4,4-tetramethyl derivative,[6] racemize rapidly at room temperature on the nmr time scale, indicating energy barriers of <12 kcal/mol. This behavior is consistent with the observation that the closest approach of vinyl methyl groups in these compounds is 2.5 Å without exocyclic bond deformation; the corresponding distance in a coplanar transition state for **2a** is only 1.4 Å. Extension of this work and optical resolution of other systems of type **1** are planned.

(16) American Chemical Society–Petroleum Research Fund Fellow, 1969–1970.

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Received April 11, 1972

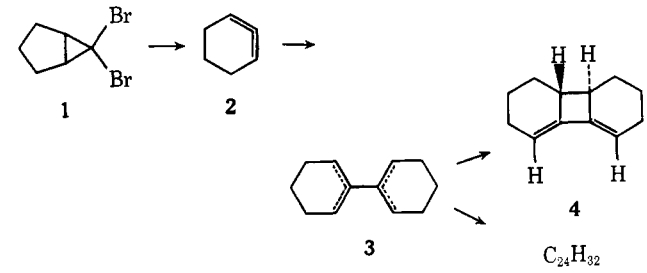
Dimerization of 1,2-Cyclohexadiene, a Model for Nonconcerted Allene Dimerization. Determination of a Secondary Deuterium Kinetic Isotope Effect by Deuterium Nuclear Magnetic Resonance[1]

Sir:

The dimerization of allenes to 1,2-dimethylenecyclobutanes has evoked much mechanistic interest.[2] In particular, one question arises repeatedly: does the addition occur in one step or is it a multistep process involving at least one intermediate? Dolbier and Dai[3] in seeking to answer this question found a negligible intermolecular secondary deuterium isotope effect in the partial dimerization of mixtures of allene-d_4 and -d_0. However, dimerization of allene-*1,1*-d_2 established that an intramolecular isotope effect was operative. In terms of forming the doubly allylic C–C bond, they reported an isotope effect of $k_H/k_D = 1.14$. From these observations, they concluded that the reaction must involve a rate-determining step devoid of isotopic discrimination followed by a product-forming step which is not. However, this conclusion is not mandatory; a one-step (concerted) mechanism could lead to the observed isotope effects.[4] Additionally, the fact that a normal intramolecular isotope effect is observed for a system undergoing an $sp^2 \rightarrow sp^3$ change is also puzzling. Both normal and inverse intermolecular isotope effects have been observed for a variety of (2 + 2) cycloadditions.[5] For example, the addition of diphenylketene to styrene shows, as expected, an inverse isotope effect at the β position of styrene, but surprisingly a substantial normal isotope effect is found at the α position. In this case Baldwin has provided an interesting rationale in terms of a concerted process.[5d]

Clearly the lack of experimental models complicates the interpretation of such isotope effects. Because of the mechanistic importance of the case of allene dimerization, we deemed it to be of prime importance to try to obtain *experimental evidence establishing the nature of the intramolecular isotope effect in the product-forming step of a related reaction where independent evidence indicates that an intermediate is involved.* In general, finding such model systems will not be easy. Fortunately, in this instance one can be developed.

In prior work,[6] we have presented compelling evidence that when 1,2-cyclohexadiene (**2**) is generated from dibromide **1**, it rapidly dimerizes to an intermediate diallylene **3** which can either cyclize to diene **4** or dimerize to two $C_{24}H_{32}$ stereoisomers. Although **2** certainly is not a typical allene, **3** should provide an excellent model for possible intermediates formed in the dimerization of normal allenes.[7]



1 2 3 4 $C_{24}H_{32}$

Labeled dibromide-**1**-*1*-*d* was treated with methyllithium in refluxing ether (generating **2**-*1*-*d* as an intermediate) and the dimer **4**-d_2 was isolated and purified.[8] Similarly, to provide a standard for analytical purposes, dimer fully labeled at the vinyl and tertiary positions, **4**-d_4, was prepared from **1**-*1,5*-d_2.[8]

The proton nmr spectrum of the d_0 dimer (Figure 1) shows that the signals due to the tertiary allylic protons are not resolved[9] from the complex signals of the remaining more shielded protons, making it impossible to make an accurate determination of the deuterium distribution by this indirect method. To solve this problem, we turned to deuterium nmr. Scattered examples of dmr have appeared in the literature,[10] but its great potential has not been exploited nor even recognized presumably because the sensitivity to D is low,

(1) Acknowledgment is made to the National Science Foundation for support of this research (GP 25216).

(2) (a) For a comprehensive review, see J. E. Baldwin and R. H. Fleming, *Fortschr. Chem. Forsch.*, **15**, 281 (1970). (b) For our preceding work, see W. R. Moore, R. D. Bach, and T. M. Ozretich, *J. Amer. Chem. Soc.*, **91**, 5918 (1969).

(3) W. R. Dolbier, Jr., and S. H. Dai, *ibid.*, **92**, 1774 (1970).

