δ 4.0 (s, OCH_3, 3 H), 6.75 (d, 3-pyr-H, $J_{3,4}$ = 9.0 Hz, 1 H), 8.13 (dd, 4-pyr-H, $J_{4,3}$ = 9.0 Hz, $J_{4,6}$ = 2.5 Hz, 1 H), 8.81 (d, 6-pyr-H, $J_{6,4}$ = 2.5 Hz, 1 H); IR (KBr) 1717 (CO_2CD_3), 1600, 1495, 1290 (vs), 1140, 1085, 1020 cm^{-1}; mass spectrum, *m/e* (relative intensity) 170 (M^+, 73), 169 (M^+ – 1, 100), 140 (42), 136 (50).

Anal. Calcd for $C_8H_6D_3NO_3$: C, 56.46;, H, 5.32; N, 8.23. Found: C, 56.17; H, 5.58; N, 7.99.

A second component was eluted with chloroform–methanol (9:1) to give 1-methyl-5-(carbomethoxy-d_3)-2(1*H*)-pyridinone as colorless crystals: 20 mg (7.3%); mp 138–139 °C; NMR ($CDCl_3$) δ 3.60 (s, NCH_3, 3 H), 6.51 (d, 3-pyr-H, $J_{3,4}$ = 9.5 Hz, 1 H), 7.83 (dd, 4-pyr-H, $J_{4,3}$ = 9.5 Hz, $J_{4,6}$ = 2.5 Hz, 1 H), 8.18 (d, 6-pyr-H, $J_{6,4}$ = 2.5 Hz, 1 H); IR (KBr) 1705 (CO_2CD_3), 1660 ($CONCH_3$), 1604, 1440, 1220, 1210, 1130, 1120, 1080 cm^{-1}; mass spectrum, *m/e* (relative intensity) 170 (M^+, 80), 136 (100), 108 (69), 95 (12).

Anal. Calcd for $C_8H_6D_3NO_3$: C, 56.46; H, 5.32; N, 8.23. Found: C, 56.31; H, 5.28; N, 8.13.

General Pyrolysis Procedure. A weighed amount of pure sample (50–100 mg) was sealed in a glass tube either at atmospheric pressure or under vacuum (ca. 10^{-1} mmHg) and heated in a sand bath for 20–48 h at 200–300 °C, as stipulated in Table I. Analysis of the reaction mixture was conducted by TLC [silica gel, eluting with ethyl acetate or a mixture of ethyl acetate–cyclohexane (1:1)] and spectrally by NMR. Purification and separation of the pure components was conducted by either (1) preparative ThLC (silica gel), (2) column chromatography, or (3) recrystallization.

1-Methyl-2(1*H*)-pyridinone:[12] bp 63 °C (0.5 mm); NMR ($CDCl_3$) δ 3.58 (s, NCH_3, 3 H), 6.24 (t, 5-pyr-H, $J_{5,4} = J_{5,6}$ = 7.0 Hz, $J_{5,3}$ = 2.0 Hz, 1 H), 6.65 (dd, 3-pyr-H, $J_{3,4}$ = 9.5 Hz, $J_{3,5}$ = 2.0 Hz, 1 H), 7.4 (m, 4,6-pyr-H, 2 H); mass spectrum, *m/e* (relative intensity) 109 (M^+, 100), 81 (78), 80 (75), 39 (10).

1-Ethyl-2(1*H*)-pyridinone:[13] bp 140 °C (0.5 mm); NMR ($CDCl_3$) δ 1.35 (t, NCH_2CH_3, *J* = 7.0 Hz, 3 H), 4.02 (q, NCH_2CH_3, *J* = 7.0 Hz, 2 H), 6.18 (dt, 5-pyr-H, $J_{5,4} = J_{5,6}$ = 6.5 Hz, $J_{5,3}$ = 1.5 Hz, 1 H), 6.57 (dd, 3-pyr-H, $J_{3,4}$ = 9.5 Hz, $J_{3,5}$ = 1.5 Hz, 1 H), 7.3 (m, 4,6-pyr-H, 2 H); mass spectrum, *m/e* (relative intensity) 123 (M^+, 86), 95 (69), 80 (70), 67 (100).

1-Methyl-3-(carbomethoxy)-2(1*H*)-pyridinone: mp 71 °C (lit.[14] mp 70–71 °C; NMR ($CDCl_3$) δ 3.62 (s, NCH_3, 3 H), 3.92 (s, CO_2CH_3, 3 H), 6.25 (t, 5-pyr-H, *J* = 7.0 Hz, 1 H), 7.63 (dd, 4-pyr-H, $J_{4,5}$ = 7.0 Hz, $J_{4,6}$ = 2.5 Hz, 1 H), 8.18 (dd, 6-pyr-H, $J_{6,5}$ = 7.0 Hz, $J_{6,4}$ = 2.5 Hz, 1 H); mass spectrum, (relative intensity) 167 (M^+, 100), 136 (95), 108 (43).

