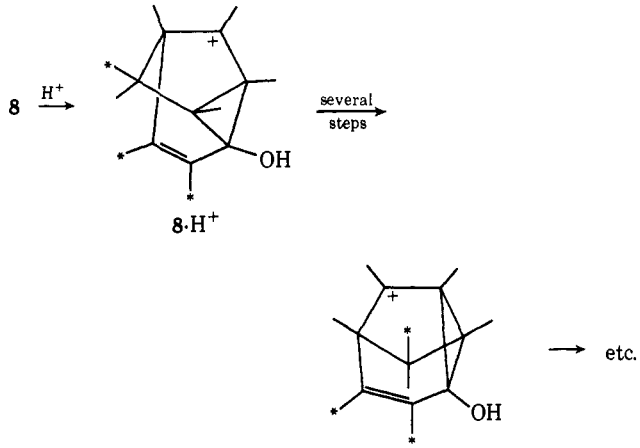
eight methyl groups underwent deuterium exchange. The singlet at τ 9.08 and two homoallylically coupled quartets at 8.15 and 8.37 remained. When exchanged **8** was treated with NaOMe–MeOD the signal at τ 8.15 disappeared and that at 8.37 sharpened to a singlet, confirming the conclusion that the two methyls on the three-carbon bridge had not exchanged under acidic conditions.

These observations are consistent with the proposed exchange mechanism; the asterisked methyls do *not* exchange.



The postulated degenerate carbonium ion **2**, while it rationalizes the experimental observations presented, may not constitute a unique explanation for the results. The mechanism's correctness and generality are being put to further experimental tests.

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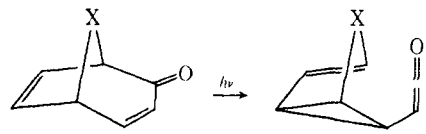
A Novel Intramolecular Ketene Cycloaddition. Functionalized Tetracyclo[3.3.0.0^{2,8}.0^{3,6}]octanes

Sir:

Compounds of the type **1** have been shown to photoisomerize to ketenes **2** (in published examples, X has been an electron pair,[1] or a CH_2, $CH{=}CH$,[2] *o*-C_6H_4,[2,3] or EtO_2CNNCO_2Et[2] group). The ketenes were detected in all cases by low-temperature infrared spectroscopy,



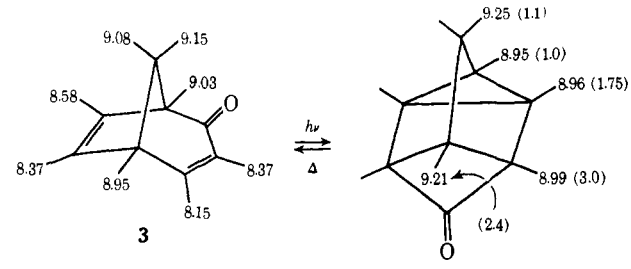
1 2

and in all but the first example by trapping with a nucleophile. In the absence of a nucleophile, ketenes **2** recyclize to **1** or dimerize.[2]

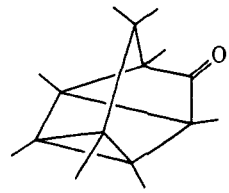
(1) O. L. Chapman and J. D. Lassila, *J. Amer. Chem. Soc.*, **90**, 2449 (1968). In this example a methoxyl group was present at C_1 or C_7.
(2) O. L. Chapman, M. Kane, J. D. Lassila, R. L. Loeschen, and H. E. Wright, *ibid.*, **91**, 6856 (1969).
(3) A. S. Kende, Z. Goldschmidt and P. T. Izzo, *ibid.*, **91**, 6858 (1969).

We wish to report that ketene **2** (X = CH_2), when completely substituted with methyl groups, reacts differently from its unsubstituted analog. It neither reacts with nucleophiles nor recyclizes to **1**, but undergoes a facile and synthetically useful intramolecular $2_\pi + 2_\pi$ cycloaddition.

