solution over a period of 30 min. The reaction flask was permitted to remain for 3 hr. at 0°. The reaction mixture was treated with 3.5 g. of 2-methyl-2-butene (50 mmoles) in 25 ml. of tetrahydrofuran. The flask was maintained for an additional 3 hr. at 0°. Water was then added to decompose residual hydride. The organoborane was oxidized at 30–50° by adding 30 ml. of 3 N sodium hydroxide, followed by 21 ml. of 30% hydrogen peroxide. The reaction mixture was then saturated with solid potassium carbonate. The upper phase formed was separated, and the aqueous phase was extracted once more with tetrahydrofuran. The tetrahydrofuran extracts were combined and dried over anhydrous sodium sulfate. The solvent was removed and the 3-methyl-2-butanol was distilled. Purification by gas chromatography gave (−)-3-methyl-2-butanol, $n^{20}\text{D}$ 1.4090, d^{23} 0.810, $[\alpha]^{20}\text{D}$ −0.91°, indicating a 17% optical purity.[9]

1-Methylcyclopentene.—Under similar experimental conditions, 100 mmoles of 1-methylcyclopentene (8.2 g.) was hydroborated with 100 mmoles of triisopinocampheyldiborane derived from (−)-α-pinene. The reaction mixture was maintained for 3 hr. at 0°. Water was then added to decompose residual hydride. The organoborane was oxidized at 30–50° by adding 50 ml. of 3 N sodium hydroxide, followed by 42 ml. of 30% hydrogen peroxide. The alcohols formed were worked up in the usual way. Distillation gave 7.62 g. of *trans*-2-methylcyclopentanol (76% yield), b.p. 58–59° at 12 mm., $n^{20}\text{D}$ 1.4510, d^{20} 0.925, $[\alpha]^{25}\text{D}$ −4.8°.

The *trans*-2-methylcyclopentanol (5.62 g., 56 mmoles) was dissolved in 20 ml. of pyridine. To this solution was added 61 mmoles of tosyl chloride. The reaction mixture was kept for 12 hr. at 4°, then was poured into a mixture of equal volumes of 6 M hydrochloric acid and ether. The upper phase was separated, and the aqueous phase extracted with ether. The combined ether extracts were washed with water, and dried. Evaporation of the ether gave 14 g. of crude tosyl ester.

In a 300-ml. flask was placed 45 ml. of isoamyl alcohol and 45 ml. of diglyme. To this mixture was added sodium hydride until 0.12 mole of hydrogen was evolved. The tosyl ester was added and the reaction mixture was heated until the olefin distilled. There was obtained 3.1 g. of 3-methylcyclopentene, b.p. 66° at 752 mm., $n^{20}\text{D}$ 1.4210, d^{25} 0.760, $[\alpha]^{25}\text{D}$ +15.2°, indicating a 17.5% optical purity.[11]

1-Methylcyclohexene.—Fifty mmoles of 1-methylcyclohexene (4.8 g.) was hydroborated with 50 mmoles of triisopinocampheyldiborane derived from (−)-α-pinene. The organoborane was oxidized, and the alcohol formed was worked up in the usual way. Purification by gas chromatography gave pure *trans*-2-methylcyclohexanol, $n^{26}\text{D}$ 1.4620, d^{20} 0.923, $[\alpha]^{25}\text{D}$ −6.9°, indicating an 18% optical purity.[17]

[Contribution from the Richard B. Wetherill Laboratory of Purdue University, Lafayette, Ind.]

Hydroboration. XX. The Reaction of Diisopinocampheylborane with Representative 2-Methyl-1-alkenes—A Convenient Synthesis of Optically Active 2-Methyl-1-alkanols

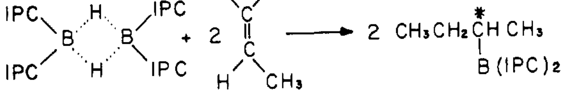
By George Zweifel, Nagaraj R. Ayyangar,[1] Takashi Munekata,[2] and Herbert C. Brown

