The melting point of a mixture with the semicarbazone of cis-9-methyl-2-decalone showed considerable depression.

Conformational Barriers in Medium-Sized Rings.
I. *trans*-Cyclodecene-1,2,4,4,9,9-d_6[1]

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The peculiar conformational situation in trans-cycloalkenes of medium ring size is discussed. It is concluded that one pair of optical isomers should exist in the odd-membered rings and two such pairs in the even-membered rings. For a given ring size, the various isomers are expected to be separated from one another by a substantial energy barrier. Cope and co-workers have shown previously that, for trans-cyclooctene, at least one of the barriers is high enough to allow isolation of two very stable optical isomers. Optically active trans-cyclononene was found to be much less stable and trans-cyclodecene gave no detectable optical activity. In the present investigation, the n.m.r. spectrum of trans-cyclodecene-1,2,4,4,9,9-d$_6$ has been studied as a function of temperature. Two processes which are slow on the n.m.r. time scale at low temperatures have been discovered. One of them, which involves rotation of the trans-alkene group through the loop formed by the methylene groups, was found to have an activation energy $\Delta E^* = 10.7 \pm 0.3$ kcal./mole and a frequency factor $A = 10^{11.7\pm0.3}$ sec.$^{-1}$. The other process, for which no accurate rates could be determined, appears to involve restricted rotation of the C-6–C-7 molecular segment in the cyclodecene ring.

Optical activity in solution can be associated with asymmetric substituted atoms or with "inherently dissymmetric" compounds. Although only relatively few classes which produce stable enantiomers are known for the latter type of isomerism,[2] the phenomenon is almost omnipresent among organic molecules when one considers all species characterized by potential-energy minima as individual entities. N.m.r. spectroscopy is particularly valuable as a tool for obtaining quantitative information about racemization processes which cannot be studied by classical means.[3] The characteristic realm of the n.m.r. line-shape method extends just from the borderline where the antipodes become too unstable to be isolated, down to interconversion barriers of a few kilocalories.

It has been proposed[4] that *trans* cyclic olefins of medium ring size should be resolvable into stable optically active conformations. Experimental evidence bearing on this prediction has been provided by Cope and his co-workers[5] who succeeded in isolating two isomers of *trans*-cyclooctene having opposite rotations. The levorotatory enantiomer was subsequently assigned the (R)-configuration.[5b] Molecular models indicate, however, that, in addition to the unsymmetrical environment of the double bond, *trans*-cyclooctene contains a second element of dissymmetry, the C-5–C-6 bond. Furthermore, it appears that rotation of the C-5–C-6 segment through the ring is about as difficult as the analogous movement of the double bond, a conclusion which is substantiated by the results to be discussed below. The reasoning leads to the four isomers **1a–d** shown in Figure 1. Interconversion of the antipodes requires two processes, which may or may not occur simultaneously, whereas either process alone would only produce the corresponding diastereomer. The sequence used by Cope and Mehta[5b] to establish the absolute configuration of a (−)-*trans*-cyclooctene isomer could not by its very nature give any information as to which pair of enantiomers of **1** these authors actually had in hand. A similar situation is found also in *trans*-cyclodecene, whereas in the odd-membered *trans*-cyclooolefins the only source of dissymmetry stems from the environment of the ethylenic linkage.

Recently the kinetics of racemization of optically active *trans*-cyclooctene have been studied[6] by the conventional polarimetric method. An activation energy of 35.6 kcal./mole was calculated from an Arrhenius plot of the rate data. It is not clear, however, whether this number refers to the true racemization process which requires two steps as pointed out above, or whether it is only a measure of the restricted rotation of the *trans* olefinic bond. It has been claimed[7] that the optical rotation of *trans*-cyclooctene mainly arises from the out-of-plane twisting of the olefinic bond system. If this is the case, differences in the relative orientation

(1) Supported in part by the National Science Foundation and the Office of Naval Research.

(2) For a review see E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(3) For a case where the n.m.r. method has been applied to a dissymmetric molecule see W. L. Meyer and R. B. Meyer, *J. Am. Chem. Soc.*, 85, 2170 (1963).

(4) A. T. Blomquist, L. H. Liu, and J. C. Bohrer, *ibid.*, 74, 3643 (1952); V. Prelog in "Perspectives in Organic Chemistry," A. Todd, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 129.

(5) (a) A. C. Cope, C. R. Ganellin, and H. W. Johnson, Jr., *J. Am. Chem. Soc.*, 84, 3191 (1962); A. C. Cope, C. R. Ganellin, H. W. Johnson, Jr., T. V. VanAuken, and H. J. S. Winkler, *ibid.*, 85, 3276 (1963). (b) A. C. Cope and A. S. Mehta, *ibid.*, 86, 5626 (1964).

