dibromide was isolated by removing through fractional recrystallization (of a bromination product) at Dry Ice temperature (*n*-pentane) as much of the solid 3,6 isomers as possible and then flash distilling [bp 40° (0.07 mm)] a small amount of the liquid. Only a very small amount of the pure isomer (nearly free of the 3,6 isomers) could be isolated with each distillation. The liquid (pure) was found to be extremely labile and rearranged to the 3,6 isomers.

The liquid dibromide was assigned the trans 3,4 structure (**4**) on the following basis: its boiling point was essentially identical with those of the 3,6 isomers; its melting point was much lower than those of the 3,6 isomers, which suggests lower molecular symmetry; the C–H absorption bands in the ir spectrum were very similar to those of the 3,6 isomers; and it (**4**) rearranged on standing in CCl_4 to give **5** and **6**. [The liquid isomer (**4**), **5**, and **6** all rearranged to identical equilibrium mixtures.] Also, nmr spectra of mixtures containing **4** did not show any signals inconsistent with its structure. Unfortunately, signals attributable to it were masked by the overlapping signals from the other two isomers, even at 220 MHz. Nmr spectra of both pure solid dibromides were recorded in CCl_4 at 60, 100 (see Figure 1), and 220 MHz: **5**, 4.304 (complex multiplet, 2, $-CH_2CH_2-$protons), 4.8268 (complex multiplet, 1, –CHBr–), 5.942 (broad d, $J = 3$ Hz, 1, –CH═CH–); **6**, 2.224 (complex multiplet, 1, $-CH_2CH_2-$protons), 4.700 (complex multiplet, 1, –CHBr–), 5.906 (sharp d, $J = 1.7$ Hz, 1, –CH═CH–). The infrared spectra (CCl_4) of **4**, **5**, and **6** all showed a fairly similar C–H stretching region (3150–2850 cm^{-1}) and additional strong–medium absorptions as follows: **4**, 1435, 1440, 1280, 1210, 1222, 1145, 1018, 922, 730, 655, 590, 545 cm^{-1}; **5**, 1440, 1400, 1201, 1080, 995, 565 cm^{-1}; **6**, 1450, 1440, 1350, 1301, 1214, 1165, 1175, 1130, 1068, 980, 887, 730, 668 cm^{-1}.

Equilibration Studies.—The equilibrium mixtures shown in Table III were obtained in every case by approaching the equilibrium position from more than one direction; *e.g.*, pure samples of two of the three cyclohexadiene dibromides (**5** and **6**) and nearly pure samples of **4** in carbon tetrachloride were allowed to stand at room temperature until each showed the same composition of dibromides (about 3 months). Equilibration times at room temperature for the other dibromides follow: cyclopentadiene dibromides, 1–2 months; 2,4-hexadiene dibromides, 75% complete in 3 months (CCl_4); bromination mixtures (in CH_3NO_2) from (*E,Z*)- and (*E,E*)-2,4-hexadiene, 1.5 months. Heating at 78–80° caused equilibration of all of the dibromides within 1–2 weeks.

Acknowledgment.—Support for this work was provided by the Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Union Oil Co. of California Foundation, Brea, Calif., and the Jet Propulsion Laboratory Director's Discretionary Fund. This paper presents results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS 7-100, sponsored by the National Aeronautics and Space Administration. We wish to thank Professor S. I. Chan, Department of Chemistry, Cal Tech, for access to the SC-220 spectrometer.

Registry No.—**1**, 42086-50-0; **2**, 42086-51-1; **3**, 17040-70-9; **4**, 42086-52-2; **5**, 42086-53-3; **6**, 42086-54-4; **7**, 42086-55-5; **8**, 42086-56-6; **9**, 42086-57-7; **10**, 42086-58-8; **11**, 42086-59-9; **12**, 42086-60-2; 1,3-cyclohexadiene, 592-57-4; cyclopentadiene, 542-92-7; (*Z,Z*)-2,4-hexadiene, 6108-61-8; (*E,Z*)-2,4-hexadiene, 5194-50-3; (*E,E*)-2,4-hexadiene, 5194-51-4.

Study of a Cope-Related System. *trans,trans*-1,5-Cyclodecadiene and *trans*-1,2-Divinylcyclohexane[1,2]

Peter S. Wharton* and Donald W. Johnson

Department of Chemistry, Wesleyan University, Middletown, Connecticut 06457

Received April 5, 1973

Rate constants were determined for the forward and reverse rearrangements of the Cope-related pair, *trans,trans*-1,5-cyclodecadiene (**3**) and *trans*-1,2-divinylcyclohexane (**4**). The rate of **4** → **3** was determined from the rate of racemization of (+)-**4** (the two rate constants are identical), an indirect approach necessitated by the large equilibrium constant favoring **4**; the ratio of forward and reverse rate constants yielded $K_{200°} = 2 \times 10^4$ with $\Delta G_{200°} = 9.4$ kcal mol^{-1}. The individual rate constants yielded $E_a = 25.0$ and 31.6 kcal mol^{-1} for **3** → **4** and **4** → **3**, respectively. The ring strain of **3** is estimated to be 12 kcal mol^{-1} relative to **4**.