Received October 3, 1963

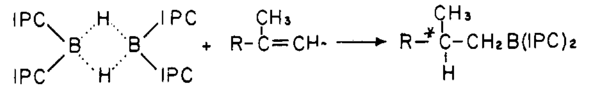
(+)-Diisopinocampheylborane readily adds to 2-methyl-1-butene, 2,3-dimethyl-1-butene, and 2-phenylpropene to produce new organoboranes containing a new asymmetric center at the 2-position. Oxidation produces optically active alcohols, all of the R-configuration: (+)-2-methyl-1-butanol, $[\alpha]\text{D}$ +1.25°, 21% optical purity; (−)-2,3-dimethyl-1-butanol, $[\alpha]\text{D}$ −1.88°, 30% optical purity; (+)-2-phenyl-1-propanol, $[\alpha]\text{D}$ +0.80°, 5% optical purity. On the other hand, the reaction of 2,3,3-trimethyl-1-butene is slow and proceeds with displacement of α-pinene from the reagent. The oxidized product, 2,3,3-trimethyl-1-butanol, exhibits $[\alpha]\text{D}$ −5.1°, of unknown absolute configuration. The model previously proposed to account for the related reaction of reactive *cis*-olefins has been adapted to permit prediction of the absolute configuration of alcohols and related products realized through the simple addition of such terminal olefins to (+)- and (−)-diisopinocampheylborane.

The success realized in achieving asymmetric syntheses through the reaction of (+)- and (−)-diisopinocampheylborane with *cis*-olefins[3,4] and of triisopinocampheyldiborane with *trans* and hindered olefins[5] led us to explore the possible extension of this asymmetric synthesis to some representative terminal olefins.

In the case of the internal olefins previously explored,[4,5] the boron becomes attached to the asymmetric center (1).

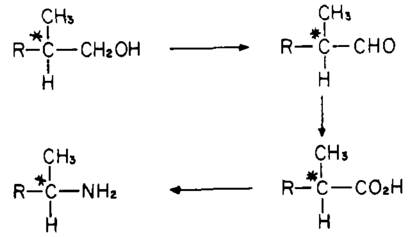

(1)

In the case of the 2-methyl-1-alkenes examined in the present study, the asymmetric center is on the carbon atom immediately adjacent to that holding the boron atom (2).


(2)

Consequently, it was anticipated that the magnitude of the asymmetric induction would be less than that realized for the *cis*-olefins.

In the case of the *cis*-olefins it proved possible to develop a model for the hydroboration stage which permitted the reliable assignment of configuration to eight products of considerably different structures.[4] For such applications it is not important that the products have high optical purities. It is far more important that the method predict reliably the configuration of the initial derivative, so that it can be used to relate the configurations of a family of derived products (3).


(3)

Accordingly, we undertook the hydroboration–oxidation of 2-methyl-1-butene, 2,3-dimethyl-1-butene, 2,3,3-trimethyl-1-butene, and 2-phenylpropene in order to examine (a) the practicality of asymmetric syntheses in terminal olefins of this type, and (b) the possibility of developing a model which would predict the absolute configurations of any optically active products thus produced.

Results

(+)-Diisopinocampheylborane, synthesized from (−)-α-pinene by hydroboration with sodium borohydride and boron trifluoride in diglyme in the usual

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[1] Postdoctorate research associate, 1961–1963, on grants (G-6273 and G-19878) provided by the National Science Foundation.

[2] Visiting Scholar, 1962–1963, on funds provided by the Kureha Chemical Industry Co., Tokyo, Japan.

[3] H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 486 (1961).

[4] H. C. Brown, N. R. Ayyangar, and G. Zweifel, *ibid.*, **86**, 397 (1964).

[5] H. C. Brown, N. R. Ayyangar, and G. Zweifel, *ibid.*, **86**, 1071 (1964).

