24 hr. The solvent was then evaporated, and the residue was diluted with D_2O and extracted with ether. The dried (anhydrous $MgSO_4$) ether extracts were evaporated and the residue (95 mg) was examined by pmr spectroscopy. The sole product was the starting aziridine **1a** with no detectable incorporation of deuterium.

The corresponding *trans*-aziridine ester was recovered unchanged and without deuterium exchange when subjected to identical reaction conditions.

Thermal Equilibration of Methyl 1-Cyclohexyl-2-(*p*-biphenyl)-3-aziridinecarboxylates (1a and 1b).—A solution of the *cis*-aziridine ester (167 mg, 0.5 mmol) in benzene-d_6 (0.3 ml) was transferred to an nmr tube, and the tube was sealed and placed in a constant-temperature bath maintained at 80 ± 0.2°. At 8-hr intervals the pmr spectrum was determined. After 40 hr, the percentages of **1a** and **1b** were determined as 68:32, respectively, by electronic integration. These percentages were not altered after an additional 16 hr at 80°.

Similarly, the corresponding *trans*-aziridine ester **1b** afforded the same equilibrium mixture after being heated to 80° for 72 hr in benzene-d_6.

Registry No.—**1a**, 19474-27-2; **1b**, 23214-20-2; **2a**, 23214-21-3; **2b**, 23214-22-4; **3a**, 23214-23-5; **3a′**, 23214-24-6; **3b**, 23214-25-7; **4a**, 23263-68-5; **4b**, 23214-26-8; **5a**, 23263-69-6; **5b**, 23214-27-9; **6a**, 23263-70-9; **6b**, 23214-28-0; **6c**, 23263-71-0; **7a**, 23214-29-1; **7b**, 23263-72-1; **8a**, 23214-30-4; **8b**, 23263-73-2; **9a**, 23214-31-5; **9b**, 23214-32-6; **10a**, 23214-33-7; **10b**, 23214-34-8; **11a**, 23214-35-9; **11b**, 23214-36-0; **12a**, 23230-36-6; **13a**, 23214-37-1; **13b**, 23214-38-2; **14a**, 23263-74-3; **14b**, 23214-39-3; *trans*-methyl *p*-phenylcinnamate, 22837-75-8; methyl 2,3-dibromo-3-(*p*-biphenyl)propionate, 23230-37-7; *cis*-methyl α-bromo-*p*-phenylcinnamate, 23214-40-6; *trans*-methyl α-bromo-*p*-phenylcinnamate, 23214-41-7; methyl α-bromo-β-d_1-*p*-phenylcinnamate (*trans*), 23214-42-8; trimethyl 1-cyclohexyl-5-d_1-5-(*p*-biphenyl)pyrrolidine-2,3,4-tricarboxylate, 23230-38-8.

Hydroboration of Dihydropyrans and Dihydrofurans

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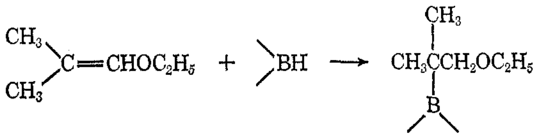
Received June 23, 1969

The hydroborations of Δ²-dihydropyran, Δ³-dihydropyran, 2-ethoxy-3,4-dihydropyran, 2,3-dihydrofuran, 2,5-dihydrofuran, and 2-methyl-4,5-dihydrofuran with diborane and with disiamylborane[bis(3-methyl-2-butyl)-borane] have been investigated. Except in the case of Δ³-dihydropyran, the hetero oxygens direct the addition of boron nearly exclusively to the β positions. Oxidation of the intermediate β-organoboranes with alkaline hydrogen peroxide affords the corresponding β-hydroxy derivatives in better than 70% yields. Addition of boron trifluoride to the β-organoboranes derived from the heterocyclic olefins results in β elimination to give, after hydrolysis, the corresponding acyclic unsaturated alcohols in 70–90% yields. Hydroboration of dihydropyrans and dihydrofurans with excess diborane followed by oxidation produces mixtures of acyclic diols.

In connection with our pursuit of certain synthetic objectives, we were confronted with the problem of developing simple, high-yield syntheses of 3-hydroxytetrahydropyrans and 3-hydroxytetrahydrofurans. We had previously synthesized 3-hydroxytetrahydropyran; however, it was obtained in only a modest yield and required a four-step synthesis starting with dihydropyran.[1] Thus we were prompted to examine the hydrations of dihydropyrans and dihydrofurans *via* the hydroboration–oxidation reaction.