(6) A. C. Cope and B. A. Pawson, to be published.

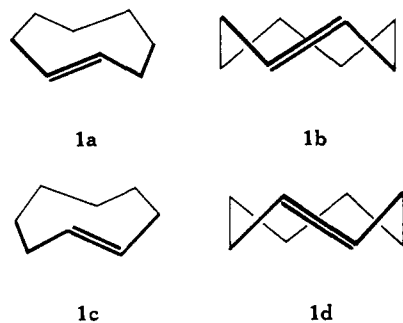(7) A. Moscowitz and K. Mislow, *J. Am. Chem. Soc.*, 84, 4605 (1962).

1a   **1b**

1c   **1d**

Figure 1. Isomers of *trans*-cyclooctene; the pairs **1a** and **1c**, and **1b** and **1d** are pairs of nonidentical mirror-image isomers.

of the double bond and the C-5-C-6 bond could go undetected by the polarimetric technique. The investigation of the molecular asymmetry of *trans*-cycloalkenes has now been extended to rings of larger sizes.[8] A rather unstable optically active *trans*-cyclononene was isolated and the barrier to interconversion determined to be 20 kcal./mole. Because *trans*-cyclononene is an odd-membered ring there exists no ambiguity as to the significance of this number. Liberation of *trans*-cyclodecene from the diastereomeric platinum complex, the method which had been successful for the eight- and nine-membered rings, produced only racemic material. An attempt[9] to prepare the dissymmetric *trans*-cyclodecene derivative **3** by asymmetric synthesis from the optically active precursor **2** also resulted in an inactive product. Both these observations suggest a relatively low barrier for the process(es) required for interconversion of the *trans*-cyclodecene enantiomers.

2   **3**
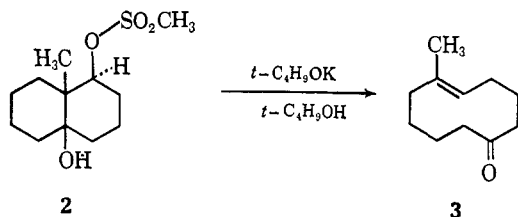
In the present investigation, we have studied the interconversion of the isomers of *trans*-cyclodecene by n.m.r. spectroscopy. The plan was to study the rate process involving rotation of the double bond through the loop of the ring by observing the spectral behavior of the allylic protons which would be nonequivalent if interconversion were slow.[10] In order to reduce the complexity of the n.m.r. spectra arising from spin-spin splitting, deuterium atoms were introduced at all positions directly adjacent to the α-methylene groups.

Synthesis. The route for preparation of *trans*-cyclodecene-1,2,4,4,9,9-d_6 is outlined in Figure 2. Diethyl adipate (**4**) was reduced with lithium aluminum deuteride (97.7% D) to 1,6-hexanediol-1,1,6,6-d_4 (**5**) which on treatment with dry hydrogen bromide yielded 1,6-dibromohexane-1,1,6,6-d_4 (**6**). The n.m.r. spectra showed the presence of less than 3% hydrogen atoms at the α positions. The dibromide **6** was

(8) A. C. Cope, K. Banholzer, H. Keller, B. A. Pawson, J. J. Wang, and H. J. S. Winkler, to be published.

(9) H. H. Westen, *Helv. Chim. Acta,* **47,** 575 (1964).

(10) *Cf.* G. M. Whitesides, D. Holtz, and J. D. Roberts, *J. Am. Chem. Soc.,* **86,** 2628 (1964), for references and discussion.