TABLE I

HYDROBORATION OF SOME REPRESENTATIVE 2-METHYL-1-ALKENES WITH (+)-DIISOPINOCAMPHEYLBORANE AT 0°

Olefin	Alcohol	α-Pinene displaced,[c] %	Rotation of alcohol, $[\alpha]^{25}D$,	Optical purity, %	Configuration of alcohol[a]
2-Methyl-1-butene	2-Methyl-1-butanol	9	+1.25°	21	*R*
2,3-Dimethyl-1-butene	2,3-Dimethyl-1-butanol	7	−1.88	30	*R*
2,3,3-Trimethyl-1-butene[b]	2,3,3-Trimethyl-1-butanol	32	−5.1		(*R*)[d]
2-Phenylpropene	2-Phenyl-1-propanol	7	+0.80	5	*R*

[a] Ref. 8. [b] The reaction was slow at 0° and was carried out at 25°. [c] Approximately 6% of the α-pinene originally used to synthesize the reagent is normally present because of an equilibrium dissociation of the diisopinocamphenylborane. [d] Assignment on basis of reasonable argument; see Discussion.

manner,[4] was utilized *in situ* at 0°. The hydroboration was carried out by adding the olefin to the suspension of the reagent in the molar ratio of one to one. Small aliquots of the reaction mixture were removed and analyzed both for residual olefin and for α-pinene which might be formed from the reagent by displacement.

The reaction involving 2-methyl-1-butene proceeded rapidly at 0°. Oxidation of the organoborane thus produced yielded 2-methyl-1-butanol in 83% yield. The alcohol was dextrorotatory, $[\alpha]^{25}D$ +1.25°, indicating an optical purity of 21%.[6] It has been established that (+)-2-methyl-1-butanol has the *R*-configuration.[7,8]

2,3-Dimethyl-1-butene also reacted rapidly with the reagent at 0°. Oxidation of the organoborane gave (−)-2,3-dimethyl-1-butanol, $[\alpha]^{25}D$ −1.88°, indicating an optical purity of 30%.[9] It has been established that (−)-2,3-dimethyl-1-butanol has the *R*-configuration.[9]

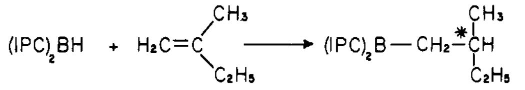
With increased branching of the alkyl chain, as in 2,3,3-trimethyl-1-butene, the rate of reaction of the reagent decreases markedly. Accordingly, the temperature of the reaction mixture was raised to 25°, but even then the reaction required some 4 hr. for completion. Moreover, in contrast to the two previous cases, there occurred a significant displacement of α-pinene (32%).

Oxidation of the reaction product yielded (−)-2,3,3-trimethyl-1-butanol, $[\alpha]^{25}D$ −5.1°. This alcohol has not previously been obtained in optically active form, so that it is not possible to report the optical purity or the configuration.

Finally, the reaction of 2-phenylpropene proceeded normally at 0°. The (+)-2-phenyl-1-propanol obtained after oxidation exhibited $[\alpha]^{25}D$ +0.80°, indicating an optical purity of 5%.[10] The *R*-configuration of the alcohol follows from its synthesis from hydratropic acid. Reduction of (−)-hydratropic acid with lithium aluminum hydride gives (+)-2-phenyl-1-propanol.[10] Since (−)-hydratropic acid has the *R*-configuration,[11] the (+)-alcohol must also have the *R*-configuration.

Discussion

In the reaction of diisopinocampheylborane with 2-methyl-1-butene, the reagent must discriminate between the very similar alkyl groups methyl and ethyl in order to achieve an asymmetric synthesis. Moreover, the discrimination must be achieved one atom removed from the developing asymmetric center (4).



$$(IPC)_2BH + H_2C{=}C(CH_3)(C_2H_5) \longrightarrow (IPC)_2B{-}CH_2{-}\overset{*}{C}H(CH_3)(C_2H_5) \quad (4)$$

Consequently, the achievement of 21% optical activity in the product must be considered both remarkable and highly satisfactory.

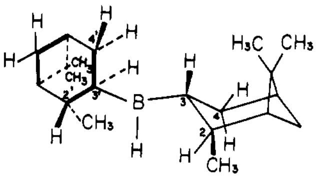
With the greater difference in the steric requirements of methyl and isopropyl in 2,3-dimethyl-1-butene, a more favorable discrimination might have been anticipated. This corresponds to the optical purity of 30% observed for the reaction product, 2,3-dimethyl-1-butanol.