trans,trans-1,5-Cyclodecadienes and *trans*-1,2-divinylcyclohexanes are formally interconvertible *via* the Cope rearrangement, and several such related pairs are now known as a result of the isolation of many sesquiterpene cyclodecadienes. In some instances there is an observable equilibrium, *e.g.*, **1**–**2**, as a result of differential effects of methyl substitution of the double bonds and the presence of a trans-fused lactone[3] which offset the strain of the cyclodecadiene. For the unsubstituted pair **3**–**4** there is insufficient counterbalancing of the high energy of the medium ring and the conversion to **4** is virtually complete. It is nevertheless still possible to explore the relationship from both sides. The rate constant k_1 for the forward Cope rearrangement can be measured directly; and the rate constant k_{-1} for the reverse Cope rearrangement can be obtained from the rate of racemization of optically active **4**, which involves Cope rearrangement to an optically active conformation of **3**, racemization of the cyclodecadiene (a relatively rapid process[4]), and reversion of the Cope rearrangement.[5] For this relationship $k_{obsd} = k_{rac} = k_{-1}$. The present paper reports on the determination of these rate constants and related thermodynamic parameters.

---

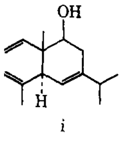
[1] The investigation was supported by Public Health Service Research Grants GM 14133 and 16338 from the Division of General Medical Sciences, U. S. Public Health Service.

[2] The article is abstracted from the Ph.D. Thesis of D. W. J., University of Wisconsin, 1970. The last year of research was carried out at Wesleyan University.

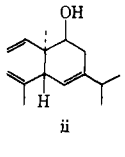
[3] T. C. Jain, C. M. Banks, and J. E. McCloskey, *Tetrahedron Lett.*, 841 (1970).

[4] For 1,5-dimethyl-*trans,trans*-1,5-cyclodecadiene, interconversion of enantiomeric conformations has been shown to be fast on the nmr time scale between temperatures of 40 and 90°. It is therefore not possible for the energy of activation for interconversion of enantiomeric conformations of **3** to be rate determining. See ref 6.

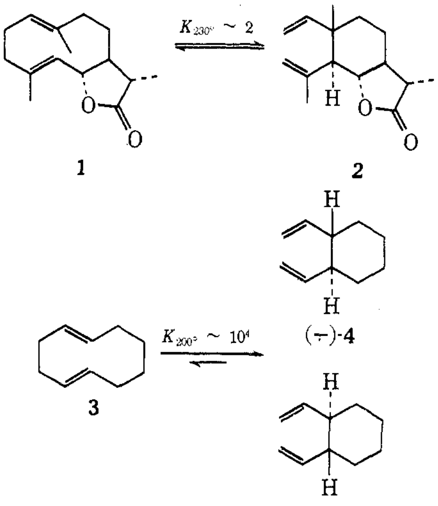
[5] This sequence corresponds to the interconversion at 200° of δ- and epi-δ-elemenol (i and ii) reported by K. Morikawa and Y. Hirose, *Tetrahedron Lett.*, 869 (1969).



i



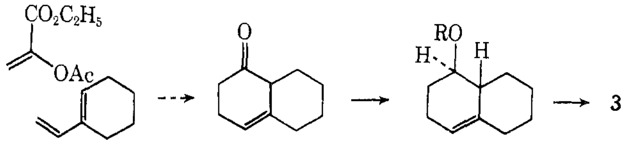
ii



1 2 3 (−)-4 (+)-4

trans,trans-1,5-Cyclodecadiene.—Experience gained in the synthesis of 1,5-dimethyl-*trans,trans*-1,5-cyclodecadienes[6,7] was responsible for our use of the same overall route to the unsubstituted ring (see Scheme I). A possible preparative route involving its reported formation *via* Hofmann elimination of the 1,6-bisquaternary ammonium salt of cyclodecane[8] was not examined.

SCHEME I



5 6a, R = H b, R = Ts

Combination of ethyl acetoxyacrylate and 1-vinylcyclohexene yielded a mixture of 1,4 cycloadducts in 86% yield. Reduction of the mixture with lithium aluminum hydride and crystallization of the resulting sludge gave a white solid, mp 75–93°, in 75% yield. That this solid was solely a mixture of epimers was shown by periodate oxidation, which afforded a single β,γ-unsaturated ketone (**5**) in 98% yield. By contrast, periodate oxidation of the total sludge of diols gave two glpc components in a ratio of 88:12, presumably corresponding to the two β,γ-unsaturated ketones obtainable from the two possible regioisomeric modes of cycloaddition.

