analyzed by gas chromatography on a Carbowax 20M column at 161° and a helium flow rate of 48 ml. per min. indicating a ratio of 71% *trans*-alcohol and 29% *cis*-alcohol. Unreduced ketone (24%) was also present. A duplicate analysis indicated 72% of *trans*-alcohol and 23% of ketone.

Reduction of DHI (7.0 g., 0.05 mole) with 0.7 g. (50% excess) of lithium aluminum hydride in the usual manner (direct addition) gave 73% *trans*-alcohol, as analyzed on a Tide column (analysis on Carbowax 20M indicated 74% *trans*). About 7% of ketone was in the product. Use of a large excess of hydride (0.0168 equivalent reducing 0.00021 mole of DHI) in another direct addition experiment gave 72% *trans*-alcohol.

Reaction of Alcohols with Lithium Aluminum Hydride in THF. Reduction of DHI.—In these experiments (except in the case of lithium aluminum tri-*t*-butoxyhydride) the alcohol was added to the stirred lithium aluminum hydride solution in THF and the hydrogen evolved was measured in a wet test meter. A solution of DHI was then added and the reaction mixture was heated under reflux for 2 hours and kept overnight at room temperature. It was then worked up in the usual manner. The products were analyzed by gas chromatography on Carbowax 20M. The results are summarized in Table V.

Acknowledgment.—This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund. We are indebted to Professor Ray Lemieux for permission to present unpublished data from his laboratory and for a discussion of this work.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND RADIATION LABORATORY* OF THE UNIVERSITY OF NOTRE DAME, NOTRE DAME, IND.]

Reductions with Metal Hydrides. XI. Solvent Effect on the Stereochemistry of Reduction with Sodium Borohydride

BY HOWARD HAUBENSTOCK AND ERNEST L. ELIEL

RECEIVED JANUARY 3, 1962

The reduction of 3,3,5-trimethylcyclohexanone with sodium borohydride in anhydrous isopropyl alcohol, anhydrous *t*-butyl alcohol or anhydrous diglyme gives 55% *trans*-3,3,5-trimethylcyclohexanol and 45% *cis* isomer, exactly as reduction with lithium aluminum hydride in ether (previous paper). Higher proportions of *trans*-alcohol (up to a maximum of 82%) are formed in aqueous isopropyl alcohol, anhydrous ethanol and aqueous methanol. The change in product composition is a result of solvent effects rather than of alkoxyborohydride formation in the latter solvents, for (a) sodium trimethoxyborohydride in isopropyl alcohol gives less *trans*-alcohol than sodium borohydride in aqueous methanol and (b) very little hydrogen (and therefore very little alkoxyborohydride) is formed when sodium borohydride is dissolved in anhydrous ethanol or methanol containing sodium methoxide.

The concepts of "steric approach control" and "product development control" applied to reductions of substituted cyclohexanones have led Dauben and co-workers to postulate that the borohydride species has a greater effective size than the aluminohydride anion.[1] Thus the reduction of menthone with lithium aluminum hydride gives 71% of menthol and 29% of neomenthol whereas with sodium borohydride in methanol it gives 49% of menthol and 51% of neomenthol. It was therefore suggested that the borohydride species, considered effectively larger than the aluminohydride anion, gave more attack from the less hindered equatorial side of the molecule to yield a greater proportion of axial alcohol, neomenthol.

Henbest and co-workers[2] found that reduction of the hindered ketone 3β-acetoxy-9α-bromoergostan-11-one (I) with sodium borohydride in methanol or *tert*-butyl alcohol gave mainly (after acetylation) 3β-acetoxyergostan-11-one while reduction of I with lithium aluminum hydride followed by acetylation gave 3β-acetoxy-9β:11β-epoxyergostane as the major product. This epoxide is presumably formed from the bromohydrin (or aluminum derivative) which is initially produced by reduction of the carbonyl group. These results, and others, were cited by Dauben[1] as further corroboration of the size difference between the aluminohydride ion and the borohydride ion.

