*J. Org. Chem.* **1983**, *48*, 945–948

**Registry No.** **5**, 6651-36-1; **6a**, 62572-35-4; *erythro*-**6b**, 13161-18-7; *threo*-**6b**, 42052-56-2; **7**, 5682-83-7; **8**, 22081-48-7; *threo*-**10**, 71444-30-9; *erythro*-**10**, 71444-29-6; *threo*-**11**, 84624-42-0; *erythro*-**11**, 84624-41-9; **12**, 84896-21-9; **13**, 60669-65-0; **14**, 84896-22-0; *threo*-**15**, 84896-23-1; *erythro*-**15**, 84896-24-2; *threo*-**16**, 81640-06-4; *erythro*-**16**, 81640-05-3; **17**, 19980-43-9; **18**, 26620-52-0; **19**, 17510-47-3; **20**, 84896-25-3; **21**, 84896-26-4; **22**, 2346-34-1; *threo*-**23**, 84896-27-5; *erythro*-**23**, 84896-28-6; **24**, 17510-46-2; **25a**, 84896-29-7; **25b**, 42052-52-8; **26**, 13735-81-4; **27**, 84896-30-0; **28**, 17082-61-0; *threo*-**29**, 84896-31-1; *erythro*-**29**, 84896-32-2; **30**, 19980-35-9; *threo*-**31**, 54322-99-5; *erythro*-**31**, 54322-98-4; **32**, 19980-33-7; **33** (isomer 1), 54323-00-1; **33** (isomer 2), 54353-03-6; **33** (isomer 3), 54323-00-1; **33** (isomer 4), 54353-01-4; **34**, 62572-34-3; **35a** (isomer 1), 62623-74-9; **35a** (isomer 2), 62572-37-6; **35a** (isomer 3), 84680-50-2; **35a** (isomer 4), 84680-51-3; **37**, 84896-34-4; *threo*-**38**, 84896-35-5; *erythro*-**38**, 84896-36-6; **39**, 84624-34-0; **40a**, 84896-37-7; *threo*-**40b**, 84896-38-8; *erythro*-**40b**, 84896-39-9; **41**, 84896-40-2; $(C_2H_5)_4NF$, 665-46-3; $(n\text{-}C_4H_9)_4NF$, 429-41-4; CsF, 13400-13-0; KF, 7789-23-3; NaF, 7681-49-4; LiF, 7789-24-4; $TiCl_4$, 7550-45-0; BTAF, 329-97-5; 2-[(trimethylsilyl)oxy]-2-(hydroxyphenylmethyl)cyclobutanone, 62248-59-3; 2-hydroxy-2-[[(trimethylsilyl)oxy]phenylmethyl]cyclobutanone, 84896-33-3; benzaldehyde, 100-52-7; *p*-nitrobenzaldehyde, 555-16-8; isobutyraldehyde, 78-84-2; fluorotrimethylsilane, 420-56-4; *p*-anisaldehyde, 123-11-5; 2-[(4-methoxyphenyl)methylene]cyclohexanone, 5765-29-7; hexamethyldisilazane, 999-97-3; trimethylchlorosilane, 75-77-4; cyclohexanone, 108-94-1; 1-(trimethylsiloxy)cyclododecene, 51584-36-2; benzophenone, 119-61-9; 2-(1-butyl-1-hydroxypentyl)cyclohexanone, 60599-75-9; 5-nonanone, 502-56-7; *N*-(trimethylsilyl)imidazole, 18156-74-6; phenyloxirane, 96-09-3; diethyl ethylidenemalonate, 1462-12-0; benzylacetone, 2550-26-7; benzaldehyde dimethyl acetal, 1125-88-8; 2,2-dimethyl-3-phenylpropanal, 6325-41-3; 5-(trimethylsiloxy)-2-methyl-5-phenyl-3-pentanone, 62572-36-5; methyl isopropyl ketone, 563-80-4; ethyl (trimethylsilyl)acetate, 4071-88-9; 2-methyl-5-phenyl-4-penten-3-one, 3160-32-5; cinnamaldehyde, 104-55-2; 3-phenylpropanal, 104-53-0; benzil, 134-81-6; furfural, 98-01-1; (*E*)-2-hexenal, 6728-26-3; tetrahydrofuran, 109-99-9; acetonitrile, 75-05-8; dimethoxyethane, 110-71-4; ether, 60-29-7; *N,N*-dimethylformamide, 68-12-2; dimethyl sulfoxide, 67-68-5.