Hydride reductions of **5** gave mixtures of anti (**6a**) and syn alcohols of variable composition. Sodium borohydride in alcohol at room temperature yielded a highly unfavorable 25:75 ratio and lithium aluminum hydride in ether at room temperature was only slightly better (35:65). Several other variations were tested, with the best (70:30) consisting of a combination of lithium aluminum hydride in diglyme at −78° which was allowed to warm slowly to room temperature. The mixture thus obtained could be enriched to 93 anti:7 syn, with 65% recovery, by acetylation of the alcohol, fractional distillation, and saponification; and this enriched product was sufficiently pure to yield anti tosylate (**6b**) without difficulty in 82% yield after two crystallizations.

Conversion of **6b** to *trans,trans*-1,5-cyclodecadiene (**3**) was effected by Marshall's method:[9] addition of diborane to the double bond and base-promoted fragmentation of the intermediate thus formed. Best results were obtained with 5 *N* sodium hydroxide for 48 hr at room temperature, the undistilled oily product consisting of 94% **3**, 1% *trans*-1,2-divinylcyclohexane (**4**), and 5% of another component (probably the expected cyclopropane[9]) in an overall yield of 65% as determined by glpc analysis.

Isolation of **3** from the crude product was complicated by the substantial losses which occurred in recovery from solutions because of its great volatility, and by the ease with which it rearranged to **4** (half-lives of 30 min at 90° and 145 hr at 40° were subsequently determined). However, it was eventually found that samples >99% pure by glpc could be reproducibly obtained by silica gel chromatography at 5° using 2-methylbutane as eluent and subsequent careful removal of solvent and low-temperature distillation.[10]

The Cope rearrangement of **3** was found to proceed at conveniently measurable rates at temperatures between 40 and 90°. Kinetics runs in *n*-decane, which served as both solvent and internal glpc standard, afforded the rate constants given[11] in Table I and a value of $E_a = 25.0 \pm 0.3$ kcal mol^{-1}.

TABLE I

RATE CONSTANTS FOR THE CONVERSION **3** → **4**

Temp, °C	k, sec^{-1}
39.78	1.35×10^{-6}
60.09	1.55×10^{-5}
75.00	7.69×10^{-5}
90.90	3.83×10^{-4}

trans-1,2-Divinylcyclohexane.—The isolation of **3** involved a chromatography which cleanly removed the minor saturated component and yielded fractions containing either pure **3** or mixtures of **3** and **4**. It was a simple matter to obtain pure **4** (>99.9% by glpc) by heating such fractions at 100°.

Partial resolution of **4** was effected by treatment of the racemic mixture with 0.5 equiv of optically active diisopinocampheylborane.[12] The volatile hydrocarbon product so obtained was found to contain much α-pinene, but this could be completely removed from pentane solutions by silica gel impregnated with silver nitrate. The final distilled product was shown to be >99.9% pure by glpc and yielded rotations as high as $[\alpha]_D$ +3.6° and $[\alpha]_{436}$ +7.5°.

Optically active **4** was found to racemize with unimolecular kinetics at conveniently measurable rates

---

[6] P. S. Wharton, Y. C. Poon, and H. C. Kluender, *J. Org. Chem.*, **38**, 735 (1973).

[7] P. S. Wharton, C. E. Sundin, D. W. Johnson, and H. C. Kluender, *J. Org. Chem.*, **37**, 34 (1972).

[8] C. A. Grob, H. Link, and P. W. Schiess, *Helv. Chim. Acta*, **46**, 483 (1963).

[9] J. A. Marshall and G. L. Bundy, *Chem. Commun.*, 854 (1967).

[10] It may be noted that the corresponding preparation of 1,5-dimethyl-*trans,trans*-1,5-cyclodecadiene was very much simpler.[6] Each of the methyl groups afforded higher stereoselectivity during the synthesis: the C-5 methyl enhanced the regiospecificity of cycloaddition and the C-1 methyl directed hydride reduction of the octalone in the desired sense. Furthermore, the two methyl groups together were responsible for straightforward isolation of the cyclodecadiene by diminishing both its volatility and tendency to rearrange.

[11] The limits were calculated at the 95% confidence level.

[12] See H. C. Brown and N. R. Ayyangar, *J. Amer. Chem. Soc.*, **86**, 397, 1071 (1964). The procedure followed was identical with that used for the partial resolution of **7**; see ref 14.

between 150 and 200°. Kinetic runs afforded the rate constants[11] given in Table II and a value of $E_a = 31.6 \pm 0.9$ kcal mol^{-1}.

Table II

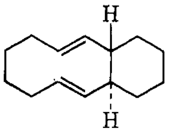
Rate Constants for the Racemization of (+)-4

Temp, °C	k, sec^{-1}
147.48	6.8×10^{-7}
170.44	6.12×10^{-6}
190.61	2.57×10^{-5}
200.18	4.96×10^{-5}

Discussion

The equilibrium constants for the rearrangement **3** ⇄ **4** obtained from the extrapolated rate constants of Tables I and II are 2.1 and 80×10^4 at 200 and 40°, respectively. The corresponding free energy differences are 9.4 and 8.5 kcal mol^{-1}. The difference in internal energy between **3** and **4**, derived from the difference in activation energies, is ~7 kcal mol^{-1}; a substantial entropy difference favoring the divinylcyclohexane is revealed.