The presence of the competing *t*-butyl and methyl group in 2,3,3-trimethyl-1-butene would appear to be even more favorable. Unfortunately, there are two difficulties in interpreting the results. First, optically active 2,3,3-trimethyl-1-butanol has not been previously synthesized, so that it is not possible at this time to proceed from the observed rotation, −5.1°, to the optical purity. Second, the reaction of this olefin with the reagent proceeds with considerable displacement of α-pinene. As discussed earlier,[5] this probably means that the hydroboration is proceeding not only through an addition of the olefin to diisopinocampheylborane (or its dimer), but also through an addition to its dissociation product, triisopinocampheyldiborane.

In view of the difference in the apparent steric requirements of methyl and phenyl, the low optical purity (5%) observed in the conversion of 2-phenylpropene to 2-phenyl-1-propanol is unexpected. However, it has been observed previously that the replacement of an alkyl group by phenyl leads to decreased optical purity of the product of an asymmetric synthesis.[12]

The observation that all three products have the same absolute configuration suggests that the reaction may be of special value as a tool in establishing the absolute configuration of optically active primary alcohols (and their derivatives) carrying a substituent in the 2-position.

In the case of the *cis*-olefins, the observed configuration of the products was rationalized in terms of an optimal steric fit for the *cis* addition of the olefin to the reagent.[4] The model selected for (−)-diisopinocampheylborane involves a diequatorial arrangement of the boron atom and the methyl group at C-2 in the pinane moiety, and an anti- or nearly antiparallel orientation of the two methyl groups (at C-2 and C-2′) in the two pinane moieties (5).[13]



(5)

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[6] F. C. Whitmore and J. H. Olewine, *J. Am. Chem. Soc.*, **60**, 2569 (1938), report $[\alpha]^{27}D$ −5.9° for (−)-2-methyl-1-butanol.

[7] K. Freudenberg and W. Hohmann, *Ann.*, **584**, 54 (1953).

[8] For the *R–S* configurational nomenclature, see R. S. Cahn, C. K. Ingold, and V. Prelog, *Experientia*, **12**, 81 (1956).

[9] P. A. Levene and R. E. Marker, *J. Biol. Chem.*, **111**, 299 (1935), report $[M]^{25}D$ +6.3° for (+)-2,3-dimethyl-1-butanol.

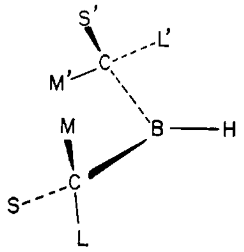
[10] R. Roger and D. G. Neilson, *J. Chem. Soc.*, 627 (1960), report $[\alpha]^{25}D$ +16.7° for 2-phenyl-1-propanol.

[11] V. Prelog and H. Scherrer, *Helv. Chim. Acta*, **42**, 2227 (1959).

[12] V. Prelog, O. Cedar, and M. Wilhelm, *ibid.*, **38**, 303 (1955).

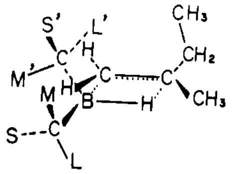
[13] The discussion is in terms of the monomer. However, no significant change is introduced if the reaction actually proceeds through the dimer.

It is convenient to simplify this model in the usual manner, using the symbols S (small) for the hydrogen atoms at C-3 and C-3′, M (medium) for the methylene groups at C-4 and C-4′, and L (large) for the methyl groups at C-2 and C-2′ (6).

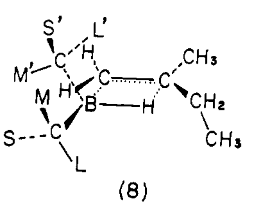


(6)

On the basis of the usual four-center transition state,[14] it is possible to draw two different transition states for the addition of a terminal olefin, such as 2-methyl-1-butene to the reagent (7, 8).

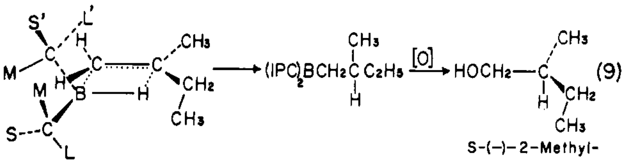


(7)



(8)

In transition state 7 the larger alkyl group, ethyl, is near the L-group of the reagent, whereas in 8 this alkyl group is closer to M. This smaller interaction of the larger group should provide a modest factor favoring transition state 8 over 7. Completion of the addition *via* 8, followed by oxidation with retention of configuration, should provide 2-methyl-1-butanol with the *S*-configuration 9.