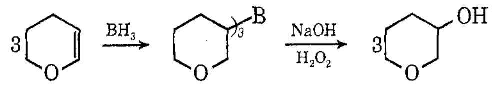
Various research groups have observed marked directive effects by alkoxy groups in the hydroboration of vinyl ethers. Thus Mikhailov and Shchegoleva reported that the hydroboration of ethyl vinyl ether produces *tris*(2-ethoxyethyl)borane in 67% yield.[2] Likewise, Pasto and Cumbo found that enol ethers undergo hydroboration predominantly at their β positions.[3] β-Ethoxystyrene gives, after hydroboration followed by oxidation of the intermediate organoborane, a 75% yield of 2-ethoxy-1-phenylethanol. Ethoxycyclohexene is converted by the same reaction sequence into *trans*-2-ethoxycyclohexanol. Finally, Brown and Sharp have recently shown that the hydroboration of isobutenyl ethyl ether results in the sterically unfavorable addition of at least 88% of the boron to the hindered tertiary carbon.[4]



$$\mathrm{(CH_3)_2C{=}CHOC_2H_5 + \rangle BH \longrightarrow CH_3\overset{CH_3}{\underset{B}{C}}CH_2OC_2H_5}$$

Results and Discussion

Hydroboration of Dihydropyrans and Dihydrofurans.—The reaction of Δ²-dihydropyran with borane (BH_3) in a 3:1 ratio in tetrahydrofuran solution at 0° proceeded rapidly to the trialkylborane stage. To assess the direction of addition of BH to the double bond, the trialkylborane was oxidized with alkaline hydrogen peroxide. Gas–liquid partition chromatography (glpc) revealed the formation of a single alcohol, 3-hydroxytetrahydropyran, in 86% yield. No evidence was obtained for the formation of any 2-hydroxytetrahydropyran. It is possible, however, that a small amount of the boron may have added to the 2 position of the pyran ring, but that the α-boron intermediate is unstable under the reaction conditions.



The hydroboration of 2-ethoxy-3,4-dihydropyran in tetrahydrofuran solvent was quite slow at 0°. However, if the hydroboration was carried out at 25° for 3 hr, analysis for residual hydride indicated that the

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[1] S. A. Barker, J. S. Brimacombe, A. B. Foster, D. H. Whiffen, and G. Zweifel, *Tetrahedron*, **7**, 10 (1959).

[2] B. M. Mikhailov and T. A. Shchegoleva, *Izv. Akad. Nauk SSSR*, 546 (1959).

[3] D. J. Pasto and C. C. Cumbo, *J. Amer. Chem. Soc.*, **86**, 4343 (1964).

[4] H. C. Brown and R. L. Sharp, *ibid.*, **90**, 2915 (1968).

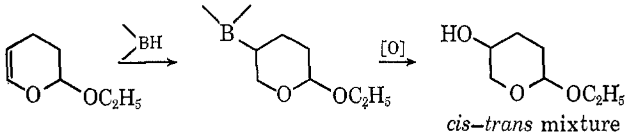
TABLE I

ALCOHOLS DERIVED FROM HYDROBORATION–OXIDATION OF DIHYDROPYRANS AND DIHYDROFURANS

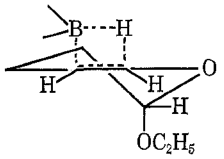
Olefin	Reacn temp, °C	Reacn time, hr	Alcohol	Yield, %[a]
Δ²-Dihydropyran	0	4	3-Hydroxytetrahydropyran	86
Δ³-Dihydropyran	25	2	3-Hydroxytetrahydropyran	55
			4-Hydroxytetrahydropyran	30
2-Ethoxy-3,4-dihydropyran	25	3	2-Ethoxy-5-hydroxytetrahydropyran	70[b]
2,3-Dihydrofuran	0	2	3-Hydroxytetrahydrofuran	78
2,5-Dihydrofuran	0	2	3-Hydroxytetrahydrofuran	84
2-Methyl-4,5-dihydrofuran	0	2	*trans*-2-Methyl-3-hydroxytetrahydrofuran	80

[a] Yield by glpc examination. [b] Yield by isolation.

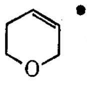
olefin was completely converted into the trialkylborane. Oxidation of the organoborane produced a 72:28 mixture of isomeric 2-ethoxy-5-hydroxytetrahydropyrans, which was isolated in 70% yield. Increasing the steric requirements of the hydroborating agent altered the *cis/trans* ratio only slightly. Thus hydroboration of the olefin with disiamylborane [bis(3-methyl-2-butyl)-borane] and subsequent oxidation gave a 92% yield (glpc) of an 80:20 mixture of 2-ethoxy-5-hydroxytetrahydropyrans.



