porcelain dish at 275 °C for 2 days. The off-white solid was stirred several times during heating to help break up the lumps and was stored in a desiccator.

General Dehydration Procedure. The alcohol to be dehydrated was placed in a round-bottomed flask containing a magnetic stirring bar and anhydrous copper(II) sulfate (0.75 molar equiv). A 7-cm Vigreux column and condenser was attached, and the mixture was immersed with vigorous stirring in an oil bath preheated to the desired reaction temperature. Heating was continued until the distillation of volatile products into an ice-cooled receiver stopped. The majority of the water layer of the product was removed by pipet, and the olefin product was filtered through a plug of cotton. In all cases the olefin product was pure as determined by NMR spectroscopy, which was also used to calculate ratios of isomeric products. Where the olefin product was higher boiling (>120 °C), aspirator vacuum (25 mm) was applied to the same experimental setup.

When dehydrations were carried out under reflux (entries 14–17), the alcohol and catalyst were heated together in a flask fitted with a condenser. The temperature and reflux time utilized were those determined for complete distillation of product in the above distillation method. The reaction mixture was cooled, ether was added, and the copper sulfate was filtered. Fractional distillation of the ether solution yielded the olefin product.

Registry No. 1-Phenylethanol, 98-85-1; 1-phenyl-1-propanol, 93-54-9; α-tetralol, 529-33-9; 2-phenyl-2-propanol, 617-94-7; 1,1-diphenylethanol, 599-67-7; 1-methylcyclohexanol, 590-67-0; 2-methyl-2-hexanol, 625-23-0; cyclohexanol, 108-93-0; 2-octanol, 123-96-6; 1-hexen-3-ol, 4798-44-1; 2-cyclohexenol, 822-67-3; geraniol, 106-24-1; linalool, 78-70-6; styrene, 100-42-5; (*E*)-β-methylstyrene, 873-66-5; (*Z*)-β-methylstyrene, 766-90-5; 1,2-dihydronaphthalene, 447-53-0; 2-methylstyrene, 300-57-2; 1,1-diphenylethylene, 530-48-3; 1-methylcyclohexene, 591-49-1; methylenecyclohexane, 1192-37-6; 2-methyl-2-hexene, 2738-19-4; 2-methyl-1-hexene, 6094-02-6; cyclohexene, 110-83-8; 1-octene, 111-66-0; 2-octene, 111-67-1; 1,3-hexadiene, 592-48-3; cyclohexadiene, 592-57-4; myrene, 123-35-3; $Cu^{II}SO_4$, 18939-61-2.

Steric Course of the Reductions of 2-Alkyltetrahydropyranones

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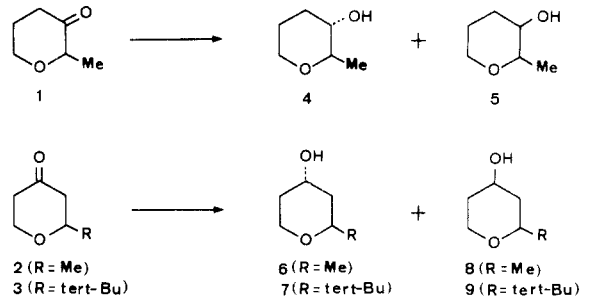
The stereoselectivity of the reductions of substituted cyclohexanones has received considerable attention over the years[1] but is still not completely understood. Our interest in the synthesis of substituted tetrahydropyrans and deoxy sugars[2-5] prompted an investigation of the stereochemistry of the reduction of alkyl-substituted tetrahydropyranones **1–3**. In particular, we have been concerned with the effect, if any, of a ring heteroatom on the stereochemical course of these reactions in comparison with those of the corresponding alkylcyclohexanones. Briefly, we found no significant deviation between the alicyclic and heterocyclic systems. Table I,[11-19] incorporating our studies and literature values, summarizes results with six reducing agents. As seen, the only differences are that the carbocyclic cases often give somewhat higher percentages of the



less stable (axial hydroxyl) isomers.

However, a recent report[6] concluded that the reduction of **2** with L-Selectride[7] affords predominantly the cis isomer **8** (equatorial OH), in contrast to the predominant attack from the equatorial side usually obtained with this bulky reagent (i.e., 85–95% equatorial attack on 3-methylcyclohexanone). This abnormal behavior was attributed to the intervention of complexation with the ring oxygen and hydride deliverance through a boat conformation.