(9)

S-(–)-2-Methyl-1-butanol

The diagrams are given in terms of (–)-diisopinocampheylborane [from (+)-α-pinene] to correspond with the models used to correlate the products from the reactive *cis*-olefins.[4] Accordingly, (+)-diisopinocampheylborane, which was used in the present study, would predict the preferential formation of the *R*-configuration, in accordance with experimental observation.

In the case of the *trans* and hindered olefins, where hydroboration proceeds with displacement of α-pinene from the reagent, it was observed that the configurations realized were the exact opposite of those predicted on the basis of the proposed model. Unfortunately, the reaction of 2,3,3-trimethyl-1-butene with diisopinocampheylborane appears to be mechanistically complex, proceeding both by displacement and addition (simple displacement would require the formation of either 50 or 100 mmoles of α-pinene in the hydroboration stage, whereas 62.8 mmoles was observed). Consequently, in this case it is not possible to apply either the model for simple addition, or the generalization proposed for hydroboration with displacement.[15]

In summary, the following rules appear applicable for the prediction of configuration of alcohols derived from the hydroboration–oxidation of olefins with (+)- or (–)-diisopinocampheylborane: A. Reactive *cis*-olefins give alcohols of high optical purity, whose absolute configuration can be related to the proposed model for the transition state having an optimal steric fit of both reagent and olefin. B. Terminal olefins give alcohols of modest optical purity. The absolute configuration can be related to the same model proposed for reactive *cis*-olefins. C. In the case of less reactive olefins, which react with diisopinocampheylborane predominantly by displacement of α-pinene, the products obtained exhibit modest optical activity and the opposite configuration to that predicted on the basis of rules A and B.

Experimental

Materials.—Purification of the solvents and reagents was carried out as described in preceding publications.[4,5] The α-pinene used exhibited $[\alpha]_D$ –47.9°. 2-Methyl-1-butene, n^{20}_D 1.3797, 2,3-dimethyl-1-butene, n^{20}_D 1.3912, and α-methylstyrene, n^{20}_D 1.5385, were products of 99% purity from the Phillips Petroleum Co. 2,3,3-Trimethyl-1-butene, b.p. 76–77° at 748 mm., n^{20}_D 1.4030, was synthesized by dehydrating with iodine 2,3,3-trimethyl-2-butanol obtained by the action of the methyl Grignard reagent on ethyl pivalate.

(+)-**2-Methyl-1-butanol.**—A suspension of 100 mmoles of (+)-diisopinocampheylborane in 125 ml. of diglyme was prepared in the usual manner.[4,5] To this reagent maintained at 0° was added 7.0 g. (100 mmoles) of 2-methyl-1-butene. The reaction mixture was maintained for 2 hr. at 0°, 10 ml. of water added to decompose residual hydride, and the organoborane product oxidized at 30 to 50° by adding 31 ml. of 3 *M* sodium hydroxide, followed by the dropwise addition of 31 ml. of 30% hydrogen peroxide (vigorous reaction!). The alcohol product was taken up in ether. Gas chromatographic analysis of the dried ether extract revealed the presence of 18 mmoles of α-pinene (9%). The ether was removed and the residue subjected to distillation. There was obtained 7.33 g. of 2-methyl-1-butanol, a yield of 83%. The alcohol, purified by gas chromatography, exhibited n^{20}_D 1.4106, $[\alpha]^{20}_D$ +1.25°.

(–)-**2,3-Dimethyl-1-butanol.**—To 50 mmoles of (+)-diisopinocampheylborane in diglyme was added 4.2 g. (50 mmoles) of 2,3-dimethyl-1-butene. The reaction was allowed to proceed for 5 hr. at 0°. After oxidation with 16 ml. of 3 *M* sodium hydroxide, followed by 16 ml. of 30% hydrogen peroxide, the product was taken up in ether. Gas chromatographic analysis of the ether extract revealed 7.3 mmoles of α-pinene (7.3%) and 47.5 mmoles of 2,3-dimethyl-1-butanol, a yield of 95%. After purification by gas chromatography, the 2,3-dimethyl-1-butanol exhibited n^{20}_D 1.4208, $[\alpha]^{20}_D$ –1.88°.