The methoxy group in 2-methoxytetrahydropyran has been reported to occupy the axial rather than the equatorial position (anomeric effect).[5] Assuming that the ethoxy group in 2-ethoxy-3,4-dihydropyran exhibits a similar conformational preference, and that the activated complex for the hydroboration reaction resembles the reactants in structure and energy,[6] the *trans*-2-ethoxy-5-hydroxytetrahydropyran should be the isomer which is formed preferentially.[7]



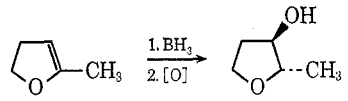
The effect of the ring oxygen on the direction of BH addition is markedly attenuated with Δ³-dihydropyran. Thus hydroboration of this olefin with diborane followed by oxidation gave a 55% yield of 3-hydroxytetrahydropyran and a 30% yield of 4-hydroxytetrahydropyran. It is noteworthy that the analogous acyclic allyl ether, crotyl ethyl ether, yields on treatment with diborane 84% β-ethoxyalkylborane derivative.[8] Both of these observations must result as a consequence of the electron-withdrawing inductive effect of the alkoxy substituent, since the oxygens in these systems are not able to affect the electron distribution by mesomeric interaction with the double bonds.



$CH_3CH{=}CHCH_2OC_2H_5$

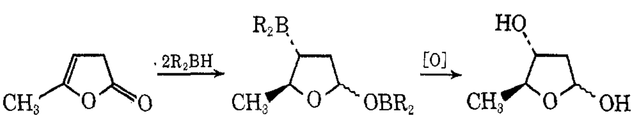
Hydroboration of the 2,3- and 2,5-dihydrofurans with diborane at 0° proceeded readily to the trialkylborane stage. Oxidation of the trialkylborane derived from 2,3-dihydrofuran gave an 78% yield of 3-hydroxytetrahydrofuran, pointing again to the strong directive influence of a vinyl ether oxygen. Hydroboration of the symmetrically substituted double bond of 2,5-dihydrofuran followed by oxidation afforded an 84% yield of 3-hydroxytetrahydrofuran.

Finally, addition of diborane to 2-methyl-4,5-dihydrofuran, which resulted in the formation of the trialkylborane, gave after oxidation an 80% yield of *trans*-3-hydroxy-2-methyltetrahydrofuran. The assignment of the *trans* configuration to the alcohol is based on the well established facts that the BH addition proceeds in a *cis* manner and that oxidation of the B–C bond occurs with retention of configuration.



A summary of the experimental results obtained from the hydroborations of the oxygen-containing heterocyclic olefins is shown in Table I.

It should be pointed out here that the hydroboration–oxidation of α,β-unsaturated dihydropyrans and dihydrofurans containing alkoxy groups adjacent to the ring oxygens provides a novel approach to the synthesis of deoxy sugars. Unsaturated lactones, such as crotonolactone and the α- and β-angelicalactones, may also serve as precursors for deoxy derivatives, since the lactone function is reduced by dialkylboranes to the corresponding hydroxyaldehyde.[9]



Relative Reactivity Studies.—In determining the reaction stoichiometries in the hydroborations of the dihydropyrans and dihydrofurans, we noticed major differences in their reactivities toward diborane. To gather more information about the effects of olefin structure on the rates of hydroboration, a number of dihydropyrans and dihydrofurans, as well as their corresponding carbocyclic analogs, were subjected to competition experiments using disiamylborane. In a typical example, 25 mmol of Δ²-dihydropyran and 25 mmol of cyclohexene were treated at 25° with 26 mmol of disiamylborane. After completion of the hydroboration, the reaction mixture was analyzed by glpc for

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(5) C. B. Anderson and D. T. Sepp, *Chem. Ind.* (London), 2054 (1964); *J. Org. Chem.*, **32**, 607 (1967).

(6) J. Klein, E. Dunkelblum, and D. Avrahami, *ibid.*, **32**, 935 (1967).

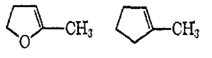
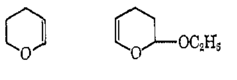
(7) A slight preference for the addition of boron *trans* to a methoxy group was also observed in the hydroborations of 3- and 4-methoxycyclohexene: D. J. Pasto and J. Hickman, *J. Amer. Chem. Soc.*, **90**, 4445 (1968).

(8) H. C. Brown and R. M. Gallivan, *ibid.*, **90**, 2906 (1968).

(9) H. C. Brown and D. B. Bigley, *ibid.*, **83**, 486 (1961).

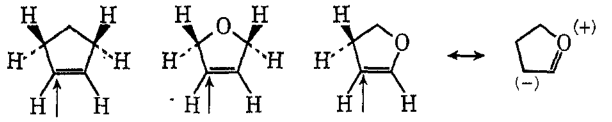
Table II

Competitions of Various Heterocyclic and Carbocyclic Olefins for Disiamylborane

Olefin pair	Reacn temp, °C	Reacn time, hr	Ratio of olefins reacted (normalized)
	0	2	54:46
	0	1	90:10
	0	1	98:2
	0	2	94:6
	25	2	53:47
	25	2	58:42

unreacted olefins using cyclohexane as an internal standard. The results of these experiments are summarized in Table II.

