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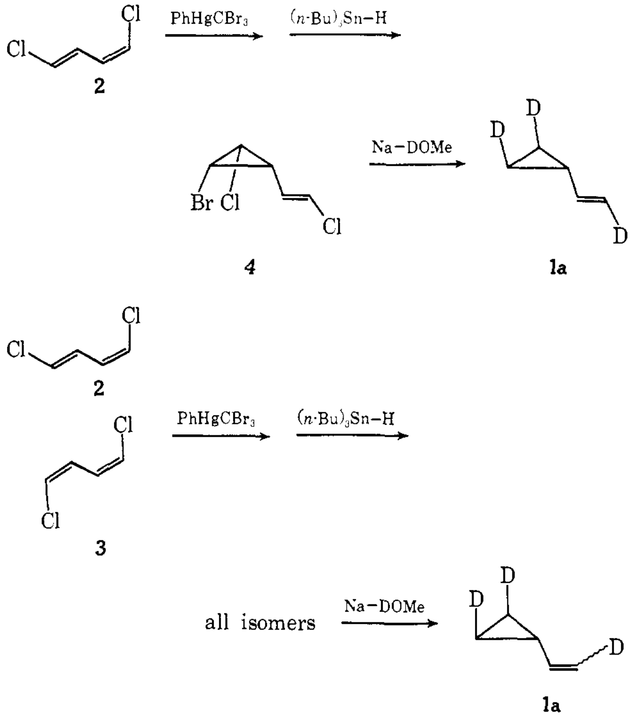
Structural Evidence for the Existence of a Symmetrical High Energy Species in the Degenerate Vinylcyclopropane Rearrangement

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 δ 1.5 (allylic H, area = 1), a doublet at δ 0.4 (cyclopropyl H *cis* to the vinyl group, area = 1.95) and a small signal at δ 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).

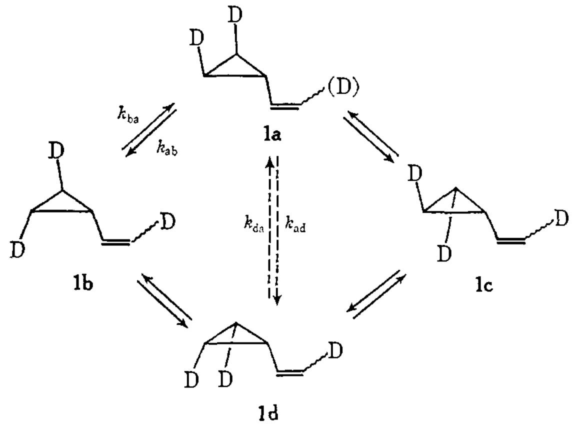
(3) D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y. Mui, H. D. Simmons, Jr., A. J. H. Treiber, and S. R. Dowd, *ibid.*, **87**, 4259 (1965).

(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).

4.[6] This adventitious synthesis provided a route to sizeable quantities of the stereospecifically labeled substrate **1a**.

Gas phase pyrolyses of aliquots of compound **1a** were conducted at 325° (pressures of 100 to 150 torr) in carefully prepared vacuum sealed glass ampoules of 15 to 20 ml volume. The reaction times ranged from 3 to 50 min, corresponding to 0.6 to 10 half-lives for the mixing of the deuterium label. The rate of this reaction was identical with that for the conversion of *trans*-2-deuterio-1-vinylcyclopropane to *cis*-2-deuterio-1-vinylcyclopropane.[5] Moreover, the ratio of the three new vinylcyclopropanes (**1b**, **1c**, and **1d**) at every extent of conversion, as monitored by the appearance of the nmr signal at δ 0.7, was found to be identical but for total intensity. Deuterium-decoupled nmr spectra simplified the δ 0.7 peak to a well-resolved six-line pattern, four lines of which are due to the *trans* compounds **1b** and **1c**, and two due to the *cis* compound **1d**. The spectrum simplification thus permitted us to measure the experimental values for ratio (**1b** + **1c**):**1d** as 2:1.[7]



