Glpc Analysis of "Kinetic" Methylation of 4-Methyl-Δ^{9}-1-octalone (7).—To a solution of 1.19 g (7.25 mmol) of **7** in 30 ml of dimethoxyethane and 4 ml of methyl iodide was added 115.8 mmol of sodium hydride obtained by removing the hydrocarbon from 5.63 g of mull by washing with dimethoxyethane. The mixture was stirred under nitrogen at room temperature.[17] Aliquots were removed at intervals, worked up, and analysed by glpc (column 1, 75°); 42, 47, 51, and 55 min components were observed. The results are recorded in Table II which appears on p 4257.

Registry No.—**1**, 13207-25-5; **2**, 17408-20-7; **4**, 17408-21-8; **7**, 13207-04-0; **8**, 17408-23-0; **9**, 17393-19-0; 4,9-demethyl-$\Delta^{5(10)}$-1-octalone, 17408-24-1.

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[17] The hydrogen evolved was measured but its rate of evolution was not found to be useful for determining the extent of reaction.

Cope Rearrangement of *trans,trans*-2,8-*trans*-Bicyclo[8.4.0]tetradecadiene[1]

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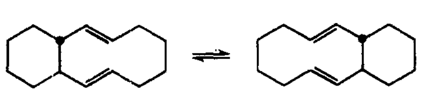
trans,trans-2,8-*trans*-Bicyclo[8.4.0]tetradecadiene[2] has been partially resolved into one of its enantiomers, $[\alpha]_D$ −58°, by selective reaction of optically active diisopinocampheylborane with the racemate.[3] Optically active diene racemizes in 2,2,4-trimethylpentane solution with first-order kinetics which yield an energy of activation of 25 kcal mol^{-1} with a frequency factor of 3×10^{11} sec^{-1} (half-life at 50° *ca.* 24 hr). These data are consistent with the occurrence of the Cope rearrangement A $\rightleftharpoons$ B, which is facilitated relative to the rearrangement of *dl*-3,4-dimethylhexa-1,5-diene (which proceeds at 180°)[4] by the combination of strain and conformation of the double bonds in the medium ring.[5] The system A $\rightleftharpoons$ B is unusual in its possession of the basic symmetry of the Cope rearrangement[6] combined with its susceptibility to extremely accurate kinetic measurement.



A B

Experimental Section

Optically Active *trans,trans*-2,8-*trans*-Bicyclo[8.4.0]tetradecadiene.—In a 25-ml flask equipped with a pressure-equalizing dropping funnel was placed 0.076 g (2.02 mmol) of sodium borohydride, 2.0 ml of diglyme, and 0.716 g (5.25 mmol) of (+)-α-pinene, bp 153.0–154.5°, $[\alpha]^{21}_D$ +53.2° (*c* 3.69, 95% ethanol). The flask was cooled to ice-bath temperature, and the contents were stirred under nitrogen throughout the course of the reaction. Boron trifluoride etherate (0.372 g, 2.62 mmol), diluted with 6.0 ml of diglyme, was first added. After 4 hr, 1.001 g (5.26 mmol) of diene, mp 48.0–49.0°, was added. After a further 4 hr, the reaction mixture was diluted with 50 ml of distilled water and extracted three times with 50-ml portions of pentane. The combined pentane extracts were washed three times with 50-ml portions of distilled water and then dried. Removal of solvent under reduced pressure and below 25° afforded 1.773 g of a clear colorless oil. The oil was dissolved in 75 ml of pentane and extracted with three 75-ml portions of 20% silver nitrate solution. The combined silver nitrate extracts were washed three times with 50-ml portions of pentane and then added to 150 ml of concentrated ammonium hydroxide at ice-bath temperature. The mixture was extracted four times with 25-ml portions of pentane. The combined pentane extracts were washed twice with 25-ml portions of distilled water and then dried. Removal of solvent under reduced pressure and below 25° afforded 0.375 g of solid, mp 41.0–46.0°, $[\alpha]^{23}_D$ −58.2° (*c* 3.65, chloroform), whose ir spectrum (CCl_4) was identical with that of pure diene. Capillary glpc indicated that the solid consisted of a single major component (99%).