However, Wheeler and Huffman[3] have pointed out that since the aluminohydride ion actually is larger than the borohydride ion, on the basis of a comparison of the Al–H and B–H bond lengths, Dauben's hypothesis rests upon the assumption that solvation of the borohydride ion gives it a greater effective size. This assumption was criticized by Wheeler and Huffman who claimed that neither borohydride ion nor aluminohydride ion is solvated. Furthermore, the different behavior of the two ions in the reduction of 3β-acetoxy-9α-bromoergostan-11-one[2] was ascribed[3] to a difference in mechanism rather than to a difference in size of reagent.

The available evidence suggests that even when consideration is restricted to reductions with sodium borohydride, differences in stereochemistry can be observed when different solvents are used. Thus Dauben found that sodium borohydride in pyridine behaves as a larger reducing agent than sodium borohydride in methanol. Even when only solvents of similar type, *e.g.*, alcohols, are considered, differences can be observed. For example, reduction of Δ^4-cholestene-3-one with sodium borohydride in isopropyl alcohol is reported to give 95% of the β-alcohol[4] while reduction with sodium borohydride in aqueous methanol gives

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* The Radiation Laboratory is operated under contract with the Atomic Energy Commission. Enquiries regarding this paper should be directed to E. L. E.

(1) W. G. Dauben, G. J. Fonken and D. S. Noyce, *J. Am. Chem. Soc.*, **78**, 2579 (1956); see also W. G. Dauben, E. J. Blanz, Jr., J. Jiu and R. A. Micheli, *ibid.*, **78**, 3752 (1956), and W. G. Dauben and R. E. Bozak, *J. Org. Chem.*, **24**, 1596 (1959).

(2) H. B. Henbest, E. R. H. Jones, A. A. Wagland and T. I. Wrigley, *J. Chem. Soc.*, 2477 (1955).

(3) D. M. S. Wheeler and J. W. Huffman, *Experientia*, **16**, 516 (1960).

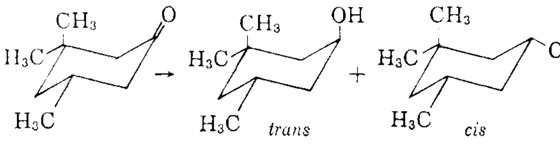
(4) O. H. Wheeler and J. L. Mateos, *Can. J. Chem.*, **36**, 1049 (1958).

74% of the β-isomer.[5] Another example, outside the steroid field, is the reduction of tropinone with sodium borohydride[6] which gives 33% of the axial alcohol tropine in isopropyl alcohol but 52% in methyl alcohol. (Here lithium aluminum hydride in ether is intermediate, giving 43% tropine, 57% ψ-tropine.)

In the present investigation, 3,3,5-trimethylcyclohexanone (dihydroisophorone) was reduced with sodium borohydride and sodium trialkoxyborohydrides under various conditions. This system,[7] unlike tropinone,[6] is devoid of complications due to the presence of a heteroatom and possesses the additional advantage of being unambiguously conformationally homogeneous, in as much as the alternate chair form would have a highly unfavorable 1,3-diaxial methyl–methyl interaction. It was therefore hoped that the present study would throw additional light on the stereochemistry of borohydride reduction.

Results and Discussion

The results of the reduction of dihydroisophorone (eq. i) with sodium borohydride in various solvents are summarized in Table I. Included are the results obtained with several other reagents.



(i)

Dihydroisophenone 3,3,5-Trimethylcyclohexanol

Comparison of entries 1 and 2 indicates, in agreement with earlier observations,[6] that the relative proportion of ketone and reducing agent does not affect the stereochemical result of the reduction.

