calibrated against the heat of fusion of indium at 156.6°, ΔH_f = 6.75 cal/g.

X-Ray Diffraction.—The X-ray powder diffraction spectra were obtained with a North American Philips Co. diffractometer and a recording geiger counter using Cu Kα radiation. Different crystalline forms were obtained by crystallization from solvent or controlled heating in the thermal analysis equipment. Lightly ground samples of each form (~10 mg) were scanned at 1° 2 θ min^{-1}. More severe grinding was avoided to prevent possible distortion of the soft crystals and decreased resolution of the pattern. The d spacing in Å (with relative intensity in parentheses) is given in Tables I–III for the most intense lines.

Acknowledgment.—The authors thank the National Science Foundation for supporting this work under the RANN Program, Grant No. GI-33645x.

Registry No.—Phenyl β-D-glucopyranoside, 1464-44-4; trehalose, 99-20-7; 1,6-anhydro-β-D-altropyranose, 10339-41-0; *p*-methoxyphenyl β-D-glucopyranoside, 6032-32-2; phenyl 2-acetamidotri-*O*-acetyl-β-D-glucopyranoside, 13089-21-9; *p*-methoxyphenyl 2-acetamidotri-*O*-acetyl-β-D-glucopyranoside, 38229-72-0; phenyl β-D-xyloside, 4756-31-4; *p*-bromophenyl 2-acetamido-2-deoxy-β-D-glucoside triacetate, 38229-74-2; *p*-iodophenyl 2-acetamido-2-deoxy-β-D-glucoside triacetate, 38229-75-3.

Stereochemistry of the Exhaustive Methylation of Alcohols with Trimethylaluminum

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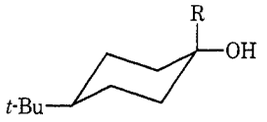
Received April 26, 1973

Exhaustive methylation of the pair of epimeric 4-*tert*-butyl-1-cyclohexanols with 1-ethyl and 1-vinyl substituents using trimethylaluminum proceeds with the loss of stereochemistry at the new quaternary carbon center. Axial and equatorial cyclohexanols give the same mixture of axially and equatorially methylated products with a preference for axial methylation. Methylation occurs *via* a common intermediate, which is not the olefin (the major side product of exhaustive methylation), since separate experiments show that methylalumination of olefin is not important under reaction conditions. A carbonium ion pair intermediate containing an oligomeric aluminum oxide counterion is proposed. Under forcing conditions, methylalumination of the olefins occurs with a strong preference for equatorial methylation. Exhaustive methylation of the allylic cyclohexanols proceeds with predominant rearrangement. Unrearranged products are formed nonstereospecifically as with the saturated analog. However, a common allylic carbonium ion intermediate cannot alone account for all the products.

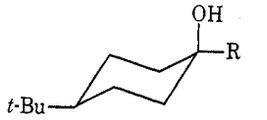
Exhaustive methylation of tertiary alcohols given in eq 1 can be achieved with trimethylaluminum.[1] Since

$$R_3COH \xrightarrow{(CH_3)_3Al} R_3CCH_3 \qquad (1)$$

the quaternization of carbon centers is a useful synthetic objective, we examined the stereochemistry of the replacement of the hydroxyl function by a methyl group in the stereoisomeric alcohols, *cis*- and *trans*-4-*tert*-butyl-1-ethylcyclohexanol (**1c** and **1t**)[2] and *cis*- and *trans*-4-*tert*-butyl-1-vinylcyclohexanol (**2c** and **2t**).[3]



1t, R = C_2H_5
2t, R = C_2H_3



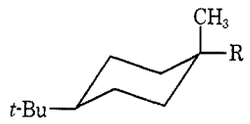
1c, R = C_2H_5
2c, R = C_2H_3

Results

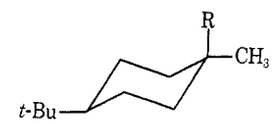
Each of the *tert*-butyl-substituted cyclohexanols (ROH) reacted vigorously with trimethylaluminum (TMA) on mixing at room temperature to afford a mixture of alkoxydimethylalanes and methane (eq 2).

