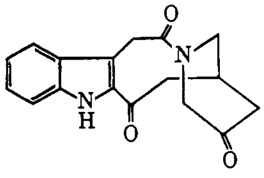
stannous chloride in hot acetic acid containing *p*-toluenesulfonic acid.[4] Oxidation[13] to the ketone **13**, mp 250–252°, followed by successive treatments with ethylmagnesium bromide in ether and with lithium aluminum hydride gave mainly the axial alcohol **14** in 0.4% yield based on **1**. Its infrared and mass spectra were identical with those of velbanamine prepared from vinblastine.[14] Further, racemic velbanamine (**14**) gave a di-*p*-toluoyl-*l*-tartrate, mp 140-140.5°, identical with the salt of "natural" velbanamine, mp 140–140.5°; mixture melting point not depressed.



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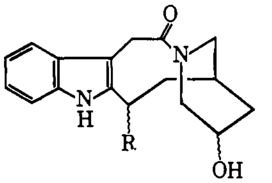
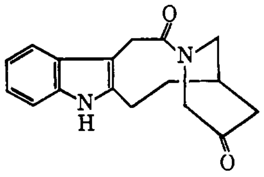


11, R = OH
12, R = H



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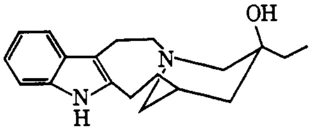

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Acknowledgment. The mass spectra were measured in the National Institutes of Health supported mass spectrometry facility at Massachusetts Institute of Technology (Grant FR 00317) under the direction of Professor K. Biemann. We are indebted to the National Institutes of Health (GM 09686) for generous financial support.

(13) K. E. Pfitzner and J. G. Moffatt, *J. Am. Chem. Soc.*, **87**, 5670 (1965).

(14) We are indebted to Dr. N. Neuss, Eli Lilly and Co., for a sample of velbanamine.

(15) National Institutes of Health Predoctoral Fellow, 1965–1967.

(16) National Institutes of Health Predoctoral Fellow, 1965–present.

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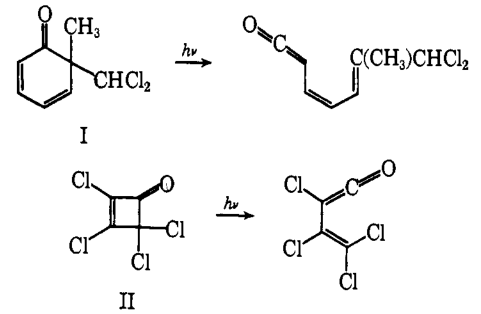
Direct Observation of Ketene Intermediates in Photochemical Reactions[1]

Sir:

Ketenes have been invoked as intermediates in many photochemical reactions of unsaturated ketones. For example, irradiation of 2,4-cyclohexadienones or cyclobutenones in the presence of nucleophiles gives acyclic adducts.[2] Evidence for the involvement of ketenes as intermediates in these reactions is indirect. We now wish to report the direct observation of ketenes as primary photoproducts of 6-methyl-6-dichloromethyl-2,4-cyclohexadienone (I)[3] and perchloro-2-cyclobuten-1-one (II), and the unexpected intrusion of a thermally unstable ketene intermediate in the interconversion of III and IV.



The infrared spectrum of the mixture produced by irradiation[4] of I as a liquid nitrogen cooled glass is shown in Figure 1. The 2118-cm^{-1} band is readily recognizable as the C=O stretch of the ketene.[5] The low-frequency region suggests that the initially formed diene ketene is the *cis*-diene ketene in accord with earlier postulates.[2] Irradiation[4] of II gave a new compound with a ketene carbonyl band at 2145 cm^{-1}.

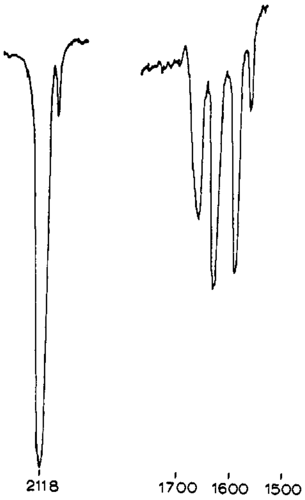


Figure 1. Low-temperature infrared spectrum of the carbonyl region after 45-min irradiation[4] of 6-methyl-6-dichloromethyl-2,4-cyclohexadienone (I).

