed kinetic treatment, with some plausible assumptions for the evaluation of the effect of secondary CO production, the primary yield of C^*O production becomes 72%. From this the relative importance of step a to step b may be estimated to have a value of ~2.6.

These results prove that in the WR of carbalkoxycarbenes, although alkoxy migration is more facile than hydrogen migration, the latter can effectively compete.

In order to obtain a deeper insight into the nature of the WR reaction we have carried out an extended Hückel molecular orbital calculation[6] for ethyl diazoacetate, ethoxyketene, and the various intermediates implicated in the mechanism. While details of the calculations will be described at a later date, the results obtained for the state energy levels are given in Figure 1. It should be noted that the extended Hückel method does not take into account electron interactions and provides only an average energy value of triplet and singlet states of a given spatial symmetry.[7,8] Therefore the excited singlet states of the diazo ester, ketene, and oxirene would be in fact slightly above, and the excited

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(1) V. Franzen, *Ann.*, **614**, 31 (1958); C. Huggett, R. T. Arnold, and T. I. Taylor, *J. Amer. Chem. Soc.*, **64**, 3043 (1942); F. Kaplan and G. K. Meloy, *ibid.*, **88**, 950 (1966); A. M. Trozzolo and S. R. Farenholtz, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968; A. Melzer and E. F. Jenny, *Tetrahedron Lett.*, 4503 (1968); W. Jugelt and D. Schmidt, *Tetrahedron*, **25**, 969 (1969); E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1960; W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964; O. A. Reutov, "Fundamentals of Theoretical Organic Chemistry," T. J. Katz, Ed., Appleton-Century-Crofts, New York, N. Y., 1967.

(2) I. G. Csizmadia, J. Font, and O. P. Strausz, *J. Amer. Chem. Soc.*, **90**, 7360 (1968).

(3) J. Shafer, P. Barnowsky, R. Laursen, F. Finn, and F. H. Westheimer, *J. Biol. Chem.*, **241**, 421 (1966); H. Chaimovich, R. J. Vaughan, and F. H. Westheimer, *J. Amer. Chem. Soc.*, **90**, 4088 (1968); T. DoMinh, O. P. Strausz, and H. E. Gunning, *ibid.*, **91**, 1261 (1969).

(4) O. P. Strausz, T. DoMinh, and H. E. Gunning, *ibid.*, **90**, 1660 (1968).

(5) T. DoMinh and O. P. Stausz, *ibid.*, **92**, 1766 (1970).

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

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

(8) O. P. Strausz, R. J. Norstrom, D. Salahub, R. K. Gosavi, H. E. Gunning, and I. G. Csizmadia, submitted for publication.

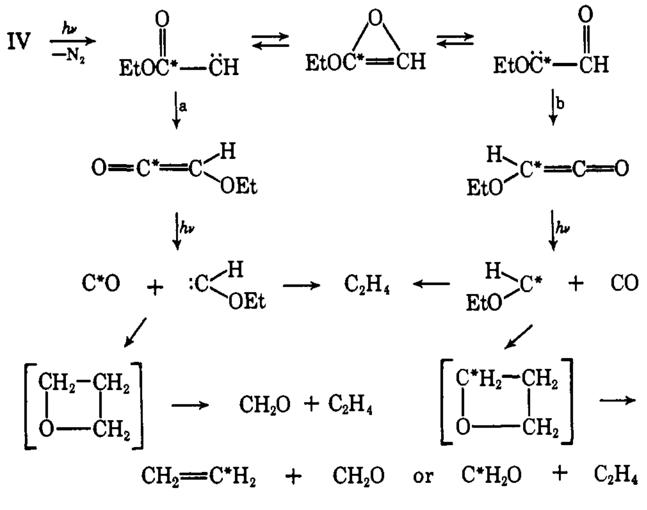
Table I. Product Yields in the Vapor-Phase Photolysis of Methyl and Ethyl Diazoacetate[a]

	Product, μmoles, of								
	N_2	CO	CO_2	CH_4	C_2H_4	C_2H_6	n-C_4H_{10}	CH_3CHO	CH_3CH_2-CHO
Methyl ester	8.3	7.6	2.4	1.6	2.0	2.8			
Ethyl ester	74.4	69.5	4.0		31.2	12.9	5.7	2.3	6.6

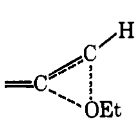
[a] Medium-pressure mercury arc, with Pyrex filter, at room temperature, at ~1-Torr pressure.

triplet states somewhat below, the extended Hückel levels. For the radical intermediates all states would be split accordingly.