1-Ethyl-3-carbethoxy-2(1*H*)-pyridinone: oil; NMR ($CDCl_3$) δ 1.30 (t, NCH_2CH_3, *J* = 7.0 Hz, 3 H), 1.41 (t, $CO_2CH_2CH_3$, *J* = 7.5 Hz, 3 H), 4.06 (q, NCH_2CH_3, *J* = 7.0 Hz, 2 H), 4.36 (q, $CO_2CH_2CH_3$, *J* = 7.5 Hz, 2 H), 6.22 (t, 5-pyr-H, *J* = 7.0 Hz, 1 H), 7.58 (dd, 4-pyr-H, $J_{4,5}$ = 7.0 Hz, $J_{4,6}$ = 2.0 Hz, 1 H), 8.05 (dd, 6-pyr-H, $J_{6,5}$ = 7.0 Hz, $J_{6,4}$ = 2.0 Hz, 1 H).

1-Methyl-5-(carbomethoxy)-2(1*H*)-pyridinone: mp 139–140 °C (lit.[15] mp 139 °C); NMR ($CDCl_3$) δ 3.62 (s, NCH_3, 3 H), 3.88 (s, CO_2CH_3, 3 H), 6.54 (d, 3-pyr-H, *J* = 9.5 Hz, 1 H), 7.87 (dd, 4-pyr-H, $J_{3,4}$ = 9.5 Hz, $J_{4,6}$ = 2.5 Hz, 1 H), 8.23 (d, 6-pyr-H, $J_{6,4}$ = 2.5 Hz, 1 H); mass spectrum, *m/e* (relative intensity) 167 (M^+, 76), 136 (100), 108 (57), 95 (12).

1-Methyl-5-(carbethoxy)-2(1*H*)-pyridinone: mp 72–73 °C (lit.[16] mp 72–73 °C); NMR ($CDCl_3$) δ 1.35 (t, $CO_2CH_2CH_3$, *J* = 7.0 Hz, 3 H), 3.64 (s, NCH_3, 3 H), 4.33 (q, $CO_2CH_2CH_3$, *J* = 7.0 Hz, 2 H), 6.53 (d, 3-pyr-H, *J* = 9.5 Hz, 1 H), 7.85 (dd, 4-pyr-H, $J_{4,3}$ = 9.5 Hz, $J_{4,6}$ = 2.5 Hz, 1 H), 8.27 (d, 6-pyr-H, $J_{6,4}$ = 2.5 Hz, 1 H); mass spectrum, *m/e* (relative intensity) 181 (M^+, 42), 153 (25), 136 (100), 108 (43).

1-Ethyl-5-(carbomethoxy)-2(1*H*)-pyridinone: mp 93–94 °C; NMR ($CDCl_3$) δ 1.40 (t, NCH_2CH_3, *J* = 7.0 Hz, 3 H), 3.87 (s, CO_2CH_3, 3 H), 4.03 (q, NCH_2CH_3, *J* = 7 Hz, 2 H), 6.52 (d, 3-pyr-H, *J* = 9.5 Hz, 1 H), 7.84 (dd, 4-pyr-H, $J_{4,3}$ = 9.5 Hz, $J_{4,6}$ = 2.0 Hz, 1 H), 8.18 (d, 6-pyr-H, $J_{6,4}$ = 2.0 Hz, 1 H); mass spectrum, *m/e* (relative intensity) 181 (M^+, 73), 153 (47), 150 (22), 122 (100).

Anal. Calcd for $C_9H_{11}NO_3$: C, 59.65; H, 6.13; N, 7.73. Found: C, 59.81; H, 6.09; N, 7.70.

1-Ethyl-5-(carbethoxy)-2(1*H*)-pyridinone:[9] bp 130 °C (0.7 mm); NMR ($CDCl_3$) δ 1.35 (t, NCH_2CH_3, *J* = 7.0 Hz, 3 H), 1.40 (t, $CO_2CH_2CH_3$, *J* = 7.0 Hz, 3 H), 4.05 (q, NCH_2CH_3, *J* = 7.0 Hz, 2 H), 4.34 (q, $CO_2CH_2CH_3$, *J* = 7.0 Hz, 2 H), 6.52 (d, 3-pyr-H, *J* = 9.5 Hz, 1 H), 7.85 (dd, 4-pyr-H, $J_{4,3}$ = 9.5 Hz, $J_{4,6}$ = 2.5 Hz, 1 H), 8.2 (d, 6-pyr-H, $J_{6,4}$ = 2.5 Hz, 1 H); mass spectrum, *m/e* (relative intensity) 195 (M^+, 83), 150 (35), 139 (85), 122 (100).

