both XCO$^+$ and XCH$_2^+$, the difference between the methoxymethyl and methoxycarbonyl ions indicates a decreased resonance stabilization of about 60 kcal/mol in the carbonyl ion. Recent evidence[6] indicates that the methoxymethyl ion may rearrange to the hydroxy carbinyl structure at the appearance potential threshold. The best estimate of the heat of formation of the methoxymethyl ion is however still approximately 170 kcal/mol, corresponding to an SE value of 66 kcal/mol. The increased inductive stabilization of the acetyl ion relative to the ethyl ion does provide evidence for enhanced inductive effects in the carbonyl ions so that the reduced resonance stabilization of the methoxy substituent is probably less than 60 kcal/mol.

Columns 5 and 6 of Table II illustrate the change of the stabilization energy if a hydrogen on the ion is replaced by a methoxy group. It appears that the HCO$^+$ ion is very similar to the H$^+$C(OCH$_3$)$_2$ ion in its stabilization effects. For the dimethoxy methyl ion both methoxy groups can compete for the charge (CH$_3{}^+$O=CHOCH$_3$ $\rightleftharpoons$ CH$_3$OCH=$^+$OCH$_3$), thus reducing the effect of conjugation of a further methoxy group with a vacant p orbital on the carbon. Therefore it is likely that in the XCO$^+$ ions the oxygen atom bears the positive charge, thereby increasing the electron density on the carbonyl carbon and reducing the effect of resonance stabilization.

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## A Ketene Intermediate in the Photochemical Solvolysis of Dihydrocoumarin[1]

*Sir:*

The photochemical solvolysis of dihydrocoumarin (**1**)[2] has received considerable attention. Conflicting opinions concerning the mechanism of this solvolysis have been presented by Plank[3] and by Gutsche and Oude-Alink.[4] Plank studied the photochemical hydrolysis in dioxane and deuterium oxide and concluded on the basis of deuterium incorporation (46.5% $d_1$, 23.6% $d_2$)[5] that the reaction proceeded *via* a ketene intermediate (**2**).[3] The photochemical conversion of **1** to **2** would be strictly analogous to processes well documented in the photochemistry of cyclic ketones.[6]

Gutsche and Oude-Alink studied the reaction in methanol and methanol-O-*d* and observed no deuterium incorporation. On this basis they concluded that a ketene intermediate was not involved in the reaction and suggested an interesting spirodienone intermediate (**3**).[4] The formation of the spirodienone is plausible in view of other photo-Fries rearrangements. Our low-temperature methods[7] seemed ideal for detecting either or both intermediates.

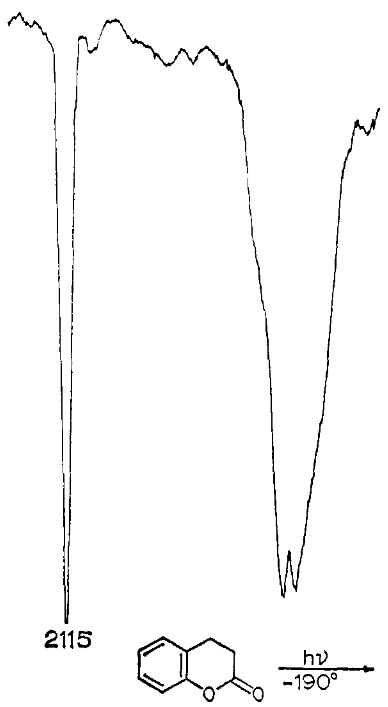
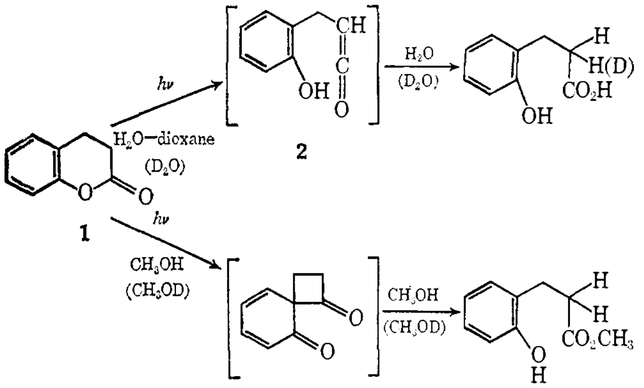


Figure 1. Infrared spectrum of 3,4-dihydrocoumarin after irradiation as a film at −190°. The new band at 2115 cm$^{-1}$ is due to the ketene.