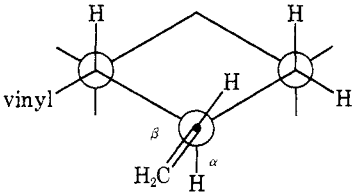
The rate of the Cope rearrangement of **4** → **3** is not very different from that of an acyclic diene: the observed E_a of 31.6 can be compared with 34.2 kcal mol^{-1} reported for 3-methyl-1,5-hexadiene.[13] By contrast the rate of the rearrangement **3** → **4** is very facile and the observed E_a of 25.0 kcal mol^{-1} is identical with that of the degenerate Cope rearrangement of **7**.[14] This correspondence is almost certainly not fortuitous because both **3** and **7** exist in a ground-state chair conformation



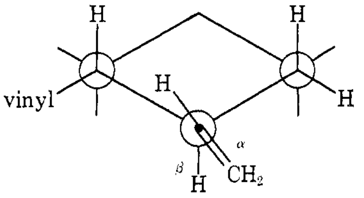
(−)-**7**

which is geometrically closely related to the transition state of the Cope rearrangement.[15] By contrast, the double bonds of **4** can rotate and thereby relieve the repulsive interaction of this conformation without generating additional interactions, as shown in the Newman projections **8** and **9**.

The difference in ground-state geometries of **7** and **4** shows up in an interesting way in their partial resolutions using (−)-diisopinocampheylborane. Both dienes can be converted *via* ozonolysis to dimethyl *trans*-1,2-cyclohexanedicarboxylate (**10**).[16] Partially resolved **7** and **4** yield **10** with negative and positive rotations in 45 and 25% optical purity, respectively.[17] Thus partial resolution preferentially destroys enantiomers of opposite bridgehead trans configuration in the two series. An explanation for these observations can be advanced on the basis that diene **7** is restricted to conformation **8**, in which each double bond presents only the α face toward an attacking reagent; the β face is shielded by the transannular double bond. By contrast, the double bonds of **4** are freer and prefer to exist substantially in conformation **9** in which the β face is not only not shielded by the adjacent double bond but is totally less hindered to an approaching reagent. Consistent with this explanation are the very different magnitudes of the specific rotations of **4** and **7**, $[\alpha]_D$ 14 and 176°, respectively.



8



9

The magnitude of the ring strain in **3** relative to **4** is considerable and can be crudely evaluated as 12 kcal mol^{-1} by adding the experimentally determined difference in internal energy of 7 kcal mol^{-1} and a 5 kcal mol^{-1} term which takes into account the differential effects of alkyl substitution of the double bonds.[18]

It is now possible to contribute to the explanation of the intriguing observation that base-induced fragmentation of boranes (as in the present synthesis), which could in principle lead to cleavages of both internal (→**3**) and peripheral bonds (→**4**), in fact, proceeds almost exclusively *via* the internal mode despite the fact that the product thus generated is much less stable than the product which would be derived from peripheral cleavage.[9,19] In both internal and peripheral cleavage, as the carbon–carbon bond breaks, there is a disrotation of the two incipient double bonds. The transition state for internal cleavage necessarily resembles the crossed chair geometry of **3** but at the corresponding point in peripheral cleavage there is no sensing of the stability of **4**; this is gained only by subsequent rotation. Thus for comparable transition-state geometries, product control is exercised by alkyl stabilization of the incipient double bonds, as suggested by Marshall. Our observation that **4** is kinetically formed to the extent of 1% or less suggests that at the transition state

---

(13) See H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969).

(14) P. S. Wharton and R. A. Kretchmer, *J. Org. Chem.*, **33**, 4258 (1968).

(15) It has been shown from nmr data that the crossed (chair) conformation of 1,5-dimethyl-**3** is no less stable than any other conformation despite the fact that it is specifically disfavored by a severe methyl–methyl repulsion (see ref 6). It can therefore be concluded that the crossed (chair) conformation of **1**, which lacks such methyl groups, is substantially more stable than other conformations. Models show that the trans bicyclic fusion present in **7** further stabilizes the crossed conformation relative to others.

(16) A. Werner and H. E. Conrad, *Chem. Ber.*, **32**, 3046 (1899). The absolute configuration of (+)-**10** was determined by D. E. Applequist and N. D. Werner, *J. Org. Chem.*, **28**, 48 (1963), and is the basis for the designations of configurations of optically active **4** and **7**.

(17) The 45% figure was established by H. C. Kluender. The rotations of optically pure **10** were determined by Werner and Conrad.[16]

(18) The value of 5 kcal mol^{-1} is obtained from Kistiakowsky's widely cited values for heats of hydrogenation of various alkyl-substituted olefins. Consideration of the effect of the additional alkyl substitution of 1,5-dimethyl-**3** (a pattern common to many sesquiterpenes) suggested that the amount of this cyclodecadiene present at equilibrium might be directly observable: the free energy difference of 9.4 kcal mol^{-1} found for the pair **3**, **4** at 200° should be reduced to ~4.7 kcal mol^{-1} assuming that there is no other differential effect of methyl substitution. Indeed, it has been found experimentally that there is 0.35% of 1,5-dimethyl-**3** present at equilibrium at 200°, an amount obtained starting from both higher and lower values. The free energy difference of 5.3 kcal mol^{-1} corresponding to this equilibrium is perhaps fortuitously close to that calculated (Y. C. Poon, Ph.D. Thesis, Wesleyan University, 1971; see also ref 6).