Inspection of the data reveals several interesting features. 2,5-Dihydrofuran reacts with disiamylborane at a rate comparable with that of cyclopentene. However, the vinyl ether, 2,3-dihydrofuran, exhibits a marked rate enhancement as compared with the 2,5-dihydro derivative or with its carbocyclic analog, although the steric environments for attack by disiamylborane should be quite similar for all three olefins.



It has been suggested that the four-center[10] or π-complexlike[11] activated complexes for the hydroboration of olefins have structures resembling the starting materials.[6] Electron donation by resonance from oxygen into the double bond[12] would explain both the favored electrophilic attack by disiamylborane at the C-3 of 2,3-dihydrofuran and its enhanced reactivity.

It must be pointed out that, although Δ^2-dihydropyran reacts with disiamylborane to give the β-organoborane in 90% yield, it does not show rate enhancement when compared with cyclohexene. Besides the increased steric hindrance factors, reduced mesomeric interaction of the nonbonded pair of electrons on oxygen with the double bond in the less planar dihydropyran may be responsible for the decreased reactivity of this olefin.

Formation of Acyclic Diols from Hydroboration of Δ^2-Dihydropyran.—It was observed that the 3-hydroxytetrahydropyrans and 3-hydroxytetrahydrofurans, produced from hydroborations of the appropriate olefins with diborane in a 3:1 ratio followed by oxidation, were obtained along with 5–10% yields of acyclic diols. Moreover, it was noticed that the amount of diols produced increased significantly when an excess of diborane was utilized in the hydroboration step. To investigate the nature of the reactions leading to the formation of diols, Δ^2-dihydropyran was hydroborated under various conditions. The experimental results are shown in Table III.

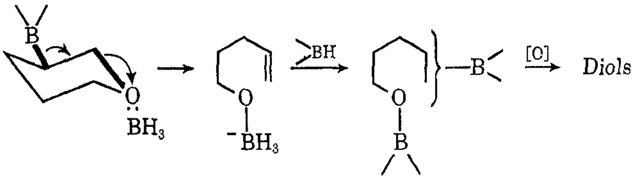
Table III

Effect of Adding Additional Borane[a] at 25° to the Trialkylborane Derived from Hydroboration of Δ^2-Dihydropyran

Hydroborating agent	Additional added borane	Reacn time, hr	Oxidation products, %[b]		
			3-Hydroxytetrahydropyran	Pentanediol	
				1,4-	1,5-
BH_3	None	2	83	4	5
		24	82	2	4
	BH_3	1	45	27	24
		24	31	27	36
		24[c]	36	20	33
R_2BH[d]	None	24	89	Trace	Trace
	R_2BH[d]	24	83	<2	<3
	BH_3	1	72	10	14
		24	49	14	23

[a] The additional borane (25 mmol) in tetrahydrofuran solution was added to 8.3 mmol of the trialkylborane in tetrahydrofuran. [b] Yield by glpc analysis. [c] Diborane (33 mmol of BH_3) was added in one portion to 25 mmol of the olefin. [d] R_2BH = disiamylborane.

A possible mechanism for formation of the diols can be envisaged as proceeding *via* a BH_3-catalyzed elimination. This produces the unsaturated derivative,[13] which is subsequently rehydroborated to afford, after oxidation, the observed diols.



Evidence in support of the proposed function of BH_3 in the elimination step comes from the observation that the β-organoborane does not undergo elimination in the presence of added disiamylborane (Table II). Disiamylborane exists as a dimer in tetrahydrofuran solution,[14] and hence cannot coordinate with the ring oxygen of the pyran ring. That a *trans* elimination should be the preferred reaction path is suggested by the arrangement of the departing groups, the boron moiety and oxygen, with the boron being in an equatorial position.

In exploring this reaction in more detail, it became apparent that the postulated unsaturated boron derivative, $H_2C{=}CH(CH_2)_2CH_2OB{<}$, could not be the sole precursor for the observed diols. To simulate the rehydroboration step, 25 mmol of 4-penten-1-ol in tetrahydrofuran was added to 25 mmol of BH_3 at 25°. Oxidation of the reaction mixture and glpc analysis revealed the formation in 86% yield of a 12:88 mixture of 1,4- and 1,5-pentanediol.[15] This ratio is markedly different from the 43:57 ratio observed in the hydroboration of Δ^2-dihydropyran with excess diborane (Table

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(10) H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **83**, 2544 (1961).