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Registry No. 3a, 15441-51-7; **3b**, 67367-26-4; **4a**, 74925-36-3; **4b**, 67367-27-5; **5a**, 13337-79-6; **5b**, 694-85-9; **6a**, 24903-80-8; **6c**, 74925-37-4; **6d**, 74357-22-5; **7a**, 24903-82-0; **7b**, 6375-89-9; **7c**, 10561-91-8; **7d**, 74925-38-5; **8**, 74925-39-6; 6-hydroxynicotinic acid, 5006-66-6; 5-(carbomethoxy-d_3)-2(1*H*)-pyridinone, 74925-39-6; 2-hydroxy-5-(carbomethoxy)pyridine, 66171-50-4; ethyl iodide, 75-03-6; 2-methoxy-5-(carbomethoxy-d_3)pyridine, 74925-40-9; *N,N*-dimethyl-2-methoxynicotinamide, 74925-41-0; 5-(dimethylcarbamoyl)-1-methyl-2(1*H*)-pyridinone, 74925-42-1.

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Intramolecular Ene Reactions of 1,2-Diallylcyclohexanes

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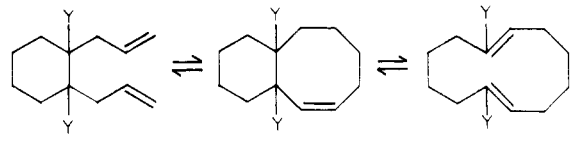
The ene reaction which interconverts 1,7-octadiene and cyclooctene is reversible and at temperatures above 300 °C the two components are in mobile equilibrium.[2] However, the reaction is limited to 1,7-dienes lacking terminal alkyl substituents.[3] There exists in this equilibrium the potential for a very interesting six-carbon ring expansion (eq 1), but so far as we can ascertain, no attempt



(1)

1 2 3

to realize this possibility has been made. Before considering any experimental studies, we need to take note of some important thermodynamic considerations. From the group values of Benson,[4] one can get some rough approximations for $\Delta H°$ and $\Delta S°$ for the various equilibria of eq 1 (Y = H).[5] For 1 ⇌ 2 $\Delta H° \simeq -16$ kcal/mol and $\Delta S° \simeq -20$ eu; for 2 ⇌ for 3 $\Delta H° \simeq +14$ kcal/mol and $\Delta S° \simeq +25$ eu; for 1 ⇌ 3 $\Delta H° \simeq -2$ kcal/mol and $\Delta S° \simeq +5$ eu. Taken at face value, these values indicate that at 600 K

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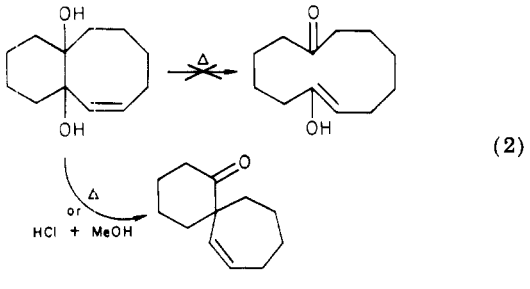
2 and 3 would be the major constituents at equilibrium. It would clearly be beneficial to bias this equilibrium further toward 3; one route to achieve this would be to use Y = OR, since enol ethers are more stable than simple double bonds by as much as 5 kcal/mol.[6] For convenience we chose (trimethylsilyl)oxy groups for an initial study.

Compound 1 (Y = OH) was prepared from 1,2-cyclohexanedione in two steps, each requiring 2 mol of allylmagnesium bromide. The diol was a liquid mixture of stereoisomers not readily separable by chromatography. When the mixture was allowed to stand at 0 °C, a small portion separated in crystalline form. However, the entire mixture was normally silylated and the resultant disilyl derivative was separated by GLC into major (62%) and minor (38%) fractions. It should be noted that under the conditions normally recommended for tertiary alcohols 1 (Y = OH) gave poor yields, but at 25 °C silylation was quantitative. When the crystalline diol was silylated it gave 1 (Y = $OSiMe_3$) equivalent with the minor product obtained from the GLC separation. Evidence permitting assignment of the minor product as *trans*-1 and the major product as *cis*-1 was obtained from two sources. At −40 °C the NMR spectrum of the major isomer (Y = $OSiMe_3$) shows two singlets, indicating two nonequivalent $SiMe_3$ groups, while the minor isomer shows one singlet. Hydrolysis of each 1 (Y = $OSiMe_3$) followed by hydrogenation gave two isomeric 1,2-dipropylcyclohexane-1,2-diols. In dilute solution in carbon tetrachloride, the dipropyl diol from the major product shows two OH stretching bands ($\Delta\tilde{\nu}$ = 48 cm^{-1}) in its infrared spectrum, while that from the minor product shows a single non-hydrogen-bonded stretch at 3613 cm^{-1}.