(19) J. A. Marshall and J. H. Babler, *Tetrahedron Lett.*, 3861 (1970); *J. Org. Chem.*, **34**, 4186 (1969).

there is operative at least half of the 5 kcal mol^{-1} influence of alkyl substitution[18] stabilizing the double bonds of **3** relative to **4**.

Experimental Section

Physical Data.—Melting points were determined using a Thomas Unimelt capillary melting point apparatus and are uncorrected. Boiling points are uncorrected. Analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Infrared spectra were recorded on Beckman IR-8 and Perkin-Elmer Infracord Model 137 spectrometers. The ultraviolet spectrum was recorded on a Cary Model 14 spectrometer. Nmr spectra were recorded using a Varian A-60A spectrometer with tetramethylsilane as an internal reference. Unless otherwise stated glpc data were obtained using 150 ft × 0.01 in. stainless steel columns in conjunction with a Perkin-Elmer Model F-11 unit, with flame ionization detection, and Disc chart integration. Fractional distillations were performed using a 24-in. Nester-Faust NFT-50 Teflon spinning bond column. Ozone was generated by a Welsbach Ozonator, Model T-408. Optical rotations were obtained at 25° using 1-dm cells in conjunction with a Rudolph Model 80 polarimeter (which happened to be modified to record *via* the faraday effect). The constant-temperature bath used in kinetic studies consisted of an insulated drum containing 12 gal of Dow Corning 510 silicone fluid, stirred with a Lightnin Model L stirrer and regulated by a YSI Model 63RA unit.

Materials.—Organic extracts were dried with either magnesium or sodium sulfate. Solvents were distilled before use (after drying when necessary) with the exceptions of anhydrous ether and alcohol. α-Pinene (Aldrich) was subjected to careful fractional distillation and a fraction was used with bp 88.0–88.5° (100 mm), >99.9% by glpc. *p*-Toluenesulfonyl chloride, *p*-nitrobenzoyl chloride, and 3,5-di-*tert*-butylcatechol were crystallized from hexane. The silica gel used was Grace, Grade 950, 80–200 mesh. For impregnation with silver nitrate 225 g of silica gel was mixed with 250 ml of 10% aqueous silver nitrate in a flask blackened externally and the water was removed at 80° on a rotary evaporator. Activation of the silica gel was accomplished by heating at 100° for at least 12 hr before use.

$\Delta^{4(10)}$-1-Octalone (5).—A mixture of 142.7 g (1.32 mol) of 1-vinylcyclohexene,[20] 186.0 g (1.18 mol) of ethyl α-acetoxyacrylate,[21] and 7.5 g of 3,5-di-*tert*-butylcatechol was heated under nitrogen at 130° for 50 hr. After cooling, distillation yielded 269.1 g (86%) of a highly viscous, colorless liquid: bp 108–110° (0.4 mm); ir (neat) 5.74 μ; nmr (CCl_4) δ 5.36 (1, broad), 4.13 (2, q, $J = 7$ Hz), 2.01 and 1.98 (3 total, singlets), and 1.24 ppm (3, t, $J = 7$ Hz).

A solution of the distillate in 1000 ml of ether was added slowly, with stirring and cooling, under nitrogen, to a mixture of 60 g (1.5 mol) of lithium aluminum hydride in 200 ml of ether. After the addition was complete the mixture was stirred for 15 hr at room temperature. Saturated magnesium sulfate solution (75 ml) was then added slowly with stirring and cooling and the mixture was allowed to stand until it was almost white (24 hr). It was then poured onto 2000 ml of ice-water, and concentrated hydrochloric acid was added to dissolve all solid. Extraction with five 500-ml portions of ether and further work-up yielded a crude product which was dissolved in ether and allowed to crystallize at 5°, affording from these repetitions a combined total of 150 g of a greenish-white solid. Crystallization of this solid from acetone gave 138.8 g (75%) of white solid: mp 75–93°; ir (CCl_4) 2.93, 6.02, and 11.64 μ; nmr (CCl_4) δ 5.30 (1, broad), and 4.0–3.0 ppm (4, broad).