4   **5**

6   **7**

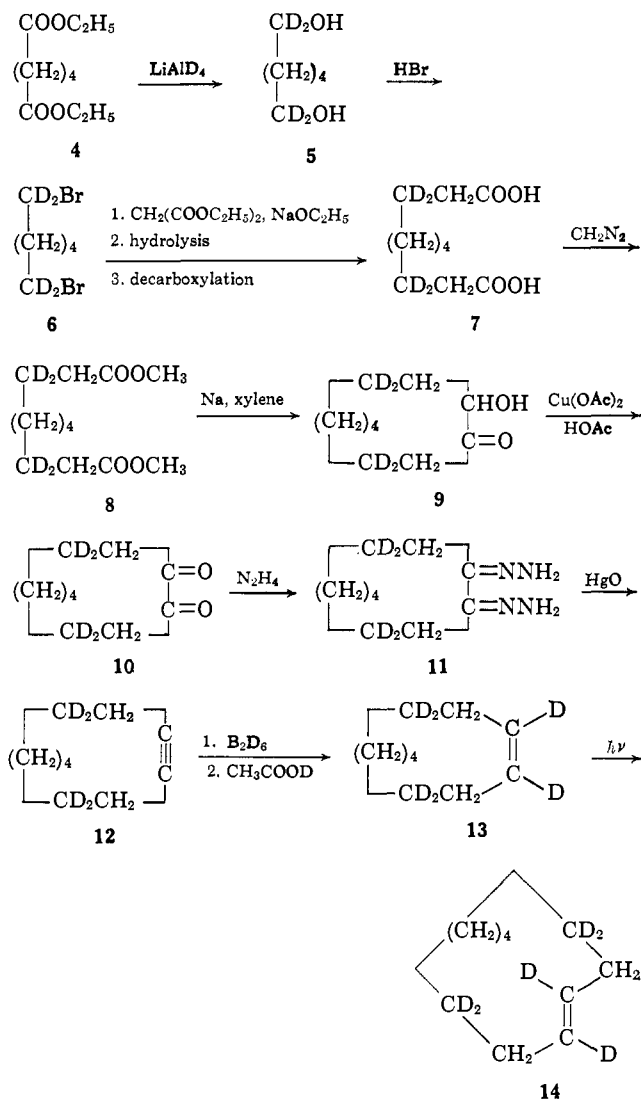**8**   **9**

10   **11**

12   **13**

14

Figure 2. Synthesis of *trans*-cyclodecene-1,2,4,4,9,9-d_6.

treated with a large excess of the sodium salt of diethyl malonate in concentrated ethanol solution in order to depress the undesired side reaction leading to ring-closed product. Simultaneous hydrolysis and decarboxylation of the product gave pure sebacic acid-$\beta,\beta,\beta',\beta'$-$d_4$ (**7**) in 76% yield. The n.m.r. spectrum of **7** in pyridine solution showed two singlets at 0.58 and 1.77 p.p.m. in the ratio 2:1, thus proving that no detectable scrambling or loss of deuterium atoms had occurred under the rather vigorous reaction conditions. The dimethyl ester **8**, obtained from the acid **7** with diazomethane, was subjected to the acyloin ring closure using a modification of the procedure previously described.[11] The acyloin **9** was oxidized to the diketone **10** and converted to the bishydrazone **11**. Treatment with an excess of yellow mercuric oxide in refluxing benzene under high-dilution conditions provided a 57% yield of cyclodecyne-4,4,9,9-d_4 (**12**). Addition of externally generated hexadeuteriodiborane and subsequent cleavage of the trivinylborane with deuterioacetic acid gave *cis*-cyclodecene-1,2,4,4,9,9-d_6 (**13**). The vapor phase chromatogram (10% Ucon Polar on Chromosorb) showed a single peak, identical

(11) N. L. Allinger in N. Rabjohn, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p. 840.
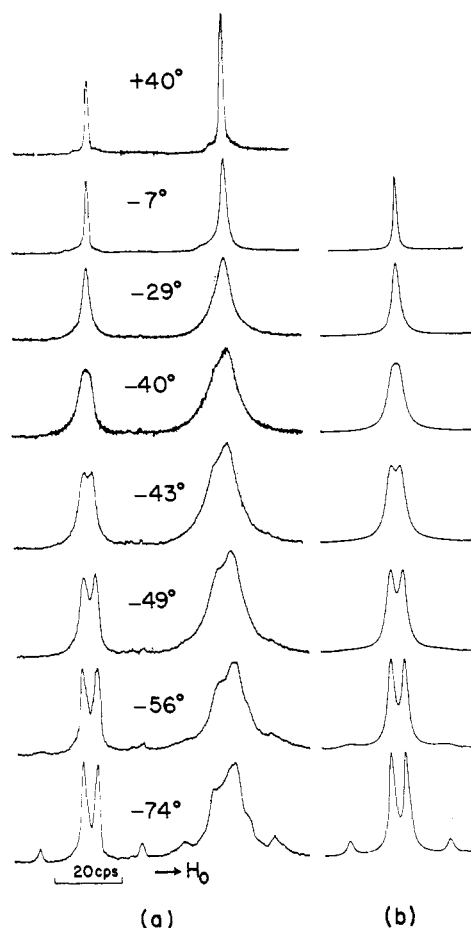
Figure 3. (a) Deuterium-decoupled, low-temperature spectra of trans-cyclodecene-1,2,4,4,9,9-d_6 in 25% vinyl chloride solution. (b) Calculated spectra of the low-field part.