The stereoisomeric mixture 1 (Y = $OSiMe_3$) was heated in solution at 300 °C or in the vapor phase at 390 °C and one major product and two minor products were obtained. The vapor-phase process was not studied thoroughly and probably could be improved. Solution reaction was slow, but good yields (80–85%) of the major product were obtained. This product was identified spectrally as 1,8-bis[(trimethylsilyl)oxy]bicyclo[6.4.0]dodec-2-ene, since it has one double bond (i.e., bicyclic) with its olefinic protons appearing in the NMR as the AB part of an ABX_2 pattern with J_{AB} = 11, $J_{AX} \rightarrow 0$, and $J_{BX} \simeq$ 6.5 Hz (CCH=CHCH_2). The (trimethylsilyl)oxy groups survive and give rise to two unequal singlets, suggesting a mixture of isomers, though separation was not achieved on GLC or TLC. One minor product (ca. 10%) was identified as spiro[5.6]dodec-7-en-1-one (see below), but the method of its generation thermally was not delineated. The second minor product (5–7%) was not identified.

The main thermal product 2 (Y = $OSiMe_3$) was hydrolyzed to 2 (Y = OH) since models indicated that 2 (Y = OH) could attain the proper geometry for a β-hydroxy olefin cleavage (eq 2). However, when 2 (Y = OH) was heated the sole produce was a nonconjugated unsaturated ketone. Its NMR spectrum shows the olefinic protons as the AB portion of an ABX_2 spectrum (J_{AB} = 11, $J_{AX} \simeq$ 6.0, $J_{BX} \rightarrow$ 0 Hz). Reduction of the double bond gave a saturated ketone, whose 2,4-DNP derivative melts at the same temperature as the derivatives of both 1-spiro-[5.6]- and 6-spiro[4.7]dodecanones.[7] The ketone was assigned the spiro[5.6]dodecanone structure because the carbonyl stretching frequencies for such compounds are 1708–1710 cm^{-1} and for the [4.7] type are near 1698 cm^{-1}.[8] Ours has $\nu_{C=O}$ = 1705 cm^{-1} and it appears that migration converting a cyclooctene to a cycloheptene would be more favorable than conversion of a cyclohexane to a cyclopentane. Compound 4 was also obtained from 2 (Y = OH) by treatment with methanolic hydrochloric acid.

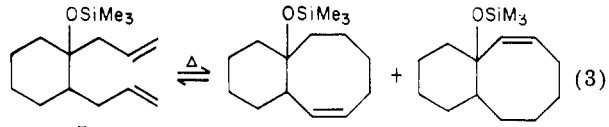


(2)

4

It is interesting that in the thermolysis of 1 (Y = $OSiMe_3$) the cis isomer reacts more rapidly than the trans. When 80% of the original sample (62% cis, 39% trans) had reacted, no cis isomer remained but 20% of the trans isomer was recovered. If it is assumed that the ene reaction is concerted and proceeds via the usual geometry for its transition state,[9] models do indeed show that the requisite geometry is more readily attained by the cis isomer. Though no actual kinetic studies were performed, it appears that the cis isomer reacts about three times faster than the trans in the solution reactions. We presume therefore that the reaction proceeds via a concerted mechanism.

This partial success, i.e., getting the cyclooctene ring closed in good yield, combined with the failure of the β-hydroxy olefin cleavage process prompted us to examine a monosubstituted example. Synthesis of 1,2-diallyl-1-[(trimethylsilyl)oxy]cyclohexane was readily achieved in good yield, though the probable mixture of stereoisomers was not separated. The ene reaction for compound 5 poses an interesting problem since the two allyl groups, differentiated by their positions relative to the (trimethylsilyl)oxy group and in some cases by virtue of occupancy of equatorial or axial positions, can react either as enoid or enophilic units. Two different products (eq 3) can arise,



(3)

5 6 7

and since both cis and trans isomers of 5, 6, and 7 may be involved, at least six transition states need to be considered. With the assumption that the reaction will be concerted and must lead to a *cis*-cyclooctene, a study of models indicated that *trans*-5 should give preferentially 6, *cis*-5 ($OSiMe_3$-eq) favors 7, and *cis*-5 ($OSiMe_3$-ax) favors 6.

In the event the mixture of stereoisomers of 5 in an unknown proportion gave a mixture of two isomeric products in the ratio of 9:1. The major isomer was identified spectroscopically as 6 since the olefinic protons constituted the AB portion of an $ABXY_2$ system with J_{AB} = 11, J_{AX} = 0, J_{AY} = 7.3, J_{BY} = 0, and J_{BX} = 8.0 Hz. Separation (GLC) of this major isomer and hydrolysis gave the alcohol corresponding to 6. These results suggest that 6 was predominantly a trans isomer which is in accord with expectations of the preferred mode of Grignard addition to a 2-alkylcyclohexanone.[10] While models suggest that

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a thermal β-hydroxy olefin cleavage would involve a hindered transition state, too little pure material was obtained to permit a test of this reaction.