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# On the Reaction of Lithium Aluminum Hydride with Alcohols

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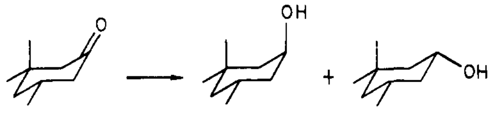
Infrared spectra of the reaction products of lithium aluminum hydride ($LiAlH_4$) with 3 molar equiv of isobutyl alcohol, 2-propanol, and the more sterically hindered 2,4-dimethyl-3-pentanol, 4, in diethyl ether were examined. Alcohol 4 reacts with $LiAlH_4$ in diethyl ether, giving a clear solution that is highly stereoselective in the reduction of 3,3,5-trimethylcyclohexanone, 1. The reaction of $LiAlH_4$ with 4 does not lead to tricoordinate aluminum species. On the basis of infrared spectra and the stereochemistry of reduction of 1, it is concluded that $LiAlH_4$ is present in solution after its reaction with 3 molar equiv of isobutyl alcohol. $LiAlH_4$ is also the initial reducing species in solution after reaction with 2-propanol. On the other hand, $LiAlH_4$ reacts with methanol, ethanol, and 4, giving lithium alkoxyaluminum hydride species. Possible pathways for the reaction of $LiAlH_4$ with alcohols are discussed.

The reaction of alcohols with lithium aluminum hydride ($LiAlH_4$) is of considerable importance although not sufficiently understood. Lithium alkoxyaluminum hydrides are intermediates in the $LiAlH_4$ reduction of carbonyl compounds. They also serve as useful selective reducing agents,[1] and many approaches to the design of chiral complex metal hydride reagents for asymmetric reductions involve the reaction of $LiAlH_4$ with chiral alcohols or phenols.[2]

Table I. Reduction of 1 with $LiAlH_4$ and Modified Reagents[a]

| entry | addend[b] | trans-axial 2,[c] % |
|---|---|---|
| 1 | | 52–55[d] |
| 2 | $CH_3OH$ | 75[e] |
| 3 | $CH_3CH_2OH$ | 83,[e] 87[f] |
| 4 | $(CH_3)_2CH\text{-}CH_2OH$ | 57,[g] 56[h] |
| 5 | $(CH_3)_2CH\text{-}CHOH\text{-}CH(CH_3)_2$, 4 | 96[i] |

[a] In diethyl ether. [b] Three molar equivalents of addend/mole of $LiAlH_4$. [c] Preparative conditions using magnetic stirring. Alcohol epimers normalized to 100%. [d] References 3, 4. [e] Reference 3. [f] This work, 33% 1 in product. [g] Reference 4. [h] This work, 26% 1 in product. [i] This work.



(1)

1 trans-2 cis-2

The stereoselectivity of reduction (eq 1) of 3,3,5-trimethylcyclohexanone, 1, has served as a simple probe for the identity (or nonidentity) of lithium alkoxyaluminum hydride reducing species in solution.[3] Thus the reduction of 1 with $LiAlH_4$ in diethyl ether gave 52–55% of *trans*-**2**,[3-5] while reduction of 1 with a reagent prepared by the reaction of $LiAlH_4$ with 3 molar equiv of methanol gave 75% *trans*-**2**.[3] On the other hand, the reduction of 1 with the reagent formed from the reaction of $LiAlH_4$ with 3 molar equiv of 2-propanol gave 54–55% *trans*-**2**,[3,4] a result

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(1) J. Málek and M. Černý, *Synthesis*, 217 (1972); E. R. H. Walker, *Chem. Soc. Rev.*, **5**, 23 (1976); H. C. Brown and S. Krishnamurthy, *Tetrahedron*, **35**, 567 (1979).