TABLE I

REDUCTION OF DIHYDROISOPHORONE WITH BOROHYDRIDES

Entry	Reagent	Solvent	Mole reagent / Mole ketone	*trans* (axial) Alcohol,[b] %
1	$NaBH_4$	Anhyd. isopropyl alc.	0.53	55.2
2	$NaBH_4$	Anhyd. isopropyl alc.	.25	56[a]
3	$NaBH_4$	Anhydr. *t*-butyl alc.	.52	55
4	$NaBH_4$	Anhydr. diglyme	.52	55
5	$NaBH_4$	65% aq. isopropyl alc.	.40	59.5
6	$NaBH_4$	Anhydr. ethanol	.40	67
7	$NaBH_4$	71% aq. methanol	.37	73
8	KBH_4	67% aq. methanol	.64	71
9	$NaB(OCH_3)_3H$	Isopropyl alc.	.75	65[c]
10	NaB(O-Pr-*i*)$_3$H	Diglyme	..	77[d]

[a] About 3.4% ketone found in product. [b] Analyses carried out by gas chromatography using a Tide detergent or Carbowax 20M column. [c] Reagent obtained from Metal Hydrides, Inc.; a large amount of unreduced ketone was obtained in the product. [d] Reduction occurred to only a small extent.

In the case of lithium aluminum hydride, we had ascribed[7] this result to disproportionation of the intermediate alkoxyhydride species. This explanation probably does not apply to borohydride, however, in as much as the tri-*sec*-alkoxyborohydrides seem to be stable species which produce different stereochemical results in reduction than does borohydride (*cf.* entry 10). Since it is known[8–10] that trialkoxyborohydrides are faster reducing agents than borohydride itself (this being contrary to the relationship between aluminohydride and trialkoxyaluminohydrides[7]), probably each molecule of borohydride is "zipped down" through all four reducing stages before another borohydride molecule enters into reaction, regardless of whether ketone or borohydride is in excess. The results in Table I, entries 1 and 2, are thus a composite of the stereochemistry of reduction of borohydride and the various alkoxyborohydrides, $BH_3(OR)$, $BH_2(OR)_2$ and $BH(OR)_3$. No change results from the use of *t*-butyl alcohol or diglyme as solvents (entries 3, 4); in all these cases the stereochemistry, perhaps fortuitously, is exactly the same as with lithium aluminum hydride in ether. Although it is dangerous to correlate reagent stereoselectivity with reagent size,[3] the present results, like the earlier ones of Beckett, *et al.*,[6] certainly lend no particular support to the hypothesis[1] that borohydride is larger than aluminohydride.

The remaining results in the 3,3,5-trimethylcyclohexanone system are generally in line with those in the tropinone system.[6] Addition of water to the isopropyl alcohol solvent (entry 5) and change of solvent to ethanol (entry 6) or methanol (entries 7, 8) increase the amount of the (less stable) axial (***trans***) alcohol formed by steric approach control. Beckett, *et al.*, explained this effect as being due to the formation of alkoxyborohydrides, these, rather than borohydride itself, being the effective reducing agents in methanol and ethanol. Our result with sodium trimethoxyborohydride (entry 9) throws doubt on this hypothesis, since this reagent gives *less* axial alcohol than does sodium borohydride in methanol (entry 7). Unfortunately the result is not entirely conclusive since there was some doubt as to the purity and homogeneity of the trimethoxyborohydride reagent (which is known to undergo disproportionation under some conditions, *e.g.*, in diglyme and in tetrahydrofuran).[11] Moreover, Beckett, *et al.*,[6] had found that the result of sodium trimethoxyborohydride reduction is strongly dependent on reaction conditions.

Fortunately, we were able to rule out intervention of sodium triethoxyborohydride (or mono- or diethoxyborohydride) in the reduction of dihydroisophorone with sodium borohydride in ethanol in another way. We were able to show that the reaction of sodium borohydride with ethanol occurs only to a small extent and thus *cannot* be a major factor in explaining the solvent effect. The data are summarized in Table II. A solution of the reagent was prepared and the hydrogen evolved was measured before and after

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[5] W. G. Dauben, R. A. Micheli and J. F. Eastham, *J. Am. Chem. Soc.*, **74**, 3852 (1952).