Experimental Section

2-Allyl-2-hydroxycyclohexanone. An ether solution of allylmagnesium bromide (from 0.82 mol of allyl bromide and 0.82 mol of magnesium in 250 mL of ether) was added under nitrogen slowly (9 h) to a cold solution containing 3.18 g (0.28 mol) of 1,2-cyclohexanedione in 250 mL of ether. The solution was stirred for 3 h longer and then the mixture was worked up with saturated ammonium chloride solution. The product was taken up in ether, the solution was dried ($MgSO_4$), and the ether was removed. Distillation, bp 46–47 °C (0.3 torr), gave 36.8 g (78%) of a clear liquid; NMR (CCl) δ 1.70 (m, 6 H), 2.10 (m, 2 H), 2.42 (m, 2 H), 5.04 and 5.70 (m, 3 H). The product was used without further purification directly in the next reaction.

1,2-Diallyl-1,2-cyclohexanediol (1, Y = OH). The above ketone (0.18 mol) was treated with allylmagnesium bromide (from 0.46 mol of magnesium) as described for 2-allyl-2-hydroxycyclohexanone. After workup 97% of a liquid product was obtained and an analytical sample was obtained by GLC (2% SE-30 on Chromosorb M at 135 °C); NMR (CCl_4) δ 1.45 (m, 8 H), 2.22 (m, cis isomer), 2.42 (d, J = 7 Hz, trans isomer), 5.12 (m, 4 H), 5.85 (m, 2 H). Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H; 10.27. Found: C, 73.42; H, 10.30.

Trans Isomer. The crude product above was cooled to 0 °C and deposited a small amount of solid: mp 89–91 °C; NMR (CCl_4) δ 1.5 (m, 8 H), 2.40 (d, J = 7 Hz, 4 H), 5.10 (m, 4 H), 5.85 (m, 2 H); IR (CCl_4) 3616, 3576 cm^{-1}. This solid was treated with hexamethyldisilazane and trimethylsilyl chloride as described below for the preparation of silyl ethers, and the product was identical (by GLC test) with that described for the trans silyl derivative.

Cis Isomer. A sample (150 mg) of *cis*-1,2-bis[(trimethylsilyl)oxy]-1,2-diallylcyclohexane was dissolved in 20 mL of a methanol solution containing 0.20 g of pyridine and 0.15 mL of concentrated hydrochloric acid. After standing for 24 h at room temperature, the solution was neutralized and the methanol was removed in vacuo. The residue was triturated with ether; the ether solution was washed with water and then dried ($MgSO_4$). The ether was removed and the diol was purified by GLC (2% SE-30 on Chromosorb M, 135 °C: NMR (CCl_4) δ 1.2–1.9 (br m, 8 H), 2.17 and 2.39 (AB part of ABX, J_{AB} = 14, J_{AX} = 6.5, J_{BX} = 7.5 Hz), 5.06 (m, 4 H), 5.88 (m, 2 H); IR (CCl_4) 3605 (sh), 3560 cm^{-1}.

1,2-Diallyl-1,2-bis[(trimethylsilyl)oxy]cyclohexane (1, Y = OSiMe$_3$). A solution containing 4.0 g (0.019 mol) of 1,2-diallyl-1,2-cyclohexanediol in 32 mL of anhydrous Me_2SO was mixed with 13.7 g (0.086 mol) of hexamethyldisilazane and 3.5 g (0.029 mol) of trimethylsilyl chloride in a bottle sealed with a septum and flushed with nitrogen. The mixture was stirred at room temperature for 48 h and the two layers were separated. The lower (Me_2SO) layer was extracted with pentane, and the extract was combined with the top layer. This solution was washed with sodium bicarbonate solution and then with water. The solution was dried ($MgSO_4$), the solvent was removed, and the product was distilled in a semimicro Hickman still at 150 °C (5×10^{-5} mm). A clear liquid, 6.0 g (90%), was isolated and GLC analysis (2% SE-30 on Chromosorb M at 135 °C) showed that two compounds, 62% and 38%, were present. These were separated by preparative GLC on an SE-30 column.

Trans Isomer. The 38% component was isolated as a clear liquid: NMR (CCl_4) δ 0.16 (s, 18 H), 1.57 (br m, 8 H), 2.35 (m, 4 H), 4.99 (m, 4 H), 5.83 (m, 2 H); an NMR spectrum ($CHCl_3$) at −40 °C showed one singlet at δ 0.10 (18 H, $SiMe_3$). Anal. Calcd for $C_{18}H_{36}O_2Si_2$: C, 63.44; H, 10.66. Found: C, 63.70; H, 10.81.