(2) D. Valentine, Jr., and J. W. Scott, *Synthesis*, 329 (1978); J. W. ApSimon and R. P. Seguin, *Tetrahedron*, **35**, 2797 (1979).

(3) H. Haubenstock and E. L. Eliel, *J. Am. Chem. Soc.*, **84**, 2363 (1962).

(4) H. Haubenstock, *J. Org. Chem.*, **38**, 1765 (1973).

(5) This product stereochemistry was observed under small-scale preparative conditions using magnetic stirring. Under these conditions it has been reported that the actual effective reducing species are $LiAlH_4$ and the lithium monoalkoxyaluminum hydride.[6]

0022-3263/83/1948-0945$01.50/0

Table II. Al-H Stretching Vibrations ($\nu_{\text{Al-H}}$) in the Infrared Spectra of Hydride Solutions

| entry | hydride species or source (molarity "hydride"[a]) | solvent | $\nu_{\text{Al-H}}$, cm$^{-1}$ |
|---|---|---|---|
| 1 | $LiAlH_4$ (0.10-0.31) | $Et_2O$ | 1736-1739[b] |
| 2 | $LiAlH_4$ (1.6) | $Et_2O$ | 1740[c] |
| 3 | $LiAlH_4$ (4.4) | $Et_2O$ | 1725[c] |
| 4 | $LiAlH(OCHPr^i{}_2)_3$, **5** (0.07) | $Et_2O$ | 1795[b] |
| 5 | $LiAlH_4$ + $3Bu^iOH$ (0.14) | $Et_2O$ | 1731-1734[b] |
| 6 | $LiAlH_4$ + $3Bu^iOH$ (0.26) | $Et_2O$ | 1730-1732[b] |
| 7 | $LiAlH_4$ + $3Pr^iOH$ (0.43) | $Et_2O$ | 1732-1735[b] |
| 8 | $LiAlH_4$ (4.0) | THF | 1655[d] |
| 9 | $LiAlH(OBu^t)_3$ | THF | 1760[e] |
| 10 | $LiAlH(OBu^t)_3$ (1.2) | THF | 1760[f] |
| 11 | $LiAlH(OCHPh_2)_3$ | THF | 1800[e] |

[a] Concentrations refer to molarity of "hydride," e.g., 0.1 M $LiAlH_4$ would be 0.4 M in "hydride". [b] This work. [c] Reference 18. [d] Reference 11. [e] Reference 10. [f] Reference 19.

identical with reduction of **1** with $LiAlH_4$. This implies, but does not rigorously require, that the actual reducing agents are the same in the two reductions. It was proposed[3] that the reaction of $LiAlH_4$ with 3 molar equiv of 2-propanol leads to the formation of **3** as a result of disproportionation (eq 2). Brown and Shoaf then demonstrated by chemical analysis that in fact $LiAlH_4$ remains in solution when reacted with 3 molar equiv of 2-propanol and that **3** is precipitated.[7] It was recognized that this behavior was not universal for *all* secondary alcohols.[8]

$$4LiAlH_4 + 12Pr^iOH \rightarrow LiAlH_4 + \underset{\mathbf{3}}{3LiAl(OPr^i)_4} + 12H_2 \qquad (2)$$

Results of the reduction of **1** with several reagents prepared by the reaction of $LiAlH_4$ with 3 molar equiv of alcohols in diethyl ether are shown in Table I. It is of particular interest that the added isobutyl alcohol gave the same stereochemical result in the reduction of **1** as did $LiAlH_4$. This suggests that $LiAlH_4$ is the predominant, if not sole, initial reducing species in the experiment, entry 4. We report infrared evidence for the presence of $LiAlH_4$ in solution after the reaction of $LiAlH_4$ with isobutyl alcohol or with 2-propanol. Additional infrared and reduction experiments are reported with ethanol and a hindered secondary alcohol, 2,4-dimethyl-3-pentanol. An explanation for the behavior of these various alcohols with $LiAlH_4$ is presented.