Figure 4. Arrhenius plot for the allylic AB methylene protons of trans-cyclodecene-1,2,4,4,9,9-d_6.

in retention time with authentic undeuterated cis-cyclodecene. The n.m.r. spectrum had two singlets with a chemical-shift difference of 49 c.p.s. in 1:2 ratio, as expected, and traces of absorption in the vinyl proton region from which the hydrogen content at the double-bond position can be estimated to be less than 5%. A wide variety of experiments designed to convert cis- to trans-cyclodecene culminated in the discovery that the isomerization could be accomplished by benzene-photosensitized irradiation in dilute solution. At the photostationary state the product mixture was found to consist of 80% cis- and 20% trans-cyclodecene. Because of side reactions resulting in polymeric material, the optimum yield of trans-cyclodecene-1,2,4,4,9,9-d_6 was obtained when the irradiation was interrupted at the point at which the trans component reached 17%. The two isomers were separated by a 16-step countercurrent distribution between cyclohexane and a silver nitrate-water–methanol phase, using a volume ratio of 8:1 calculated to be of optimum efficiency from the experimentally determined distribution coefficients (28.5 and 2.8 for the cis- and trans-cyclodecenes, respectively). The trans-cyclodecene-1,2,4,4,9,9-d_6 thus obtained was contaminated with less than 0.5% of the cis compound.

N.m.r. Spectra. The room-temperature 60-Mc.p.s. proton n.m.r. spectrum of trans-cyclodecene-1,2,4,4,-9,9-d_6 in 25% vinyl chloride solution consists of two
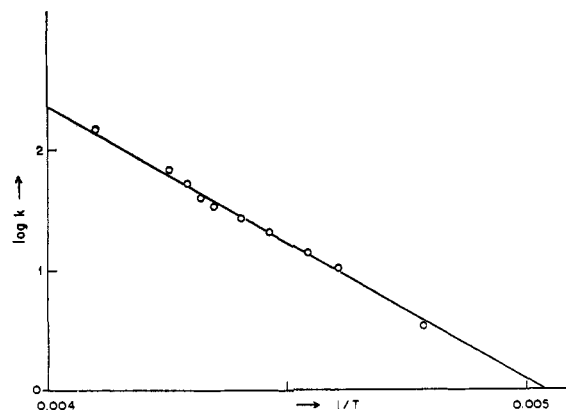
lines, one at 82.5 c.p.s. (1.37 p.p.m.) with a width at half-height of 2.5 and the other at 122.5 c.p.s. (2.04 p.p.m.) with a width at half-height of 4.5 c.p.s. in the integral ratio 2:1. On double irradiation at a frequency of 9,209,785 c.p.s. both peaks sharpen and show line widths of 1.1 c.p.s. and extensive ringout. At about 0°, the peak at 1.37 p.p.m. broadens and this is followed by broadening of the allylic resonance at around −20°. On further lowering the temperature, the allylic protons split into an AB pattern with a chemical-shift difference of 11.4 c.p.s. and a coupling constant $J = -12.8$ c.p.s., the coalescence temperature being at −40°. The peak which in the high-temperature limit is centered at 1.37 p.p.m. changes into an unsymmetrical pattern of overlapping lines. Some of the decoupled, low-temperature spectra are reproduced in Figure 3a.

On going to −143° the spectrum broadens again. At −164°, one observes two featureless, partially overlapping peaks with line widths of about 30 c.p.s. The TMS signal at −164°, however, is already 8 c.p.s. wide due to viscous broadening and this limits the further detection of significant changes in the spectrum at still lower temperatures.

From the observed line widths at the high- and low-temperature limits of 1.1 and 2.1 c.p.s., respectively, "apparent" transverse relaxation times T_2 were calculated. At intermediate temperatures, T_2 was approximated by assuming a linear dependence with temperature between the two limits. The allylic resonances of a series of upfield and downfield spectra were matched by theoretical spectra computed by a Fortran IV coded program based on Alexander's density-matrix treatment of exchanging spins[12] (Figure 3b). An Arrhenius plot of the rate constants thus obtained is shown in Figure 4. The activation parameters determined by a least-squares treatment are[13] $\Delta E^* = 10.7 \pm 0.3$ kcal./mole, $A = 10^{11.7 \pm 0.3}$ sec.$^{-1}$.