Cis Isomer. The 62% component was isolated as a clear liquid: NMR (CCl_4) δ 0.16 (s, 18 H), 1.26–1.90 (m, 8 H), 2.36 and 2.54 (AB part of ABX, J_{AB} = 14, J_{AX} = J_{BX} = 7 Hz), 4.97 (m, 4 H), 5.85 (m, 2 H); NMR ($CHCl_3$, −40 °C) 0.08 (s, 9 H), 0.15 (s, 9 H). Anal. Calcd for $C_{18}H_{36}O_2Si_2$: C, 63.44, H, 10.66. Found: C, 63.67; H, 10.80.

1,8-Bis[(trimethylsilyl)oxy]bicyclo[6.4.0]dodec-2-ene (2, Y = OSiMe$_3$). A solution containing 3.0 g (8.7 mmol) of 1,2-diallyl-1,2-bis[(trimethylsilyl)oxy]cyclohexane (mixture of isomers) in 30 mL of methylcyclohexane was degassed and sealed in a carefully cleaned and dried bottle. This was placed in a 500-mL steel hydrogenation bomb, 30 mL of methylcyclohexane was added to equalize the pressure, and the bomb was sealed. The bomb was heated at 300 ± 10 °C for 90 h. After the solvent had been distilled, 2.63 g of crude material was recovered and GLC analysis (2% SE-30 column at 180 °C) showed that this contained one product (80%) and 20% of the trans isomer of the reactant. A pure sample of product was obtained by preparative GLC; NMR (CCl_4) δ 0.08, 0.12 (2 s, 18 H), 1.09–2.25 (br m, 16 H), 5.47 and 5.75 (AB part of ABX_2, J_{AB} = 11, $J_{AX} \simeq 0$, $J_{BX} \simeq$ 6.5 Hz). Anal. Calcd for $C_{18}H_{36}O_2Si_2$: C, 63.44; H, 10.66. Found: C, 63.25; H, 10.50.

A sample run under the same conditions as above except that the temperature was 325 °C gave 64% of the above product along with two additional products, 12% and 7%. The 12% fraction was identified spectrally and by GLC comparison with an authentic sample (below) as spiro[5.6]dodec-7-en-1-one. The lesser byproduct was not identified.

A 2-g sample of 1,2-diallyl-1,2-bis[(trimethylsilyl)oxy]cyclohexane was pyrolyzed in the vapor phase at 390 °C and a 50-s contact time, using nitrogen as a carrier gas. GLC analysis of the pyrolysate showed that it contained 30% 1,8-bis[(trimethylsilyl)oxy]bicyclo[6.4.0]dodec-2-ene, 38% of the cis isomer and 21% of the trans isomer of the reactant, and several minor unidentified components. About 0.6 g of dark polymer was washed from the pyrolysis column.

2-Bicyclo[6.4.0]dodecene-1,8-diol (2, Y = OH). A solution containing 1.0 g (2.3 mmol) of 1,8-bis[(trimethylsilyl)oxy]bicyclo[6.4.0]dodec-2-ene, 0.65 g of pyridine, and 0.5 mL of hydrochloric acid in 75 mL of methanol was allowed to stand for 24 h at room temperature. The acid was neutralized and the methanol was removed in vacuo. The product was taken up in ether and the ether solution was washed with water and dried ($MgSO_4$). The diol was isolated by preparative GLC (2% SE-30 column at 145 °C); NMR (CCl_4) δ 1.2–2.1 (br m, 16 H), 3.15 (br, 2 H, OH), 5.73 (m, 2 H). Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.67; H, 10.13.

The diol was also obtained in 80% yield by refluxing 0.6 g of the silyloxy derivative for 5 h in 0.1 M sodium methoxide in methanol.

Spiro[5.6]dodec-7-en-1-one (4). A solution containing 150 mg (0.69 mmol) of 2-bicyclo[6.4.0]dodecene-1,8-diol and 0.3 mL of hydrochloric acid in 75 mL of methanol was refluxed for 6 h. The acid was neutralized and the methanol was removed by distillation. The product was taken up in ether and the ether solution was dried ($MgSO_4$). The ketone was isolated by preparative GLC (2% SE-30 at 135 °C); NMR (CCl_4) δ 1.25–1.85 (br m, 12 H), 2.00 (X_2 of ABX_2), 2.36 (m, 2 H), 5.58 and 5.80 (AB part of ABX_2, J_{AB} = 11, $J_{AX} \simeq$ 6, $J_{BX} \simeq$ 0 Hz).