## Results

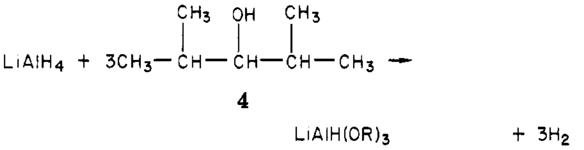
**Infrared Spectra.** Isobutyl alcohol (3 molar equiv) was allowed to react with $LiAlH_4$ in diethyl ether under nitrogen. A portion of the reaction mixture was filtered under nitrogen and the clear filtrate examined by infrared spectroscopy. The experiment was carried out twice (Table II, entries 5 and 6) and the near identity of the Al–H stretching vibration ($\nu_{\text{Al-H}}$) with that of $LiAlH_4$ in the same concentration range (Table II, entry 1) suggests that $LiAlH_4$ is present as a major species[9] after the reaction with isobutyl alcohol. This can explain the identical stereoselectivities within experimental error observed in the reduction of **1** (Table I, entries 1 and 4). The reaction of $LiAlH_4$ with 2-propanol is known to result in a solution of $LiAlH_4$.[3,7] The infrared spectrum of the filtered solution from this reaction confirmed this and showed the same value of $\nu_{\text{Al-H}}$ (Table II, entry 7) as observed from the reaction with isobutyl alcohol.

Table III. Infrared Spectra of Products of Reaction of $AlH_3$[a] with **4**

| **4**, mmol | $AlH_n(OR)_{3-n}$[b] | concn[c] | $\nu_{\text{Al-H}}$, cm$^{-1}$ |
|---|---|---|---|
|  | $AlH_3$ | 0.39 | 1783 |
| 3.8 | $AlH_2OR$ | 0.2 | 1845 |
| 7.8 | $AlH(OR)_2$ | 0.08 | 1883 |
| 11.6[d] | $AlH(OR)_2$ | 0.07 | 1883 |

[a] 3.8 mmol of $AlH_3$. Solvent is diethyl ether. $AlH_3$ was prepared by the reaction of $LiAlH_4$ with anhydrous $ZnCl_2$.[14] [b] R = 2,4-dimethyl-3-pentyl. [c] Concentrations refer to molarity of "hydride"; see Table II, footnote *a*. [d] Hydrogen evolution corresponded to formation of the dialkoxyaluminum hydride.

There is little data available on infrared spectra of lithium alkoxyaluminum hydrides. A value of 1690 cm$^{-1}$ ($\nu_{\text{Al-H}}$) has been reported for $LiAlH_4$ and its mono- and trimethoxy derivatives in THF.[10] However, other lithium trialkoxyaluminum hydrides show a shift in $\nu_{\text{Al-H}}$ to higher frequencies compared with that of $LiAlH_4$ (Table II, entries 9–11) and the same trend has been observed with lithium aryloxyaluminum hydrides[11] and alkoxy derivatives of aluminum hydride (Table III). Data has been unavailable in diethyl ether due to the general insolubility of lithium alkoxyaluminum hydrides.[10] Fortunately, we have found that the reaction of $LiAlH_4$ with 3 molar equiv of 2,4-dimethyl-3-pentanol, **4**, in diethyl ether results in clear, colorless solutions with no precipitation. The product of this reaction is represented as the trialkoxy species **5** expected on the basis of the reactant stoichiometry and the evolution of 3 molar equiv of hydrogen (eq 3). The infrared spectrum of **5** in ether shows $\nu_{\text{Al-H}}$ = 1795 cm$^{-1}$ (Table II, entry 4), considerably higher than that for $LiAlH_4$. Disproportionation to $LiAlH_4$ does not occur in this case probably because of steric hindrance in the tetraalkoxy species.[12] Heating the solution under reflux for 1 h did not change the spectrum.



