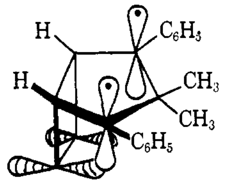
138° (60% isolated yield);[6] $\lambda_{\max}^{\text{isooctane}}$ 234 nm (ϵ 8900); $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 1.03 (s, 6, $-CH_3$), 2.02 (s, 4, cyclopropyl), and 7.29 (s, 10, aryl). The identical substance was isolated from the thermal decomposition of **5** at 135° in $Cl_2C{=}CCl_2$. When the thermolysis of this azo compound at different temperatures was monitored by nmr spectroscopy, it was noted that nitrogen evolution and quadricyclane production were quite slow at 125°. At 135°, however, the conversion was complete after several hours.

Assignment of the quadricyclane structure to **7** follows from its ultraviolet absorption[9] and the highly symmetrical nature of its nmr spectrum. In particular, the absence of vinyl protons demands that the molecule be tetracyclic. Chemical substantiation of the quadricyclane formulation was derived by thermal rearrangement of **7** ($Cl_2C{=}CCl_2$ solution) at 175°. At this temperature, **7** was converted cleanly to the norbornadiene derivative **8**: mp 188–190°;[6] $\lambda_{\max}^{\text{isooctane}}$ 253 (ϵ 670), 258 (ϵ 695), and 266 nm (ϵ 485); $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 0.83 (s, 6, $-CH_3$), 7.07 (s, 4, vinyl), and 7.40 (s, 10, aryl). Irradiation of **8** in hexane solution through quartz optics resulted in reconversion to **7**.

Since the thermal rearrangement of **6** to **7** is the formal result of a ${}_{\sigma}2_{s} + {}_{\pi}2_{s}$ cycloaddition, a concerted rebonding process is intrinsically orbital-symmetry forbidden.[10] Rather, the C_2–C_5 bond almost certainly suffers homolytic rupture with formation of 1,3-diradical **9**.[11] Intramolecular trapping of the diradical appears to occur to the exclusion of other possible reactions, in contrast with earlier attempts to trap other 1,3-diradicals on an intermolecular basis with such simple olefins as isobutylene.[12] Because the thermal decomposition of azo compound **5** requires temperatures (135°) in excess of those required for the **6** → **7** rearrangement (100°), no firm conclusions regarding the mechanism of this fragmentation can be drawn at the present time. However, one might expect that, if the required ${}_{\sigma}2_{s} + {}_{\sigma}2_{s} + {}_{\pi}2_{s}$ transformation were concerted, a more ready fragmentation would be encountered. Since the cost of symmetry forbiddenness is necessarily a function of the reaction under study, a firm answer must await the synthesis of the *exo* isomer of **5** and a comparison of the two rates of decomposition.



9

The ready availability of *trans*-tricyclo[4.1.0.0^{2,5}]hept-3-enes by means of this direct and apparently general synthesis[13] now causes these alicyclic molecules to became an attractive focus of further synthetic and mechanistic study. Those aspects of this research presently under active investigation will be reported in subsequent papers.

Acknowledgment. We thank Dr. Paul Demarco for the NOE determinations and Badische Anilin und Soda Fabrik for their generous gift of cyclooctatetraene.

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(9) The ultraviolet spectrum of phenylcyclopropane serves as a rough analogy: M. T. Rogers, *J. Amer. Chem. Soc.*, 69, 2544 (1947).

(10) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, 81, 797 (1969); *Angew. Chem. Intern. Ed. Engl.*, 8, 781 (1969).

(11) Obviously, it is not known whether C_2 and C_5 in **9** are formally sp^2-hybridized and therefore planar. For a summary of those reactions in which 1,3-diradicals are presumed to occur, see D. R. Arnold, A. B. Evnin, and P. H. Kasai, *J. Amer. Chem. Soc.*, 91, 784 (1969), ref 1.

(12) G. L. Closs, L. R. Kaplan, and V. I. Bendall, *ibid.*, 89, 3376 (1967).

(13) L. M. Leichter, unpublished observations.

(14) National Institutes of Health Predoctoral Fellow, 1969–present.

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Cycloaddition of Ethoxyketene to Olefins

Sir:

We wish to report the preparation and subsequent cycloaddition of the elusive ethoxyketene intermediate to a series of simple olefins. An interesting facet of these cycloadditions is their unusual stereoselectivity[1] which appears to show a gratifying correlation with the Woodward–Hoffmann orbital symmetry conservation rule.

Ethoxyketene was prepared *in situ* by two independent methods, the photochemical Wolff rearrangement of ethyl diazoacetate[2] and the dehydrochlorination of ethoxyacetyl chloride with triethylamine in anhydrous media.