[6] A. H. Beckett, N. J. Harper, A. D. J. Balon and T. H. E. Watts, *Tetrahedron*, **6**, 319 (1959).

[7] See also H. Haubenstock and E. L. Eliel, *J. Am. Chem. Soc.*, **84**, 2363 (1962).

[8] H. C. Brown, E. J. Mead and B. C. Subba Rao, *ibid.*, **77**, 6209 (1955).

[9] H. C. Brown, E. J. Mead and C. J. Shoaf, *ibid.*, **78**, 3616 (1956).

[10] E. R. Garrett and D. A. Lyttle, *ibid.*, **75**, 6051 (1953).

[11] H. C. Brown, E. J. Mead and P. A. Tierney, *ibid.*, **79**, 5400 (1957).

the addition of the ketone. Only one fourteenth of the available hydride was converted to hydrogen. Similar results were obtained in methanol, although in this case addition of sodium methoxide was required to inhibit extensive reaction of the borohydride with solvent (see Table II, footnote).

TABLE II

REDUCTION OF DIHYDROISOPHORONE

$NaBH_4$, mole	Solvent[a]	Mole H_2 evolved before ketone addn.	Total H_2 evol., mole	% Axial isomer in alc. obtd.[b]
0.014	Ethanol	Neglig.	0.004	63–64
0.016	Methanol	>0.014	0.048	80[c]

[a] Anhydrous solvent. [b] Gas chromatographic analysis on Carbowax 20M. [c] The ketone was only about half reduced since the sodium borohydride had completely reacted (with ketone and solvent) before addition of the ketone was complete. ADDED IN PROOF: Since the publication of the paper by R. E. Davis and J. A. Gottbrath, *J. Am. Chem. Soc.*, **84**, 895 (1962), Mr. J. Dorsey in our laboratory has repeated the reduction of dihydroisophorone with sodium borohydride in absolute methanol containing sodium methoxide. Regardless of the order of addition, the product again contained 80–82% axial alcohol. Less than one-tenth the available hydride was converted to hydrogen.

Our present findings and some of those reported in the accompanying paper[7] may be summarized as: (1) Sodium borohydride in inert solvent brings about the same steric result in the reduction of dihydroisophorone as does lithium aluminum hydride in ether. (2) The stereochemistry of sodium borohydride reduction is subject to a solvent effect which cannot be adequately explained in terms of alkoxyborohydride formation. The effect of using methanol and ethanol as a solvent is to increase the stereoselectivity of the reagent. (3) A similar effect is found in lithium aluminum hydride reduction when the solvent is changed from diethyl ether to tetrahydrofuran.[7] These findings strongly imply, contrary to a recent assertion,[3] that both borohydride and aluminohydride ions are solvated,[11] at least in some of the common solvents used for reduction, since solvation of the reducing species would seem the most likely explanation for the variation in steric result.[12] A possible alternative is differential solvation of the transition states leading to equatorial and axial product such as to move them along the reaction coördinate and change their relative steric requirements.

Experimental

Reductions of Dihydroisophorone (DHI) with $NaBH_4$ in Various Solvents.—The reduction of DHI with $NaBH_4$ in dry methanol and ethanol are described below in detail, as is the preparation and reaction of sodium triisopropoxyborohydride. The other reductions were carried out similarly. Analyses were effected by gas chromatography on a Tide detergent or Carbowax 20 M column using peak height–half-width measurement of peaks.