We have carefully reexamined the reduction of **2** with L-Selectride and conclude that the *trans isomer* **6** *is the major product in THF at −78 °C*[8] *and ether at room temperature.*[6]

As previously observed,[6] direct NMR analysis of the alcohols **6** and **8** was hampered by overlap of the C-2 and C-6 protons with the diagnostic ones at C-4. However, this problem was conveniently overcome by conversion to the *p*-nitrobenzoates which shifted the signals of the C-4 protons away from the offending peaks of C-2 and C-6.

In this manner, assignment of the proper configurations was straightforward and confirmed the previous determinations; the signals for the protons at C-4 of the esters had exactly the same shapes as those reported for the corresponding hexadeuterated alcohols.[6] Likewise, analysis of mixtures of **6** and **8** by GLC was difficult, as reported.[6] However, the corresponding trimethylsilyl ethers were readily separated (OV-17 column), and this provided a convenient and accurate method of analysis. As indicated in Table I, L-Selectride consistently afforded a predominance of the trans alcohol **6**, in accord with results with cyclohexanones and other tetrahydropyranones. We conclude that a ring oxygen in position 3 or 4 of a six-membered-ring ketone has no significant effect on the stereochemistry of reductions.

The discrepancy between our and previous[6] results is perhaps due to the latter's analysis by NMR. The presence of 2-butanol, produced in the peroxide oxidation of L-Selectride reductions, would artificially enhance the perceived amount of cis isomer **8** since the CHOH proton

(1) For recent reviews see: D. C. Wigfield, *Tetrahedron*, **35**, 449 (1979); H. C. Brown and S. Krishnamurthy, *ibid.*, **35**, 561 (1979).
(2) G. Berti, G. Catelani, and L. Monti, *Chim. Ind. (Milan)*, **56**, 571 (1974).
(3) G. Berti, G. Catelani, M. Ferretti, and L. Monti, *Tetrahedron*, **30**, 4013 (1974).
(4) C. Anselmi, G. Berti, G. Catelani, L. Lecce, and L. Monti, *Tetrahedron*, **33**, 2271 (1977).
(5) C. Anselmi, G. Berti, G. Catelani, F. Coppa, and L. Monti, *Gazz. Chim. Ital.*, **109**, 41 (1979).
(6) D. C. Wigfield and S. Feiner, *Can. J. Chem.*, **56**, 789 (1978).
(7) Lithium tri-*sec*-butylborohydride (trademark of Aldrich Chemical Co. Inc.).
(8) H. C. Brown and S. Krishnamurthy, *J. Am. Chem. Soc.*, **94**, 7159 (1972).
(9) E. L. Eliel and Y. Senda, *Tetrahedron*, **26**, 2411 (1970).
(10) C. J. Pouchert and J. R. Campbell, Eds., "The Aldrich Library of NMR Spectra", Vol. 1, Aldrich Chemical Co. Inc., Milwaukee, Wis., 1974, no. 850.
(11) H. E. Ashby, J. R. Boone, and J. P. Oliver, *J. Am. Chem. Soc.*, **95**, 5427 (1973).
(12) H. C. Brown and H. R. Deck, *J. Am. Chem. Soc.*, **87**, 5620 (1965).
(13) D. C. Wigfield and D. J. Phelps, *J. Am. Chem. Soc.*, **96**, 543 (1974).
(14) B. Rickborn and M. T. Wuenthoff, *J. Am. Chem. Soc.*, **92**, 6894 (1970).
(15) H. C. Brown and V. Varma, *J. Org. Chem.*, **39**, 1631 (1974).
(16) W. G. Dauben and R. E. Bazak, *J. Org. Chem.*, **24**, 1596 (1959).
(17) D. C. Wigfield and D. J. Phelps, *J. Org. Chem.*, **41**, 2396 (1976).
(18) E. L. Eliel and R. S. Ro, *J. Am. Chem. Soc.*, **79**, 5992 (1957).
(19) H. C. Brown and W. C. Dickason, *J. Am. Chem. Soc.*, **92**, 709 (1970).