Discussion

Molecular models show that all conformations of trans-cyclodecene not possessing a high degree of

(12) S. Alexander, J. Chem. Phys., 37, 967, 974 (1962); 38, 1787 (1963); 40, 2741 (1964); J. L. Beauchamp, Undergraduate Thesis, California Institute of Technology, 1964.

(13) The actual errors for these values are probably somewhat higher than the r.m.s. errors given above due to systematic errors arising from various sources.
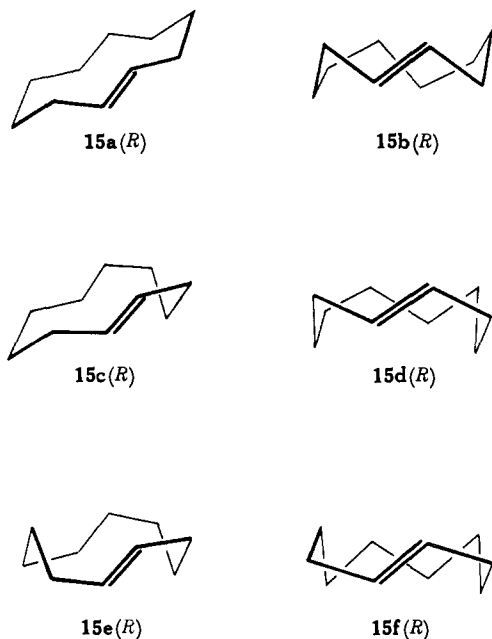
a

15a(R)   15b(R)

15c(R)   15d(R)

15e(R)   15f(R)

Figure 5. Conformational isomers of *trans*-cyclodecene; (R)-series.

16a(R)   16c(S)

16b(R)

16d(S)

b

17(R)

18(S)

HB

HA

strain can be derived by slight distortions from a rather limited number of conformational classes. All these classes are obtained by joining together two parallel, more-or-less planar, four-carbon zigzag chains at both ends by methylene bridges. One of these chains consists of the carbon atoms 1, 2, 3, and 10 and contains the double bond; the other is formed by the carbon atoms 5, 6, 7, and 8. This result is not surprising in view of the fact that analogous conformations have been claimed to be the most favorable ones for cyclodecane.[14,15] Introduction of a *trans* double bond accentuates this type of conformational preference. It is found that one has to consider 12 species, differing in the configuration around the double bond, the C-6-C-7 bond, and in the position of the 4- and 9-methylene groups. Those having the (R)-configuration[16] with respect to the *trans* double bond are shown in Figure 5. Except for conformation 15b which contains two eclipsed ethane segments and is therefore probably not populated to a significant extent, all the other forms are almost completely staggered and show no severe interactions across the ring. The species 15a and f are remarkable for their flexibility whereas the others are more or less rigid.

Three types of rate processes can be visualized. The first involves flipping of the C-4 and C-9 methylene groups, thus interconverting the species 15a, c, e, and 15b, d, f, respectively. Models clearly indicate that this process should require only a very small activation energy and should, in fact, be comparable to the ease with which two cyclohexane boat forms can be interconverted. It seems certain that the methylene flip will occur orders of magnitude faster than the other two movements of atoms and bonds coupled with the

(14) J. Sicher in "Progress in Stereochemistry," Vol. 3, P. B. D. de la Mare and W. Klyne, Ed., Butterworth Inc., Washington, D. C., 1962, p. 202.
(15) J. B. Hendrickson, *J. Am. Chem. Soc.*, 86, 4854 (1964).
(16) For nomenclature see R. S. Cahn, C. K. Ingold, and V. Prelog, *Experientia*, 12, 81 (1956).
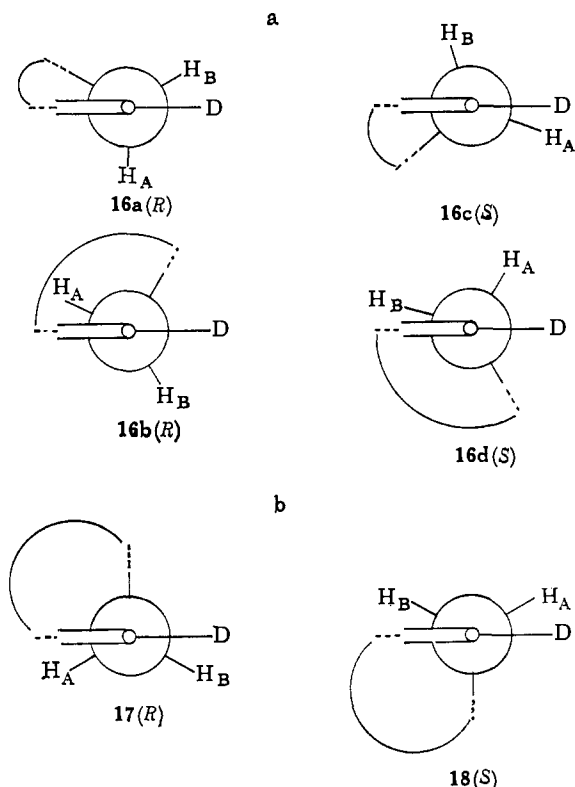
Figure 6. (a) Newman projections of carbon atoms 2 and 3 in the conformational isomers of *trans*-cyclodecene. (b) Newman projections of carbon atoms 2 and 3 in the time-averaged conformations of *trans*-cyclodecene. Note that the position of HB in 17 is the same as an average of HB in 16a and 16b while that of HB in 18 is the same as an average of HB in 16c and 16d.