Irradiation of dihydrocoumarin at −190° as a thin film or as a glass containing methanol in a liquid nitrogen-cooled infrared cell using previously described techniques[7] gave a product with a strong ketene band at 2115 cm$^{-1}$ (see Figure 1). No new bands which could be attributed to spirodienone **3** were observed. Warming the methanol-containing glasses above −70° caused concurrent disappearance of the 2115-cm$^{-1}$ band and appearance of the 1737- and 1716-cm$^{-1}$ bands of methyl 3-(*o*-hydroxyphenyl)propionate. The ketene mechanism suggested by Plank is clearly operating under these conditions. In order to determine the significance of this mechanism at room temperature, we reinvestigated the deuterium-labeling experiments in deuterium oxide and methanol-O-*d*. Irradiation of dihydrocoumarin in deuterium oxide–dioxane gave 3-(*o*-hydroxyphenyl)-propionic acid 52.0% $d_1$ and 5.5% $d_2$ and in methanol-

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(1) Photochemical Transformations. XXXIII.

(2) J. C. Anderson and C. B. Reese, *J. Chem. Soc.*, 1781 (1963).

(3) D. A. Plank, Ph.D. Thesis, Purdue University, 1966.

(4) C. D. Gutsche and B. A. M. Oude-Alink, *J. Amer. Chem. Soc.*, **90**, 5855 (1968).

(5) Plank[3] attributed the production of $d_2$ species to thermal recyclization of the product to dihydrocoumarin followed by a second photochemical cleavage to the ketene and incorporation of a second deuterium.

(6) R. Srinivasan, *Advan. Photochem.*, 1, 83 (1964).

(7) O. L. Chapman and J. D. Lassila, *J. Amer. Chem. Soc.*, **90**, 2449 (1968); L. L. Barber, O. L. Chapman, and J. D. Lassila, *ibid.*, **90**, 5933 (1968); **91**, 531 (1969).

O-$d$ gave 43.5% $d_1$ and 5.5% $d_2$ (analysis by mass spectroscopy).[8] The dark solvolysis is quite sensitive to acid present on the surface of the vessel,[9] and we found irradiations in polyethylene vessels with quartz covers gave more reproducible results. The deuterium incorporation results together with direct observation of the ketene clearly show that the ketene mechanism suggested by Plank[3] is responsible for the major portion of the product. The nature of the mechanism which produces product without deuterium incorporation is not known.

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[8] A recheck by Gutsche and Oude-Alink (private communication) of their data showed that the purified sample of methyl β-(2-hydroxyphenyl)propionate contained no carbon-bound deuterium, as indicated by a ratio of 1.0 for the $CH_2$/ArH resonances in the nmr. The nmr of the crude photolysis product, however, showed a $CH_2$/ArH ratio of 0.89, corresponding to a 45% incorporation of deuterium into a methylene group. The reasons for the apparent (or real?) absence of deuterium in the purified product are not known, and we are informed that these authors are engaged in further investigation of these circumstances.

[9] A film builds up on the vessel during irradiation and must be removed by washing with chromic acid. Traces of residual acid strongly catalyze the dark reaction and lower deuterium incorporation significantly.

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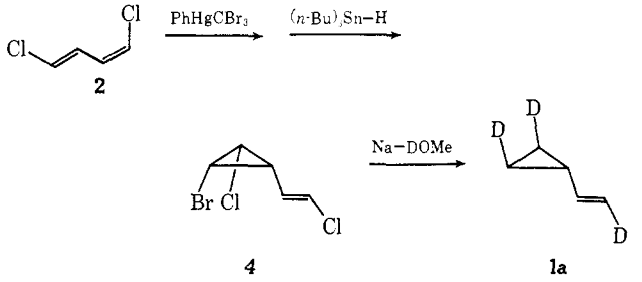
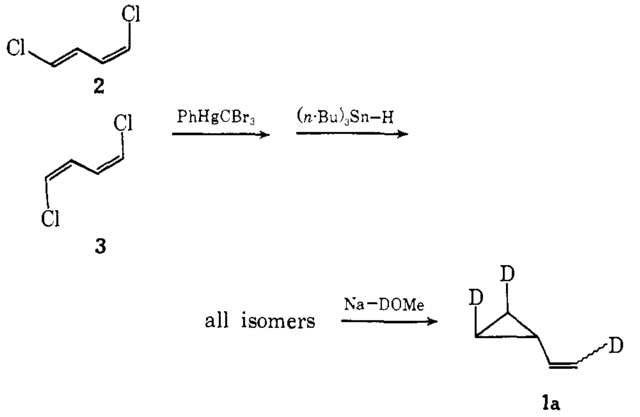
## Structural Evidence for the Existence of a Symmetrical High Energy Species in the Degenerate Vinylcyclopropane Rearrangement