$$ROH + (CH_3)_3Al \longrightarrow ROAl(CH_3)_2 + CH_4 \qquad (2)$$

Heating the benzene solution of the alkoxydimethylalanes with a threefold excess of trimethylaluminum and a small amount of water in sealed tubes afforded the expected methylated products as a mixture of cis and trans isomers. Significant amounts of elimination

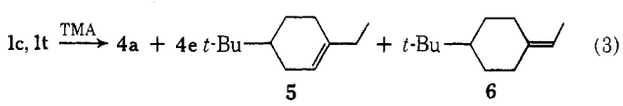


4a, R = C_2H_5
7a, R = C_2H_3



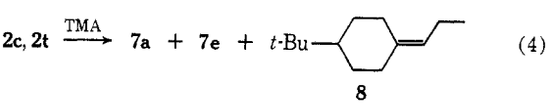
4e, R = C_2H_5
7e, R = C_2H_3

products **5** and **6** shown in eq 3 were also formed. The



(3)

5 **6**



(4)

8

allylic isomer of **2c** and **2t**, the cyclohexylidene alcohol **3**, also afforded in eq 5 the same products as those

(5)

3

derived from **2c** and **2t**, although in different isomeric ratios, as shown in Table I.

The structures of the axial and equatorial methylation products (**4a** and **4e**) were assigned by an analysis of the nmr spectra of isolated samples. The C-1 methyl resonance (δ 0.77) in **4e** appears at higher field than the corresponding methyl resonance (δ 0.80) in **4a** owing to steric deshielding of the axial methyl by the axial 3 and 5 hydrogens.[4] These assignments were confirmed by

(1) A. Meisters and T. Mole, *J. Chem. Soc., Chem. Commun.*, 595 (1972).
(2) G. D. M. Meakins, R. K. Percy, E. E. Richards, and R. N. Young, *J. Chem. Soc. C*, 1106 (1968).
(3) R. J. Ouellette, K. Liptak, and G. E. Booth, *J. Org. Chem.*, **31**, 546 (1966).
(4) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley-Interscience, New York, N. Y., 1972, p 43.

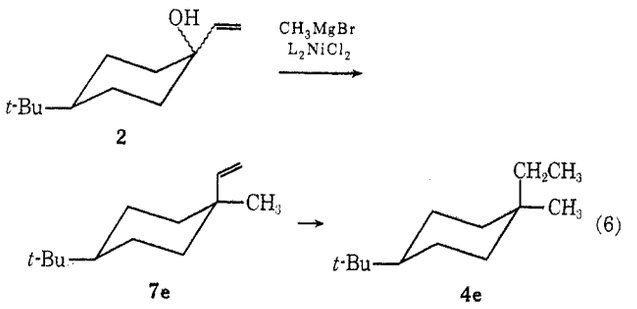
TABLE I

EXHAUSTIVE METHYLATION OF *tert*-BUTYLCYCLOHEXANOLS

Reactant	Temp, °C	Methylation products: Relative yield, % 4a	4e		Overall yield, %	Elimination products yield, % 5 + 6
1c[a]	150	70	30		49	34
1t[b]	150	67	33		14	16
		7a	7e	8		
2c	150	6	7	88	23	
	115	11	11	78	32	
2t	150	6	7	87	29	
	115	11	12	77	30	
3	115	3	80	17	75	

[a] Average of six runs. [b] Average of three runs.

an independent synthesis of **4e** by hydrogenation of the corresponding olefin (**7e**), the major product[5] of



exhaustive methylation of a mixture of the epimeric alcohols (**2**)[6] with methylmagnesium bromide in the presence of bis(triphenylphosphine)nickel dichloride.[7] The elimination products 4-*tert*-butyl-1-ethylcyclohexene (**5**) and 4-*tert*-butyl-1-ethylidenecyclohexane (**6**) were identified by comparison with authentic samples,[8] as were the methylation products **7a**, **7e**, and **8**.[5]

The overall yields from the saturated alcohols **1c** and **1t** varied considerably from run to run, but the product ratios of **4a** and **4e** were reasonably constant. The unreacted alcohol accounted for the remainder of the material balance shown in Table I and was recovered unisomerized from each epimer.

