$-14.1°$ (c 1.0, methanol); R_f 0.60 (methanol); ν_{max} 3300 broad (OH), 2900 (CH), 1740 (C=O), 1670 very broad (C=O and urethan), 1393 and 1669 (*t*-butyl), 1165 (CO), and 695 (Ph) cm^{-1}; λ_{max} 247, 252, 258, 261, 264, and 267 mμ (ε 162, 160, 180, 143, 145, and 100).

Anal. Calcd for $C_{29}H_{41}N_7O_9 \cdot H_2O$ (649.7): C, 53.61; H, 6.66; N, 15.09. Found: C, 53.88; H, 6.46; N, 15.62.

The tetrapeptide was alternatively prepared by use of N,N'-dicyclohexylcarbodiimide, but only an oily product was obtained in spite of many crystallization attempts.

Registry No.—III, 17115-09-2; XI, 17791-44-5; XII, 17791-45-6; XVII, 17791-46-7; XX, 17791-47-8; XXI, 17791-48-9; XXIII, 17791-49-0; XXVII, 2488-14-4; XXVIII, 17791-51-4; XXIX, 17791-52-5; XXXI, 13734-45-7; XXXII, 17791-54-7; XXXIII, 17818-04-1.

Acknowledgment.—The authors are indebted to the National Science Foundation for Grant GB-587, which supported this investigation.

Angular Methylation of 4-Methyl-$\Delta^{4(10)}$-1-octalone[1]

P. S. WHARTON AND C. E. SUNDIN,

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Received May 27, 1968

This Note reports the direct angular methylationof 4-methyl-$\Delta^{4(10)}$-1-octalone (**1** → **2**), a synthetic step previously suggested[2] for $\Delta^{4(10)}$-1-octalones in general but unrealized[3] in one attempt to methylate $\Delta^{4(10)}$-1-octalone itself. In conjunction with a synthesis of $\Delta^{4(10)}$-1-octalones *via* 1,4 cycloaddition to 1-vinylcyclohexenes[4] the present work forms the basis of a useful synthetic approach to germacrane and elemane sesquiterpenes.[5]

4-Methyl-$\Delta^{4(10)}$-1-octalone (**1**) is rapidly and completely isomerized by ethanolic sodium hydroxide to its corresponding conjugated double-bond isomer (**7**).[6] The dire consequences of this isomerization were anticipated, but their establishment proved to be useful.[7] Addition of methyl iodide to the enolate mixture formed by stirring equimolar amounts of **7** and sodium hydride in dimethoxyethane for 36 hr to ensure partial, if not complete, equilibration of enolate ions gave a multicomponent distillate in 85% yield from which the predominant component (47% by glpc) was isolated and shown to be 4,9-dimethyl-$\Delta^{5(10)}$-1-octalone, a product of angular methylation but with undesirable double-bond isomerization. Thus, of the five interconvertible enolates in this system, the most stable is the $\Delta^{1(9),5(10)}$-hexalin, in accord with the relative stabilities of the unsubstituted hexalins and other related systems.[8]

Methylation of **7** under conditions favoring kinetic control of enolate formation[9] yielded no trace of **2**. Treatment of **7** in dimethoxyethane at room temperature with an excess of both sodium hydride and methyl iodide gave in high yield 2,2,4-trimethyl-Δ^9-1-octalone (**9**) *via* the glpc detectable intermediates, *cis*- and *trans*-2,4-dimethyl-Δ^9-1-octalones (**8**, see the lower half of Scheme I). This result is consistent with exemplary data indicating that α' protons of α,β-unsaturated ketones can be more acidic than γ protons in the kinetic, if not thermodynamic, sense.[10]