(4) One of us has pointed out (private communication to Professor Dolbier cited in footnote 13 of ref 3) that a one-step mechanism could accommodate the data provided that $(k_H/k_D)_A(k_H/k_D)_V \simeq 1$, where $(k_H/k_D)_A$ is the isotope effect at the methylene group involved in forming the doubly allylic bond and $(k_H/k_D)_V$ is that at the vinylic position. This possibility was rejected[3] on the grounds that a one-step mechanism would not have $(k_H/k_D)_A > 1$. However, normal isotope effects have been observed in reactions considered to be concerted; *cf.* ref 5d.

(5) (a) T. J. Katz and R. Dessau, *J. Amer. Chem. Soc.*, **85**, 2172 (1963); (b) W. R. Dolbier, Jr., and S. H. Dai, *ibid.*, **90**, 5028 (1968); (c) E. K. von Gustorf, D. V. White, J. Leitich, and D. Henneburg, *Tetrahedron Lett.*, 3113 (1969); (d) J. E. Baldwin and J. A. Kapecki, *J. Amer. Chem. Soc.*, **92**, 4874 (1970).

(6) W. R. Moore and W. R. Moser, *ibid.*, **92**, 5469 (1970); *J. Org. Chem.*, **35**, 908 (1970).

(7) Although dimer **4** is not formed quantitatively from **1**, it is stable to the reaction conditions, making it a valid monitor of an intramolecular kinetic isotope effect. A meaningful intermolecular kinetic isotope effect cannot be determined since the rate-determining step probably precedes formation of **2** which also has other reaction paths open to it.

(8) (a) Dibromides *1*-*1*-*d* and **1**-*1,5*-d_2 were prepared by addition of dibromocarbene to the deuterated cyclopentenes. Cyclopentene-*1*-*d* was prepared by the xanthate dehydration of cyclopentanol-*1*-*d*, obtained from reduction of cyclopentanone with $LiAlD_4$. Cyclopentene-*1,2*-d_2 was prepared by reduction of 1,2-dibromocyclopentene with sodium in 1-methylcyclohexanol-*O*-*d*. (b) In each case dimer **4** was isolated by reduced pressure distillation and purified by recrystallization from methanol followed by sublimation twice. No impurities could be detected spectroscopically or by glc. (c) Low voltage mass spectral analysis: **4**-d_2, 94.8% d_2, 5.2% d_1; **4**-d_4, 96.5% d_4, 3.5% d_3.

(9) Partial, but inadequate, resolution was obtained in benzene.

(10) P. Diehl and Th. Liepert, *Helv. Chim. Acta*, **47**, 545 (1964); R. C. Dougherty, G. D. Norman, and J. J. Katz, *J. Amer. Chem. Soc.*, **87**, 5801 (1965); L. K. Montgomery, A. O. Clause, A. M. Crelier, and L. E. Applegate, *ibid.*, **89**, 3453 (1967); R. Wylde and J. Grinaud, *C. R. Acad. Sci., Ser. C*, **271**, 597 (1970); E. Casadevall and P. Metzger, *Tetrahedron Lett.*, 4199 (1970); R. E. Santini, *Anal. Chem.*, **43**, 801 (1971).

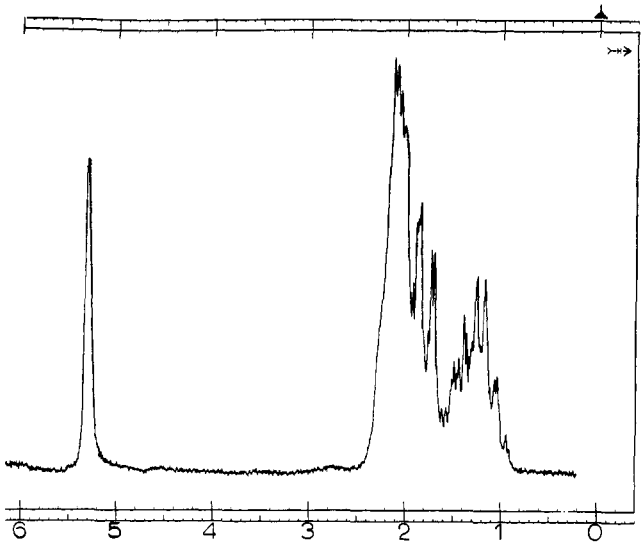


Figure 1. 100-MHz proton nmr spectrum of **4** in CCl_4; values in ppm at decreased shielding from tetramethylsilane.