Heating of either 4-*tert*-butyl-1-ethylidenecyclohexane (**6**) or 4-*tert*-butyl-1-ethylcyclohexene (**5**) with 1 equiv of dimethyl methyoxyaluminate and excess trimethylaluminum in benzene at 175° for 60 hr gave mostly unreacted olefin and less than 3% of a mixture of **4e** and **7e**. No trace of **4a** was detected in the reaction mixtures.

(5) (a) M. Joly-Goudket, Thesis, University of Paris-Sud Centre d'Orsay, 1972. (b) These structural assignments were based on the synthesis of **7a** and **7e** from the corresponding 4-*tert*-butyl-1-methylcyclohexylacetic acids whose structures were established (C. Amsterdamsky, Thesis, Universite de Paris-Sud Centre d'Orsay, 1969) by the Barbier–Wieland degradation to the corresponding methyl 4-*tert*-butyl-1-methylcyclohexanecarboxylates, since the axial acid, *cis*-4-*tert*-butyl-1-methylcyclohexanecarboxylic acid, was known [H. O. House and T. M. Bare, *J. Org. Chem.*, **33**, 943 (1968)]. In addition, it was shown that the methyl ester of the equatorial acid is saponified much more readily than the hindered axial epimer. These esters also exhibit infrared bonds characteristic of equatorial (1253 cm^{-1}) and axial (1170, 1195, 1220 cm^{-1}) esters [*cf.* M. Fetizon and S. Bory, *Bull. Soc. Chim. Fr.*, 570 (1964)].

(6) K. W. Egger and A. T. Cocks, *J. Amer. Chem. Soc.*, **94**, 1810 (1972), and references cited therein.

(7) C. Chuit, H. Felkin, C. Frajerman, G. Roussi, and G. Swierczewski, *Chem. Commun.*, 1604 (1968).

(8) (a) E. J. Corey and G. T. Kwiatkowski, *J. Amer. Chem. Soc.*, **88**, 5652 (1966); (b) D. J. Pasto and F. M. Klein, *J. Org. Chem.*, **33**, 1468 (1968).

Discussion

Exhaustive methylation of the stereoisomeric saturated tertiary alcohols **1c** and **1t** affords methylation products **4e** and **4a** by a nonstereospecific substitution. A mechanism which incorporates a common intermediate such as a carbonium ion would accommodate the experimental results. The axial alcohol **1c** is more reactive than the equatorial isomer **1t**, and suggests that acceleration due to release of steric strain accompanies a rate-determining cleavage of the C–O bond. Preferential delivery of the methyl group to the resulting tertiary cyclohexyl carbonium ion intermediate from the axial direction is preferred, since torsional interactions of the ethyl substituent with the equatorial hydrogens on C-2 and C-6 (which develop during equatorial bond formation) hinder "equatorial" delivery of a methyl group.[9] In addition, the counterion in an ion-pair intermediate (*vide infra*) could shield one side of the cyclohexane ring. The "equatorial" ion pair would be favored over the more sterically congested "axial" ion pair, resulting in preferential shielding of the "equatorial" side of the cyclohexane ring.

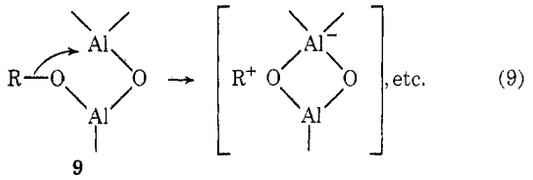
It was previously noted that the temperature and the time required for exhaustive methylation may be lowered significantly by the addition of a few mole per cent of water.[1] This observation could indicate the formation of oxygen-bridged polynuclear aluminum alkoxides such as **9**, as reactive intermediates in the following manner.