A 2,4-dinitrophenylhydrazone prepared by the procedure of Curtin, Shriner, and Fuson[11] melted at 103–105 °C.

1-Spiro[5.6]dodecanone. A sample of the above enone (33 mg, 0.12 mmol) was reduced at atmospheric pressure in ethanol over 5% Pt/C catalyst. The product was isolated by GLC (2% SE-30 at 130 °C); NMR (CCl_4) δ 1.2-2.1 (br m, 18 H), 2.30 (br t, $J \simeq$ 6 Hz). A 2,4-dinitrophenylhydrazone prepared as above melted at 128–129 °C (lit.[7] mp 127 °C).

1,2-Diallylcyclohexanol (5, Y = OH). A solution containing 0.027 mol of allylmagnesium bromide in 25 mL of ether was added slowly to 4.0 g (0.022 mol) of 2-allylcyclohexanone in 30 mL of ether. The reaction was worked up as described for 2-allyl-2-hydroxycyclohexanone. GLC analysis of the crude product, 5.15 g (93%), showed it to contain a single product. An analytical sample was purified by preparative GLC (2% SE-30 at 130 °C; NMR (CCl_4) δ 1.0–1.90 (br m, 9 H), 2.18–2.50 (br m, 4 H), 5.18 (m, 4 H), 5.58 (m, 2 H). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.88; H, 11.20.

1,2-Diallyl-1-[(trimethylsilyl)oxy]cyclohexane (5, Y = OSiMe$_3$). A mixture of 1.88 g (0.010 mol) of 1,2-diallylcyclohexanol, 1.0 g (0.008 mol) of trimethylchlorosilane, 3.91 g (0.024 mol) of hexamethyldisilazane, and 12 mL of anhydrous Me_2SO

(11) Shriner, R. L.; Fuson, R. C.; Curtin, D. Y. "Systematic Identification of Organic Compounds"; John Wiley and Sons: New York, 1964; p 253.

was stirred under nitrogen for 48 h. The layers were separated, and the bottom layer was extracted with pentane. The extracts were combined with the top layer and this solution was washed with sodium bicarbonate solution and then with water. The solution was dried ($MgSO_4$) and the product was distilled in a semimicro Hickman still (bath 150 °C, 5×10^{-5} torr) to give 2.44 g (93%). An analytical sample was collected by GLC; NMR (CCl_4) δ 0.14 (s, 9 H), 1.20–2.02 (br m, 9 H), 2.20 (m, 2 H), 2.54 (m, 2 H), 4.99 (m, 4 H), 5.75 (m, 2 H). Anal. Calcd for $C_{15}H_{28}OSi$: C, 71.34; H, 11.18. Found: C, 71.19; H, 11.03.

1-[(Trimethylsilyl)oxy]bicyclo[6.4.0]dodec-2- (and -6-) enes (6 and 7). A sample, 0.90 g (3.6 m mol), of 1,2-diallyl-1-[(trimethylsilyl)oxy]cyclohexane in 30 mL of methylcyclohexane was pyrolyzed as described for 1,8-bis[(trimethylsilyl)oxy]bicyclo-[6.4.0]dodec-2-ene at 290 °C for 76 h. After removal of the solvent, 0.76 g (84%) of product was recovered. GLC analysis (2% SE-30 at 115 °C) found two products in a 9:1 ratio, and pure samples of each were obtained by preparative GLC. The major product has NMR (CCl_4) δ 0.06 (s, 9 H), 1.2–1.96 (br m, 14 H), 2.15 (m, 3 H), 5.28 and 5.57 (AB part of Y_2ABX, $J_{AB} = 11$, $J_{AY} = 7.3$, $J_{AX} = J_{BY} = 0$, $J_{BX} = 8$ Hz); minor product, NMR (CCl_4) δ 0.30 (s, 9 H), 1.35–1.95 (br m, 14 H), 2.29 (m, 2 H), 2.87 (m, 1 H), 5.85 (m, 2 H).

6-Bicyclo[6.4.0]dodecen-1-ol. The major product above, 0.10 g, was heated for 12 h under reflux in 35 mL of 0.1 N sodium methoxide in methanol. The solution was neutralized and the methanol was removed in vacuo. The organic product was taken up on ether, and the ether solution was washed with water and then dried ($MgSO_4$). The product was isolated by GLC (2% SE-30 at 120 °C; NMR (CCl_4) δ 1.2–1.9 (br m, 14 H), 2.20 (m, 3 H), 5.34 and 5.62 (AB part of Y_2ABX, $J_{AB} = 11$, $J_{AY} = 7.8$, $J_{AX} = J_{BY} = 0$, $J_{BX} = 8.2$ Hz). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 80.00; H, 11.22.