$$LiAlH_4 + 3CH_3-\underset{\mathbf{4}}{\overset{CH_3}{\overset{|}{CH}}-\overset{OH}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}}-CH_3 \rightarrow LiAlH(OR)_3 + 3H_2 \qquad (3)$$

**5**, R = 2,4-dimethyl-3-pentyl

The reaction product **5**, unlike $LiAlH_4$ is highly stereoselective in the reduction of **1**, giving 96% of *trans*-**2** (Table I, entry 5).

The possibility that the reaction of $LiAlH_4$ with **4** leads to tricoordinate species,[11,13] for example, via the process

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(6) R. J. McMahon, K. E. Wiegers, and S. G. Smith, *J. Org. Chem.*, **46**, 99 (1981).

(7) H. C. Brown and C. J. Shoaf, *J. Am. Chem. Soc.*, **86**, 1079 (1964).

(8) References 3, 4; also O. Červinka, *Collect. Czech. Chem. Commun.*, **30**, 2403 (1965).

(9) Examination of the deformation vibration region ($\delta_{\text{Al-H}}$) of the infrared spectra showed that in addition to absorption near 760 cm$^{-1}$ (which is also present in the spectra of $LiAlH_4$ and the reaction product of $LiAlH_4$ with 2-propanol), there is an absorption peak near 730 cm$^{-1}$. Therefore, $LiAlH_4$ is not the sole species present in solution after the reaction of $LiAlH_4$ with isobutyl alcohol.

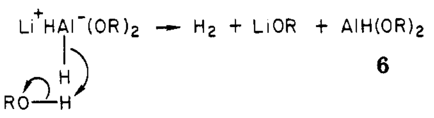
(10) E. C. Ashby, F. R. Dobbs, and H. P. Hopkins, Jr., *J. Am. Chem. Soc.*, **97**, 3158 (1975).

(11) H. Haubenstock, T. A. Mester, Jr., and H. Zieger, *J. Org. Chem.*, **45**, 3443 (1980).

(12) $LiAlH_4$ reacted readily with 3 molar equiv of **4** at ice-bath temperature, but addition of a fourth molar equiv of **4** did not occur as shown by very little gas evolution. There is no appreciable reaction at room temperature (ca. 20 °C), but some additional hydrogen is evolved on refluxing the ether solution.

(13) The term tricoordinate is used in reference to the empirical formula $AlH_n(OR)_{3-n}$, $n$ = 0–3 without regard to the probable association of such species or to their interaction with solvent.

shown by eq 4, was investigated. Diethyl ether solutions



(4)

6

R = 2,4-dimethyl-3-pentyl

of $AlH_n(OR)_{3-n}$ were prepared by the reaction of 4 with $AlH_3$. The infrared Al–H stretching frequencies ($\nu_{Al-H}$) for these tricoordinate compounds are shown in Table III. The Al–H stretching frequency observed for $AlH_3$, 1783 $cm^{-1}$, agrees with the value reported by Ashby and coworkers.[14,15] The higher values of $\nu_{Al-H}$ for the alkoxyaluminum hydrides are consistent with those reported for the analogous isopropoxy derivatives[16,17] and with bis(aryloxy)aluminum hydride.[11] A comparison of infrared $\nu_{Al-H}$ values shown in Tables II and III shows that tricoordinate aluminum species are not formed in the reaction of $LiAlH_4$ with 4. Furthermore, the reduction of ketone 1 (in excess) with 6 gave 33% *trans*-**2**, in marked contrast to reduction of 1 with 5.