$$ROAl(CH_3)_2 + H_2O \longrightarrow ROAl(CH_3)OH + CH_4 \quad (7)$$

$$ROAl(CH_3)OH + (CH_3)_3Al \xrightarrow{-CH_4} ROAl(CH_3)OAl(CH_3)_2, \text{ etc.} \quad (8)$$

9

The lack of epimerization of the aluminum alkoxides during the reaction indicates that C–O bond cleavage is irreversible. Thus, if the reaction involves heterolysis of the C–O bond, the resulting oxyanion must be a relatively poor nucleophile. The effect of water as well as the nonnucleophilicity of the postulated anionic aluminum oxide leaving group would be explained by the concerted (anchimerically assisted) formation of a polynuclear aluminum anion.[10] from an oxygen-bridged polynuclear aluminum alkoxide as shown in eq 9. Thus, instead of forming an oxy anion by simple



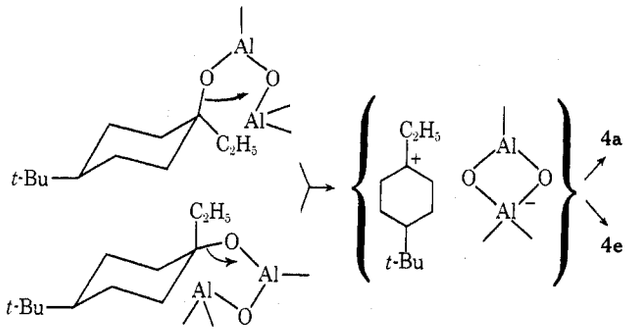
9

C–O heterolysis, a neighboring aluminum atom may act as an internal Lewis acid catalyst. The sequestering of the oxygen atoms of the resulting aluminum

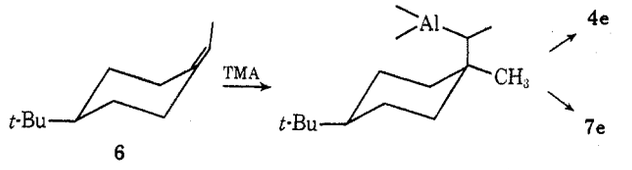
(9) (a) F. R. Jensen, L. H. Gale, and J. E. Rodgers, *J. Amer. Chem. Soc.*, **90**, 5793 (1968); (b) S. D. Elakovich and J. G. Traynham, *J. Org. Chem.*, **38**, 873 (1973).

(10) (a) The partial structure indicated in the scheme for this anion is only one of many possibilities. The actual structure may even be polymeric and several structurally different species may be involved. (b) Alternatively, Dr. E. C. Ashby has kindly suggested ionization of the dimer, *e.g.*, $[ROAl(CH_3)_2]_2 \rightleftharpoons R^+ + OAl_2(CH_3)_4OR^-$, etc.

oxide anion by chelation would lead to their diminished nucleophilic reactivity.



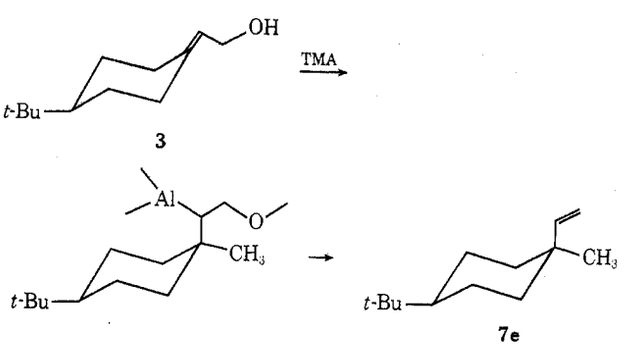
Olefins **5** and **6** are the major side products of the exhaustive methylation reaction. The possibility that methylation of **1c** and **1t** might proceed indirectly *via* methylalumination of **5** and **6** was examined. Under the conditions of the exhaustive methylation (*i.e.*, 150°) no reaction was detected. Under more forcing conditions (*i.e.*, 175°), a low yield of **4e** but no **4a** was observed. A small amount of **7e** was also formed,



6

presumably by dehydroalumination of an alkylaluminum intermediate. Methylalumination of **5** and **6** must vary in importance during the course of the exhaustive methylation, being favored at higher temperatures and as the concentrations of these olefins build up.