To a solution of this solid (0.76 mol) in 2000 ml of 50% aqueous alcohol was added, with cooling and stirring under nitrogen, 182.8 g (0.795 mol) of sodium metaperiodate in one portion. After the solution was stirred at room temperature for 1.5 hr, 2000 ml of water was added and the mixture was extracted with two 500-ml portions of pentane. The aqueous phase was then diluted to 8000 ml and extracted with four 1000-ml portions of pentane. The combined pentane extracts were washed with 500 ml of water, 500 ml of 0.5 *N* sodium thiosulfate solution, 500 ml of water, and 500 ml of saturated sodium chloride solution. Drying and removal of solvent yielded 112.6 g (98.5%) of a colorless liquid: ir (neat), 5.85 and 8.34 μ; uv max (95% ethanol) 285 nm (ϵ 30.5); nmr (CCl_4) δ 5.50 ppm (1, broad).

***anti*-$\Delta^{4(10)}$-1-Octalol and Its Derivatives (6).**—To a mixture of 11.0 g (275 mmol) of lithium aluminum hydride in 2000 ml of diglyme, cooled to −78° in a Dry Ice–acetone bath, was added over a period of 1.5 hr, with stirring, under nitrogen, a solution of 112.6 g (0.749 mol) of $\Delta^{4(10)}$-1-octalone in 500 ml of diglyme. After stirring for an additional 5 hr at −78° the mixture was allowed to warm to room temperature. Saturated magnesium sulfate solution (75 ml) was then added slowly, with cooling, and the mixture was allowed to stand until it was nearly white (24 hr). Addition of 450 g of powdered anhydrous magnesium sulfate yielded a mixture which could be filtered easily. The separated solid was washed thoroughly with ether. The combined organic solutions were distilled, eventually at 50 mm, until the head temperature reached 87°, in order to remove most of the diglyme. The residue was diluted with 1000 ml of water and then extracted with three 500-ml portions of pentane. The combined pentane extracts were washed with four 500-ml portions of water and 250 ml of saturated sodium chloride solution. After drying, removal of solvent afforded 105.2 g (92%) of a yellow oil: nmr (CCl_4) δ 3.85 and 3.38 ppm (1 total, complex), attributable to syn and anti isomers, respectively, in a 31:69 ratio (best determined after removal of the OH absorption by adding D_2O).

To a solution of this yellow oil in 1000 ml of pyridine was added 400 ml of acetic anhydride. After 30 hr at room temperature the solution was poured over ice and the mixture was stirred for 1 hr. Addition of 3000 ml of water and extraction with four 500-ml portions of ether gave, after further work-up and a rapid distillation at 0.5 mm, 128.8 g (96%) of a colorless, fragrant liquid. The distillation product was then subjected to a careful fractional distillation at 0.3 mm (head temperature *ca.* 60°) and the per cent anti alcohol in the distillate was determined by glpc at 160° (Apiezon L): fraction 1, 45.2 g (95.4%); fraction 2, 25.6 g (91.2%); fraction 3, 30.9 g (74.8%); fraction 4, 26.3 g[22] (3.2%). Redistillation of fraction 3 afforded a further 20.0 g (96.5%) which was combined with fractions 1 and 2 (totaling 90.8 g, 94.5% anti).

This combined distillate (90.8 g) was saponified in a solution of 1250 ml of methanol and 125 ml of water containing 75 g of 85% potassium hydroxide. After 14 hr at 40° under nitrogen, the methanol was removed under reduced pressure, 2000 ml of water was added, and the mixture was extracted with four 500-ml portions of ether. Further work-up yielded 75.4 g of a yellow oil which afforded, upon distillation, 67.5 g (95%) of a colorless oil: bp 70.7–73.0° (0.7 mm); nmr (CCl_4) δ 5.27 (1, broad) and 3.38 ppm (1, m). A small portion yielded crystals from a pentane solution at −78°; and further crystallization from pentane at −20° gave a white solid, mp 40.1–42.2°.

From the distilled oil, a crystalline *p*-nitrobenzoate was obtained by a standard procedure, mp 71.0–71.3°.

Anal. Calcd for $C_{17}H_{19}NO_4$: C, 67.67; H, 6.36; N, 4.65. Found: C, 67.87; H, 6.13; N, 4.66.

The *p*-toluenesulfonate was prepared from 40.0 g (0.263 mol) of the distilled oil, which was dissolved in 300 ml of pyridine and treated with 55.0 g (0.288 mol) of *p*-toluenesulfonyl chloride. The solution was allowed to stand at 5° for 80 hr. Excess *p*-toluenesulfonyl chloride was then destroyed by the addition of 5 ml of water. Further work-up afforded 80.6 g of a white solid which gave, after two crystallizations from methanol at −20°, with pentane washing, 65.9 g (82%) of white crystals: mp 44.7–45.4°; nmr (CCl_4) δ 5.28 (1, broad) and 4.34 (1, m).

Anal. Calcd for $C_{17}H_{22}O_3S$: C, 66.65; H, 7.24; S, 10.44. Found: C, 66.79; H, 7.28; S, 10.36.