Scheme II



The results are illuminating. Within the Pyrex transparency region (λ >2800 Å, ~102 kcal) two or three different excited states of the *cis*-diazo ester can be populated by optical excitation, which by loss of N_2 can give rise to four different carbethoxycarbenes. Oxirene formation requires a total excitation energy of ~100 kcal, though isomerization of the carbethoxycarbene to the ketene is an exothermic process even for ground-state carbene. Thus the MO calculation seems to suggest that only a fraction of the carbethoxycarbene, which is sufficiently energy rich, forms oxirene, while the rest isomerizes to the ketene, bypassing the oxirene state. Therefore, high pressure of inert gases should have a suppressing effect on oxirene formation, which would explain why oxirene formation could not be observed in the condensed phase. The bond dissociation energy of *cis*-ethyl diazoacetate is somewhat above 26.5 kcal. In thermolysis only the lowest singlet state of the carbethoxycarbene would be produced without a substantial excess of vibrational energy. Since isomerization of the carbene involves a strained cyclic activated complex, it should be a slow, inefficient process in thermolysis, and in fact it does not occur at all.[5] In triplet benzophenone sensitization (E_T = 69 kcal) rearrangement to ground-state ketene would be spin forbidden, while rearrangement to the lowest excited triplet ketene would be an energetically uninviting process, and again it does not seem to occur.[5]



Further studies are in progress.

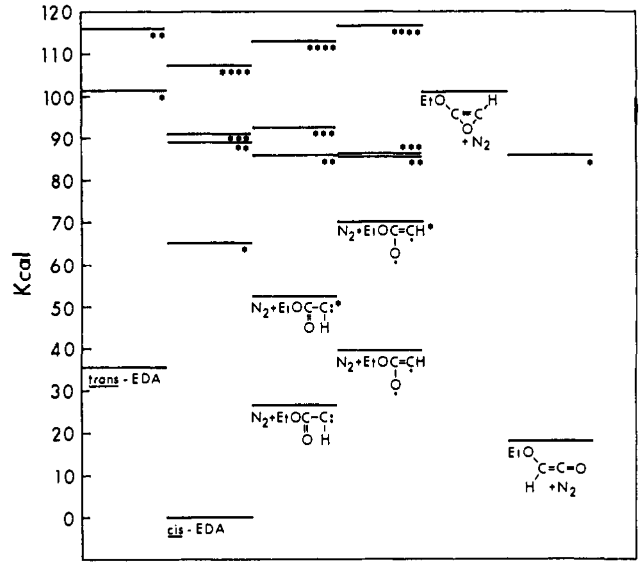


Figure 1. Extended Hückel state energy levels. Asterisks indicate excited states.

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Stevens Rearrangement of 3-Dimethylamino-3-methyl-1-butyne Methiodide. Product Evidence for a Radical Mechanism

Sir:

Recent reports[1] have cited nmr evidence showing that 1,2-electrophilic rearrangements (Stevens, Wittig, etc.) commonly proceed *via* radical intermediates. We wish to describe a new reaction of this type with particularly significant product features.

Reaction of 3-dimethylamino-3-methyl-1-butyne methiodide[2] (68 g, 0.27 mol) with sodamide (29 g, 0.75 mol) in liquid ammonia (1500 ml) with stirring at atmospheric pressure for 5 hr followed by addition of ammonium

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(1) (a) R. W. Jemison and D. G. Morris, *Chem. Commun.*, 1226 (1969); (b) A. R. Lepley, *ibid.*, 1460 (1969); (c) U. Schöllkopf, U. Ludwig, G. Ostermann, and M. Patsch, *Tetrahedron Lett.*, 3415 (1969).

(2) C. Ainsworth and N. R. Easton, *J. Org. Chem.*, 26, 3776 (1961); G. F. Hennion and C. V. DiGiovanna, *ibid.*, 30, 3696 (1965).