Reduction of DHI with $NaBH_4$ in Ethanol.—Sodium borohydride (0.537 g., 0.014 mole) was placed in a 200-ml. 3-neck flask equipped with a magnetic stirrer, condenser leading to a wet test meter, and two pressure-equalized addition funnels. One funnel contained 50 ml. of dry ethanol and the other a solution of dihydroisophorone (5.6 g., 0.04 mole) in 5 ml. of ethanol. The ethanol was added to the $NaBH_4$ over a 5-min. interval. The solution was then stirred for 17 min. At this stage a negligible amount (13 ml.) of hydrogen was evolved. The ketone solution was then added dropwise, and the rate of hydrogen evolution increased. A total of 0.0004 mole of hydrogen was evolved, which represents only $^1/_{14}$ of the initially available hydride. No precipitation occurred during the addition of the ketone. The solution was stirred for 2.5 hours. On acidification with 10% H_2SO_4, 0.011 mole of hydrogen was evolved. The reaction mixture was diluted with salt solution and the product was extracted with ether. The ether extract was washed with saturated sodium bicarbonate solution and with salt solution, and dried over anhydrous magnesium sulfate. Distillation of the solvent gave a concentrated residue weighing 8.1 g. which was analyzed by gas chromatography on a Carbowax 20 M column at 164° giving 64% *trans*-alcohol and 36% *cis*-alcohol. No ketone was present.

In another experiment in which 0.3 g. of $NaBH_4$ was added to a solution of DHI (2.74 g.) in dry ethanol, the reaction mixture was heated under reflux for 1.5 hours and allowed to stand overnight. After workup of the reaction in the usual manner, analysis on a Tide detergent column gave 67% *trans*-alcohol and 33% *cis*-alcohol. No ketone was present.

Reduction of DHI with $NaBH_4$ in Dry Methanol.—Sodium borohydride (0.609 g., 0.016 mole) was placed in a 200-ml. 3-neck flask equipped with a magnetic stirrer, a condenser leading to a wet test meter, and two pressure-equalized addition funnels. Dry methanol was added (50 ml.) and hydrogen evolution started rapidly. The rate of hydrogen evolution increased and continued after all the methanol had been added. By the time the ketone addition was started, more than 500 ml. of hydrogen (>0.019 mole) had been evolved. When a portion of the ketone solution (5.6 g., 0.04 mole, in 5 ml. of methanol) was added, the reaction became markedly exothermic and the rate of hydrogen evolution rose rapidly, so that all the hydrogen left had been evolved before the addition of the ketone was completed. No precipitation occurred. The reaction mixture was stirred for 2.5 hr. and was decomposed with 10% NaOH. The product was extracted with ether after dilution with salt solution. The ether solution was washed several times with salt solution and dried over anhydrous magnesium sulfate. A residue of 6.6 g. was obtained after distillation of solvent. Analysis on a Carbowax 20M column at 162° gave 80% *trans*-alcohol and 20% *cis*-alcohol. Only about 50% reduction had occurred.

In the presence of sodium methoxide,[13] little hydrogen was evolved and the reduction proceeded to the extent of 86–96%, yet the composition of the product was essentially the same (80–82% *trans*).

In another experiment a solution of $NaBH_4$ (1.4 g., 0.037 mole) in 30 ml. of water was added to a solution of

TABLE III

Reagent	Mole reagent	Solvent	Mole DHI	Product composition,[a] % *trans*	*cis*
$NaBH_4$	0.0264	Isopropyl alcohol	0.05	55	45
$NaBH_4$	.0125[b]	Isopropyl alcohol	.05	56[c]	44
$NaBH_4$	.0079	65% aq. isopropyl alc.	.02	59	41
$NaBH_4$	.013	*t*-Butyl alc.	.025	55[d]	45
$NaBH_4$	.026	Diglyme	.05	55[e]	45
$NaB(OCH_3)_3H$[f]	.0375	Isopropyl alc.	.05	66[g]	34