## Discussion

The reaction of $LiAlH_4$ with 2-propanol results in a solution of $LiAlH_4$. Reaction of $LiAlH_4$ with isobutyl alcohol appears to give a solution containing $LiAlH_4$ as a significant species. It is possible that this occurs through disproportionation of intermediate species. However, it is also possible that a series of reactions leads sequentially to the tetraalkoxy species (Scheme I). This latter scheme is possible because of the rapidity of the reactions involved, and under the relatively inefficient mixing conditions employed in preparative work, a local high concentration of alcohol exists during its addition to the hydride solution.[6] The present data do not distinguish between these two alternative reaction paths leading to the tetraalkoxy species.

Scheme I[a]

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

[a] R = $Bu^i$ or $Pr^i$.

On the other hand, lithium alkoxyaluminum hydride species are clearly the reaction products in the addition of 3 molar equiv of methanol or ethanol to $LiAlH_4$ as shown by the stereoselectivity of reduction of 1 (Table I, entries 2 and 3). In these cases it is probable that the tetraalkoxy species are also rapidly formed. However, with these less sterically hindered alcohols, and in contrast to the branched isopropyl or isobutyl alcohols, the tetraalkoxy species back-reacts with $LiAlH_4$ to form the trialkoxy species (eq 5).[20] This process has been demonstrated for

$$3LiAl(OR)_4 + LiAlH_4 \rightarrow 4LiAlH(OR)_3 \quad (5)$$
$$R = Me \text{ or } Et$$

methanol[7] and we have now demonstrated its feasibility for ethanol by the following experiment. The tetraethoxy species was prepared by the reaction of $LiAlH_4$ with 4 molar equiv of ethanol (4 equiv of hydrogen was evolved). This was followed by the addition of a one-third molar equivalent of $LiAlH_4$ in accordance with eq 5, and the resulting reaction mixture was used to reduce 1. The result was the formation of 86% *trans*-**2**, identical within experimental error with that shown in Table I, entry 3.

In summary, the back-reaction of $LiAl(OEt)_4$ leads to lithium ethoxyaluminum hydride species (eq 5). There is a reduced tendency for this to occur in the reaction of $LiAlH_4$ with isobutyl alcohol. No evidence for back-reaction exists with 2-propanol. In the case of the highly hindered doubly branched alcohol 4, the tetraalkoxy species is not formed under the reaction conditions.[12]

## Experimental Section

2,4-Dimethyl-3-pentanol was obtained from the Aldrich Chemical Co. Alcohols were kept over 4A molecular sieve. Diethyl ether (anhydrous grade) was distilled from $CaH_2$ under dry nitrogen.[21] It was usually predried over KOH pellets. Infrared spectra were recorded on a Beckman 4260 spectrophotometer. Spectra of hydride solutions were taken with 0.1-mm NaCl solution cells fitted with septa, purged with nitrogen, and filled by syringe.

Lithium aluminum hydride solutions were prepared by refluxing the solid reagent (obtained from Alfa-Ventron) with dry ether under nitrogen. After the residue settled, the solution was filtered under positive nitrogen pressure.[22,23] The hydride solutions were standardized by titration.[24] Analyses of reduction products were carried out by gas chromatography. The reduction products are readily separated on Carbowax 20 M columns.