(–)-**2,3,3-Trimethyl-1-butanol.**—Triglyme was substituted for diglyme as the solvent to facilitate recovery of the product. To a suspension of 100 mmoles of (+)-diisopinocampheylborane in triglyme was added 9.8 g. (100 mmoles) of 2,3,3-trimethyl-1-butene. The reaction mixture was maintained at 0° for 2 hr. Since gas chromatographic examination revealed that little of the olefin had reacted, the reaction vessel was allowed to come to room temperature and kept there for 20 hr. After oxidation and extraction, distillation yielded 2,3,3-trimethyl-1-butanol contaminated by α-pinene. The alcohol was then purified by gas chromatography on a glycerol column. The 2,3,3-trimethyl-1-butanol isolated had n^{20}_D 1.4294, $[\alpha]^{25}_D$ –5.1°.

In a separate experiment, it was observed that the hydroboration of the 2,3,3-trimethyl-1-butene was essentially complete in 4 hr. at 25°, and that the reaction proceeds with the formation of 62.8 mmoles of α-pinene (31%).

(+)-**2-Phenyl-1-propanol.**—The usual suspension of 50 mmoles of (+)-diisopinocampheylborane in diglyme was treated with 5.91 g. (50 mmoles) of α-methylstyrene. After 4 hr. at

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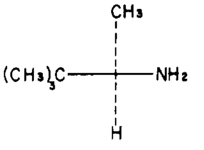
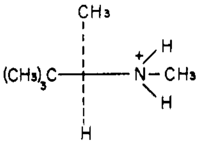
[14] H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 2544 (1961).

[15] Although the absolute configuration of 2,3,3-trimethyl-1-butanol has not been established, it is likely that the $-NH_2CH_3$ (11) and the $-CH_2OH$ group (12) produce a similar rotatory effect. Therefore, the three compounds (–)-pinacolylamine (10), (–)-N-methylpinacolylammonium ion (11), and (–)-2,3,3-trimethyl-1-butanol (12) should be configurationally related (private communication from Professor J. H. Brewster, Purdue University). Since (–)-pinacolylamine has the *R*-configuration, the levorotatory alcohol obtained *via* the hydroboration of 2,3,3-trimethyl-1-butene with (+)-diisopinocampheylborane should have the *R*-configuration.



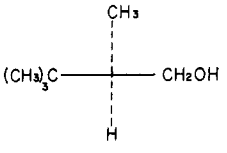
(–)-R

(10)



(–)-R

(11)



(–)-R

(12)

0°, oxidation yielded 6.9 mmoles of α-pinene (6.9%) and 38.5 mmoles of 2-phenyl-1-propanol, a yield of 77%. 2-Phenyl-1-propanol was first separated from the isopinocampheol by liquid phase chromatography on alumina, eluting the isopinocampheol with ether and the 2-phenyl-1-propanol with a mixture of ether-methanol. The solvents were removed and the product was further purified by gas chromatography: $n^{20}\text{D}$ 1.5250, $[\alpha]^{26}\text{D}$ + 0.80°.

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY, LAFAYETTE, IND.]

Selective Reductions. III. Further Studies of the Reaction of Alcohols with Lithium Aluminum Hydride as a Route to the Lithium Alkoxyaluminohydrides[1]

BY HERBERT C. BROWN AND CHARLES J. SHOAF[2,3]