The photochemical rearrangement of III to IV has been described.[6] Labeling of positions 4 and 6 with alkyl groups defined the rearrangement of atoms as shown. It was suggested[6] that electronic excitation of III, 4,6-bond formation, rearrangement (V → VI), and electron redistribution gave IV. This mechanistic rationalization satisfactorily accounted for related rearrangements reported later.[7] We wish to describe evidence for a path from III to IV which implicates a thermally unstable ground-state intermediate.

Irradiation[4] of III gave rise to a new product with a

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(1) Photochemical Transformations. XXVI.

(2) D. H. R. Barton, *Helv. Chim. Acta*, **42**, 2604 (1959); D. H. R. Barton and G. Quinkert, *J. Chem. Soc.*, 1 (1960); J. E. Baldwin and M. C. McDaniels, *J. Am. Chem. Soc.*, **89**, 1537 (1967); P. M. Collins, and H. Hart, *J. Chem. Soc.*, 1197 (1967); G. Quinkert, *Angew. Chem. Intern. Ed. Engl.*, **4**, 211 (1965).

(3) The sample of 6-methyl-6-dichloromethyl-2,4-cyclohexadienone was provided by Professor John Baldwin. The photochemical transformations of I in the presence of nucleophiles will be reported shortly by J. Baldwin and M. McDaniel.

(4) Neat glasses were irradiated in a liquid nitrogen cooled infrared cell mounted in a vacuum shroud with sodium chloride windows. Pyrex filters were used for all irradiations.

(5) The weak band at 2060 cm^{-1} is due to the natural abundance ^{13}C=O ketene band as in the spectrum of ketene: W. F. Arendale and W. H. Fletcher, *J. Chem. Phys.*, **26**, 793 (1957).

(6) W. G. Dauben, K. Koch, S. L. Smith, and O. L. Chapman, *J. Am. Chem. Soc.*, **85**, 2616 (1963); **83**, 1768 (1961).

(7) T. Mukai and T. Miyashi, *Tetrahedron*, **23**, 1613 (1967); T. Mukai and T. Shishido, *J. Org. Chem.*, **32**, 2744 (1967).

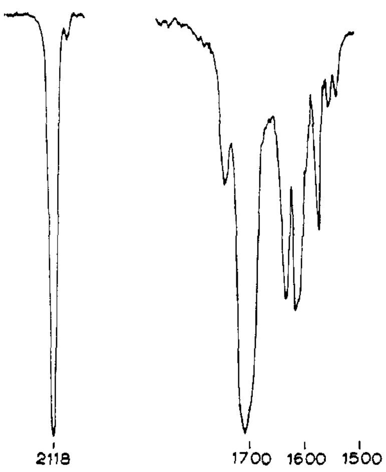
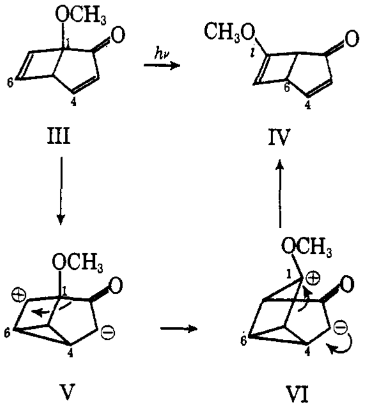


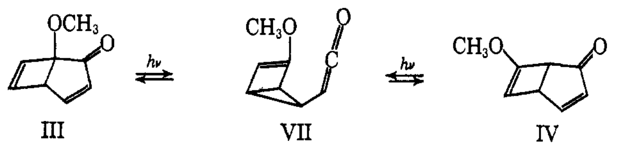
Figure 2. Low-temperature infrared spectrum of the carbonyl region after 50-min irradiation[4] of 1-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one (III).

ketene carbonyl band at 2118 cm^{-1} (Figure 2)[5,8] which could be observed after 2-min irradiation and which reached a maximum at 1-3 hr. The intermediate was stable in the dark for 12 hr at $< -180°$. Above $-70°$ the intermediate disappeared rapidly in the dark. The only products observed by infrared analysis, gas chromatography, and nmr spectra were III and IV.[9] Analysis of the low-temperature infrared spectra and the behavior of the various bands during warm-up to room temperature permit assignment of bands at 1620 (enol ether double bond) and 825 cm^{-1} and tentative assignment of bands at 1320, 1280, and 1223 cm^{-1} to the intermediate.