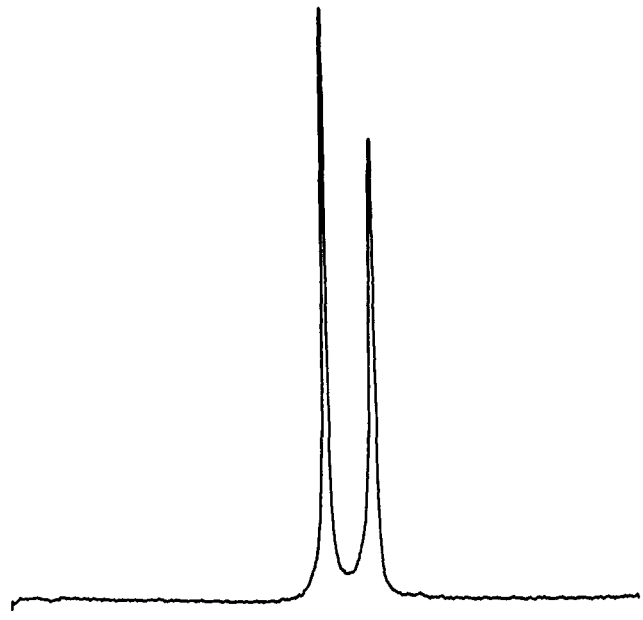


Figure 2. Deuterium nmr spectrum of **4**-d_2 in CCl_4 (96 pulses), decreased shielding to the left.

amounting to only 1% that of H. To achieve a high signal-to-noise ratio, which is absolutely essential for a problem such as ours, would require unusually stable conditions and prolonged time averaging for spectra obtained in the usual continuous wave (CW) mode. However, just as with the more publicized ^{13}C, signal enhancement can be obtained readily by utilizing the Fourier transform of the free induction decay obtained from appropriate multipulsing experiments.[11]

As can be seen from the example shown in Figure 2, the spectra obtained[12] are remarkably simple, consisting of only two broad lines with a spacing of 3.1 ppm—the value predicted from the proton spectrum. (The peak assignments are certain because there is a 1:1 correlation between D and H chemical shifts.) The data from integrations establishing the deuterium distribution are summarized in Table I. Although the observed ratio of vinyl-D/allyl-D of 1.04 (4) is small, statistical analysis indicates that it really differs from unity with a high probability (>98%).

If, as is usually done, the kinetic isotope effect is defined in terms of replacement of a single H by D, then in the present case in terms of forming the doubly allylic C–C bond the composite[13] k_H/k_D is 1.04 (4). The isotope effect of 1.14 reported by Dolbier and Dai[3] is based on replacing two H by two D and thus, as defined above, refers to $(k_H/k_D)^2$. Hence for allene, k_H/k_D = 1.06 (8). When the combined uncertainties in the two systems are considered, it is apparent that one cannot say whether or not the difference between 1.04 (4) and 1.06 (8) is significant. What is important is that both systems show a small normal secondary deuterium kinetic isotope effect.[14] *Inasmuch as we have examined a model system in which independent evidence indicates that the product-forming step involves the closure of an intermediate diallylene to a 1,2-dimethylenecyclobutane, this correspondence provides experimental support for Dolbier and Dai's interpretation of their kinetic isotope effects.*

Finally, we believe that the solution of this problem by application of deuterium nmr should provide graphic evidence of the potential of this method and hope that it will provide impetus to the more extensive use of dmr.[15]

Table I. Deuterium Distribution in **4**

Sample[a]	Obsd peak area[b] ratio, vinyl/allylic	Std dev
d_4	1.02 (0)	0.010
d_2	1.05 (2)	0.016
d_2	1.05 (8)	0.010
d_2	1.08 (4)	0.021
d_2 mean	1.06 (5)	0.017
Normalized, vinyl-D/allyl-D:	1.06 (5)/1.02 (0) = 1.04 (4)	

[a] The d_2 values refer to three separate reactions. [b] Peak areas were determined by integration using the appropriate computer program. Data were all recorded consecutively under invariant nmr conditions.

(11) Dmr spectra were obtained utilizing a Bruker HFX-90 spectrometer interfaced with a Digilab FTS/NMR-3 data system. Lacking deuterium transmitter and receiver systems for our spectrometer, we lowered the Bruker magnetic field from its normal value of 21.138 to 18.652 kG causing deuterium to resonate at 12.201 MHz, which is the frequency of a transmitter–receiver system we use to obtain ^{17}O nmr at 21.138 kG. The adaptations to the lock system as well as the full details for utilizing this general technique will appear elsewhere: D. D. Traficante, *Rev. Sci. Instrum.*, in press.

(12) A typical spectrum was obtained on a solution of 100 mg of **4**/ml of CCl_4 utilizing the following parameters: 2048-point transform, 2000-Hz sampling frequency, 1.0-sec delay tine, and 224 pulses. The d_2 and d_4 spectra were indistinguishable to the eye.

(13) It is wise to note that although one can focus attention on forming the doubly allylic C–C bond, the intramolecular isotope effect actually reflects simultaneous changes at *both* the (forming) allylic and vinylic positions.

(14) Professor Dolbier has provided a possible (and interesting) interpretation of this normal isotope effect: S. H. Dai and W. R. Dolbier, Jr., *J. Amer. Chem. Soc.*, **94**, 3946 (1972). We wish to thank Professor Dolbier for a preprint of this paper.

(15) Although we fully labeled our compounds, note that a knowledge of the extent of labeling is not necessary. In many experiments, a relatively low labeling level could be used while still retaining reasonable accuracy by increasing the number of pulses.

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Received February 23, 1972