RECEIVED OCTOBER 18, 1963

The reactions of methyl, ethyl, isopropyl, and *t*-butyl alcohols with lithium aluminum hydride in ethyl ether, tetrahydrofuran, and diglyme were studied in order to establish whether these reactions provide convenient synthetic routes to lithium di- and trialkoxyaluminohydrides. As reported earlier, the reaction of *t*-butyl alcohol can be controlled to yield lithium di- and tri-*t*-butoxyaluminohydride without difficulty. Similarly, the reaction of methanol with lithium aluminum hydride appears to lead, without complications, to the formation of lithium di- and trimethoxyaluminohydride, insoluble in ethyl ether, but highly soluble in tetrahydrofuran and diglyme. Lithium trimethoxyaluminohydride can also be prepared by the reaction of lithium aluminum hydride with lithium tetramethoxyaluminohydride. The reaction of ethyl alcohol with lithium aluminum hydride appears to lead to products which are predominantly lithium di- and triethoxy derivatives, but the reaction is less simple than the previous cases. Finally, both isopropyl and *sec*-butyl alcohol react to yield complex mixtures, involving the formation and precipitation of major amounts of the tetraalkoxy derivative. Utilization of acetone in place of isopropyl alcohol yields similar results. Lithium di-*t*-butoxyaluminohydride reacts with 1 mole of methanol to give a mixed alkoxy derivative, lithium monomethoxydi-*t*-butoxyaluminohydride. Lithium trimethoxyaluminohydride is a far more powerful reducing agent than the tri-*t*-butoxy derivative, but not as active as the parent compound. Preliminary experiments revealed that the product obtained by reaction of 3 moles of ethyl alcohol per mole of lithium aluminum hydride is a promising reagent for the reduction of both aromatic and aliphatic nitriles to aldehydes in good yield.

The alkali metal borohydrides[4] and the corresponding alkali metal aluminum hydrides[5] constitute two families of reducing agents of vastly different characteristics. Thus sodium borohydride, at one extreme, reduces only aldehyde, ketone, and acid chloride groups at a convenient rate,[6] whereas lithium aluminum hydride, at the other extreme, rapidly reduces practically all functional groups.[7]

For organic syntheses there would be obvious advantages in having available not merely these two extremes but rather an entire series of reagents of graduated activities. In line with this objective, we have been investigating means of increasing the activity of the borohydride reagents, and of decreasing the activity of the aluminum hydride compounds. Thus it was observed that the activity of sodium borohydride could be increased by the addition of certain metal salts[8] and by the introduction of alkoxy substituents.[9] On the other hand, the introduction of three ethoxy[10] or *t*-butoxy[11] substituents considerably diminishes the reducing power of the alkali metal aluminum hydride.[12]

Lithium tri-*t*-butoxyaluminohydride, conveniently synthesized *in situ* by the reaction of 3 moles of *t*-butyl alcohol with lithium aluminum hydride in an appropriate solvent,[11] has proved to be an excellent reagent for the reduction of acid chlorides to aldehydes,[11,13] for the stereospecific reduction of steroids,[14] as well as for other selective reductions.[15,16] On the other hand, sodium triethoxyaluminohydride has found relatively little application in organic synthesis. It is probable that the synthesis, *i.e.*, the reaction of sodium hydride with freshly prepared, monomeric aluminum ethoxide in tetrahydrofuran at 70 to 90° in an autoclave,[10,17] is too inconvenient for the preparation of small quantities of the reagent required for an individual reaction.

Our success in synthesizing lithium tri-*t*-butoxyaluminohydride by the reaction of *t*-butyl alcohol with the parent compound encouraged us to make a detailed examination of the reaction of methyl, ethyl, and isopropyl alcohols with lithium aluminum hydride with the primary objective of ascertaining whether the reactions could be controlled to provide a convenient synthetic route to the corresponding di- and trialkoxyaluminohydrides.

Results and Discussion

Lithium aluminum hydride and its alkoxy derivatives are highly reactive materials, exceedingly sensitive to traces of water, oxygen, carbon dioxide, etc. In view of the special objectives of this investigation, it was decided that major emphasis should be placed on a determination of the nature of the species formed by treating lithium aluminum hydride in solution with 1, 2, and 3 moles of the appropriate alcohol.

$$\mathrm{LiAlH_4 + ROH \longrightarrow LiAlH_3OR + H_2}$$
$$\mathrm{LiAlH_3OR + ROH \longrightarrow LiAlH_2(OR)_2 + H_2}$$
$$\mathrm{LiAlH_2(OR)_2 + ROH \longrightarrow LiAlH(OR)_3 + H_2}$$
$$\mathrm{LiAlH(OR)_3 + ROH \longrightarrow LiAl(OR)_4 + H_2}$$

Ethyl ether, tetrahydrofuran, and diglyme were selected as representative solvents. Standardized solu-

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(1) Addition Compounds of the Alkali Metal Hydrides. XIII.

(2) Based upon a thesis submitted by Charles J. Shoaf, in 1957, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Research assistant on Contract DA-33-008-ORD-992 supported by the Office of Ordnance Research, U. S. Army.

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