rotation of the double bond and C-6-C-7 bond segment, respectively. As has already been pointed out, either of these latter processes alone will produce the corresponding diastereomer whereas both of them are necessary to convert a species to its enantiomer. Models furthermore suggest that a vinylic hydrogen can pass through the ring most easily when one starts from one of the flexible forms 15a or f. The rigid forms 15c or d, on the other hand, seem to be more favored as starting points for the rotation of the C-6-C-7 bond segment.

The conclusion that the flipping of the C-4 and C-9 methylene groups is fast compared to the processes involving a passing of hydrogen atoms through the loop has an interesting consequence for the n.m.r. spectrum. This can easily be seen from the Newman projections of the carbon atoms 2 and 3 in Figure 6. All the conformation isomers 15a-f belonging to the (R)-series can be represented by either 16a or 16b and those in the (S)-series by 16c or d. The fast methylene flipping process results in the time-averaged projections 17 and 18 for the (R)- and (S)-series, respectively. The exact time-averaged positions of the protons A and B depend on the relative populations of the conformers 15a-f. By the interconversion 17 ⇄ 18, the protons A and B interchange their magnetic environments. It follows that the only process that can cause the allylic resonance to split into an AB pattern at low temperature involves rotation of a vinyl deuterium through the loop formed by the methylene groups. The restricted rotation of the C-6-C-7

segment is not expected to have any significant influence on this part of the spectrum.

The fast flipping of the C-4 and C-9 methylene groups also causes the equatorial and axial hydrogen atoms at C-5 and C-8 to become magnetically equivalent. The pair of hydrogens at carbon atoms 6 and 7 which point to the inside of the ring and are therefore affected by the anisotropy of the carbon–carbon double bond can only be averaged on the n.m.r. time scale with those pointing away from the double bond by rotation of the C-6–C-7 segment. The fact that the peak at 1.37 p.p.m. starts to broaden at a temperature which is about 20° higher than that at which the first detectable change in the allylic resonance occurs seems to indicate that the activation energy for the rotation of the C-6–C-7 bond is slightly higher than that of the double bond.

The data of the present investigation taken along with those obtained by Cope and co-workers demonstrate dramatically the effects of strain and of non-bonded interactions on the optical stability of *trans*-cycloalkenes. In fact, the half-lives of the optical forms calculated at room temperature range over more than *16 powers of ten*, from 10^5 years for *trans*-cyclooctene to 10 sec. for *trans*-cyclononene, to 10^{-4} sec. for *trans*-cyclodecene.

Experimental Section

The 60-Mc.p.s. proton n.m.r. spectra were recorded with a Varian Model V-4300 spectrometer equipped with a variable-temperature probe. The instrument was operated in HA mode down to $-80°$ and in HR mode below that temperature. The sample was double irradiated with a frequency of 9,209,785 c.p.s. generated by a Nuclear Magnetic Resonance Specialties Model SD-60 spin decoupler and monitored by use of a Hewlett Packard Model 5245L megacycle counter. Spectra were taken on a degassed, 25% solution of *trans*-cyclodecene-1,2,4,4,9,9-d_6 in vinyl chloride with TMS as internal standard on calibrated Varian HA-60 chart paper at a sweep width of 100 c.p.s.

1,6-Hexanediol-1,1,6,6-d_4 (5). A solution of 46.0 g. of diethyl adipate (228 mmoles) in 100 ml. of dry ether was added to a stirred mixture of 10.0 g. of lithium aluminum deuteride (97.7% D; 0.23 mole) in 150 ml. of anhydrous ether at room temperature over a period of 1.5 hr. The mixture was heated at reflux for 2 hr. and then allowed to stand overnight. A solution of 30 ml. of concentrated sulfuric acid in 170 ml. of water was added with cooling. The ether layer was separated, the ether was removed by distillation, and the aqueous phase was extracted 15 times with 50-ml. portions of chloroform. Distillation of the extract yielded 25.0 g. of colorless liquid (90%), b.p. 125° (1 mm.) which crystallized on standing at room temperature.