In relation to the angular methylation of **1**, the foregoing results emphasized the need for a procedure involving kinetic control of enolate formation from the β,γ-unsaturated ketone. Treatment of **1** in dimethoxyethane at room temperature with 1 equiv of sodium hydride and excess methyl iodide afforded a multicomponent distillate in 83% yield, from which was obtained, by repetitive preparative glpc, a sample of the desired ketone **2**. Determination of the efficacy of this chosen[11] procedure was effected by analyzing the reaction of **1** with an excess of both sodium hydride and methyl iodide. Analysis and separation were simplified by treating each aliquot removed from the reaction vessel with base to ensure complete isomerization of β,γ-unsaturated ketones **5** and **6** to α,β-unsaturated ketones **8** and **9**. Results of the glpc analysis are shown in Table I and Figure 1. A seven-component mixture developed and converged to a single final product which was isolated and character-

TABLE I

"KINETIC" METHYLATION OF 1[a]

Time min	%						
	4	*trans*[b] **3**	**2**	*cis*[b] **3**	*trans*[b] **8**	**7**	*cis*[b] **8**
0						100	
18			3.3			96.7	
33			18.4			81.0	0.6
42		0.8	41.1	1.7	1.2	48.2	6.8
49		2.1	57.0	5.7	2.1	24.5	8.4
60	1.1	7.5	66.6	12.7	0.4	0.7	10.6
82	10.0	27.7	18.4	41.4	0.6	0.3	1.4
159	55.5	18.5		26.0			
258	76.3	10.7		13.0			
645	88.9	9.9		1.2			
1530	99.4	0.3		0.3			
2055	99.6	0.1		0.3			

[a] Compounds are listed in order of increasing glpc retention time. Other detectable peaks never amounted to more than 0.8%. [b] Arbitrary isomer assignments based on a rationalization of steric interference with adsorption.

(1) This investigation was supported by Public Health Service Research Grant GM 09759 and GM 14133 from the Division of General Medical Sciences, U. S. Public Health Service. Acknowledgment is also made of National Science Foundation Grant G 19108 which contributed to the purchase of the nmr spectrometer used in this research.

(2) A. J. Birch, J. A. K. Quartey, and H. Smith, *J. Chem. Soc.*, 1768 (1952).

(3) J. A. K. Quartey, *J. Ind. Chem. Soc.*, **37**, 731 (1960).

(4) P. S. Wharton and B. T. Aw, *J. Org. Chem.*, **31**, 3787 (1966); B. T. Aw and C. E. Sundin, Ph.D. Theses, University of Wisconsin, 1966–1967.

(5) The continuation is most simply envisaged *via* the fragmentation sequence developed by J. A. Marshall and G. L. Bundy [*Chem. Commun.*, 854 (1967)].

(6) The 4-methyl group does not stabilize the β,γ-unsaturated isomer sufficiently to produce a detectable amount at equilibrium. *Cf.* K. G. Lewis and G. J. William, *Tetrahedron Lett.*, 4573 (1965).

(7) For a general discussion of the alkylation of α,β-unsaturated ketones, see J. M. Conia, *Rec. Chem. Progr.*, **24**, 43 (1963).

(8) R. B. Bates, R. H. Carnighan, and C. E. Staples, *J. Amer. Chem. Soc.*, **85**, 3030 (1963), and references therein; M. S. Newman, V. DeVries, and R. Darlak, *J. Org. Chem.*, **31**, 2171 (1966).

(9) For a general discussion of enolate anions, their formation, and alkylation, see H. O. House, *Rec. Chem. Progr.*, **28**, 98 (1967).

(10) A. J. Birch, *J. Chem. Soc.*, 2325 (1950); H. J. Ringold and A. Turner, *Chem. Ind.* (London), 211 (1962).

(11) (a) Trityl and amide ions have been used extensively as bases to obtain enolates from ketones. We did not investigate these and other procedures. (b) See ref 9 and H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, Chapter 7.