**Reaction of $LiAlH_4$ with Isobutyl Alcohol.** A solution of $LiAlH_4$ in ether (10.0 mL of 1.22 M $LiAlH_4$, 12.2 mmol of $LiAlH_4$) was added by syringe to a 100-mL, three-neck flask equipped with condenser, equilibrated addition funnel, and septa. The apparatus had been flamed under dry nitrogen. A solution of isobutyl alcohol (38.3 mmol in 20 mL of ether) was added dropwise with magnetic stirring. Hydrogen gas evolution (36.0 mmol) was measured with a wet test meter. After addition of the alcohol, the reaction mixture was diluted with 10 mL of ether and a portion was filtered through a sintered glass funnel under nitrogen. The filtrate was sampled by syringe for infrared analysis. The filtered solid residue was washed with dry ether, placed in a flask attached to the wet test meter, and hydrolyzed. No gas evolution occurred. It is possible, however, that the solid contained active hydride species prior to the ether washing.

In a similar experiment 1 was added to the reaction mixture after a portion had been removed for filtration and infrared analysis.

**Reaction of $LiAl(OEt)_4$ with $LiAlH_4$. Reduction of 1.** In an apparatus similar to that described above, a solution of ethanol (48.8 mmol in 8 mL of ether) was added to 10.0 mL of 1.21 M $LiAlH_4$ (12.1 mmol of $LiAlH_4$) and 44.7 mmol of hydrogen evolution measured on the wet test meter. An additional 3.3 mL of 1.21 M $LiAlH_4$ (4.0 mmol of $LiAlH_4$) was then added followed by a solution of 1 (10.0 mmol in 8 mL of ether). After workup in the usual manner, gas chromatographic analysis showed 86% *trans*-**2**, 14% *cis*-**2** (normalized to 100%), and 2% 1.

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(19) E. C. Ashby, J. P. Sevenair, and F. R. Dobbs, *J. Org. Chem.*, **36**, 197 (1971).

(20) The triethoxy species is undoubtedly not a unique product of this reaction. It is present as a mixture with other lithium ethoxyaluminum hydride species.[7]

(21) D. R. Burfield, K.-H. Lee, and R. H. Smithers, *J. Org. Chem.*, **42**, 3060 (1977).

(22) H. C. Brown, "Organic Syntheses via Boranes", Wiley, New York, 1975, Chapter 9.

(23) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, 1969.

(24) H. Felkin, *Bull. Soc. Chim. Fr.*, 347 (1951). A solution of iodine in toluene was used instead of benzene.

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**Registry No.** 1, 873-94-9; 4, 600-36-2; 5, 84752-55-6; $LiAlH_4$, 16853-85-3; $CH_3OH$, 67-56-1; $CH_3CH_2OH$, 64-17-5; $(CH_3)_2CHCH_2OH$, 78-83-1; $LiAl(OEt)_4$, 18460-81-6; 2-propanol, 67-63-0.

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# Palladium-Catalyzed Syntheses of Conjugated Polyenes

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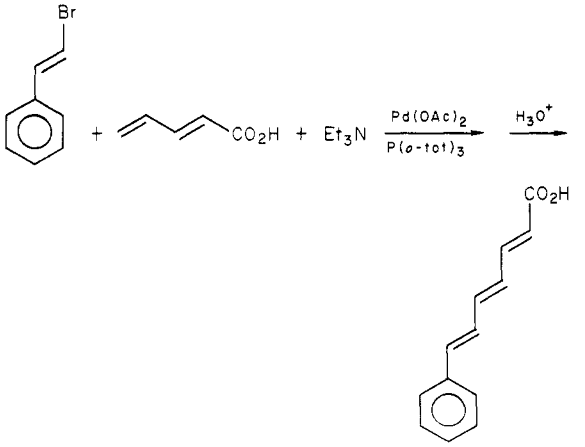
Conjugated trienes have been prepared by the palladium-catalyzed reaction of vinylic bromides with 2,4-pentadienoic acid and its 3-methyl derivative, in the presence of triethylamine. Methyl (*E*)-3-bromo-2-methylpropenoate also forms conjugated trienes and in some instances also tetraenes when it is reacted with 1,3-dienes under similar conditions. Some loss of stereochemistry in the starting vinylic bromide or, more often, in the diene may occur in the reactions presumably because equilibrating $\pi$-allylic intermediates are involved. 1,3,5-Hexatriene and 2 equiv of methyl (*E*)-3-bromo-3-methylpropenoate form orange-red dimethyl (*E,E,E,E,E*)-2,11-dimethyl-2,4,6,8,10-dodecapentaenedioate in modest yield.

