exo,endo epimer **14c** was suggested from high resolution nmr in the region of the sharp methyl doublets of **14a** and **14b** (τ 8.8–9.1). Each of the two doublets appeared to contain a barely resolved further doublet of low intensity similar to those of **10c**. However, this was not investigated further by glc.

In a further experiment the reaction mixture was investigated by nmr for a possible epimerization of **14a** and **14b** under the experimental conditions. While this method was not very accurate, a change in the ratio of **14a**:**14b** was not discernible after 3 days.

Comments on Debromination in Acetone. The major by-product in these reactions was the parent ketone and diacetone alcohol. For example, 2,4-dibromo-2-methyl-3-pentanone (**6b**) and furan afforded the adduct **8** (35%), 2-methyl-3-pentanone (51%), diacetone alcohol (7%), and an unidentified compound (7%). Debromination under rigorously dry conditions using acetone (distilled from (i) $KMnO_4$ and (ii) P_4O_{10}) and furan (refluxed over Na for 30 hr) in a 50:50 mixture (v/v) led to recovery of α,α'-dibromo ketone.

Comments on Debromination in Glyme. Initially, the zinc–copper couple was added in one batch, when it was found that substantial amounts of α,α'-dibromo ketone could be recovered at the end of the reaction. In order to bring about complete debromination it is advantageous to introduce the zinc–copper couple in several portions. Under these conditions the cycloaddition is very efficient and provides a most simple route to seven·membered unsaturated ketones.

Secondary Deuterium Isotope Effects in Allene Cycloadditions

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Abstract: *Intra*molecular kinetic secondary deuterium isotope effects were obtained for the reactions of allene-*1,1-d₂* with acrylonitrile, 1,1-dichloro-2,2-difluoroethylene, tetracyanoethylene oxide, hexachlorocyclopentadiene, and 5,5-dimethoxytetrachlorocyclopentadiene and for the dimerizations of allene-*1,1-d₂* and 1,2-cyclononadiene-*1-d*. *Inter*molecular effects were obtained for the acrylonitrile and hexachlorocyclopentadiene reactions as well as for the allene dimerization. The results lead to the conclusion that all [2 + 2] cycloaddition processes of allenes, including dimerizations, proceed *via* a multistep pathway, while the [2 + 3] and [2 + 4] cycloadditions proceed *via* concerted mechanisms.

Within the past few years, a surge of general interest in the chemistry of allenic compounds has generated a great deal of mechanistic investigations in the cycloadditions of allenes. A number of kinetic[2] and stereochemical[2b,3] studies are now available, with the stereochemical results seeming to suggest that allene cycloadditions are quite stereoselective. Some observations of stereospecific [2 + 2] cycloadditions led to conclusions that such reactions were multicenter, concerted reactions,[2b] with allene acting in an antarafacial manner similar to the way that ketene has been demonstrated to behave,[4] while most preferred to explain their results on the basis of multistep mechanisms.

We wish to present a rather broad series of studies which seem to support the latter conclusion, and which seem to relegate allene to the category of being just another relatively reactive alkene.[5] In these studies secondary deuterium isotope effects have been utilized as the major mechanistic probe. *Intra*molecular competitive studies provided information about the *product-determining* steps while *inter*molecular competition experiments gave knowledge of the *rate-determining* steps.

A broad spectrum of cycloaddition reactions was investigated: two Diels–Alder reactions ([2 + 4] cycloadditions), the reactions of allene with hexachlorocyclopentadiene (**1**)[6] and with 5,5-dimethoxytetrachlorocyclopentadiene (**2**); one [2 + 3] cycloaddition the 1,3-dipolar cycloaddition of tetracyanoethyleneoxide(**3**) with allene;[7] two [2 + 2] cycloadditions, the reaction of allene with acrylonitrile (**7**)[8] and with, 1,1-dichloro-2,2-difluoroethylene (**9**)[9]; and two dimeriza-