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Registry No. *cis*-1 (Y = OH), 74930-46-4; *trans*-1 (Y = OH), 74930-47-5; *cis*-1 (Y = $OSiMe_3$), 74930-48-6; *trans*-1 (Y = $OSiMe_3$), 74930-49-7; *cis*-2 (Y = $OSiMe_3$), 74930-50-0; *trans*-2 (Y = $OSiMe_3$), 74930-51-1; *cis*-2 (Y = OH), 74930-52-2; *trans*-2 (Y = OH), 74930-53-3; 4, 74930-54-4; 4 DNP derivative, 74930-55-5; dihydro-4, 73223-35-5; dihydro-4 DNP derivative, 1050-65-3; *cis*-5 (Y = OH), 74930-56-6; *trans*-5 (Y = OH), 74930-57-7; *cis*-5 (Y = $OSiMe_3$), 74930-58-8; *trans*-5 (Y = $OSiMe_3$), 74930-59-9; *cis*-6, 74930-60-2; *trans*-6, 74930-61-3; *cis*-7, 74947-54-9; *trans*-7, 74930-62-4; 2-allyl-2-hydroxycyclohexanone, 60277-96-5; allyl bromide, 106-95-6; 1,2-cyclohexanedione, 765-87-7; 2-allylcyclohexanone, 94-66-6; *cis*-6-bicyclo[6.4.0]dodecen-1-ol, 74930-63-5; *trans*-6-bicyclo[6.4.0]dodecen-1-ol, 74930-64-6.

Stereochemistry of Molybdenum Peroxide Oxidation of Organoboranes

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Evans[3] has recently reported that organoboranes are efficiently oxidized to alcohols with the molybdenum peroxide reagent MoO_5·py·HMPA (MoOPH). The MoOPH reagent is reported to be an anhydrous reagent capable of oxidizing organoboranes under mild (ambient temperature) conditions. We recently required such a reagent for the oxidation of optically active allylborane derivatives which are prone to undergo protonation and allylic rearrangement.[4] We have noted that the stereochemistry of oxidation of organoboranes with MoOPH has not been reported. Free-radical intermediates have been suggested in the oxidation of Grignard reagents by molybdenum peroxide reagents.[5] If radicals are also involved in organoborane oxidations, then the MoOPH oxidations could lead to a serious loss of stereochemistry.[6] We herein report that oxidation of organoboranes with MoOPH proceeds with complete retention of configuration.

The hydroboration–oxidation of 1-methylcyclohexene was chosen for the study (eq 1). Conventional oxidation

(1)

with basic hydrogen peroxide produces >99% isomerically pure *trans*-2-methylcyclohexanol.[7] Oxidation with MoOPH likewise gave >99% of the trans isomer. None of the cis isomer (prepared by K-Selectride reduction of 2-methylcyclohexanone[8]) could be detected by VPC or NMR. The MoOPH oxidation of organoboranes thus presumably does not occur by a free-radical process since such a process should lead to an epimeric mixture of alcohols. The reagent is thus a mild alternative to trialkylamine *N*-oxides which often require elevated temperature or prolonged reaction times for oxidation of organoboranes under anhydrous conditions.[9] Unfortunately, with the oxidation conditions employed for alkylboranes, the MoOPH reagent failed to oxidize allylboranes to allylic alcohols in high yield.

Experimental Section

All reactions were run in dry glassware under nitrogen by using syringe and double-ended-needle techniques.[10] 1-Methylcyclohexene (Aldrich) was distilled from a small quantity of lithium aluminum hydride. The MoOPH was prepared by the method of Vedejs.[11] The NMR spectra were recorded on a Varian EM390 instrument.

Hydroboration–Oxidation of 1-Methylcyclohexene. A 50-mL flask equipped with a septum-capped inlet, magnetic stirring bar, and a reflux condenser attached to a nitrogen bubbler was charged with 6 mL of tetrahydrofuran and 6 mmol of 1-methylcyclohexene. Then 3 mmol of borane–methyl sulfide was added and the solution stirred at 0 °C for 1 h followed by warming to room temperature for 2 h. Methanol (3 mmol) was added and the solution stirred for 30 min to produce the methoxyborane. The solution was then cooled to 0 °C. A separate round-bottomed flask was charged with 4.4 g of MoOPH (10 mmol) and flushed with nitrogen. The side arm of the flask was attached via a Tygon tube to the side arm of the flask containing the organoborane. The MoOPH was then added to the organoborane over a 5-min period. The mixture was stirred at 0 °C for 30 min and then warmed to room temperature. After 1 h, 5 mL of 3 M sodium hydroxide was added. Hexadecane was added as an internal standard and the mixture analyzed by VPC (10% DC710). There was found 5.65 mmol (94%) of *trans*-2-methylcyclohexanol. The mixture was extracted with ether, washed with water and then 1 N hydrochloric acid, and dried (potassium carbonate). The ether

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