The ketene intermediate is also formed on irradiation of IV. In fact, a steady state involving III, IV, and the intermediate can be approached from either III or IV.

The intermediate possesses a ketene carbonyl group and an enol ether double bond and it is thermally unstable at temperatures above $-70°$. The thermal rearrangement leads predominantly to IV. These considerations lead us to assign structure VII to the intermediate. The thermal instability of VII has excellent analogy in the apparent thermal isomerization of *cis*-1,2-divinylcyclopropane generated *in situ* below $-40°$ to 1,4-cycloheptadiene[10,11] and in the degenerate valence isomerizations of tricyclo[3.3.2.0^{4,6}]deca-2,7,9-triene (bullvalene),[10–14] tricyclo[3.3.1.0^{4,6}]nona-2,7-dien-9-one (barbaralone),[11,15] and tricyclo[3.3.2.0^{4,6}]deca-2,7-diene[14] which are not frozen out at $-50°$. Formation of VII from either III or IV is easily understood as an example of the well-known α-cleavage reaction of n,π^* excited stages,



Ketene intermediates analogous to VII can be considered for many photochemical reactions. These possibilities are under active investigation.

Acknowledgment. This investigation was supported by Grant 14305 from the National Institute of General Medical Sciences, National Institutes of Health. Samples of III and IV were provided by Mr. R. L. Reierson.

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(8) The possibility that the 2118-cm^{-1} band might be due to carbon monoxide was excluded by irradiation of a freeze-thaw degassed glass of I followed by warm-up and mass spectrometric examination of the gaseous products. A trace of residual nitrogen could be detected but no carbon monoxide.

(9) After prolonged (12 hr) irradiation of the intermediate some absorption in the 1720–1780-cm^{-1} region was observed.

(10) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

(11) W. von E. Doering and W. R. Roth, *Angew. Chem. Intern. Ed. Engl.*, **2**, 115 (1963).

(12) G. Schröder, *Angew. Chem.*, **75**, 722 (1963).

(13) M. Saunders, *Tetrahedron Letters*, 1699 (1963).

(14) R. Merenyi, J. F. M. Oth, and G. Schröder, *Ber.*, **97**, 3150 (1964).

(15) J. B. Lambert, *Tetrahedron Letters*, 1901 (1963).

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Conformational Analysis in Multisulfur Heterocycles. II. Isolation of the Conformationally Pure Twist-Boat Form of Duplodithioacetone

Sir:

Although many studies have dealt with the measurement of the rate of very fast conformational equilibrations[1] in solution, little effort has been expended to isolate conformers in solution when the barrier $(\Delta F^{\ddagger})$ to conformational interconversion is about 16 kcal/mole or less.[2] Once the barrier to conformational equilibration has been measured, *e.g.*, by variable-temperature nuclear magnetic resonance (nmr) spectroscopy, appropriate low temperatures can be selected at which the half-life of a given conformer is many hours.

Recently, the unusual observation was made that the twist-boat conformer of duplodithioacetone (tetramethyl-*s*-tetrathiane) was more stable than the chair form ($\Delta F° = -0.8$ kcal/mole at 0° in CS$_2$).[3]

Examination of the nmr spectrum[4] of duplodithioacetone at 35° reveals a set of two broadened resonances of unequal intensities at δ 2.00 and 1.66 ppm. Upon

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(1) J. E. Anderson, *Quart. Rev.* (London), **19**, 426 (1965); F. G. Riddell, *ibid.*, **21**, 364 (1967).

(2) F. R. Jensen and C. H. Bushweller, *J. Am. Chem. Soc.*, **88**, 4279 (1966).

(3) C. H. Bushweller, *ibid.*, **89**, 5978 (1967).

(4) The nmr spectra were recorded on a Varian Associates A-60 nmr spectrometer using a V-6040 temperature controller. Temperature was measured using a methanol sample.