Both stereoisomeric allylic alcohols (**2c** and **2t**) produce the same relative yields of unrearranged quaternary methylation products (**7a** and **7e**). As with the saturated analogs, the lack of stereospecificity suggests a common intermediate prior to the formation of these products. The relative yield of **7a** and **7e** from the exhaustive methylation of the alcohol **3** is much different from that observed from the alcohols **2c** and **2t**. Moreover, exhaustive methylation of the allylic alcohols **2c**, **2t**, and **3** proceeds with predominant allylic rearrangement. A common intermediate from **2c**, **2t**, and **3**, such as an allylic carbonium ion, cannot alone account for all of the products. The preferential formation of the equatorially methylated **7e** from the hydroxyethylidenecyclohexane **3** is reminiscent of the



3 **7e**

preferential formation of **4e** by methylalumination of the ethylidenecyclohexane **6**. A preference for "equatorial" methylalumination of **3** or **6** is expected since "axial" methylalumination would be sterically hindered by axial hydrogens. Neighboring heteroatoms are known to facilitate alkylmetalation of olefins.[11] Thus methylalumination of **3** followed by elimination is a reasonable mechanism for production of **7e**. A similar mechanism may be operative for the production of **8** from **2c** or **2t**. Other mechanisms, such as S_N2' or S_Ni processes, may also be operative.

Experimental Section

Materials.—Trimethylaluminum was obtained from the Ethyl Corp. and used as such. The stereoisomeric alcohols *cis*- and *trans*-4-*tert*-butyl-1-ethylcyclohexanol (**1c** and **1t**) and *cis*- and *trans*-4-*tert*-butyl-1-vinylcyclohexanol (**2c** and **2t**) were prepared by known procedures.[2,3] 4-*tert*-Butyl-1-(2′-hydroxyethylidene)-cyclohexane (**3**) was prepared by the lithium aluminum hydride reduction of ethyl-4-*tert*-butylcyclohexylidene acetate.[12]

Preparative gas chromatography (vpc) was carried out with a Varian A-90 chromatograph. Analytical vpc utilized a Varian Hy Fi instrument. Trimethylaluminum was vacuum transferred into a cooled receiver. Benzene was distilled from sodium benzophenone ketyl under nitrogen. Nmr spectra were recorded with a Varian A-60 spectrometer. Mass spectra were measured with a Varian CH7 instrument. Microanalyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich.

Exhaustive Methylation.—The appropriate alcohol (200 mg, 1.09 mmol) was combined with a solution of trimethylaluminum in benzene (1.4 ml of a 3 *M* solution) with judicious cooling. Water (2 μl) was added cautiously and the mixture was sealed in a heavy-walled glass tube (about 20 ml volume). The mixture was then heated in a steel bomb using benzene as an external solvent for pressure equalization. The reaction mixture was cooled with liquid nitrogen and carefully opened (methane produced). After dilution with pentane (50 ml) followed by hydrolysis with 5% hydrochloric acid (20 ml), the clear pentane extract was washed with saturated aqueous $NaHCO_3$, dried with $MgSO_4$, and concentrated by distillation of the solvent through a 20-cm Vigreux column. Product yields from **1c** and **1e** were determined (after addition of *n*-tetradecane as internal standard) by vpc on a 10 ft × 0.125 in. column packed with 20% FFAP on 60/80 AW Chromosorb W. Relative retention times follow: **4e**, 0.73; **4a**, 0.79; **6**, 0.87; **5**, 0.90; *n*-tetradecane, 1.00. Products were isolated by vpc on a 10 ft × 0.25 in. column packed with Apiezon J on firebrick at 160°, on which the olefins **5** and **6** have shorter retention times than the hydrocarbons **4e** and **4a**. The sample of **4e** thus obtained was further purified by vpc on 9 ft × 0.25 in. column packed with 15% FFAP on Chromosorb W. The products **4e**, **5**, and **6** were identified by comparison with authentic samples. In addition, **4e** and **4a** were characterized by elemental analysis.