(11) A. Streitwieser, L. Verbit, and R. Bittman, *J. Org. Chem.*, **32**, 1530 (1967).

(12) Hückel molecular orbital calculations on enol ethers predict the greatest electron density at the β carbon: A. Hassner, R. E. Barnett, P. Catsoulacos, and S. H. Wilen, *J. Amer. Chem. Soc.*, **91**, 2632 (1969).

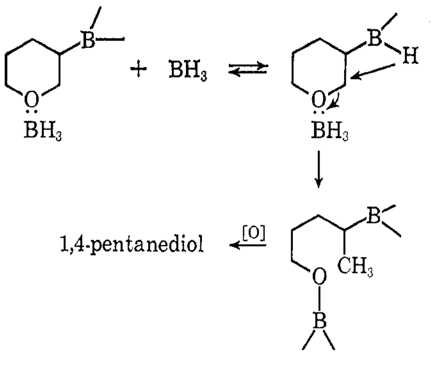
(13) The reaction may involve the intermediacy of a cationic boron species which is stabilized by solvation with the electron-donating solvent tetrahydrofuran (>B$^+$THF).[8]

(14) H. C. Brown and G. J. Klender, *Inorg. Chem.*, **1**, 204 (1962).

(15) Hydroboration of 3-buten-1-ol with diborane followed by oxidation yielded a 15:85 mixture of 1,3- and 1,4-butanediol: H. C. Brown and M. K. Unni, *J. Amer. Chem. Soc.*, **90**, 2902 (1968).

III). Consequently, at least part of the 1,4 diol must have arisen *via* an alternate route.

Possible mechanisms which could account for formation of the extra 1,4 diol are cleavage of the tetrahydropyran ring by diborane[16] and/or intramolecular transfer of hydride from boron to C-2.[17] In the latter case a redistribution reaction would have to precede the transfer reaction.



The results in Table III also indicate that the elimination–rehydroboration reaction proceeds at a much slower pace when diborane is added to the organoborane derived from Δ^2-dihydropyran and disiamylborane. It is conceivable that the bulky siamyl groups hinder coordination of tetrahydrofuran with boron, which should facilitate the *trans* elimination.[13,18]

Routes to Unsaturated Alcohols *via* Hydroboration of Dihydropyrans and Dihydrofurans.—The use of a Lewis acid which does not react with double bonds should permit the synthesis of unsaturated alcohols from dihydropyrans and dihydrofurans *via* the hydroboration–elimination sequence postulated earlier. Pasto and Snyder have reported that β-ethoxyorganoboranes undergo *trans* elimination in the presence of boron trifluoride.[17]

Addition of boron trifluoride etherate to the β-organoboranes derived from hydroboration of Δ^2-dihydropyran, 2,3- and 2,5-dihydrofuran, and 2-methyl-4,5-dihydrofuran with diborane resulted in formation of the corresponding unsaturated alcohols as predicted. The experimental results are summarized in Table IV.

TABLE IV

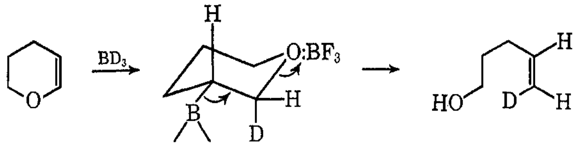
UNSATURATED ALCOHOLS OBTAINED BY ADDITION OF BF_3 ETHERATE AT 25° TO THE TRIALKYLBORANES IN TETRAHYDROFURAN SOLUTION DERIVED FROM HYDROBORATION OF Δ^2-DIHYDROPYRAN AND VARIOUS DIHYDROFURANS

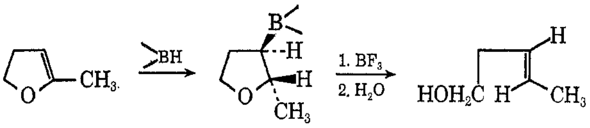
Organoborane derived from	Ratio of BF_3: olefin	Reacn time, hr	Product	Yield, %[a]
Δ^2-Dihydropyran	...	12	3-Hydroxytetrahydropyran	81
			4-Penten-1-ol	0
	1:10	12	3-Hydroxytetrahydropyran	36
			4-Penten-1-ol	50
	1:1	12	3-Hydroxytetrahydropyran	1
			4-Penten-1-ol	81
2,5-Dihydrofuran	1:1	2	3-Buten-1-ol	71
2,3-Dihydrofuran	1:1	2	3-Buten-1-ol	70
2-Methyl-4,5-dihydrofuran	1:1	1	*trans*-3-Penten-1-ol	88

[a] Yields by glpc analysis.