1,6-Dibromohexane-1,1,6,6-d_4 (6). A rapid stream of dry hydrogen bromide was bubbled through 25.0 g. of the diol 5 (205 mmoles) at 100° until saturation was reached and then a slow stream of hydrogen bromide was passed in for 10 hr. with the mixture at 130–135°. Water and chloroform were added, the organic phase was separated, washed with sodium carbonate solution, dried with calcium chloride, and

distilled. The yield of 6 was 39.5 g. (78%), b.p. 121–126° (25 mm.).

Sebacic Acid-$\beta,\beta,\beta',\beta'-d_4$ (7). To a solution of 28 g. (1.22 g.-atoms) of sodium dissolved in 300 ml. of anhydrous ethanol was added 200 g. of diethyl malonate (1.25 moles). To the mixture was added dropwise a solution of 39.5 g. of the dibromide 6 (159 mmoles) in 100 ml. of anhydrous ethanol over 1.5 hr. at a temperature just below the reflux point. The mixture was then heated for another 2 hr., poured into 300 ml. of water, and allowed to stand overnight. Concentrated sulfuric acid (300 ml.) was then added and the mixture was heated and stirred while the ethanol was removed by distillation. After 520 ml. of distillate, boiling between 75 and 90°, was collected, vigorous gas evolution took place. Another 120 ml. of distillate was then collected, the heating was interrupted, 100 ml. of water was added, and the mixture was heated under reflux for 1 hr. The black reaction mixture was allowed to stand overnight at room temperature. The crude product was removed by filtration through a sintered-glass Büchner funnel, washed thoroughly with water, dissolved in aqueous potassium hydroxide solution, heated with Norit, filtered, precipitated with hydrochloric acid, collected on a filter, washed with cold water, and dried. The yield was 25.0 g. (76%) of colorless crystals, m.p. 127–129° (lit.[17] m.p. of sebacic acid 134°).

Dimethyl sebacate-$\beta,\beta,\beta',\beta'-d_4$ (8) was obtained from the acid 7 in 92% yield by methylation with diazomethane in ether solution, followed by distillation under reduced pressure.

Sebacoin-4,4,9,9-d_4 (9). A solution of 28.5 g. of dimethyl sebacate-$\beta,\beta,\beta',\beta'-d_4$ (8) (111 mmoles) in 450 ml. of dry xylene was added over 15 hr. to a suspension of 11.5 g. of sodium (0.5 g.-atom) in 150 ml. of dry xylene at reflux temperature. Isolation of the product according to the literature directions[11] afforded sebacoin-4,4,9,9-d_4 in 72% yield.

Cyclodecane-1,2-dione-4,4,9,9-d_4 (10) was prepared from 9 in 94% yield by the procedure described in the literature.[18]

Cyclodecane-1,2-dione-4,4,9,9-d_4 Bishydrazone (11). Hydrazine hydrate (20 g., 400 mmoles) was dissolved in 120 ml. of anhydrous ethanol and a solution of 12.9 of dione 10 (75 mmoles) in 35 ml. of ethanol was added over 15 min. at 0°. The white slurry was stirred for 0.5 hr. at room temperature and a clear solution resulted. It was then heated for 45 min. in a bath at 90° and about two-thirds of the ethanol was removed by slow distillation over 3 hr., keeping the bath temperature below 105°. When the mixture was cooled, colorless crystals were formed which were removed by filtration and washed with cold ethanol. Evaporation of the mother liquor in a rotary evaporator to about 20 ml. yielded a second crop of crystals. Both crystal fractions melted between 120–130° under decomposition; the combined yield was 14.0 g. (93%).

Cyclodecane-4,4,9,9-d_4 (12). A suspension of 14.0 g. (70 mmole) of the bishydrazone 11 in 300 ml. of

(17) M. D. Soffer, N. S. Strauss, M. D. Trail, and K. W. Sherk, *J. Am. Chem. Soc.*, **69**, 1684 (1947).
(18) A. T. Blomquist and A. Goldstein in "Organic Syntheses," Coll. Vol. IV, N. Rabjohn, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, p. 838.