Irradiation of **3**[4] (1% solution in methanol, Pyrex) gave a single photoproduct, $\nu_{C=O}$ 1760 cm^{-1} (cyclobutanone), no nmr allylic methyl signals, in 100% chemical yield. We assign the product the tetracyclic structure **4** (1,2,3,4,5,6,7,7,8-octamethyltetracyclo[3.3.0.-0^{2,8}.0^{3,6}]octan-4-one). The nmr spectrum consisted of five sharp singlets, three of which (τ 9.25, 8.99, and 8.96) were twice the area of the other two (all assigned as shown in the formula). Europium shift reagent



caused downfield shifts of all the signals[5] but caused no broadening of the signals assigned to degenerate methyl pairs. These data favor structure **4** over the other plausible but asymmetric cyclobutanone structure **5**.



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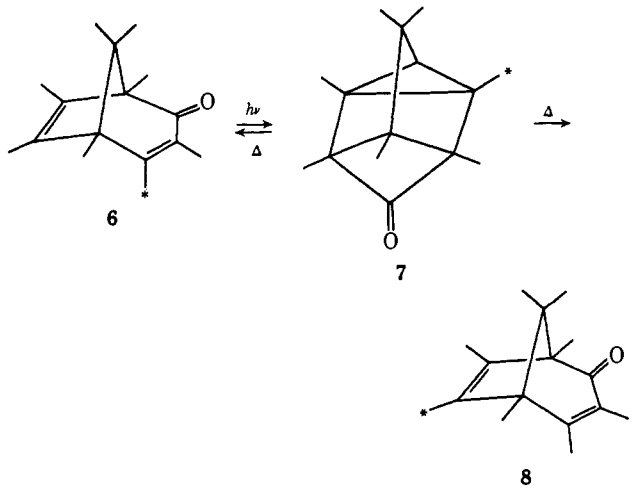
Photoproduct **4** isomerizes thermally to **3** in carbon tetrachloride at 100° with a half-life of 50 min. Advantage was taken of this thermal rearrangement to unequivocally demonstrate the symmetric structure of **4**. Ketone **3**, when treated with NaOMe–MeOD, gave the trideuterio compound **6** (which lacked the low-field methyl signal at τ 8.15; the asterisked methyl is CD_3). Irradiation of **6** gave **7** (peak at τ 8.96 in **4** reduced 50% in area). When **7** was heated, the expected 1:1 mixture of **6** and **8** was obtained (1.5 protons at τ 8.15, 4.5 protons at τ 8.37), clearly demonstrating the symmetry of the photoproduct **4**.

A similar rearrangement of **4** to **3** appears to occur on electron impact.[6] Although the mass spectra of **4** and **3** were virtually identical at 70 eV (base peak at *m/e* 217 due to M − CH_3, and the peak at *m/e* 204 due to M − CO was relatively minor), when the ionizing voltage was lowered to 20 eV the peak due to

(4) Synthesized as described in the accompanying communication; H. Hart and G. Love, *ibid.*, **93**, 6264 (1971). The numbers in the formula are the nmr chemical shifts of the methyl signals, in τ (CCl_4 solvent).
(5) The numbers in parentheses are the relative slopes of these signals with added Eu(DPM)$_3$, the lowest slope arbitrarily taken as 1.0. These slopes, as well as experiments with three differently labeled samples of **3** (CD_3 in place of certain CH_3 groups), permit the unequivocal nmr assignment shown.
(6) The inlet temperature was kept as low as possible, approximately 70°, to avoid the thermal isomerization.



6 7 8

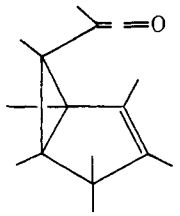
M − CO became the base peak. The data in Table I suggest that the M − CH_3 peak arises mainly from

Table I. Selected Peaks in the Mass Spectrum of **4**

Ionizing voltage, eV	Relative peak intensities m/e 232	217	204
70	47	100	20
20	32	70	100
17.5	30	50	100
15	35	35	100
13	56	16	100

3, and the M − CO peak mainly from **4**.