(1) (a) Taken in part from the Ph.D. dissertation of S.-H. Dai, University of Florida, June 1971; (b) Alfred P. Sloan Foundation Fellow, 1970–1972.
(2) (a) A. Roedig, *Angew. Chem., Int. Ed. Engl.,* **8**, 150 (1969); (b) E. F. Kiefer and M. Y. Okamura, *J. Amer. Chem. Soc.,* **90**, 4187 (1968).
(3) (a) J. E. Baldwin and U. V. Roy, *J. Chem. Soc. D,* 1225 (1969); (b) W. R. Moore, R. D. Bach, and T. M. Ozretich, *J. Amer. Chem. Soc.,* **91**, 5918 (1969); (c) A. Roedig and N. Defzer, *Justus Liebigs Ann. Chem.,* **710**, 1 (1967); (d) J. J. Gajewski and W. A. Black, *Tetrahedron Lett.,* 899 (1970); (e) T. L. Jacobs, J. R. McClenon, and O. J. Muscio, Jr., *J. Amer. Chem. Soc.,* **91**, 6038 (1969); (f) E. V. Dehmlow, *Tetrahedron Lett.,* 4283 (1969).
(4) (a) R. Huisgen and P. Otto, *J. Amer. Chem. Soc.,* **90**, 5342 (1968); (b) R. Huisgen, L. A. Feiler, and P. Otto, *Tetrahedron Lett.,* 4485 (1968); (c) W. T. Brady and R. Roe, Jr., *J. Amer. Chem. Soc.,* **92**, 4618 (1970); (d) H. M. Frey and N. S. Issacs, *J. Chem. Soc. B,* 830 (1970); (e) J. E. Baldwin and J. A. Kapecki, *J. Amer. Chem. Soc.,* **92**, 4868 (1970); (f) R. Montaigne and L. Ghosez, *Angew. Chem., Int. Ed. Engl.,* **7**, 221 (1968).
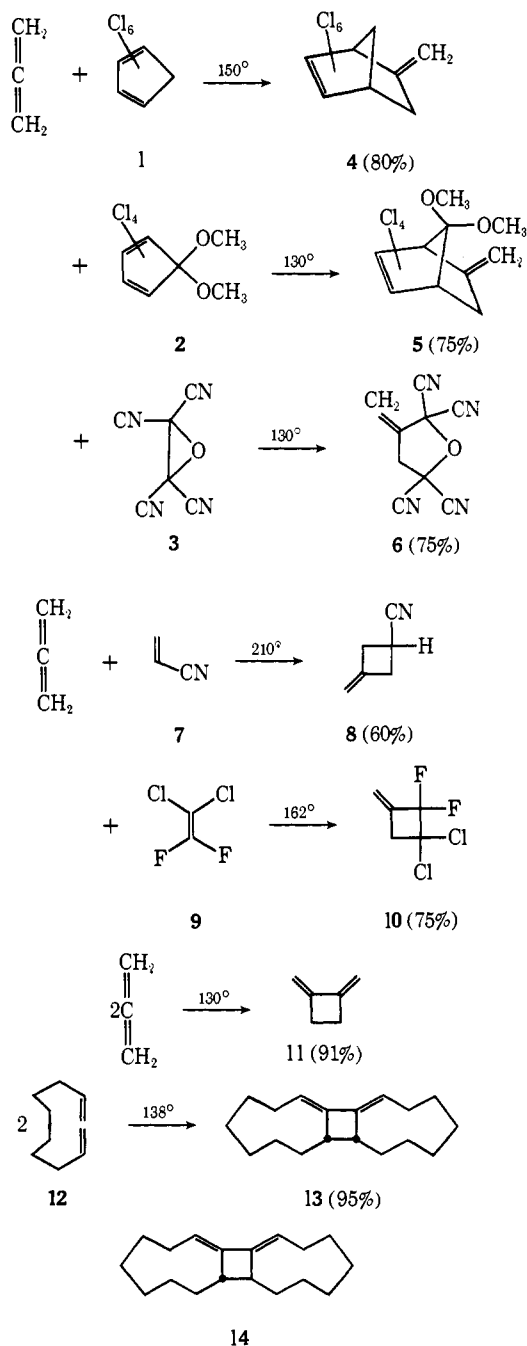
(5) This work has been partially reported in a series of preliminary communications: W. R. Dolbier, Jr., and S.-H. Dai, *J. Amer. Chem. Soc.,* **90**, 5028 (1968); **92**, 1774 (1970); *Tetrahedron Lett.,* 4645 (1970).
(6) H. Pledger, *J. Org. Chem.,* **25**, 278 (1960).
(7) W. J. Linn and R. E. Bensen, *J. Amer. Chem. Soc.,* **87**, 3657 (1965).
(8) H. N. Cripps, J. K. Williams, and W. H. Sharkey, *ibid.,* **81**, 2733 (1959).
(9) D. R. Taylor and M. R. Warburtan, *Tetrahedron Lett.,* 3277 (1967).

CH₂=C=CH₂ schemes in left column:

1 + (cyclopentadiene with Cl₆) →(150°) **4 (80%)**

2 + (diene with Cl₄, OCH₃, OCH₃) →(130°) **5 (75%)**

3 + (CN, CN, O, CN, CN) →(130°) **6 (75%)**

CH₂=C=CH₂ **7** + (CN) →(210°) **8 (60%)**

9 + (Cl, Cl, F, F) →(162°) **10 (75%)**

2 CH₂=C=CH₂ **11 (91%)** →(130°)

2 (cyclononadiene) **12** →(138°) **13 (95%)**

14

tion processes (formally also [2 + 2] cycloadditions), that of allene itself[10] and of 1,2-cyclononadiene (**12**).[11]

Experimental Section

Melting points were determined in a Thomas-Hoover capillary melting point apparatus and are uncorrected. All glpc work was performed on a Model A-90-P3 Varian Aerograph gas chromato· graph equipped with a Varian Model G2010 strip chart recorder. Nmr spectra were obtained using Varian A-60 spectrometers and mass spectra were obtained using a Hitachi Model RMU-6E spectrometer. Essentially all of the reactions used for isotope effect studies have been previously investigated. However, the procedures given are generally quite different from those reported, owing to the special requirements of the isotope effect studies.

Allene-1,1-d_2 was prepared by the reaction of either 1,3-dichloropropyne or propargyl-1-d chloride with a stirred, refluxing mixture

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(10) S.-H. Dai and W. R. Dolbier, Jr., *J. Org. Chem.*, **37**, 950 (1972) and references therein.

(11) L. Skattebøl and S. Solomon, *J. Amer. Chem. Soc.*, **87**, 4506 (1965).

of D₂O, zinc dust, and dioxane. The former procedure has been described in detail by Morse and Leitch.[12] Purification was then achieved by bubbling the gaseous product mixture through a AgNO₃-NH₄OH solution to remove propyne. Isotopic analysis was accomplished by low-voltage mass spectrometry (11 eV).

Allene-d_4 was prepared by the reaction of hexachloropropene with a stirred, refluxing mixture of D₂O, zinc dust, and dioxane. This procedure is also described in detail by Morse and Leitch.[12] Purification and isotopic analysis were accomplished as above.

Mixtures of allene-d_0 and allene-d_4 for intermolecular isotope effect studies were generally prepared in such a way that the mole fractions were about equal. The procedure was as follows. The allene-d_4 (d_4 = 91.3, d_3 = 8.7%) was allowed to vaporize in a closed vacuum system (vol = 1230 ml) until the pressure showed 400 mm. This allene was then condensed in a collecting tube on the vacuum line. Allene-d_0 was then expanded into the system to a pressure of 370 mm, and this amount condensed in the same tube. The tube was sealed, warmed to room temperature, shaken carefully for 15 min, and allowed to stand overnight. To sample the homogeneous mixture, the mixture was allowed to expand entirely into a larger vacuum line. After standing for several minutes, a mass spectrum bulb was opened to collect a gas sample for low-voltage (~9 eV) mass spectral analysis. Hand scanning of the peaks gave flat-top peaks. The process was repeated four times and the peak height averaged to give the isotopic composition of the allene mixture: 48.4 ± 0.3, 4.6 ± 0.1, 47.0 ± 0.3 for allene-d_0, $-d_3$, and $-d_4$, respectively. The measured allene-d_0 proportion is slightly overestimated if only part of the allene mixture is expanded into the vacuum system for sampling.