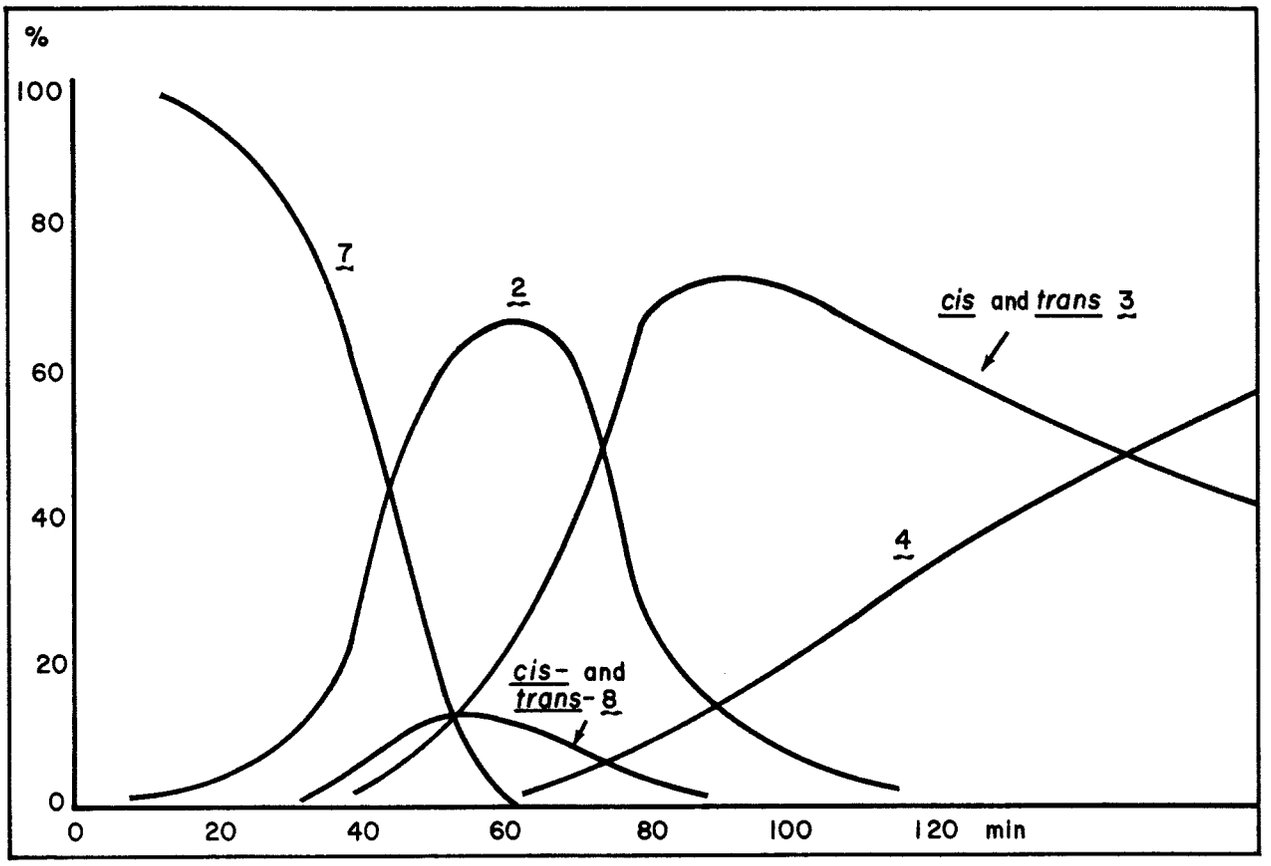
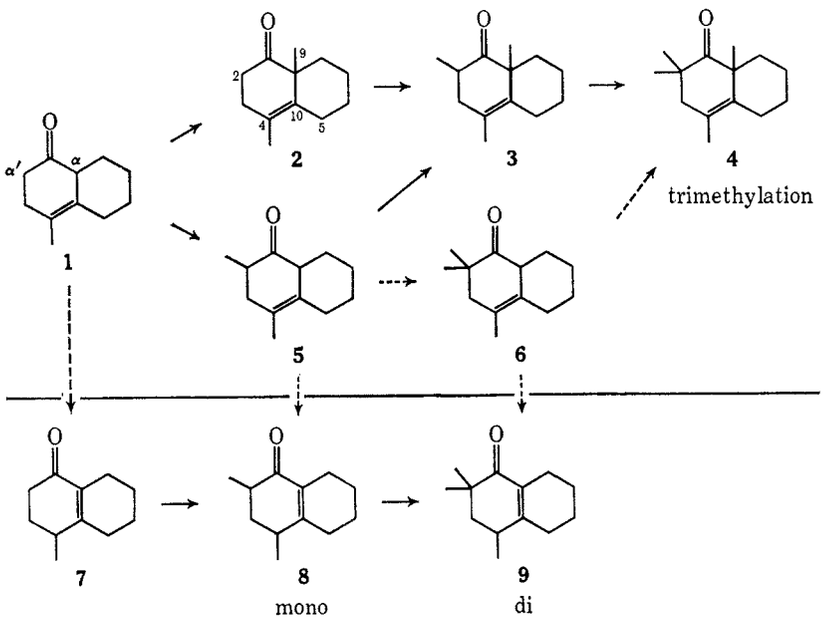