We find it convenient to formalize the three limiting cases for the motion of the -CHD groups by writing the four ring isomers in the array as shown here, and then considering the rate constants interconnecting them. Those rates connecting **1a**, **1b**, **1c**, and **1d** (k_{ab}, k_{bc}, etc.) are equal by symmetry.[8] The rates connecting compounds **1a** and **1d** (k_{ad}, k_{da}) are also equal, but need not have the same value as k_{ab}. Three different time-dependent behaviors of the system starting from pure **1a** can be generated when we consider relative magnitudes of k_{ab} and k_{ad}. The rate k_{ad} may be much faster than all others (case I), or nonexistent (case II), or equal to k_{ab} (case III). The first mechanism, ruled out by our data, demands formation of compounds **1a** and **1d** with exclusion of compounds **1b** and **1c**. Mechanisms II and III are similar, but solution of the rate expressions by use of random-walk techniques, or by analog computation, reveals that when the nmr peaks which appear at δ 0.7 (from **1b** + **1c** + **1d**) have increased to 50% of their final value the concerted path (case II) has a 6:1 ratio while the random path (case III) has a 2:1 ratio for (**1b** + **1c**):**1d**. Thus, our experimental result is consistent only with a mechanism in which stereochemistry is lost simultaneously at two centers (case III).

It is possible to identify this sharply defined result as evidence for the intervention of a diradical.[9] Extrapolation of the diradical hypothesis to other cyclopropane reactions is obvious, but three recent examples deserve special mention. The Berson–Balquist account of the simultaneous racemization and geometrical isomerization of tetramethylcyclopropane-d_6 leaves no question that the diradical which is generated re-forms the cyclopropyl σ bond faster than the geminal dimethyl groups rotate.[10] Carter and Bergman's[11] observations of simultaneous racemization and geometrical isomerization of (–)-*cis*-1-methyl-2-ethylcyclopropane are explained in terms of a diradical formed by $CHCH_3$–CHC_2H_5 bond scission which then collapses to *cis* and *trans* isomers at slightly different rates. Crawford and Lynch have found that the loss of optical activity from (–)-*trans*-1,2-diphenylcyclopropane is 1.5 times the rate of formation of the *cis* compounds,[12] results exactly predicted by a free rotating diradical intermediate, even if bulky phenyl groups are involved.

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[6] The vinyl substituent contained both *trans*-2-deuteriovinyl and *cis*-2-deuteriovinyl groups, but this partial stereochemistry is not crucial to the present discussion, so we shall omit further mention of it. The fact that all possible starting materials produce the same mixture of trideuteriovinylcyclopropanes raises some interesting mechanistic points which are now under investigation.

[7] The accuracy of the nmr method is such that a ratio of (2.0 ± 0.2):1.0 is not likely to be experimentally significant; however, a ratio of 3:1 is easy to determine and well outside our experimental error. The details of the nmr spectra of all the compounds reported in this paper will be published separately.

[8] This argument ignores equilibrium isotope effects, an assumption which seems valid.

[9] The diradical hypothesis requires that our observations are adequate to describe the behavior at a single molecule during the course of the reaction. If this criterion is not met, then we can only discuss an average symmetry for the entire set of molecules. For this particular case the average symmetry is equivalent to claiming a planar intermediate for the reaction.

[10] J. A. Berson and J. M. Balquist, *J. Am. Chem. Soc.*, **90**, 7343 (1968).

[11] W. L. Carter and R. G. Bergman, *ibid.*, 90, 7344 (1968).

[12] R. J. Crawford and T. R. Lynch, *Can. J. Chem.*, 46, 1457 (1968).

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Allylic Palladium Acetate Systems. Acetate Bridge Inversion

Sir:

Recent reports have indicated that π-allylic palladium acetate systems are catalytic intermediates in a variety of diene-oligomerization reactions.[1a] As part of a general study of the nature and reactivity of π-allylic ligands, we have carried out variable-temperature nmr studies of several π-allylic palladium acetates.[1b]

In the solid state allylpalladium acetate, $[Pd_2(OAc)_2(C_3H_5)_2]$, has been shown to have structure Ib.[2] Three

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[1] (a) R. Van Helden, C. F. Kohl, D. Medema, G. Verberg, and T. Joukhoff, *Rec. Trav. Chim. Pays-Bas*, 87, 961 (1968), and references therein. (b) Allylic palladium acetate complexes were prepared by the method reported by S. D. Robinson and B. L. Shaw, *J. Organometal. Chem.*, 3, 367 (1965).

[2] M. R. Churchill and R. Mason, *Nature*, **204**, 777 (1964). Ib is a diagrammatic representation of one side of the structure. The arrows represent a side view of the π-allylic ligands, the arrow heads showing the position of the central carbon atoms. The planes defined by the three carbons of the π-allyl ligands are set at angles greater than 90° with respect to the planes defined by the oxygen–palladium–oxygen units (*ca.* 110 and 125°).