Reaction of Allene with Acrylonitrile.[8] Allene (0.4 g, 0.01 mol) and 2.1 g (0.04 mol) of acrylonitrile were sealed in a 10-ml pyrolysis tube as a benzene solution. The sealed tube along with several pieces of Dry Ice (0.6-1.0 g) then was sealed inside a small, stainless-steel autoclave (inside capacity of 45 ml). The autoclave was then heated under the conditions seen in Table I. After open-

Table I. Intramolecular Isotope Effects in the Allene–Acrylonitrile System

Reaction temp, °C[a]	Reaction time, hr	Allene deuterium content[b,c]	Nmr ratio,[d] allyl/vinyl	$k_H/k_D{}^g{}_{cor}$[h]
210 ± 4	12	100% d_0	2.50 ± 0.02[e]	
206 ± 5	10	91.2% d_2 7.03% d_1	4.28 ± 0.03[e]	1.21 ± 0.02
225 ± 1	12	92.2% d_2 5.90% d_1	4.18 ± 0.04[f]	1.15 ± 0.02
225 ± 1	14	92.2% d_2 5.90% d_1	4.14 ± 0.05[f]	1.13 ± 0.02

[a] Reactions using benzene as solvent were run in sealed tubes and heated in a tube furnace. [b] Deuterium content was measured by low-voltage mass spectrometry. [c] Deuterium content of allene recovered from reaction mixture was virtually unchanged. [d] Errors denoted in all tables are standard deviations for at least ten measurements, in this case nmr ratios. [e] The chemical shift of the hydrogen α to the nitrile group is identical with that of the allyl hydrogens. [f] For k_H/k_D = 1.00, one would expect an nmr ratio of 4.0. [g] k_H/k_D in each table expresses the preference for hydrogen to end up in the *saturated* position. [h] The calculated isotope effect is corrected for d_1 and d_0 content by assuming that $(k_H/k_D)d_1{}^2 = (k_H/k_D)d_2$.

ing the tube at $-78°$, unreacted allene was removed on the vacuum line. The volatile product was then transferred *via* vacuum line (room temperature to $-195°$). The adduct, 3-methylenecyclo· butanecarbonitrile (**8**), was then separated from starting materials by glpc (10% Carbowax 1500, 8-ft × 0.25 in. column at 150°) and was obtained in >60% yield. Its spectroscopic properties were identical with those reported previously.[8]

Kinetic Intramolecular Isotope Effects in the Allene–7 System. After purification of the adduct of allene-1,1-d_2 and 7 a careful nmr spectrum, with multiple intergrations, was obtained. At least ten integrations were averaged to obtain the value of the allylic

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(12) A. T. Morse and L. C. Leitch, *J. Org. Chem.*, **23**, 990 (1958).

Table II. Equilibrium Isotope Effects in the Allene–Acrylonitrile System

Reaction temp, °C	Reaction time, hr	Nmr ratio, allyl/vinyl	k_H/k_D
287 ± 5	15	3.26 ± 0.02	0.92 ± 0.01
280 ± 5	34	3.28 ± 0.04	0.93 ± 0.01
280 ± 5	48	3.26 ± 0.04	0.92 ± 0.01

to vinylic proton ratio for each run as seen in Table I. The intramolecular isotope effect could be easily calculated from this ratio and the value could be corrected for the small amount of allene-d_1 component.

Table III. Intermolecular Isotope Effects in the Allene and Acrylonitrile System

Allene composition before reaction	Allene d_0/d_4	Nmr ratio, allyl/vinyl	Adduct d_0/d_4	k_H/k_D
d_4 50.8 ± 0.03 d_0 49.2 ± 0.03	0.97 ± 0.02	4.01 ± 0.03	1.00 ± 0.3	1.03 ± 0.05
d_4 50.2 ± 0.03 d_0 49.8 ± 0.03	0.99 ± 0.02	3.94 ± 0.03	1.04 ± 0.02	1.05 ± 0.04
			Av	1.04 ± 0.05

Table IV. Intramolecular Isotope Effects in the Allene–9 System

Reaction temp, °C	Reaction time, hr	Nmr ratio, allyl/vinyl	$k_H/k_{Dcor}{}^a$
190	48	1.00 ± 0.01	b
170	48	1.12 ± 0.02	1.15 ± 0.03
170	48	1.12 ± 0.03	1.15 ± 0.04
162	40	1.19 ± 0.03	1.24 ± 0.03
200	48	1.12 ± 0.03^c	1.15 ± 0.04
		Av	1.17 ± 0.04

$^a k_H/k_D$ value corrected for 13.5% d_1 and 2.8% d_0 species present in allene-$1,1$-d_2. ^{b} Control run with 100% allene-d_0. ^{c} When the adduct is heated to 287° for 4.5 hr, the nmr ratio diminishes to 1.01 ± 0.02.

sealed in a thick-walled tube in the presence of a small amount of hydroquinone. The tube was heated in a manner similar to that described for the allene–7 reaction at temperatures varying from 162 to 200° for periods from 40 to 48 hr. About 1.3 g of volatile starting materials was recovered after the reaction. The remaining product mixture was analyzed and the components were isolated by glpc (10% tricresyl phosphate, 15 ft × 0.25 in. column at 75°). There were two main components in a ratio of 2:3, the earlier eluting component being the dimer of 9 while the latter component was 2,2-difluoro-3,3-dichloromethylenecyclobutane (10): bp 123°; nmr δ 3.31 (t, 2), 5.46 (m, 1), and 5.75 ppm (m, 1). The nmr indicated that this isomer comprised at least 95% of the [2 + 2] adduct mixture.

Kinetic Intramolecular Isotope Effects in the Allene–9 System. The method employed was identical with that used in the allene–7 system. See Table IV for the results.

Reaction of Allene with Hexachlorocyclopentadiene.[6] Allene (~1.0 g) was transferred *via* vacuum line to a pyrolysis tube (~10-ml capacity) containing an 1.5–2.0 molar excess of **1**. The tube was sealed under vacuum, wrapped with glass wool, and heated in a tube furnace for the desired time. Then after cooling to −78°, the tube was opened and the product purified by molecular distillation (115° (0.5 mm)). Further purification could be done by a rapid distillation. Yields of purified 1,2,3,4,7,7-hexachloro-5-methylene-2-norbornene were generally ~80%: nmr δ 3.12 (quart., 2 H), 5.41 (sext, 1 H), and 4.25 ppm (sext, 1 H).

Kinetic Intramolecular Isotope Effects in Allene–1 System. The method employed was identical with that used in the allene–7 system. Table V contains the results.