It should be noted that boron trifluoride acts catalytically, since a 1:10 ratio of BF_3 to olefin afforded a 50% yield of 4-penten-1-ol. Consequently, the hydroboration of olefins containing functional groups that are prone to undergo elimination must be carried out with diborane which is free of boron trifluoride.[19]

The catalytic role of boron trifluoride in these reactions can be depicted as facilitating the breaking of the carbon–oxygen bond, and resultant loss of boron, by coordination with the oxygen. Based on stereoelectronic considerations, one would predict, as mentioned earlier, that the elimination should proceed in a *trans* manner. This prediction was confirmed by the observation that *cis*-5-*d*-4-penten-1-ol was obtained after work-up from the β-organoborane derived from hydroboration of Δ^2-dihydropyran with deuterioborane (BD_3). Also, hydroboration of 2-methyl-4,5-dihydrofuran with diborane, followed by subsequent addition of boron trifluoride, afforded only *trans*-3-penten-1-ol.





It was pointed out in the preceding discussion that the reaction of Δ^2-dihydropyran with excess diborane affords a 43:57 mixture of 1,4- and 1,5-diols, whereas hydroboration of 4-penten-1-ol gives a 12:88 distribution. Therefore, a combination of the hydroboration–elimination–rehydroboration sequence should convert Δ^2-dihydropyran mainly into 1,5-pentanediol. Treatment of Δ^2-dihydropyran with the stoichiometric amount of diborane, followed by addition of boron trifluoride etherate and rehydroboration of the unsaturated intermediate with diborane, yielded after oxidation 72% 1,5-pentanediol and only 9% 1,4 isomer. This 11:89 distribution of 1,4- to 1,5-diols is similar to the ratio of diols obtained from the hydroboration of 4-penten-1-ol.

Experimental Section

Materials.—Tetrahydrofuran, diglyme, and boron trifluoride etherate were purified as described previously.[20] Sodium borohydride (98% pure) and lithium deuteride (98% D) were obtained from Metal Hydrides, Inc. Diborane was generated from boron trifluoride etherate and sodium borohydride,[19] and was bubbled through a solution of sodium borohydride in diglyme before being passed into freshly distilled tetrahydrofuran. Likewise, diborane-d_6, prepared as described previously,[20] was bubbled through a suspension of lithium deuteride in diglyme before being passed into tetrahydrofuran. The preparation of disiamylborane in tetrahydrofuran has been previously described.[21]

Commercial samples of Δ^2-dihydropyran (Matheson Coleman and Bell), 2-ethoxy-4,5-dihydrofuran (K & K), 2,5-dihydrofuran (Aldrich), and 2-methyl-4,5-dihydrofuran (Aldrich) were puri-

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(16) J. Kollonitsch, *J. Amer. Chem. Soc.*, **83**, 1515 (1961).

(17) D. J. Pasto and S. R. Snyder, *J. Org. Chem.*, **31**, 2777 (1966).

(18) A similar explanation was offered by Brown and Knights regarding the greater stability of the *trans* β adducts derived from hydroboration of 3-cyclopentene derivatives with disiamylborane: H. C. Brown and E. F. Knights, *J. Amer. Chem. Soc.*, **90**, 4439 (1968).

(19) To ensure the absence of traces of boron trifluoride, which could catalyze the elimination reaction, the diborane generated from BF_3 etherate and $NaBH_4$ was bubbled through a solution of $NaBH_4$ in diglyme before being passed into freshly distilled tetrahydrofuran.

(20) G. Zweifel and H. Arzoumanian, *ibid.*, **89**, 291 (1967).

(21) G. Zweifel, K. Nagase, and H. C. Brown, *ibid.*, **84**, 190 (1962).

fied before use by fractional distillation. Δ^3-Dihydropyran[22] and 2,3-dihydrofuran[23] were prepared according to published procedures.

Stoichiometry and Product Studies.—In a typical experiment, 4.4 ml of a 2.0 *M* solution of borane in tetrahydrofuran (26.4 mequiv of hydride) was added to 2.1 g (25 mmol) of Δ^2-dihydropyran in 20 ml of tetrahydrofuran at 25°. After the reaction mixture had been stirred for a given period of time, 1:1 glycerol-water was added and the hydrogen evolved was measured volumetrically with a gas buret. The organoborane was oxidized at 30–50° by adding 5 ml of 3 *N* sodium hydroxide, followed by dropwise addition of 3 ml of 30% hydrogen peroxide. The reaction mixture was saturated with potassium carbonate ($K_2CO_3 \cdot 1^1/_2H_2O$), and the organic layer formed was separated. The aqueous phase was extracted twice with ether, and the combined organic layers were dried ($MgSO_4$). The yields of 3-hydroxytetrahydropyran, 1,4-pentanediol, and 1,5-pentanediol were determined by glpc using internal standards as references. The experimental results are summarized in Table I.