[a] Analyses carried out by gas chromatography on a Tide detergent column. [b] In this experiment the reagent was added in small portions over a 2.5-hour interval. [c] About 3% ketone was present. [d] A synthetic mixture of 3,3,5-trimethylcyclohexanols containing 69.4% *trans*-alcohol was subjected to the same workup conditions as in the reduction experiment and the recovered alcohol mixture analyzed for 68.9% *trans*-alcohol on a Tide column. [e] A synthetic mixture consisting of 72.2% of *trans*-alcohol was subjected to the same workup conditions as in the reduction experiment and the recovered alcohol mixture analyzed for 71.8% *trans*-alcohol on a Tide column. [f] Reagent obtained from Metal Hydrides, Inc. [g] A large amount of ketone was present in the product.

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(12) The solvent effect is much less marked in unhindered systems, such as 3- and 4-methylcyclohexanone, where changing the solvent from isopropyl alcohol to methanol changes product composition by only 3–4%: M. G. Combe and H. B. Henbest, *Tetrahedron Letters*, 404 (1961).

(13) R. E. Davis and J. A. Gottbrath, *J. Am. Chem. Soc.*, **84**, 895 (1962).

DHI (14.1 g., 0.1 mole) in 75 ml. of methanol. After an hour of reflux and standing at room temperature for 2 hours, the reaction mixture was decomposed with 10% sodium hydroxide and worked up in the usual way. Analysis of the product on a Tide detergent column gave 73% *trans*-alcohol and 27% *cis*-alcohol. No ketone was found.

A similar reduction using KBH_4 in 67% aqueous methanol gave the same product composition within experimental error.

Reductions of DHI with $NaBH_4$ in anhydrous isopropyl alcohol, 65% aqueous isopropyl alcohol, anhydrous diglyme, *t*-butyl alcohol and with sodium trimethoxyborohydride in isopropyl alcohol are summarized in Table III.

Preparation of $NaB(O\text{-}Pr\text{-}i)_3H$ and Reduction of DHI.—Sodium hydride (1.14 g.) was added to isopropyl borate[9] (8.6 g., 0.045 mole) in 100 ml. of sodium-dried diglyme in a flask which was previously flamed under a nitrogen atmosphere. During the entire operation dry nitrogen was passed through the system. The reaction mixture was heated at about 130° for 85 min. At one point the temperature reached about 135° and the contents turned brown.

A solution of DHI (3.9 g., 0.028 mole) in 20 ml. of diglyme was added and the reaction mixture was stirred overnight, then heated on a steam-bath for 3 hours and kept overnight at room temperature. The reaction mixture was hydrolyzed with water and 10% sulfuric acid and diluted with about 1 liter of water. The product was extracted with ether and the ether solution was washed with saturated sodium bicarbonate solution and with water and dried over anhydrous magnesium sulfate. The ether was distilled leaving a concentrated orange residue weighing 6 g. which was analyzed with a Carbowax 20M column at 155° and contained 77% *trans*-alcohol and 23% *cis*-alcohol. Reduction had occurred to only a limited extent.

Acknowledgment.—This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND RADIATION LABORATORY[1] OF THE UNIVERSITY OF NOTRE DAME, NOTRE DAME, IND.]

Reduction with Metal Hydrides. XII. Reduction of Acetals and Ketals with Lithium Aluminum Hydride–Aluminum Chloride

BY ERNEST L. ELIEL, VICTOR G. BADDING AND MARK N. RERICK

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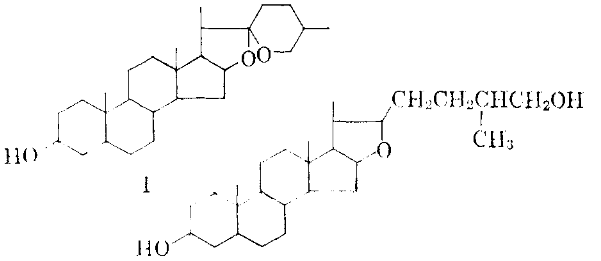
The reduction of acetals and ketals to ethers in high yield by means of lithium aluminum hydride–aluminum chloride is described.