Intermolecular Isotope Effects in Allene–1 System. Using a large excess (21-fold) of allene-d_0 and -d_4 with **1** the reactions and purifications were identical with those for other such reactions

Table V. Intramolecular Isotope Effects in the Allene–1 System

Reaction temp, °C	Reaction time, hr	Allene deuterium content	Nmr ratio, allyl/vinyl^a	k_H/k_{Dcor}
150 ± 3	12	100% d_0	1.006 ± 0.006	
150 ± 3	15	91.2% d_2 7.03% d_1	0.894 ± 0.004	0.89 ± 0.01
145 ± 2	12	91.2% d_2 7.03% d_1	0.87 ± 0.01	0.87 ± 0.01
145 ± 2	15	91.2% d_2 7.03% d_1	0.93 ± 0.01	0.93 ± 0.01
135 ± 1	12	91.2% d_2 7.03% d_1	0.923 ± 0.004	0.92 ± 0.01

^{a} Heating the product mixture at temperatures as high as 200° caused virtually no change in the nmr ratio.

Equilibrium Isotope Effects in the Allene–7 System. The adduct of allene-d_4 and 7 was heated to 280–287° for 15–48 hr in a sealed tube. The results are shown in Table II.

Intermolecular Isotope Effects with Allene–7 System. A mixture of allene-d_0 and allene-d_4 was allowed to react with a fourfold excess of acrylonitrile in a manner similar to that described above. However, the temperature of the reactions was maintained at 190–210° so as to be able to control the rate of the reaction. The reactions were terminated when the conversion to adduct 8 was only ~10%. The allyl/vinyl proton ratio was determined by nmr as described earlier and, with the three protons of 7 being used as an internal proton standard, the values of k_H/k_D can easily be obtained algebraically. They are summarized in Table III.

Reaction of Allene and 1,1-Dichloro-2,2-difluoroethylene.[9] A mixture of 0.5 g (0.013 mol) of allene and 2.5 g (0.019 mol) of **9** was

except that the excess allene was recovered. An internal proton standard $CHCl_3$ was used, weighing out appropriate amounts of adduct and $CHCl_3$ to give near identical peak integrations. The relative amount of heavy and light adduct could then be deduced knowing the moles of total adduct (from weighing) and the moles of light adduct (from adduct/$CHCl_3$ proton ratio). Then k_H/k_D = $(f_H/f_D)_{adduct} \times (d_4/d_0)_{starting\ allene}$. Table VI shows the results.

1,2,3,4,7,7-Hexachloro-5-(chloromethyl-d_2)-2-norbornene. Allyl-$1,1$-d_2[13] chloride (~0.75 g) and an approximate twofold excess of **1** (4.5 g) were sealed in a 15-ml, thick-walled tube. After heating at 130° for 15 hr in a tube furnace, the tube was cooled and opened.

(13) R. D. Schuetz and F. W. Millard, *J. Org. Chem.*, **24**, 297 (1959).

Table VI. Intermolecular Isotope Effects in the Allene–1 System

Mole ratio allene/diene	Reaction temp, °C	Reaction time, hr	k_H/k_{Dcor}
21.1	135 ± 3	19	0.93 ± 0.04
21.1	135 ± 3	10	0.88 ± 0.04

Table VII. Intramolecular Isotope Effects in the Allene–2 System

Reaction time, hr	Reaction temp, °C	Nmr ratio, vinyl/allyl	k_H/k_D
10	125 ± 3	1.09 ± 0.01	0.92 ± 0.01
10	125 ± 3	1.10 ± 0.01	0.91 ± 0.01
10	125 ± 3	1.09 ± 0.02	0.92 ± 0.02
10	125 ± 3	1.10 ± 0.02	0.91 ± 0.02
			Av 0.92 ± 0.02

Table VIII. Intramolecular Isotope Effects in the Allene–3 System

Mole ratio, allene/3	Reaction temp, °C	Reaction time, hr	Nmr ratio, vinyl/allyl	k_H/k_{Dcor}
3.20	130–135	10	0.99 ± 0.01	0.93 ± 0.01
3.42	130–135	10	1.07 ± 0.01	0.92 ± 0.01
2.95	130–135	10	1.06 ± 0.01	0.94 ± 0.01
				Av 0.93 ± 0.01

The liquid product was distilled and a pale yellow oil obtained: bp 96–99° (0.01 mm); nmr δ 2.36 (quart., J_{AB} = 3.8 cps, J_{AX} = 12.5 cps, 1 H), 3.17 (q, J_{BX} = 8.6 cps, J_{AX} = 12.5 cps, 1 H), and 3.62 ppm (q, J_{AB} = 3.8 cps, J_{AX} = 8.6 cps, 1 H).

1,2,3,4,7,7-Hexachloro-5-(methylene-d_2)-2-norbornene (18).[14] A mixture of 1,2,3,4,7,7-hexachloro-5-(chloromethyl-d_2)-2-norbornene (3.0 g, 8.6 mmol), KOH (0.56 g, 10 mmol), and 20 ml of absolute EtOH was refluxed for 3 hr. The solution was then filtered and solvent distilled at reduced pressure. The product was collected (2.2 g, 82%) as a colorless, viscous oil: bp 76–80° (0.010 mm); nmr (CCl₄) δ 2.98 (q, J_{AB} = 15.1 cps, 2 H), 5.32 and 5.68 (m, <0.01 H).

Pyrolysis of 1,2,3,4,7,7-Hexachloro-5-(methylene-d_2)-2-norbornene (18). Pyrolyses were carried out by heating **18** as a solution in a large excess of pentane or hexane or neat (gas phase) in a sealed tube. Temperatures varied from 150 to 310° and time of heating from 12 to 5 hr, respectively. In all cases the unrearranged **18** was recovered, although after 5 hr at 310° only 15% could be recovered.