Conjugated trienes often have been obtained as minor products in the palladium-catalyzed reactions of vinylic bromides with conjugated dienes and piperidine or morpholine.[1] In these reactions $\pi$-allylic palladium complexes were intermediates, and they underwent nucleophilic substitution with the secondary amine present more easily than they underwent elimination to form the conjugated trienes. The relative ease of elimination vs. substitution, however, depends significantly upon the substituents in the vinylic bromide and diene. We have reported the formation of a conjugated triene in reasonably good yield (57%) when a carboxyl group is conjugated with the diene group in the reaction employing triethylamine as the base.[2] (eq 1). The aromatic ring conjugated with the double bond in the vinylic bromide probably also assisted the reaction since it appears, not unexpectedly, that the $\pi$-allylic complexes in these reactions are relatively destabilized because decomposition by elimination gives highly conjugated systems. We have observed this effect frequently in reactions of vinylic halides with various alkenes.[3]



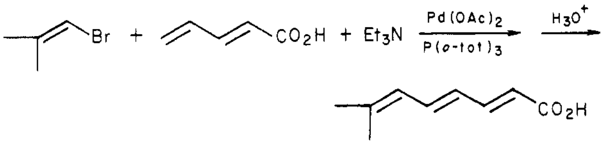
(1)

We now report further studies on the synthesis of conjugated polyenes by the reaction.

## Results and Discussion

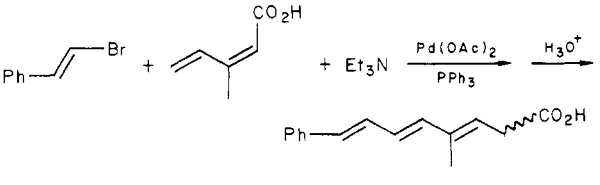
**Conjugated Trienes.** Several additional reactions of vinylic bromides with conjugated dienes have been studied to better define the scope of the reaction.

It is not necessary to have an aryl group in the vinylic bromide as well as the carboxyl group in the diene in order for the elimination to occur with triethylamine. 2-Methyl-1-bromo-1-propene reacts with (*E,E*)-2,4-pentadienoic acid with the usual $Pd(OAc)_2$–$P(o\text{-}tol)_3$ catalyst and triethylamine to form (*E,E,E*)-7-methyl-2,4,6-octatrienoic acid in 50% yield (eq 2). The low yield is probably mainly due to instability of the product and reactants under the reaction conditions. We were unable to isolated a product from a similar reaction of (*E*)-1-bromo-1-propene with 2,4-pentadienoic acid.



(2)

The reaction of (*E*)-$\beta$-bromostyrene with (*Z*)-3-methyl-2,4-pentadienoic acid was carried out to determine the stereoselectivity of the reaction. If the reaction proceeds by way of a $\pi$-allylic palladium intermediate, equilibration of isomers would be expected, and the *E,E,E* product should be formed since syn-$\pi$-allylic complexes are favored. The reaction at 100 °C gave a 70:30 2*Z*,4*E*,6*E*/2*E*,4*E*,6*E* triene isomer mixture in 40% yield with 6% triphenyl phosphine and 2% $Pd(OAc)_2$ as a catalyst (eq 3). These conditions were the most favorable found for



(3)

retention of the stereochemistry in reactions forming 2,4-

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(2) Patel, B. A.; Dickerson, J. E.; Heck, R. F. *J. Org. Chem.* **1978**, *43*, 5018.

(3) Kim, J.-I.; Patel, B. A.; Heck, R. F. *J. Org. Chem.* **1981**, *46*, 1061.