We have thus far been unable to trap the ketene **9** with a nucleophile. Irradiation of **3** in ether containing a large excess of dimethylamine, either at room temperature or at −190°, or in methanol under similar conditions, gave only **4**. But direct evidence for the intermediacy of **9** was obtained when a solution of **3**



9

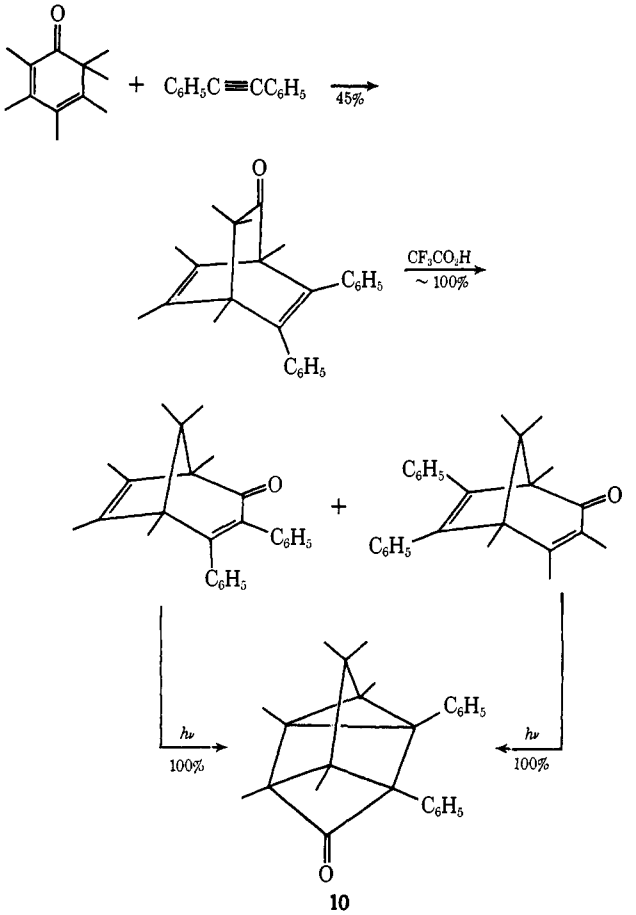
in pentane was frozen as a thin solid film and irradiated in an infrared cell[7] at about −190°. The expected sharp ketene absorption at 2110 cm^{-1} appeared quite quickly; however, even slight warming resulted in rapid conversion of the ketene to **4** (1760-cm^{-1} band). There is, therefore, no doubt that the reaction proceeds *via* a ketene intermediate.

Interconversions of the type **3** ⇌ **4** are probably quite general if the ring systems are highly substituted. For example, we have prepared the diphenyl analog **10** in essentially quantitative yield after the first step, by the following reaction sequence.[8,9]

(7) A Hanovia UV 100 irradiation system was used as the energy source.

(8) The first step and preliminary work on the second step were carried out by T. Kakihana, M.S. Thesis, Michigan State University, 1966.

(9) Experimental conditions and structural evidence will be presented in a full paper; they are unexceptional.



10

The accelerating effect of alkyl groups on the intramolecular cycloaddition of the type **9** → **4** is reminiscent of similar substituent effects on the cyclization of diene ketenes to conjugated cyclohexadienones[10] and bicyclo[3.1.0]hexenones.[11,12]

The parent hydrocarbon of the tetracyclic ring system present in **4** and **10** has been reported,[13] but we believe this is the first preparation of functional derivatives of the system.

We are exploring the scope of the intramolecular cycloaddition reaction described, as well as the chemistry of the interesting ring system which it generates.

Acknowledgment. We are indebted to the National Science Foundation and the National Institutes of Health for their generous support.

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(12) H. Hart, P. M. Collins, and A. J. Waring, *ibid.*, **88**, 1005 (1966); P. M. Collins and H. Hart, *J. Chem. Soc. C*, 895 (1967); H. Hart and D. C. Lankin, *J. Org. Chem.*, **33**, 4398 (1968); M. R. Morris and A. J. Waring, *Chem. Commun.*, 526 (1969); H. Perst and K. Dimroth, *Tetrahedron*, **24**, 5385 (1968).

(13) P. K. Freeman, V. N. M. Rao, and G. E. Bigam, *Chem. Commun.*, 511 (1965).

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Electrophilic Opening of the Thiazolidine Ring in Penicillins

Sir:

In recent years the selective opening of the thiazolidine ring of the penicillin nucleus in which the azeti-