Reaction of Allene with 5,5-Dimethoxy-1,2,3,4-tetrachlorocyclopentadiene. (2) Allene (1.2 g, 30 mmol) and **2** (2.53 g, 9.6 mmol) were sealed in a thick-walled tube (10-ml capacity) and heated to 130° for 12 hr in a tube furnace. After cooling to −78°, the tube was opened, the unreacted allene transferred, and the residual oil fractionated to give 2.35 g (78%) of colorless product, **5**: bp 78–80° (0.035), 105–106° (0.25 mm); nmr (CCl₄) δ 2.45 (d with fine splitting to t, J_{AB} = 14.2 cps, J_{AX} = 1.8 cps, 1 H), 2.95 (d split to t, J_{AB} = 14.2 cps, J_{BX} = 2.2 cps, 1 H), 3.47 (s, 3 H), 3.51 (s, 3 H), 4.98 (t, J_{AX} = 1.8 cps, 1 H), and 5.30 (t, J_{BX} = 2.2 cps, 1 H).

Intramolecular Isotope Effects in Allene–2 System. The procedure employed was identical with that used in the allene–7 system. Table VII shows the results.

Reaction of Allene with Tetracyanoethylene Oxide[7] (3). **3** (0.65 g, 4.5 mmol) dissolved in 6 ml of p-dioxane was transferred to a 20-ml thick-walled tube and allene (15.4 mmol) was condensed into it via vacuum line. The tube was sealed under N₂ and heated to 130–135° for ~10 hr. Allene was recovered on the vacuum line by transfer from −78 to −195°, the residual liquid was filtered, and the dioxane evaporated. The crude solid (0.55 g, 75%) was recrystallized from benzene and sublimed to provide a pale yellow solid, **6**: mp 113–115°; nmr (acetone-d_6) δ 4.12 (t, J = 2.2 cps, 2 H) and 6.23 ppm (m, 2 H).

Intramolecular Isotope Effect Study in the Allene–3 System. The analysis of the adduct **6** was accomplished as in the allene–7 system. The results are in Table VIII.

Dimerization of Allene. The procedure described optimizes the yield of 1,2-dimethylenecyclobutane (**11**) while minimizing the over conversion of allene.[10] To a 15-ml, thick-walled tube were added 2.4 g of benzene and 0.8 g of allene via vacuum line. After sealing in $vacuo$, the tube was wrapped in glass wool and heated at 130° for 14 hr, whence the unreacted allene (95%) was recovered by vacuum line transfer from −78 to −195°. Of the residue, 91% was determined by glpc (10%, 10 ft × 0.25 in. Carbowax 1500 column at 80°) to be **11**. The only other components in the mixture were the three trimers. The dimer was collected by glpc and shown to display the previously reported spectral characteristics:[15] nmr (CCl₄) δ 2.63 (sext, 4 H), 4.69 (sext, 2 H), and 5.13 ppm (sext, 2 H); uv (EtOH) λ_{max} 255 mμ (ε 10,100), 246 (12,300), and 240 (11,000).

Intramolecular Isotope Effects for Allene Dimerization. The procedure followed was essentially the same as that employed for the allene–7 system. Table IX shows the results.[16]

Intermolecular Isotope Effects for the Allene Dimerization System. The allene-d_0 and -d_4 composition before reaction was determined as described earlier and was used to calculate the $statistical$ isotopic composition of dimer if k_H/k_D = 1. The $actual$ isotopic composi-

Table IX. Intramolecular Isotope Effects for the Dimerization of Allene[a]

Allene deuterium content,[b] %	Nmr ratio, allyl/vinyl	Allene deuterium content,[b] %	Nmr ratio, allyl/vinyl
100 d_0	1.00 ± 0.03	95.7 d_2	1.13 ± 0.01
95.5 d_2	1.16 ± 0.02	8.30 d_1	
3.86 d_1		95.5 d_2	1.14 ± 0.01
		3.72 d_1	

[a] Temperature of all runs was 140 ± 2°, the reaction times ranged from 13 to 24 hr, the ratio of benzene/allene from 1.2 to 1.9, and the per cent of allene reacted from 5 to 8%. [b] The deuterium content of the recovered allene from each run, as measured by low-voltage mass spectrometry, was virtually identical with that of the starting allene.

tion of dimer was then determined by low-voltage mass spectrometry (<11 eV) where >95% of the observed peaks were parent peaks. The intramolecular isotope effect could then easily be calculated and they are tabulated in Table X.

Cyclooctanol-1-d was prepared from cyclooctanone in 93% yield using LiAlD₄ in ether in a standard procedure.

Cyclooctene-1-d. To a solution of 30.2 g (0.24 mol) of cyclooctanol-1-d in 160 ml of toluene was added 5.8 g (0.25 g-atom) of sodium. The mixture was heated under reflux and stirred for 18 hr, whence the mixture was cooled to room temperature and the unreacted sodium removed with a wire. CS₂ (18.0 g, 0.24 mol) was then added dropwise to the mixture and a slightly yellow solid was formed during the addition. The mixture was then refluxed for 8 hr. After cooling to room temperature 32 g (0.2 mol) of methyl iodide was added dropwise and the mixture warmed to 60° overnight. The mixture was cooled and the NaI precipitate filtered. The NaI was washed with ether, the ether combined with the filtrate, and the filtrate evaporated on a rotary evaporatory. The toluene was distilled at room temperature (0.5 mm). Some unreacted cyclooctanol was also distilled and recovered (~9.5 g). The xanthate residue was pyrolyzed in a 50-ml, pear-shaped flask topped with a short condenser, by heating on an oil bath at 170°

(14) W. K. Johnson and V. Mark, J. Org. $Chem$., **26**, 4105 (1961).

(15) B. Weinstein and A. H. Fenselau, J. $Chem$. Soc. C, 368 (1967).

(16) As pointed out by Witta Priester, the ratio of allyl to vinyl protons in this case as in the case of 1,2-cyclononadiene-1-d dimer, is not a true measure of k_H/k_D, with the actual value undoubtedly significantly larger.