0022-3263/80/1945-0919$01.00/0

Table I. Percentage of Trans Isomer[a]

substrate	$LiAlH_4$	$NaBH_4$	B_2H_6 (THF)	L-Selectride	$Al(O\text{-}i\text{-}Pr)_3$	Raney Ni
1	85[b]			<1[c]	72[b]	
2-methylcyclohexanone	79[d,e]	73,[f] 60[g]	74[h]	0.7[i]	85[j]	
2	5[b]	7.5,[b] 19[k]	18[b]	70,[b,l] 76,[b] 27[k]		
3-methylcyclohexanone	15[h]	23,[g] 14[m]	23[h]	94.5,[i] 88[k]	22[n]	
3	5.5[b]	10.3[b]	10.7[b]	76[b]	21.5[b]	22.5[b]
3-*tert*-butylcyclohexanone	15,[o] 18[h]	24[g]	30[h]	72[p]		

[a] Percent of trans alcohol in the mixture of cis + trans isomers taken as 100. [b] This work. [c] Reference 3. [d] Reference 11. [e] Reference 12. [f] Reference 13. [g] Reference 14. [h] Reference 15. [i] Reference 8. [j] Reference 16. [k] Reference 6. [l] Under the same conditions as described in ref 6. [m] Reference 17. [n] Reference 18. [o] Reference 19. [p] Since the data on the reduction with L-Selectride have not been reported, we include the value obtained with another bulky reagent, lithium perhydro-9b-boraphenalylhydride.[19]

signal is very similar in chemical shift (and shape) to the septet of the C-4 proton of 8.

Experimental Section

The preparation and characterization of the ketones **1** and **3** and of the alcohols **4–9** have been previously described.[3,4]

2-Methyltetrahydropyran-4-one (**2**) was prepared by oxidation of alcohol **8** with Jones' reagent. The following general procedure was utilized: The alcohol **8** (10 g, 0.1 mol) dissolved in acetone (250 mL) was treated with a slight excess of Jones' reagent and left 1 h at room temperature. The excess of reagent was destroyed with 2-propanol, and the solution was neutralized with solid K_2CO_3. Evaporation and distillation gave **2** (6.6 g): bp 88–90 °C (43 mmHg); n^{17}_D 1.4452 [lit.[20] bp 70 °C (20 mmHg); n^{20}_D 1.4469]. Characterization was accomplished as the 2,4-dinitrophenylhydrazone, mp 140–141 °C (lit.[20] mp 140 °C).

Analytical Procedure. All GC analyses were performed on a Perkin-Elmer F-11 (FID) chromatograph under the following conditions. For the reduction products of **1**, a 2.5-m glass column with 15% Carbowax 20M on 80–100-mesh silanized Chromosorb W (125 °C) was used; the ratio of the retention times of **5** and **4** was 1.00:1.75. For the reduction products of **2**, the standard procedure was used to convert the crude products into the trimethylsilyl ethers. A 2.5-m glass column with 3% OV-17 on 80–100-mesh silanized Chromosorb W (75 °C) was used for the chromatography; the ratio of the retention times of the trimethylsilyl ethers of **6** and **8** was 1.00:1.24. The accuracy of the analysis was ensured by subjecting mixtures of different compositions of pure **6** and **8** to the same procedure; the response factor was 1.04 ± 0.02. The data reported in Table I should be accurate within ±2%. For the reduction products of **3** the same column used for **1** was employed (140 °C); the ratio of the retention times of **7** and **9** was 1.00:1.08.

Reduction Conditions. $LiAlH_4$. The ketone (1 mmol) and $LiAlH_4$ (2.6 mmol) in Et_2O (20 mL) were refluxed for 3 h and hydrolyzed with H_2O (0.1 mL), 3 N NaOH (0.1 mL), and H_2O (0.3 mL). In the reduction of **1** and **3** GC analysis was performed directly on the ether solution; for **2**, the ether was evaporated on a steam bath before trimethylsilylation.

$NaBH_4$. The ketone (1 mmol) and $NaBH_4$ (2.6 mmol) in 2-propanol (10 mL) were reacted for 2 h at 0 °C, the mixture was hydrolyzed with H_2O (10 mL), acidified with 10% H_2SO_4, and extracted with Et_2O (3 × 10 mL), and the extract was analyzed as above.