3-Hydroxytetrahydropyran.—To 8.4 g (0.10 mol) of Δ^2-dihydropyran in 60 ml of tetrahydrofuran was added 17.5 ml of a 2.0 *M* solution of borane in tetrahydrofuran (0.105 equiv of hydride) at 0–5°. After the reaction mixture had been stirred at 0° for 3 hr, the temperature was raised to 25° and the mixture was stirred at this temperature for an additional 2 hr. The organoborane formed was oxidized at 30–50° by adding 18 ml of 3 *N* sodium hydroxide followed by dropwise addition of 12 ml of 30% hydrogen peroxide. After the reaction mixture had been stirred for 1 hr at room temperature, sodium chloride was added and the upper phase formed was separated. The aqueous phase was extracted with ether and the combined extracts were dried ($MgSO_4$). Distillation yielded 7.1 g (70%) of 3-hydroxytetrahydropyran, bp 90° (21 mm), $n^{21}D$ 1.4572. The 3,5-dinitrobenzoate derivative was obtained, mp 133–134° [lit.[1] bp 92–95° (12–15 mm), $n^{21}D$ 1.4571].

2-Ethoxy-5-hydroxytetrahydropyran.—To 12.8 g (0.10 mol) of 2-ethoxy-3,4-dihydropyran in 60 ml of tetrahydrofuran was added 18.5 ml of a 1.9 *M* solution of borane in tetrahydrofuran (0.105 equiv of hydride) at 25°. After the reaction mixture had been stirred at room temperature for 5 hr, the organoborane formed was oxidized at 30–50° by adding 15 ml of 3 *N* sodium hydroxide and 12 ml of 30% hydrogen peroxide. After the mixture had been stirred for 1 hr, the aqueous phase was saturated with potassium carbonate ($K_2CO_3 \cdot 1^1/_2H_2O$) and the organic layer formed was separated. The aqueous phase was extracted twice with 35-ml portions of tetrahydrofuran, and the combined extracts were dried ($MgSO_4$). Distillation gave 10.2 g (70%) of 2-ethoxy-5-hydroxytetrahydropyran, bp 64–66° (1 mm), $n^{22}D$ 1.4505.

Anal. Calcd for $C_7H_{14}O_3$: C, 57.49; H, 9.65. Found: C, 57.42; H, 9.70.

***trans*-2-Methyl-3-hydroxytetrahydrofuran.**—To 2.1 g (25 mmol) of 2-methyl-4,5-dihydrofuran in 20 ml of tetrahydrofuran was added 3.6 ml of a 2.42 *M* solution of borane in tetrahydrofuran (26.4 mequiv of hydride) at 0°. After the mixture had been stirred at this temperature for 2 hr, it was oxidized by adding 5 ml of 3 *N* sodium hydroxide and 3 ml of 30% hydrogen peroxide and was extracted repeatedly with ether. Distillation yielded 1.4 g (55%) of *trans*-2-methyl-3-hydroxytetrahydrofuran, bp 91° (21 mm), $n^{22}D$ 1.4420. The 3,5-dinitrobenzoate derivative was obtained, mp 113–114°.

Anal. Calcd for $C_{12}H_{12}N_2O_7$: C, 48.65; H, 4.08; N, 9.46. Found: C, 48.54; H, 4.14; N, 9.36.

Competitive Hydroboration Experiments.—In a typical experiment, 2.10 g (25 mmol) of Δ^2-dihydropyran, 2.05 g (25 mmol) of cyclohexene, and 1.76 g (21 mmol) of cyclohexane in 5 ml of tetrahydrofuran were placed in a 100-ml flask. To this mixture was added 22 ml of a 1.2 *M* solution of disiamylborane in tetrahydrofuran (26.4 mequiv of hydride) at 25°. Aliquots were removed after 0.5, 1.0, and 2.0 hr, quenched in an ice-cooled mixture containing 3 *N* sodium hydroxide and *n*-pentane, and analyzed by glpc for remaining olefins by using the cyclohexane as an internal standard. The experimental results are summarized in Table II.

Elimination Reactions with Diborane.—In a typical experiment, 4.17 ml of a 2.0 *M* solution of borane in tetrahydrofuran (25 mequiv of hydride) was added to 2.3 g (27.5 mmol) of Δ^2-dihydropyran in 5 ml of tetrahydrofuran at 25°. After the mixture had been stirred for 2 hr at this temperature, an additional 12.5 ml of a 2.0 *M* solution of borane (25 mequiv) in tetrahydrofuran was added. The reaction mixture was maintained at 25° for 24 hr before being oxidized with alkaline hydrogen peroxide (5 ml of 3 *N* sodium hydroxide and 3 ml of 30% hydrogen peroxide). The yields of 3-hydroxytetrahydropyran and of the pentanediols were determined by glpc using internal standards as references. The experimental results are summarized in Table III.