Table X. Intermolecular Isotope Effects for the Dimerization of Allene[a,b]

Allene composition before reaction[c]	Allene composition recovered[c]	Dimer isotopic composition obsd[c]	k_H/k_D[d]	$k_H/k_D)^2$[e]
d_4 49.3 ± 0.1	d_4 50.5 ± 0.1	d_8 24.2 ± 0.4		
d_0 50.7 ± 0.1	d_0 49.5 ± 0.1	d_4 49.7 ± 0.2	1.021 ± 0.028	1.020 ± 0.036
		d_0 26.1 ± 0.3		
d_4 49.9 ± 0.3	d_4 49.3 ± 0.5	d_8 24.5 ± 0.2		
d_0 50.1 ± 0.3	d_0 50.7 ± 0.5	d_4 49.9 ± 0.1	1.022 ± 0.018	1.036 ± 0.037
		d_0 25.6 ± 0.1		
d_4 48.7 ± 0.1	d_4 48.0 ± 0.2	d_8 23.6 ± 0.2		
d_0 51.3 ± 0.1	d_4 50.1 ± 0.1	d_4 50.1 ± 0.1	0.997 ± 0.013	1.004 ± 0.024
		d_0 26.3 ± 0.2		
			Av 1.013 ± 0.020	1.020 ± 0.032

[a] The temperature of all reactions was 130°, the time of reaction ranged from 12 to 14 hr, and the per cent conversion ranged from 4.1 to 6.3%. [b] The yields of 1,2-dimethylenecyclobutane were 92–95%. [c] Only d_4 and d_0 allenes were considered and d_8, d_4, and d_0 dimers since the small amount (<6%) of d_3 allene did not complicate the mass spectral analysis. [d] Calculated from the d_4/d_0 ratio of dimers as obtained from low-voltage mass spectra where generally less than 5% fragments were observed. [e] Calculated from the d_8/d_0 ratio.

Table XI. Intramolecular Isotope Effects for the Dimerization of **12**-1-d

Dimer	Mp, °C	Mole ratio 13 or 14/CHCl₃, A	Nmr ratio, vinyl/CHCl₃, B	A/B (k_H/k_D)
14 d_0	80–82	1.229	1.22 ± 0.01	1.01 ± 0.01
14 d_2	80–82	1.129	1.03 ± 0.02	1.10 ± 0.03
14 d_2	80–82	0.8834	0.799 ± 0.006	1.11 ± 0.01
14 d_2	80–82	1.108	0.987 ± 0.013	1.12 ± 0.02
				Av 1.10 ± 0.03
13 d_0	109–110	1.035	1.02 ± 0.01	1.01 ± 0.01
13 d_2	109–110	0.9890	0.935 ± 0.02	1.06 ± 0.02

for 2 hr. A colorless gas, COS, was evolved during the heating. The residue was distilled through a Vigreux column to give 11.1 g (62%) of cyclooctene-1-d: nmr (CCl₄) δ 1.13–2.04 (broad, 8 H), 2.04–2.67 (broad, 4 H), and 6.53 ppm (t, J = 7.9 cps, 1 H).

9,9-Dibromobicyclo[6.1.0]nonane-1-d. Potassium (10 g, 0.26 g-atom) was treated with 300 ml of *tert*-butyl alcohol, under N₂, to give a solution to which 26.0 g (0.24 mol) of cyclooctene-1-d was added, followed by slow addition of 78.0 g (0.31 mol) of bromoform with stirring and cooling in an ice–salt bath. The addition took 3 hr and the color of the reaction mixture changed gradually from yellow to brown. When the addition was complete, the mixture was allowed to warm to room temperature and stirred overnight. Water (100 ml) was added and the organic layer separated. Three ether extractions of the aqueous layer were combined with the organic layer and dried over MgSO₄. The solvent was evaporated and distillation provided 26.4 g (40%) of 9,9-dibromo[6.1.0]nonane-1-d, bp 107–110° (1 mm).[17]

1,2-Cyclononadiene-1-d was prepared in 98% yield from the 9,9-dibromobicyclo[6.1.0]nonane-1-d and ethereal methyllithium using the known procedure.[17] Nmr indicated that only one vinyl hydrogen was present.

Dimerization of 12.[11] A sealed tube containing 2.62 g (22 mmol) of **12** was heated at 138 ± 2° for 24 hr. Extraction of the solid product with hot EtOH and evaporation gave 2.42 g (93%) of a white solid (mp 68–70°). The cis and trans dimers **13** and **14** could be separated by column chromatography using a 2-ft alumina column with hexane as eluting solvent. Each dimer was further purified by recrystallization from 1-propanol to yield three parts of trans dimer[11] **14** [mp 80–83; nmr (CCl₄) δ 0.89–2.45 (broad m, 26 H), 5.50 (t, J = 8.5 cps, 2 H)] and one part of cis dimer[11] **13** [mp 108–110°; nmr (CCl₄) δ 0.89–2.51 (broad, 24 H), 3.12 (broad, 2 H), 5.50 ppm (t, J = 8.5 cps, 2 H)] (33% overall recovery). The deuterated dimers showed similar properties except that the vinyl protons were sharp triplets with *no* fine splitting.

Intramolecular Isotope Effects for 1,2-Cyclononadiene System. Estimation of the intramolecular isotope effect was obtained using the trans and cis dimers from the **12**-1-d dimerization, by using CHCl₃ as an internal proton standard. Knowing the relative weights of CHCl₃ and **13** or **14** as well as the nmr ratio of CHCl₃ proton and **13** or **14** vinylic protons, one could easily calculate the desired isotope effect (see Table XI).

(17) L. Skattebøl, *Acta Chem. Scand.*, 17, 1683 (1963).

Discussion

Secondary deuterium isotope effects are being utilized with increasing frequency in mechanistic investigations of cycloaddition reactions, with varying degrees of success. There often has been, however, a difficulty in predicting even the nature (whether they be normal or inverse) of expected isotope effects for these reactions. It is hoped that this work, along with that of numerous other research groups will help alleviate this problem and thus make secondary isotope effects a viable mechanistic tool in the study of cycloaddition reactions.

It seems that there can be little doubt regarding the *basic* conclusions to be drawn from the isotope effects described above. Allene is quite a unique molecule. In a concerted cycloaddition, it behaves as if it has two identically "isolated," double bonds. Deuterium substitution on one of the double bonds, such as in allene-1,1-d₂, should then give rise to the same order and magnitude of *intramolecular* isotope effects as had previously been obtained intermolecularly (*i.e.*, with a mixture of protiated and deuterated alkene).[18]

Of equal significance is the fact that in *non*concerted cycloadditions, allene apparently consistently forms the initial C–C bond at the center, sp-hybridized carbon.[8] This, significantly, should give rise to an allylic radical intermediate where, again, unsymmetrical deuterium labeling can give the molecule an isotopically discriminatory product-forming step.