Figure 1.—Kinetic methylation of 4-methyl-$\Delta^{4(10)}$-1-octalone (1).

SCHEME I



ized as **4**.[12] This ketone was one of a group of four β,γ-unsaturated ketones well separated from a group of three α,β-unsaturated ketones by glpc retention times. Comparison with the retention times of components formed in the "kinetic" methylation of **7** revealed the presence of *cis* and *trans* **8**, *but complete absence of* **9**, establishing the formation of *cis* and *trans* **8** exclusively by isomerization of *cis* and *trans* **5** in the work-up and not by formation during the reaction (either by isomerization of **5**, or by isomerization of **1** followed by methylation). The over-all pattern of methylation of **1** is therefore completely defined by the upper half of Scheme I.

Figure 1 reveals that, under the chosen conditions, the maximum realizable yield of **2** is at least 55% (66% based on recovered distillate), a demonstration that direct angular methylation of $\Delta^{4(10)}$-1-octalones represents a viable synthetic procedure. This contrasts with the indirect approaches which have been employed

(12) (a) Although not expected, competitive γ and O alkylation would have complicated the observed methylation pattern; see ref 7. (b) Conditions were not controlled and no over-all kinetic analysis of the results was attempted. For convenience in sampling at short reaction times the reaction was started at 0° and then allowed to warm to room temperature.

to introduce an angular methyl group into 1-decalones.[11b] The effect of the 4(10) double bond is apparent in a comparison of the (apparent)[13] kinetic acidities of the α and α' protons of **1** and *trans*-1-decalone: the α proton is seven times *less* acidic than the α' protons in *trans*-1-decalone[14] and four times *more* acidic in **1**.[12b,15]

Experimental Section

Physical Data.—Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill. Infrared spectra were recorded on Perkin-Elmer 137 Infracord and Beckman IR-8 spectrometers. Nmr spectra were recorded on Varian A-60 and A-60A spectrometers using tetramethylsilane as an internal standard. Mass spectra were obtained on a Consolidated CEC 103 spectrometer with samples introduced *via* a heated glass inlet system maintained at 200°. Glpc data were obtained using (1) capillary columns in conjunction with a Perkin-Elmer F-11 unit (flame ionization) and (2) packed columns in conjunction with an Aerograph A-90-P2 unit (thermal conductivity). Component composition is given in terms of peak areas determined by using a Disc chart integrator. Glpc columns used were (1) Ucon Polar 50-HB-2000, 150 ft capillary; (2) 5% Carbowax on Teflon 6, 5 ft × 1/4 in.; (3) 20% didecylphthalate on 60/80 Chromosorb P, 5 ft × 1/4 in.; (4) 20% SF-96 on 60/80 firebrick, 5 ft × 1/4 in.

Materials and Procedure.—Dimethoxyethane was distilled from lithium aluminum hydride and stored over molecular sieves (activated Linde Type 13X). Methyl iodide was distilled and stored over molecular sieves. Where not described, the work-up was typically carried out by pouring the reaction mixture into saturated sodium chloride solution containing a small amount of sodium thiosulfate. The aqueous phase was extracted with several portions of ether; the ether extracts were combined and washed several times with saturated sodium chloride solution. The ether solution was dried over sodium or magnesium sulfate, filtered, and evaporated under reduced pressure.