Racemization of Optically Active *trans,trans*-2,8-*trans*-Bicyclo[8.4.0]tetradecadiene.—For each kinetic run, a solution of optically active diene in 2,2,4-trimethylpentane was prepared in a 25-ml volumetric flask, and the flask was suspended in a constant-temperature bath with ±0.03° temperature control. After allowing at least 30 min for the solution to reach thermal equilibrium, 2.0-ml aliquots were periodically removed and, except for measurements at 30°, quenched at ice-bath temperature. The optical rotation of these aliquots was measured at the sodium 589-mμ line at *ca.* 23° with an estimated accuracy of ±0.004°. Infinity points were measured after at least ten half-lives. The results of these measurements are compiled in Table I.

TABLE I

RACEMIZATION DATA[a]

Temp, °C	α_0	α_∞	k_α,[b] sec^{-1}
29.85	−0.452	+0.008[c]	$7.36 \pm 0.54^{d} \times 10^{-7}$
48.86	−0.570	+0.024	$7.74 \pm 0.50^{d} \times 10^{-6}$
59.58	−0.435	+0.10	$3.17 \pm 0.17^{d} \times 10^{-5}$

[a] *Ca.* 0.02 *M* diene in 2,2,4-trimethylpentane. [b] $2k_{\text{Cope}} = k_a = 2.303/t \times \log(\alpha_0 - \alpha_\infty)/(\alpha_t - \alpha_\infty)$. [c] Measured after finally heating for 71 hr at 60°. [d] Standard deviation.

After the kinetic run at 48.86°, evaporation of solvent yielded a solid, mp 43.0–47.0°, whose ir spectrum (CCl_4) was identical with that of pure diene.

Registry No.—(−)-*trans,trans*-2,8-*trans*-Bicyclo[8.4.0]tetradecadiene, 17510-76-8; (±)-*trans,trans*-2,8-*trans*-bicyclo[8.4.0]tetradecadiene, 17510-77-9.

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[1] This investigation was supported by Public Health Service Research Grant GM 09759 from the Division of General Medical Sciences, U. S. Public Health Service, and by a National Institutes of Health Predoctoral Fellowship to R. A. K. Acknowledgment is also made of National Science Foundation Grant G19108 which contributed to the purchase of the nmr spectrometer used in this research.

[2] P. S. Wharton, Y. Sumi, and R. A. Kretchmer, *J. Org. Chem.*, **30**, 234 (1965).

[3] This resolution is a direct application of an established method of synthesis of optically active alcohols from olefins. The reaction of *trans* double bonds is normally very slow, not so those of our strained diene. See H. C. Brown and N. R. Ayyangar, *J. Amer. Chem. Soc.*, **86**, 397, 1071 (1964).

[4] W. von E. Doering and W. R. Roth, *Tetrahedron*, **18**, 67 (1962).

[5] The parent system, *trans,trans*-1,5-cyclodecadiene, is reported to undergo the Cope rearrangement at slightly higher temperatures, rearranging irreversibly over a period of 3 days at 70° to *trans*-1,2-divinylcyclohexane: C. A. Grob, H. Link, and P. W. Schiess, *Helv. Chim. Acta*, **46**, 483 (1963).

[6] The observed rearrangement is degenerate in a previously unobserved sense; reactant and product are structurally identical but enantiomeric. For the first of several reported degenerate Cope rearrangements, previously observed solely by nmr spectroscopy, see W. von E. Doering and W. R. Roth, *Angew. Chem. Intern. Ed. Engl.*, **2**, 115 (1963). For an example of asymmetric induction in the Cope rearrangement, see R. K. Hill and N. W. Gilman, *Chem. Commun.*, 619 (1967).