The exact *nature* of the intermediate, where it exists, will not be considered at length here. Reactions with

(18) (a) D. E. Van Sickle and J. O. Rodin, *J. Amer. Chem. Soc.*, 86, 3091 (1964); (b) S. Selzer, *ibid.*, 87, 1534 (1965); (c) T. J. Katz and R. Dessau, *ibid.*, 85, 2172 (1963); (d) W. F. Bayne and E. I. Snyder, *Tetrahedron Lett.*, 2263 (1970); (e) P. Brown and R. C. Cookson, *Tetrahedron*, 21, 1993 (1965).

optically active allenes indicate that a totally symmetrical intermediate cannot be formed *where alkylated allenes are used*.[3a,d] Whether these stereochemical results derived from (rigid or nonrigid) nonplanar intermediates,[19] or whether they are due to a combination of nonbonded interactions and rapid formation of product from the initially formed intermediate, will not concern us greatly in this paper. Of interest primarily will be *whether* an intermediate is formed or not.
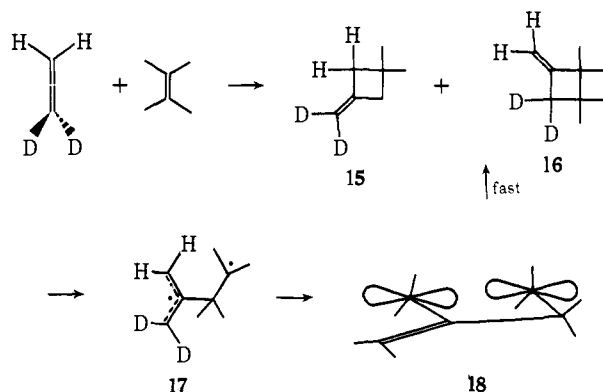
A discussion of those isotope effects which might be expected for the two mechanisms, depicted above for a [2 + 2] cycloaddition, is presented below.

Secondary isotope effects are generally considered to arise from changes in out-of-plane C–H bending force constants. Usually, but not always, such changes have been associated with concomitant hybridization changes.

A synchronous formation of both new σ bonds should give rise to a predominance of isomer 16 since the reaction would involve a rate-determining change of hybridization at C-1 or C-3 from sp^2 to sp^3. Thus both the intra- and intermolecular competitions should result in k_H/k_D being <1.

On the other hand, the rate-determining step of the two-step mechanism involves *no* change in hybridization at C-1 or C-3, and should thus give rise to at best a small *inter*molecular isotope effect. Only recently, Pryor and coworkers[21] have demonstrated that the conversion $sp^2 \rightarrow$ radical not only should, but does experimentally give rise to a small normal deuterium isotope effect (*i.e.*, $k_H/k_D \approx 1.03$). It is of course possible that there could also result some intermolecular effect due to other molecular interactions.[22] The product-forming step would, however, involve a change in hybridization which could give rise to intramolecular competition. The effect need *not*, however, be comparable to that observed in a rate-determining step such as in the concerted reaction. In the concerted reaction, discrimination is being effected in a moderately high activation energy step, where the transition state might reasonably be expected to be far along the reaction coordinate (*i.e.*, significant σ bond formation). On the other hand, intramolecular discrimination in

the two-step process takes place in a fast, relatively low activation energy step where the transition state should be *early* along the reaction coordinate. In fact, simple combination of radicals might be thought to have negligible activation energy. The fact that there apparently is a small, but significant activation energy for combination of such stabilized diradicals as 17 would seem to indicate that the bulk of the activation energy for such a process derives from the *rotation* of a methylene group from the planar configuration toward the orthogonal geometry, 18, which is necessary for σ bond formation. Thus the transition state for product formation in the two-step process may in actuality have little or no σ bond character. Any observed isotope effect for such a process consequently should not be due to a change in hybridization, but due to a change from allylic radical $\rightarrow$ primary radical. One possible source of potential isotope effects in such a process might be relief of nonbonded interactions and torsional interactions which would be found in the planar allylic, but not in the nonplanar radical system. This could be considered a "steric" isotope effect whereby the hydrogen would rotate more rapidly out of a sterically congested situation.[23]

A system similar in many ways which has been studied extensively and which gives a strong indication of steric inhibition to planarity is the trimethylenemethane diradical system. In this system, in spite of the predicted inherent stability[25] of the planar trimethylenemethane diradical, it seems clear that *any* alkyl substitution is sufficient to prohibit planarity of the π system.[26] Hückel calculations back up this experimental conclusion,[26,27] and Dewar has recently determined that the singlet parent trimethylenemethane species should be most stable in a nonplanar conformation.[28]

Carrying this analogy over to the various allylic diradicals which one would invoke for the [2 + 2] reactions and dimerizations of allenes, one might propose that the stereospecific reactions observed for *substituted* allenes do not necessarily make inconsistent a proposal of essentially planar, symmetrical intermediates for the apparent two-step reactions of *unsubstituted* allene that we have studied.

Two basic types of intramolecular isotope effects were observed. A normal (*i.e.*, $k_H/k_D > 1$) effect was observed in all [2 + 2] reactions, including the dimerizations. While a normal effect is not consistent with expectations for a concerted reaction, it can be rationalized, as discussed above, in terms of a two-step reaction. Moreover, Crawford, earlier, had observed an analogous normal effect for the ring closure of the trimethylenemethane diradical.[29] An important piece of corroborative evidence pointing to distinct rate-determining and product-forming steps in the [2 + 2] cycloadditions, was the observation of only relatively small (not significant relative to error) intermolecular isotope

(19) Baldwin has suggested[3a,20] that both the kinetic isotope effects and the stereochemical results could be accommodated by an orbital symmetry controlled formation of a disymmetric allyl radical and orbital symmetry controlled destruction of this disymmetric intermediate.

(20) J. E. Baldwin and R. H. Fleming, *Fortsch. Chem. Forsch.*, 15, 281 (1970).

(21) We wish to thank Professor W. Pryor for communicating his results to us prior to publication.

(22) *I.e.*, rotation of one of the allene methylene groups into the plane of the other in the rate-determining transition state.

(23) A significant and related, "steric" isotope effect has only recently been reported by Winter and Honig.[24]

(24) R. E. K. Winter and M. L. Honig, *J. Amer. Chem. Soc.*, 93, 4616 (1971).