*Sir:*

Diradical intermediates have been claimed in many thermal isomerization reactions using the powerful, but indirect, methods of thermodynamics and kinetics, a situation imposed by the fact that no one has been able to observe directly any chemical or physical evidence for a diradical.[1] Whether the description of cyclopropane rearrangements, such as that of *cis*- to *trans*-1,2-dideuteriocyclopropanes,[2] involves a diradical intermediate or only a transition state, there are still but three limiting sets of molecular motions: (I) a simultaneous epimerization at two of the three carbon atoms in the ring, (II) an epimerization exclusively at one carbon atom in the ring, and (III) randomization of the stereochemistry at two of the three carbon atoms in the ring at each observable event. Most cyclopropane rearrangements have been carried out using substrates with a symmetry such that two, or even all three, of these descriptions ambiguously fit the kinetic and stereochemical results, thereby forcing the differentiation of mechanism to be made by carefully chosen structural tests. We wish to record here the synthesis of a *cis*-2,3-dideuteriovinylcyclopropane and its subsequent thermolysis as unequivocal evidence for a high energy species in which randomization of stereochemistry occurs simultaneously at two centers (case III).





Reaction of phenyl(tribromomethyl)mercury[3] with a large excess of *cis,trans*-1,4-dichlorobutadiene (**2**) led to the expected dibromodichlorovinylcyclopropanes, which on cautious reduction with 1 mol of tri-*n*-butyltin hydride[4] at 30° produced four stereoisomers of 1-(2-chlorovinyl)-2-bromo-3-chlorovinylcyclopropane. Separation of all four isomers was accomplished by preparative vapor phase chromatography. After identification of the purified isomers by nuclear magnetic resonance and mass spectra data, compound **4** was treated with sodium in methanol-O-$d$[5] to produce a good yield of 1-(*trans*-2-deuteriovinyl)-*trans,trans*-2,3-dideuteriocyclopropane (**1a**). The *cis* arrangement of the cyclopropyl hydrogens in compound **1a** was assured when the upfield portion of the 100-MHz nmr spectrum exhibited a complex multiplet at $\delta$ 1.5 (allylic H, area = 1), a doublet at $\delta$ 0.4 (cyclopropyl H *cis* to the vinyl group, area = 1.95) and a small signal at $\delta$ 0.7 (cyclopropyl H *trans* to vinyl group, area less than 0.1). The surprising inversion of configuration on the cyclopropyl ring which occurred during sodium–deuterio alcohol reduction of compound **4** to **1a** was made credible when we found that the trideuteriovinylcyclopropanes produced by carrying all isomers from a mixture of *cis,cis*- and *cis,trans*-1,4-dichlorobutadienes (**2** and **3**) through the same sequence possessed the identical (*cis*-2,3-) stereochemistry on the cyclopropyl ring as the vinylcyclopropane produced by reduction of pure compound

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[1] The literature dealing with this subject is voluminous. For a summarizing viewpoint in favor of diradicals see: (a) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968). (b) S. W. Benson, "Thermochemical Kinetics," John Wiley & Sons, Inc., New York, N. Y., 1968. For a theory and experiments from which one can construct a counter viewpoint see: (c) R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 1475 (1968). (d) R. J. Crawford and A. Mishra, *ibid.*, **87**, 3768 (1965); **88**, 3963 (1966).

[2] E. W. Schlag, B. S. Rabinovitch, and K. B. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958); E. W. Schlag and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **82**, 5996 (1960).

[3] D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y. Mui, H. D. Simmons, Jr., A. J. H. Treiber, and S. R. Dowd, *ibid.*, **87**, 4259 (1965).

[4] D. Seyferth, H. Yamazaki, and D. L. Alleston, *J. Org. Chem.*, **28**, 703 (1963).

[5] M. R. Willcott and V. H. Cargle, *J. Am. Chem. Soc.*, **89**, 723 (1967).