***trans,trans*-1,5-Cyclodecadiene (3) and *trans*-1,2-Divinylcyclohexane (4).**—To a solution of 20.0 g (65.2 mmol) of *anti*-$\Delta^{4(10)}$-1-octalyl *p*-toluenesulfonate in 50 ml of tetrahydrofuran, stirred and cooled in an ice–water bath and under nitrogen, was added, over a period of 15 min, 70 ml of a solution of 1 *M* borane in tetrahydrofuran (Alfa). The mixture was stirred for an additional 90 min at room temperature. To it was added cautiously,

---

[20] 1-Vinylcyclohexene was prepared from 1-ethynylcyclohexanol *via* the sequence elimination–reduction (not the converse) described by E. D. Bergman and A. Becker, *J. Amer. Chem. Soc.*, **81**, 225 (1959).

[21] Ethyl α-acetoxyacrylate was prepared according to the procedure described for the methyl ester by J. Wolinsky, R. Novak, and R. Vasileff, *J. Org. Chem.*, **29**, 3598 (1964).

[22] This fraction was characterized as *syn*-$\Delta^{4(10)}$-1-octalyl acetate and yielded *syn*-$\Delta^{4(10)}$-1-octanol, mp 50–51°, and *syn*-$\Delta^{4(10)}$-1-octalyl *p*-toluenesulfonate, mp 58.6–59.3° dec.

with cooling in an ice-water bath, first 15 ml of water and then 25 ml of 5 *N* sodium hydroxide solution. The mixture was stirred at room temperature for 48 hr and then 25 ml of 30% hydrogen peroxide was added with external cooling. The mixture was stirred for an additional 3 hr at room temperature. Work-up involved addition of 500 ml of water and extraction with five 100-ml portions of 2-methylbutane. The combined 2-methylbutane extracts were extracted with four 100-ml portions of water and then dried. Removal of most of the solvent was effected by fractional distillation and the residue was chromatographed on a 250-g column of silica gel; 100-ml fractions of 2-methylbutane eluent were collected and the solvent was removed by fractional distillation. Fraction 2 yielded a mixture probably containing tricyclo[5.3.0.0^{1,6}]decane: ir (film) 3.35 and 9.80 μ; nmr (CCl_4) δ 0.95–0.5 ppm (2, complex). Fraction 3 gave 1.22 g of a colorless liquid which was shown to be a mixture of 70% **3** and 30% **4** by glpc at 50° (SF-96). Fraction 4 afforded 4.67 g of a colorless liquid which was shown to be **3** containing less than 2% of **4** by glpc. Fractions 5 and 6 yielded oils similar in composition to fraction 4. Fractions 3–6 were combined and heated overnight at 100° under nitrogen. Short-path distillation of the resulting oil gave 5.50 g (62%) of *trans*-1,2-divinylcyclohexane (**4**) (>99.9% by glpc): bp 46.0–46.5° (10 mm); ir (film) 3.28, 5.50, 6.10, 10.10, and 11.01 μ; nmr, ratio of olefinic to paraffinic hydrogens, 6:10.

From similar runs *trans,trans*-1,5-cyclodecadiene (**3**) was obtained from individual fractions. For example, a 2.78-g chromatography fraction (>98% **3** by glpc) afforded 1.58 g of **3** (99% by glpc) upon short-path distillation at room temperature and 0.3 mm: ir (film) 3.36, 6.02, 10.11, 10.41, 12.78, and 13.65 μ; nmr (CCl_4), ratio of olefinic to paraffinic hydrogens, 4:12, main olefinic H signal a broad band centered at δ 4.7 ppm with $W_{1/2}$ = 14 Hz.

(+)-*trans*-1,2-Divinylcyclohexane.—To a solution of 0.997 g (26.4 mmol) of sodium borohydride and 9.60 g (70.2 mmol) of α-pinene, $[\alpha]_D$ +53.4° (95% ethanol), in 75 ml of diglyme, cooled to −10 to −20° in an ice–salt bath, was added slowly, with stirring under nitrogen, 4.98 g (35.1 mmol) of boron trifluoride etherate. The mixture was stirred for an additional 4 hr at −10 to −20°. Racemic **4** (9.58 g, 70.2 mmol) was added in one portion and the mixture was stirred at −10 to −20° until it became homogeneous (6 hr). To the cold solution was added cautiously first 5 ml of water and then 20 ml of 5 *N* sodium hydroxide solution. The ice–salt bath was removed, 20 ml of 30% hydrogen peroxide was added, and the mixture was allowed to stand overnight with stirring. It was then poured into 500 ml of water. Further work-up afforded 6.85 g of a colorless oil, bp 50–60° (10 mm), glpc analysis (SF-96) showing it to be a 65:34 mixture of **4** and α-pinene. The mixture was placed on a 180-g column of silica gel impregnated with 10% silver nitrate. Pentane was passed through the column until no trace of pinene in the eluent could be detected by glpc (this required 600 ml of pentane). The pentane in the column was displaced by 2-methylbutane and the column packing was then dumped into 400 ml of cold, concentrated ammonium hydroxide. Extraction with three 150-ml portions of 2-methylbutane and further work-up afforded, after distillation, 2.17 g of a colorless oil: bp 43–45° (10 mm); >99.9% **4** by glpc; $[\alpha]_{436}$ +9.00° (cyclohexane).