In 1951, Doukas and Fontaine reported[2] that spirostanes such as I are reduced to furostanols, such as II, by the addition of solid lithium aluminum hydride (LAH) to an ethereal solution of the spirostane saturated with anhydrous hydrogen chloride or hydrogen bromide. This report was noteworthy for two reasons. The combination of reagents employed was rather unusual. (Neither LAH nor hydrogen halides by themselves affected I and combinations of LAH with hydrogen sulfide, sulfur dioxide and *p*-toluenesulfonic acid were also ineffective.) Also conversion of I to II exemplifies reduction of a ketal to an ether for which no procedures giving acceptable yields were then available. In general, of course, the ketal function is resistant to the attack of LAH and, in fact, ketal formation often is employed to protect ketone groups during the reduction of other functions (such as ester groups) in a molecule.[3]



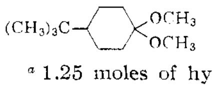
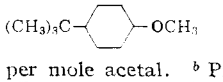
I

II

When subsequent work in our laboratory and elsewhere[4] disclosed that the reducing properties of LAH may be considerably modified by the addition of Lewis acids, especially aluminum chloride, it became likely that the active ingredient in the reagent employed by Doukas and Fontaine[2] was a LAH–aluminum chloride combination. We therefore studied[5] the action of such a combination on a variety of acetals and ketals with the results shown in Table I.

TABLE I

REDUCTION OF ACETALS AND KETALS

Compound reduced	Product	Yield, %
$C_6H_5CH(OCH_3)_2$	$C_6H_5CH_2OCH_3$	88
$C_6H_5CH(OC_2H_5)_2$	$C_6H_5CH_2OC_2H_5$	73^a
$n\text{-}C_3H_7CH(OC_2H_5)_2$	$n\text{-}C_4H_9OC_2H_5$	*ca.* $47^{a,b}$
$C_6H_5C(OC_2H_5)_2CH_3$	$C_6H_5CH(CH_3)OC_2H_5$	81
$(CH_3)_2C(OC_4H_9\text{-}n)_2$	$(CH_3)_2CHOC_4H_9\text{-}n$	84^c
$C_6H_{10}(OCH_3)_2{}^d$	$C_6H_{11}OCH_3{}^e$	74
$C_6H_{10}(OC_2H_5)_2{}^d$	$C_6H_{11}OC_2H_5{}^e$	78
$C_6H_{10}(OC_3H_7\text{-}n)_2{}^d$	$C_6H_{11}OC_3H_7\text{-}n^e$	74
$C_6H_{10}(OC_4H_9\text{-}n)_2{}^d$	$C_6H_{11}OC_4H_9\text{-}n^e$	61
		92^f

^{a} 1.25 moles of hydride per mole acetal. ^{b} Product codistilled with ethanol. ^{c} Product codistilled with 1-butanol. ^{d} C_6H_{10} is cyclohexylidene. ^{e} C_6H_{11} is cyclohexyl. ^{f} 75.5% *trans* isomer, 16.5% *cis* isomer by gas chromatography.

The reductions all proceeded to give ethers: $RR'C(OR'')_2 \rightarrow RR'CHOR''$. Yields were good,

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[1] The Radiation Laboratory is operated under contract with the Atomic Energy Commission. This paper is taken in part from the Ph.D. dissertation of Victor G. Badding.

[2] H. M. Doukas and T. D. Fontaine, *J. Am. Chem. Soc.*, **73**, 5917 (1951); **75**, 5355 (1953).

[3] N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, pp. 673–680.

[4] For a review and references, see E. L. Eliel, *Rec. Chem. Progr.*, **23**, 129 (1961).

[5] For a preliminary communication of some of these results, see E. L. Eliel and M. N. Rerick, *J. Org. Chem.*, **23**, 1088 (1958).