We have found that the photolysis of ethyl diazoacetate (**1**) in olefinic solvents affords, in addition to products attributed to insertion and addition reactions of carbethoxymethylene, substantial yields (up to 18%) of products which can only be rationalized in terms of a Wolff rearrangement of the carbethoxymethylene[3] followed by cycloaddition of the resulting ethoxyketene to the olefin. These products have apparently been overlooked in earlier studies.

The ketene produced by the classical method was generally allowed to react *in situ* with the olefin with or without a solvent. At −78° it appears to be rather stable. At room temperature it slowly forms a polymeric material and some ketene dimer can be isolated. Cycloaddition readily occurs at 80–100° to give cyclobutanones in moderate to good yields.

A typical experiment with vinyl ethyl ether consists of mixing equimolar olefinic solutions of ethoxyacetyl chloride and triethylamine at Dry Ice–acetone temperature. The reaction mixture is carefully sealed in a

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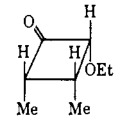
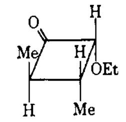
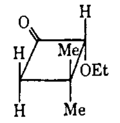
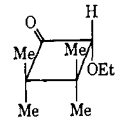
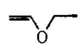
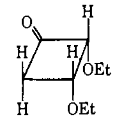
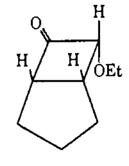
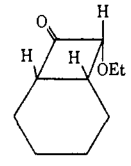
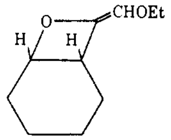
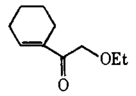
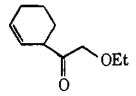
(1) Stereospecific cycloadditions of ketoketenes to double bonds are well established: R. Montaigne and L. Ghosez, *Angew. Chem.*, 80, 194 (1968); T. Huisgen, L. A. Feiler, and P. Otto, *Tetrahedron Lett.*, 4485 (1969); R. Huisgen and P. Otto, *ibid.*, 4491 (1968); W. T. Brady and H. R. O'Neal, *J. Org. Chem.*, 32, 612 (1967); W. T. Brady and E. F. Hoff, *J. Amer. Chem. Soc.*, 90, 6256 (1968). After the present article had been submitted a brief communication by W. T. Brady, E. F. Hoff, R. Roe, Jr., and F. H. Parry, Jr. (*ibid.*, **91**, 5679 (1969)), appeared describing somewhat similar observations on the stereospecific aspect of the cycloaddition of monohalo- and monomethylketene to cyclopentadiene as those found in this work.

(2) J. Shafer, P. Barnowsky, R. Laursen, P. Finn, and F. H. Westheimer, *J. Biol. Chem.*, 241, 421 (1966); O. P. Strausz, Th. DoMinh, and H. E. Gunning, *J. Amer. Chem. Soc.*, 90, 1660 (1968); H. Chaimovich, R. J. Vaughan, and F. H. Westheimer, *ibid.*, 90, 4088 (1968); D. E. Thornton, R. K. Gosavi, and O. P. Strausz, *ibid.*, **92**, 1768 (1970).

(3) Ketene formation was observed only in direct photolysis; triplet benzophenone sensitization of **1** afforded triplet carbene which adds nonstereospecifically to olefins and abstracts hydrogen to yield ethyl acetate. Thermolysis of **1** (at 140°) produced singlet carbene, probably in the lowest lying excited singlet state which adds stereospecifically to olefins without giving ethoxyketene.

Table I Cycloaddition of Ethoxyketene to Olefins

Olefin	Compd	Structure	Yield, % Classical	Yield, % Photochemical
	2		45	16
	3		31	17
	4		30	18
	5		43	
	6		55	
	7		56	
	8		46	
	9		18	
	10			18
	11			

heavy glass tube and placed in an 80° oven for 15 hr. The precipitate of triethylammonium chloride is removed and the residue distilled (bp 130–135° (16 mm)) to give pure *cis*-2,3-diethoxycyclobutanone in 55% yield.