L-Selectride.[7] The ketone (1 mmol) in 10 mL of anhydrous THF at −78 °C was treated with 1 M L-Selectride in THF (2.0 mL) and the mixture was left for 3 h at −78 °C. The solution was brought to room temperature, hydrolyzed with 3 M NaOH (0.3 mL), treated with 36% H_2O_2 (0.3 mL), stirred for 1 h, dried with K_2CO_3, and analyzed by GC as in the other reductions. The ratio of alcohols **6** and **8** was 76:24. The ketone **2** was also reduced under the conditions described by Wigfield and Feiner.[6] The ratio of alcohols **6** and **8** was 70:30.

B_2H_6. To the ketone (1 mmol) in 10 mL of anhydrous THF was added 1 M BH_3 in THF (1 mL) and the solution kept 6 h at 0 °C before being hydrolyzed with 3 N NaOH (0.5 mL), oxidized with 36% H_2O_2 (0.5 mL, 1 h of stirring), and dried with K_2CO_3. The solution was analyzed as described above.

(20) E. Hanschke, *Chem. Ber.*, 88, 1053 (1955).

$Al(O\text{-}i\text{-}Pr)_3$ Reduction. The ketone (1 mmol) and aluminum isopropoxide (0.5 g) in 20 mL of 2-propanol were refluxed for 3 h and the 2-propanol was evaporated under reduced pressure. The residue was hydrolyzed with crushed ice and acidified with concentrated HCl (1.5 mL), and the mixture was extracted with Et_2O (3 × 10 mL), washed with aqueous $NaHCO_3$, dried ($MgSO_4$), and analyzed as described above.

Equilibration of 7 and 9. The method of Eliel and Senda[9] was used. A solution of **3** (0.5 mmol) and **9** (0.5 mmol) in benzene (10 mL) was refluxed in the presence of purified Raney nickel, the equilibration being monitored by GC, until a constant **7**:**9** ratio was reached.

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Registry No. **1**, 30448-27-2; **2**, 1193-20-0; **3**, 23659-44-1; **4**, 55230-29-0; **5**, 55230-31-4; **6**, 55230-32-5; **7**, 55522-90-2; **8**, 33747-08-9; **9**, 33747-10-3.

Dipole Moment and Spectral Data of the (*Z*)- and (*E*)-Enol Ethers, 2-(1-Methoxyethylidene)-5-hydroxypentanoic Acid Lactone[1]

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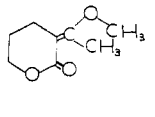
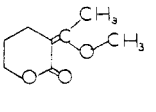
The observation of certain spectral anomalies associated with the rather flexible structures of the β-alkoxy derivatives of α,β-unsaturated esters[2] prompted the synthesis and study of model compounds of fixed conformation.[3] Two of these, the methyl enol ethers of α-acetyl-δ-valerolactone [2-(1-methoxyethylidene)-5-hydroxypentanoic acid lactone], are the subjects of this report. The *E* isomer has the fixed conformation, trans-s-cis, the *Z* isomer, cis-s-cis.



E



Z

(1) Presented in part at the Rocky Mountain Regional Meeting, American Chemical Society, Laramie, WY, June 1976.

(2) (a) Rhoads, S. J.; Hasbrouck, R. W.; Pryde, C.; Holder, R. W. *Tetrahedron Lett.* **1963**, *10*, 669. (b) Rhoads, S. J.; Gilbert, J. C.; Decora, A. W.; Garland, T. R.; Spangler, R. J.; Urbigkit, M. J. *Tetrahedron* **1963**, *19*, 1625. (c) Rhoads, S. J.; Decora, A. W. *Ibid.* **1963**, *19*, 1645. (d) Rhoads, S. J.; Pryde, C. *J. Org. Chem.* **1965**, *30*, 3213. (e) Rhoads, S. J. *Ibid.* **1966**, *31*, 171.

(3) The initial work on this problem is detailed in Harrod, C. E. M.S. Thesis, University of Wyoming, June, 1969. Other information comes from undergraduate research reports of D.R.B. and the Honors Thesis of T.G.B.

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