4-Methyl-Δ^9-1-octalone[4] (**7**) was recovered in 98% yield from base-catalyzed isomerization of 4-methyl-$\Delta^{4(10)}$-1-octalone: glpc (column 1, 85°) 38 min (98%); ir max 6.02 μ; uv max (95% EtOH) 247 mμ (ϵ 12,500); mass spectrum (70 eV) *m/e* (rel intensity) 164 (13), 149 (5), 136 (19), 122 (16), 107 (16), 93 (4), 51 (100).

2,2,4-Trimethyl- and 2,4-Dimethyl-Δ^9-1-octalones (9 and 8).—To a solution of 976 mg (5.95 mmol) of **7** in 18 ml of dimethoxyethane and 2 ml of methyl iodide was added, with stirring under nitrogen, 262 mg (5.92 mmol) of sodium hydride as a 54% mull. After stirring at room temperature for 18 hr a test for sodium hydride was negative. Work-up afforded 982 mg of a colorless distillate (bath temp 70–90° at 0.1 mm): glpc (column 1, 75°) 43 (0.3), 48 (7.6), 52 (91.4), and 56 min (0.7%); the 52 min component corresponded to the starting material. To a solution of 941 mg of distillate in 17 ml of dimethoxyethane and 2 ml of methyl iodide was added 769 mg (17.9 mmol) of sodium hydride as a 60% mull. After 62 hr at room temperature work-up yielded 1.01 g of distillate: glpc (column 1, 75°) 27 (1.2), 43 (41.5), 48 (51.8), and 56 min (5.5%). Preparative glpc (column 2, 130°) afforded an analytical sample of the 43 min component (**9**): ir max (film) 5.99 μ; nmr (CCl_4) δ 1.02 (s, 6), 1.09 (d, 3, J = 8 Hz); mass spectrum (70 eV) *m/e* (rel intensity) 192 (42), 177 (4), 163 (2), 149 (15), 137 (34), 136 (100), 135 (31), 121 (10), 107 (23), 95 (95).

Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.45; H, 10.35.

Preparative glpc also afforded an analytical sample of the 48 min component (**8**): ir max (film) 5.99 μ; nmr (CCl_4) δ 1.08 (d, 3, J = 9.5 Hz) and 1.18 (d, 3, J = 9.0 Hz).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.66; H, 10.16.

4,9-Dimethyl-$\Delta^{5(10)}$-1-octalone.—To a solution of 1.27 g (7.76 mmol) of **7** in 18 ml of dimethoxyethane was added 322 mg (7.79 mmol) of sodium hydride as a 58% mull. After stirring under nitrogen at room temperature for 36 hr the dark brown solution was cooled in an ice–water bath. Methyl iodide (0.7 ml) was added, and the mixture was stirred for 5 min. Work-up gave 1.18 g of distillate (bath temp 50–80° at 0.2 mm): glpc (column 1, 75°) 11 (1.9), 26 (10.3), 27 (1.1), 29 (46.8), 32 (5.7), 51 (27.7), 58 (2.2) and 63 min (4.3%). Preparative glpc (column 2, 142° and column 3, 140°) afforded an analytical sample of the 29 min component, 4,9-dimethyl-$\Delta^{5(10)}$-1-octalone: ir max (film) 5.82 μ; nmr (CCl_4) δ 1.07 (d, 3, J = 6.7 Hz), 1.25 (s, 3) and 5.42 (m, 1); mass spectrum (70 eV) *m/e* (rel intensity) 178 (88), 163 (36), 149 (11), 136 (61), 135 (73), 123 (83), 122 (15), 121 (28), 107 (62), 93 (100).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.65; H, 10.16.