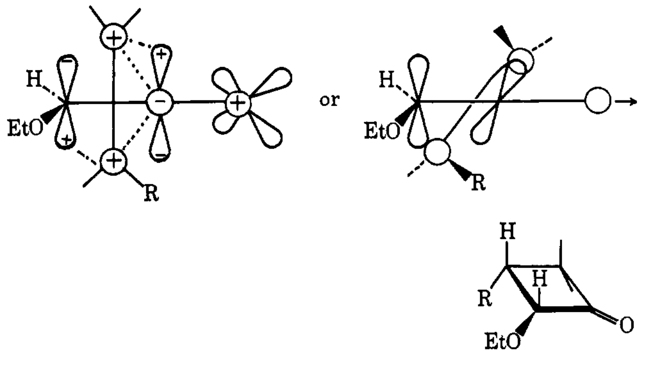
The cycloadducts obtained with various olefins are summarized in Table I. The products were generally characterized by uv, ir, and nmr spectroscopy in conjunction with high-resolution mass spectrometric and/or elemental analysis. Structural assignments were based on high-resolution nmr (Varian HA-100) utilizing spin decoupling techniques. In all cyclobutanones, a much larger coupling constant for vicinal ring protons in the *cis* configuration was found ($J_{cis} \sim 9$–10 Hz *vs.* $J_{trans} \sim 5$ Hz) along with relatively large cross ring coupling ($J \sim 3$ Hz). These data are in excellent agreement with recent nmr analyses for cyclobutanones by Braillon[4] and by Sutcliffe and Walker.[5]

Relative rates of cycloaddition were measured for four olefins (*cis*-2-butene (A), *trans*-2-butene (B), 2-methylpropene (C), and 2,3-dimethyl-2-butene (D)) by direct competition. The values at 100° are as follows: $k_D = 1.0$; $k_B = 1.7$; $k_C = 3.0$; and $k_A = 25.0$. From a temperature study $E_a(B) - E_a(A) = 0.26$ kcal and $A(A)/A(B) = 16.2$. Finally, at least in the case of cyclohexene, not only cyclobutanone **8** was found in good yield but a considerable amount of the oxetane **9** was also isolated. The identification of this product is based on the following data: mol wt (MS-12) 168; negative test with 2,4-DNP, but positive with bromine in CCl_4; no carbonyl band in the ir, but a medium-intensity band at 1680 cm^{-1}, attributed to vinyl ether. The nmr spectrum indicated resonances at τ 8.82 (t, 3 H), 7.7–8.8 (broad m, 9 H), 6.40 (q, 2 H), 6.0–6.3 (m, 1 H), 5.3 (s, 1 H).

The reaction is characterized by a threefold isomeric relation. First, the geometrical configuration of the parent olefin is maintained. Second, the orientation of the ethoxy group is such that it is always *syn* to the adjacent substituent in the products. The cycloadduct is either *cis-syn* or *trans-syn*, but never *anti*. Third, with unsymmetrical olefins only the cycloadducts having a substituent in a position vicinal to the ethoxy group are formed (head-to-head cycloadduct).

The large difference in reactivity between *cis*- and *trans*-butene is due to steric effects; the activation energy difference is quite small. Steric effects are probably of paramount importance with other olefins as well.

Woodward and Hoffman[6] consider ketenes as vinylium ylides ($>C{=}C^+{-}O^-$) and, as such, to play an antarafacial role in the concerted $[\pi_s^2 + \pi_a^2]$ cycloaddition. The place of the vacant p orbital of the simple vinylium ion is taken by the unoccupied $\Pi_{C=O}^*$ orbital of the ketene, and the high electrophilic reactivity of ketene is a consequence of the exceptionally low-lying position of this orbital.[6] Thus the cycloaddition may be represented as



Steric repulsion would prevent the approach of the olefin on the side of the ethoxy group. Moreover, the ap-

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[4] B. Braillon, *J. Mol. Spectrosc.*, 27, 313 (1968).
[5] L. H. Sutcliffe and S. M. Walker, *J. Phys., Chem.*, 71, 1555 (1967).
[6] R. B. Woodward and R. Hoffmann, *Angew. Chem.*, in press.

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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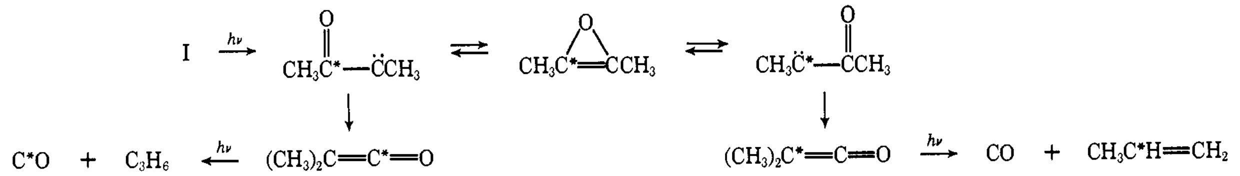
Mechanism of the Wolff Rearrangement. II

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, $CH_3\ddot{O}CH$, 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.