Configurational Correlation of (+)-4 with (+)-Dimethyl *trans*-1,2-Cyclohexanedicarboxylate.—One sample of (+)-**4**, 61 mg (0.448 mmol), $[\alpha]_D$ +3.61°, $[\alpha]_{436}$ +7.53° (cyclohexane), in 25 ml of methylene chloride was cooled to −78° and treated with an excess of ozone. The solution was allowed to warm to room temperature and remain at that temperature for 60 min. Solvent was then removed and to the residue was added 3 ml of 5 *N* sodium hydroxide solution and 2 ml of 30% hydrogen peroxide. The mixture was stirred overnight and excess peroxide was then destroyed with a small amount of 5% palladium on carbon. Further work-up yielded 20 mg (26%) of a white, solid acid.

A second sample of (+)-**4**, 59 mg (0.435 mmol), $[\alpha]_D$ +3.61°, $[\alpha]_{436}$ +7.53° (cyclohexane), in 2 ml of chloroform at −30° was treated with an excess of ozone. The solution was then allowed to stand at room temperature for 60 min. Thereafter the chloroform was removed by dropwise addition to 10 ml of water maintained at 95°. The aqueous mixture was then cooled slightly before adding to it 0.5 g of silver oxide and 1 ml of 5 *N* sodium hydroxide solution. This mixture was heated at 90° for 1 hr and then filtered hot. Further work-up afforded 17 mg (23%) of a slightly yellow oily acid.

The acidic products obtained from the two ozonolyses were combined, 38 mg, and esterified with an ethereal solution of diazomethane. Work-up gave 44 mg of a yellow oil which, subjected to preparative glpc at 150° (5 ft × 0.25 in. column packed with 5% Carbowax 20M on 40/60 Chromosorb T) afforded 29 mg of a colorless oil with ir and glpc characteristics indistinguishable from those of authentic dimethyl *trans*-1,2-cyclohexanedicarboxylate, $[\alpha]_D$ +7.29°, $[\alpha]_{436}$ +12.89° (acetone).

Kinetic Studies. A. Cope Rearrangement.—Samples of **3** in *n*-decane were degassed and then sealed under nitrogen and heated in a constant-temperature bath (±0.01°). Over the period of observation (approximately 2 half-lives) no side reactions could be detected by glpc and no residue was left upon distillation. The extent of conversion was determined by glpc analysis (50°, SF-96), each analysis in duplicate or triplicate, using the *n*-decane as a reference in two independent determinations: (1) the rate of disappearance of **3** and (2) the rate of appearance of **4**. At each of four temperatures two runs were made; for each run approximately ten sample tubes were heated. The glpc areal ratios were slightly changed by using a correlation line obtained with standard weighed mixtures; inexplicably, this did not quite pass through the origin for the mixture of **3** and *n*-decane. A good value of $[\mathbf{4}]_\infty$ was difficult to obtain directly (it was probably obscured by polymerization) and it was finally assigned the value of $[\mathbf{3}]_0$; varying this value by ±5% was found to have a negligible effect on the results. The total set of rate constants thus obtained yielded Arrhenius parameters from a General Electric Mark I computer using the least squares program SIXCR\$.

B. Racemization.—Samples of (+)-**4** were degassed and then sealed under vacuum and heated in a constant-temperature bath (±0.02°). Approximately ten samples were analyzed for each run, which extended over approximately 2 half-lives (except at the lowest temperature when there were only four observations taken up to ~20% conversion). Each sample tube was cooled and opened and the contents were distilled from the tube at room temperature and 0.3 mm into a small Dry Ice–acetone trap. The contents of the trap were removed with a small amount of cyclohexane and their weight was determined by difference. For determination of rotations each cyclohexane solution was made up to 1 ml in a volumetric flask. The specific rotation at t_∞ was taken to be zero and was actually found to be $[\alpha]_{436}$ 0.000 ± 0.004° after 10 half-lives. For each separate determination of rotation an individual rate constant was calculated from the first-order rate equation, yielding an average rate constant for each temperature. The total set of rate constants thus obtained yielded Arrhenius parameters from the computer program referred to above.

Registry No.—**3**, 10573-77-0; (±)-**4**, 41727-77-9; (+)-**4**, 41727-78-0; **5**, 41718-12-1; **6a**, 41727-79-1; *syn*-**6a**, 41727-80-4; **6a** *p*-nitrobenzoate, 41727-81-5; *syn*-**6a** acetate, 41727-82-6; **6b**, 41727-83-7; *syn*-**6b**, 41727-84-8; 1-vinylcyclohexene, 2622-21-1; ethyl α-acetoxyacrylate, 22807-79-0; 1,4-cycloadduct regioisomer A, 41718-15-4; 1,4-cycloadduct regioisomer B, 41718-16-5; epimer A, mp 75–93°, 41727-85-9; epimer B, mp 75–93°, 41727-86-0; tricyclo[5.3.0.0^{1,6}]decane, 41718-17-6; (+)-α-pinene, 7785-70-8.