Spectro Grade benzene was added in small portions during 2.5 hr. to a vigorously stirred mixture of 80 g. of yellow mercuric oxide (0.37 mole), 3 g. of powdered potassium hydroxide, and 60 g. of anhydrous sodium sulfate in 300 ml. of benzene at the reflux temperature. The mixture was heated for another 2 hr., cooled, and filtered through a sintered-glass Büchner funnel. The residue was washed with three 50-ml. portions of benzene. The benzene was removed from the combined solutions by distillation through a Vigreux column. Reduced-pressure distillation of the residue yielded 6.50 g. (57%) of colorless 12, b.p. 91–92° (27 mm.).

Deuterioacetic Acid. Commercially available acetic anhydride, containing 3.0% acetic acid, was distilled through a 3-ft. column packed with glass turnings and a middle fraction of constant boiling point (137.7°) was collected. This material still contained 1.6% acetic acid. The distillate was stirred with small pieces of sodium with a high-speed stirrer (10,000 r.p.m.) for 12 hr. and the acetic anhydride was removed *in vacuo* in a thoroughly dried apparatus. The distillate showed no carboxylic proton peak in the proton n.m.r. spectrum. To 87 g. of stirred, purified acetic anhydride was added 15.6 ml. of deuterium oxide over 1 hr. at 70°. The mixture was then heated overnight at 70°. The resulting deuterioacetic acid contained 99.2% D, calculated from the n.m.r. integral ratio of this material and a sample to which a known amount of ordinary acetic acid had been added.

cis-Cyclodecene-1,2,4,4,9,9-d_6 (13) was prepared by addition of hexadeuteriodiborane to 12 followed by treatment with deuterioacetic acid. The procedure described for the synthesis of *cis*-cyclodecene-1,2-d_2[19] was adopted except that a 50% excess of hexadeuteriodiborane had to be used to obtain 13 completely free of the acetylene 12. This modification resulted in a 61% yield of 13 in which no impurities could be detected in the v.p.c. (Ucon Polar). The v.p.c. retention time of 13 was identical with that of authentic *cis*-cyclodecene.

Irradiation of cis-Cyclodecene-1,2,4,4,9,9-d_6. A 2.5% solution of 13 (3.50 g.) in purified benzene was put in 10-mm. (i.d.) quartz tubes and degassed in high vacuum through three freeze–thaw cycles. The tubes were sealed, then exposed to the direct ultraviolet irradiation from a battery of low-pressure, mercury-vapor, germicidal lamps for 72 hr. The benzene was removed by distillation through a column and when the residue was distilled at 25 mm., it afforded 2.85 g. (81%) of a mixture containing 83% of the *cis* isomer 13 and 17% of the trans isomer 14. V.p.c. analyses were carried out on an 8-ft. analytical column packed with 10% Ucon 50 HB 2000 Polar (Loenco, Inc.) on Chromosorb HMDS.

Separation of cis- and trans-Cyclodecene-1,2,4,4,-9,9-d_6. A solution of 300 g. of silver nitrate in 600 ml. of water was made up with methanol to 2 l. and then equilibrated with 500 ml. of cyclohexane which resulted in a cyclohexane phase I and an aqueous silver nitrate–methanol phase II. The distribution coefficients (I/II) were determined by v.p.c. to be 28.5 for 13 and 2.8 for 14. The 83:17 mixture of 13 and 14 (2.85 g.) was dissolved in 20 ml. of I and subjected to a 16-step countercurrent distribution. Each extraction was carried out with 20 ml. of I and 160 ml. of II. The usual countercurrent distribution scheme[20] was followed up to cycle 7. Starting with step 8, phases I were withdrawn from the end containing pure 13 and phases II from the opposite end containing pure 14. The experimental distribution curves were determined after step 10 by v.p.c. and found to be in substantial agreement with the theoretical curves calculated from the distribution coefficients. After 16 steps, the phases II containing the *trans*-cyclodecene-1,2,4,9,9,9-d_6 (14) were combined and concentrated under reduced pressure at a rotary evaporator to about half of their volume, poured into 600 ml. of concentrated ammonia and ice, and extracted five times with 300 ml. of pentane each. The solution was dried over sodium sulfate and the pentane was removed. Distillation under reduced pressure in a microapparatus yielded 307 mg. of the *trans* isomer 14. Gas chromatographic analysis showed that this material contained less than 0.5% of the *cis* compound 13.

(19) A. C. Cope, G. A. Berchtold, P. E. Peterson, and S. H. Sharman, *J. Am. Chem. Soc.*, 82, 6370 (1960).

(20) For a review see L. C. Craig and D. Craig in "Technique of Organic Chemistry," Vol. III, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1950, p. 171.