Elimination Reactions with Boron Trifluoride.—In a typical experiment, 27.5 mmol of Δ^2-dihydropyran was converted into the organoborane as described above. To this was added 28 mmol of boron trifluoride etherate. The reaction mixture was stirred at 25° for 12 hr; then enough 3 *N* sodium hydroxide was added to make the mixture basic. The organoborane was oxidized at 30–50° by adding 3 ml of 30% hydrogen peroxide and the products formed were analyzed by glpc. The reaction time and amount of boron trifluoride etherate added were varied in individual experiments. The results of these investigations are summarized in Table IV.

4-Penten-1-ol.—To 9.2 g (0.11 mol) of Δ^2-dihydropyran in 60 ml of tetrahydrofuran was added 13.1 ml of a 2.55 *M* solution of borane in tetrahydrofuran (0.10 equiv of hydride) at 0–5°. The reaction mixture was maintained at 0–5° for 3 hr and then at 25° for 2 hr. To the organoborane formed was added 0.110 mol of boron trifluoride etherate. The reaction mixture was stirred at 25° for 24 hr, made basic by adding 3 *N* sodium hydroxide, and saturated with sodium chloride. Distillation yielded 5.1 g (60%) of 4-penten-1-ol, bp 70° (52 mm), $n^{21}D$ 1.4288 [lit.[24] bp 76° (60 mm), $n^{20}D$ 1.4299]. The 3,5-dinitrobenzoate derivative was obtained, mp 44–45° (lit.[25] mp 44–45°).

Hydroboration of Δ^2-Dihydropyran with BD_3 Followed by Addition of Boron Trifluoride Etherate.—To 2.3 g (27.5 mmol) of Δ^2-dihydropyran in 20 ml of tetrahydrofuran was added at 0° 6.4 ml of a 1.3 *M* solution of deuterioborane (25 mequiv of deuteride) in tetrahydrofuran. The solution was stirred for 2 hr at 0–5° and for an additional one hr at 25°. The reaction mixture was then treated with 28 mmol of boron trifluoride etherate, stirred at 25° for 24 hr, made basic by adding 3 *N* sodium hydroxide, and saturated with potassium carbonate. The organic layer was separated, dried ($MgSO_4$), filtered, and distilled to give *cis*-5-*d*-4-penten-1-ol, bp 68° (35 mm), $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 5.16 (d, 1, J = 11 Hz, *cis* DHC=CH) and 6.07 ppm (m, 1, *cis* DHC=C**H**).

1 5-Pentanediol.—In a 125-ml flask was placed 2.31 g (27.5 mmol) of Δ^2-dihydropyran in 5 ml of tetrahydrofuran. Hydroboration was achieved by dropwise addition of 4.2 ml of a 2.0 *M* solution of borane (25 mequiv of hydride) in tetrahydrofuran. The solution was stirred for 2 hr at room temperature treated with 28 mmol of boron trifluoride etherate, and stirred for 12 hr at 25°. After having been diluted with 25 ml of tetrahydrofuran followed by the addition of 4.2 ml of a 2.0 *M* solution of borane (25 mequiv of hydride) in tetrahydrofuran, the reaction mixture was stirred for 1 hr at 25°. The organoborane formed was oxidized at 30–40° by adding 5 ml of 3 *N* sodium hydroxide followed by dropwise addition of 3 ml of 30% hydrogen peroxide. The reaction mixture was stirred for an additional 1 hr and then saturated with potassium carbonate ($K_2CO_3 \cdot 1^1/_2H_2O$), and the organic phase was separated and dried ($MgSO_4$). Analysis by glpc on a silicone–sorbitol column revealed the formation of 72% 1,5-pentanediol and 9% 1,4-pentanediol.

Registry No. 3-Hydroxytetrahydropyran, 19752-84-2; 2-ethoxy-5-hydroxytetrahydropyran, 23062-30-8; *trans*-2-methyl-3-hydroxytetrahydrofuran, 23061-82-7; *trans*-2-methyl-3-hydroxytetrahydrofuran 3,5-dinitrobenzoate, 23061-83-8; *cis*-5-*d*-4-penten-1-ol, 23061-84-9.

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[22] J. Cologne and R. Boisde, *Bull. Soc. Chim. Fr.*, 824 (1956).

[23] R. Paul, M. Fluchaire, and G. Collardeau, *ibid.*, 668 (1950).

[24] M. S. Kharasch and C. F. Fuchs, *J. Org. Chem.*, **9**, 359 (1944).

[25] H. P. Thomas and C. L. Wilson, *J. Amer. Chem. Soc.*, **73**, 4803 (1951).