4,9-Dimethyl-$\Delta^{4(10)}$-1-octalone (2).—To a solution of 733 mg (4.46 mmol) of **1** in 17 ml of dimethoxyethane and 2 ml of methyl iodide was added 205 mg (4.62 mmol) of sodium hydride as a 54% mull. The mixture was stirred under nitrogen at room temperature for 1.5 hr. Work-up afforded 661 mg of distillate (bath temp 50–70° at 0.2 mm): glpc (column 1, 100°) 18 (3.8), 19 (0.8), 21 (6.9), 23 (64.2), and 25 min (24.2%).[16] Preparative glpc (column 4, 144°) yielded an analytical sample of the 23 min component (**2**): ir max (film) 5.83 μ; nmr (CCl_4) δ 1.19 (s, 3) and 1.69 (s, 3); mass spectrum (70 eV) *m/e* (rel intensity) 178 (6), 163 (2), 149 (1), 121 (15), 107 (10), 93 (25), 39 (100).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C 80.73; H, 10.22.

2,2,4,9-Tetramethyl-$\Delta^{4(10)}$-1-octalone (4).—To a solution of 374 mg (2.28 mmol) of **1** in 13 ml of dimethoxyethane and 0.5 ml of methyl iodide was added 600 mg (13.4 mmol) of sodium hydride as a 54% mull. The mixture was stirred under nitrogen at room temperature for 10 hr. Work-up afforded 430 mg of distillate (bath temp 75° at 0.3 mm): glpc (column 4, 130°) 21 (0.4), 32 (6.6), and 51 min (92.4%), from which was obtained an analytical sample of the 51 min component (**4**): ir max (film) 5.86 μ; nmr (CCl_4) δ 1.08 (s, 6), 1.12 (s, 3), and 1.71 (s, 3); mass spectrum (70 eV) *m/e* (rel intensity) 206 (32), 191 (7), 163 (29), 150 (19), 136 (100), 122 (17), 121 (85), 107 (55), 93 (74).

Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.29; H, 10.73.

Glpc Analysis of "Kinetic" Methylation of 4-Methyl-$\Delta^{4(10)}$-1-octalone (1).—To a mixture of 2.06 g (49.6 mmol) of sodium hydride as a 58% mull, 50 ml of dimethoxyethane and 4 ml of methyl iodide, contained in a flask cooled in ice–water, was added a solution of 944 mg (5.74 mmol) of **1** in 10 ml of dimethoxyethane. The mixture was allowed to warm to room temperature and was stirred at this temperature under nitrogen. (After 14 hr a further 16 mmol of sodium hydride was added.) Aliquots were removed at intervals and added to 5-ml portions of cold 95% ethanol. Each solution was then boiled for 10 min, cooled, worked up, and analyzed by glpc (column 1, 75°); 22, 27, 29, 32, 40, 45, 50, and 56 min components were observed. The results are recorded in Table I in the text.

TABLE II

"KINETIC" METHYLATION OF **7**[a]

Time, min	%			
	9	*trans*[b] **8**	**7**	*cis*[b] **8**
11			100	
29		3.6	96.2	0.2
55		26.8	68.2	5.0
98	0.3	38.1	54.8	6.8
161	2.3	56.3	31.0	10.3
230	8.4	71.0	9.7	10.9
520	32.6	61.3	0.2	5.9
2260[c]	73.1	25.5		1.4
7450[d]	90.1	9.9		

[a] Compounds are listed in order of increasing glpc retention times. [b] Arbitrary isomer assignments based on a rationalization of steric interference with adsorption. [c] 1.0% at 22 min. [d] 3.4% at 22 min.

(13) The possibility of *partial* equilibration of enolates cannot be discounted.

(14) H. O. House and B. M. Trost, *J. Org. Chem.*, **30**, 1341 (1965).

(15) The relative kinetic acidity of the α' proton of **5** is even less, the 2-methyl group suppressing the formation of **6**. See H. O. House and V. Kramar, *ibid.*, **28**, 3362 (1963).

(16) This experiment was carried out before adopting a standard base treatment in the work-up which ensured complete isomerization. The glpc results cannot therefore be directly correlated with those of other runs because of uncertainty with respect to the extent of isomerization.

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.

(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]

P. S. WHARTON AND R. A. KRETCHMER

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Received May 13, 1968

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

A B

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.

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] $2k_{Cope} = k_a = 2.303/t \times \log (\alpha_0 - \alpha_\infty)/(\alpha_t - \alpha_\infty)$. [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.

(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).