4-*tert*-Butyl-*cis*-1-ethyl-*trans*-1-methylcyclohexane (4e).—*Anal.* Calcd for $C_{13}H_{26}$: C, 85.63; H, 14.37. Found: C, 85.76; H, 14.27.

4-*tert*-Butyl-*trans*-1-ethyl-*cis*-1-methylcyclohexane (4a).—*Anal.* Calcd for $C_{13}H_{26}$: C, 85.63; H, 14.37. Found: C, 85.74; H, 14.42.

Product yields from **2c**, **2t**, and **3** were determined (after addition of *n*-pentylbenzene as internal standard) by vpc on the above FFAP column. Relative retention times follow: **7e**, 0.53; **7a**, 0.62; **8**, 0.82; *n*-pentylbenzene, 1.00. The mass spectra of these products as well as their vpc retention times were identical with those of authentic samples prepared by known procedures.[5]

4-*tert*-Butyl-*trans*-1-methyl-*cis*-1-vinylcyclohexane (7e).—The title compound was prepared by bis(triphenylphosphine)nickel(II) dichloride catalyzed exhaustive methylation of a mixture of *cis*- and *trans*-4-*tert*-butyl-1-vinylcyclohexanols (**2**)[6] with methyl-

(11) (a) J. K. Crandall, and A. C. Clark, *J. Org. Chem.*, **37**, 4236 (1972), and references cited therein. (b) A. H. Veefkind, J. v. d. Schaff, F. Bickelhaupt, and G. W. Klumpp, *Chem. Commun.*, 722 (1971), and references cited therein.

(12) H. O. House, W. L. Respess and G. M. Whitesides, *J. Org. Chem.*, **31**, 3128 (1966).

magnesium bromide.[7] Distillation of the product mixture under reduced pressure yielded a sample of the title compound (**7e**) as the major component of the reaction mixture (about 90% pure), bp 74–76° (0.6 mm).[5]

Hydrogenation of the Olefin 7e.—The olefin was stirred under a blanket of hydrogen in methyl acetate solution with a suspension of 5% Pd/C to afford a hydrocarbon whose nmr spectrum and vpc retention time were identical with that of the equatorially methylated isomer **4e**.

Methylalumination of 5 and 6.—The olefins **5** or **6** plus 1 equiv of methanol were substituted for the tertiary alcohols in the exhaustive methylation procedure described above. A component of the reaction mixture in each case had a vpc retention time identical with that of **4e** and **7e**. The mass spectrum of this component resembled that obtained by the superposition of spectra of authentic samples of **4e** and **7e**.

4-*tert*-Butyl-1-(2′-hydroxyethylidene)cyclohexane (3).—Ethyl-4-*tert*-butylcyclohexylidene acetate[3] was reduced in the usual manner with $LiAlH_4$ in ether, giving **3**, bp 82–83° (0.4 mm), in 86.4% yield.

Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 78.97; H, 12.21.

Acknowledgment.—We wish to thank the National Science Foundation for financial support of this work, the Ethyl Corporation for a gift of trimethylaluminum, and Dr. Hugh Felkin for results concerning the vinyl alcohols (**2a** and **2e**) and methyl derivatives (**7a** and **7e**) prior to publication.

Registry No.—**1c**, 17328-78-8; **1t**, 25143-76-4; **2c**, 7103-35-7; **2t**, 7103-36-8; **3**, 41498-18-4; **4a**, 41498-76-4; **4e**, 41498-77-5; **7e**, 41498-78-6; trimethylaluminum, 75-24-1; methyl bromide, 74-83-9.