(25) See P. Dowd, *ibid.*, 88, 2587 (1966), and references therein.

(26) W. R. Dolbier, Jr., K. Akiba, J. M. Riemann, C. A. Harmon, M. Bertrand, A. Bezaquet, and M. Santelli, *ibid.*, 93, 3933 (1971).

(27) M. Vala and J. Wrobel, unpublished work.

(28) M. J. S. Dewar and J. S. Wasson, *J. Amer. Chem. Soc.*, 93, 3081 (1971).

(29) R. J. Crawford and D. M. Cameron, *ibid.*, 88, 2589 (1966).

Table XII. Summary of Secondary Deuterium Isotope Effects

Cyclo-addition type	System	Intra-molecular k_H/k_D	Inter-molecular k_H/k_D	Equi-librium k_H/k_D
[2 + 2]	Allene–7	1.13–1.21	1.05	0.92
[2 + 2]	Allene–9	1.17		
[2 + 2]	Allene–allene	1.14	1.02	
[2 + 2]	**12–12**	1.10		
[2 + 3]	Allene–3	0.93		
[2 + 4]	Allene–1	0.90	0.90	
[2 + 4]	Allene–2	0.92		

effects in the allene–acrylonitrile reaction and the allene dimerization (Table XII).[30]

An interesting sidelight to the allene–acrylonitrile reaction was the fact that the [2 + 2] cycloaddition was complicated by a concomitant thermal isomerization of a degenerate methylene–cyclobutane type.[31] From Table I, one can see the isotope effect became minimized by this equilibration process. Indeed, if carried to complete equilibrium, one was able to measure the equilibrium isotope effect and as expected,[32] it was inverse (k_H/k_D = 0.92 ± 0.01), and thus could not be responsible for the observed *kinetic* effect.

The possibility that the normal intramolecular effect was due to a "ponderal" effect as suggested by Crawford[29] could be safely ruled out by the observation of a substantial isotope effect for the 1,2-cyclononadiene dimerization system.

In the [2 + 3] and [2 + 4] reactions which were investigated an *inverse* kinetic intramolecular secondary deuterium isotope effect was invariably observed. As discussed earlier, such an effect was entirely consistent with a concerted process being involved for these cycloadditions. Essentially all previous isotope effect studies of concerted suprafacial–suprafacial cycloadditions[35] have resulted in the observation of inverse secondary deuterium isotope effects.[18]

Again corroborative evidence came from the intermolecular competitive studies where the allene–1 [2 + 4] cycloaddition gave rise to an intermolecular isotope effect which, within experimental error, could not be distinguished from the intramolecular effect.[37] This result is precisely that which would have been predicted on the basis of a concerted mechanism where

the rate-determining and product-forming steps would be one and the same.

An additional control reaction was conducted to ensure against either equilibrium isotope effects or some selective decomposition of either of the isotopically different isomers being involved. First, the value of k_H/k_D was found to be essentially constant after further heating of the adduct mixture and, second, **19** was specifically synthesized and shown not to thermally convert to isomer **20**.

19   20
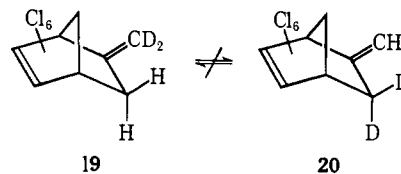
Concluding Remark

While there are still many unanswered questions about the mechanism of allene cycloadditions, particularly concerning the exact nature of intermediates, where they are formed, it does appear on the basis of our isotope effect studies, that allene behaves as a reasonably normal electron-rich alkene in its cycloaddition reactions, that is, it seems to undergo synchronous [2 + 3] and [2 + 4] and multistep [2 + 2] cycloadditions. There is *no* kinetic evidence for antarafacial behavior of allene in [2 + 2] processes, contrary to the behavior of ketene whose carbon–carbon double bond *will not* undergo [2 + 4] cycloadditions and which does give strong evidence for antarafacial behavior in most [2 + 2] processes.[4] Moreover allene does not, of course, have the "vinyl cation" character to which Woodward and Hoffmann have attributed ketene's strange behavior.[38, 39]

An equally important conclusion that we would like to draw from this work is that, within the scope of the reactions studied, which are a rather broad selection of allene cycloadditions, the use of kinetic secondary deuterium isotope effects as a mechanistic probe has been very effective in leading to reasonably definitive conclusions. Other reactions of allene may also be conducive to mechanistic elucidation through the utilization of this tool.

It does appear that secondary deuterium isotope effects can provide a *very* sensitive probe into the exact nature of the transition states of reactions. It remains for us to learn how to precisely interpret them. It is hoped that the apparent intensification of utilization of this tool will lead to such knowledge.

(30) Baldwin has also reported a lack of significant intermolecular discrimination in the allene–acrylonitrile reaction.[20]

(31) W. von E. Doering and J. C. Gilbert, *Tetrahedron, Suppl.*, 7, 397 (1967).

(32) Equilibrium isotope/effects apparently depend upon differences in ground state vibrational energies.[33,34]

(33) E. R. Thornton, *Annu. Rev. Phys. Chem.*, 17, 349 (1966).

(34) R. Malojcic, K. Humski, S. Borcic, and D. E. Sunko, *Tetrahedron Lett.*, 2003 (1969).

(35) Some cycloadditions which apparently have the $_\pi 2_s$ and $_\pi 2_a$ capability give an inverse intermolecular effect at one end of the double bond and a normal effect at the other end.[36]

(36) (a) J. E. Baldwin and J. A. Kapecki, *J. Amer. Chem. Soc.*, 92, 4874 (1970); (b) E. K. von Gustorf, D. V. White, J. Leitich, and D. Henneberg, *Tetrahedron Lett.*, 3113 (1969).

(37) An intermolecular isotope effect was also measured for the allene–2 system. However, due to slight impurities in the adduct, the isotope effect, although corroborative, was very imprecise; *i.e.*, $k/_H k_D$ = 1.10 ± 0.13.

(38) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Academic Press, Weinheim/Bergstr., 1970, p 163.

(39) Further circumstantial evidence against any similarity between ketene and allene in their cycloaddition reactions derives from the fact that *cis*-alkenes react faster with ketenes in the $_\pi 2_s - _\pi 2_a$ process, while allenes apparently react faster with trans alkenes.[2b]