Preparation of Organometallic Complexes by Reduction of Magnesium Alkyls with Alkali Metals

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Received March 7, 1973

The reduction of dialkylmagnesium compounds in hydrocarbon solution by alkali metals was studied and found to yield organometallic complexes of definite stoichiometries involving magnesium and alkali metals. In most cases, the reduction appeared to occur according to the stoichiometry below, *i.e.*, a 1:1 complex was formed: $2M + 3R_2Mg \rightarrow 2R_3MgM + Mg\downarrow$. Lithium reacted to form both the 1:1 complex and a 3:1 complex, R_3MgLi_2. Results with sodium were not so straightforward, but it appeared that this metal reduced dialkylmagnesium compounds to form a 1:2 complex (R_5Mg_2Na) as well as the 1:1 complex. Potassium, rubidium, and cesium also reduced dialkylmagnesium compounds to yield 1:1 complexes. These intermetallic reagents are viewed as complexes between alkali metal alkyls and magnesium alkyls; this complex formation solubilizes and stabilizes the alkali metal alkyls. The latter compounds, with the exception of lithium alkyls, had previously been known only as insoluble, relatively unstable species. A structure for the hydrocarbon-soluble 1:1 complexes was proposed in which a di-*sec*-butylmagnesium unit in the di-*sec*-butylmagnesium dimer is replaced by an organoalkali compound.

In 1951 Wittig,[2] Meyer, and Lange reported that reaction of diphenylmagnesium and phenyllithium resulted in the formation of a 1:1 complex in ether (eq 1). After the addition of xylene, the complex

$$PhLi + Ph_2Mg \longrightarrow Ph_3MgLi \quad (1)$$

precipitated as a crystalline compound, mp 212°. Recently there has been considerable interest in the preparation of additional examples of intermetallic complexes involving magnesium and alkali metals illustrated for the general case with magnesium in eq 2, where R is alkyl, aryl, or hydrogen and M is alkali metal.

$$nR_2Mg + RM \longrightarrow [R_2Mg]_n \cdot [RM] \quad (2)$$

The preparation of "lithium *n*-butyldimethylmagnesium" complex was reported by Coates and Heslop.[3] Removal of solvent after reaction of *n*-butyllithium with dimethylmagnesium in diethyl ether yielded a viscous liquid of stoichiometry $[n\text{-BuLi}] \cdot [Me_2Mg] \cdot [OEt_2]$. Coates and Heslop also attempted to prepare alkali metal–alkylmagnesium hydride complexes analogous to $NaEt_2BeH$[4] and $NaH \cdot 2Et_2Zn$.[5] These attempts were unsuccessful owing to cleavage of the solvent ether by the alkali metal hydride.

More recently, Ashby and Arnott[6] have reported the preparation and characterization of several complexes between alkali metal hydrides and dialkylmagnesium compounds. Their initial attempts to prepare these species by reaction of magnesium alkyls in ether with alkali metal hydrides resulted in extensive ether cleavage, consistent with the results of earlier work by Coates and Heslop.[3] However, Ashby and Arnott were able to isolate one stable complex from an ether solution by reaction of diphenylmagnesium with potassium hydride at room temperature. The complex precipitated from the ethereal reaction mixture and analysis showed it to be $KH \cdot 2Ph_2Mg$. By reaction of the hydrocarbon-soluble di-*sec*-butylmagnesium[7] with solid potassium hydride, a relatively stable solution of a 1:1 complex was obtained which was soluble in cyclohexane and benzene. Reaction of sodium hydride with di-*sec*-butylmagnesium resulted in the formation of $[NaH] \cdot 2[sec\text{-}Bu_2Mg]$, but lithium hydride would not react.

Seitz and Brown[8] have studied organometallic exchange reactions by lithium-7 and proton nuclear magnetic resonance, and have reported that alkyllithium

(1) Correspondence should be addressed to D. B. Malpass, Texas Alkyls, Inc., P. O. Box 600, Deer Park, Texas 77536.

(2) G. Wittig, F. J. Meyer, and G. Lange, *Justus Liebigs Ann. Chem.*, **571**, 167 (1951).

(3) G. E. Coates and J. A. Heslop, *J. Chem. Soc. A*, 514 (1968).

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