Preparation and Properties of Di-*sec*-butylmagnesium

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New synthetic procedures for obtaining dialkylmagnesium reagents are illustrated with the preparation of di-*sec*-butylmagnesium. The procedures, which can yield magnesium reagents with or without solvation by a Lewis base, involve either direct synthesis of the magnesium alkyl from alkyl chloride and metal under conditions causing magnesium halide to precipitate, or reaction of a magnesium halide with an alkyllithium reagent causing lithium chloride to precipitate. The latter reaction will occur in a hydrocarbon medium, free of basic solvent, if one employs an activated form of magnesium chloride. A number of characteristics of di-*sec*-butylmagnesium are reported, including formation of crystalline complexes ($R_2Mg \cdot base$) with the bicyclic bases triethylenediamine and methyltriethylenediamine. When free of basic solvation, di-*sec*-butylmagnesium is a mobile liquid which is completely miscible with hydrocarbons; this property distinguishes it from all previously characterized magnesium alkyls. A dimeric structure (R_4Mg_2) is proposed for the *sec*-butylmagnesium reagent, analogous in size to tetrameric *sec*-butyllithium (R_4Li_4).

The preparation and properties of unsolvated dialkylmagnesium reagents have received relatively little attention. By direct reaction of amyl chloride with magnesium, Glaze and Selman[1] have recently produced di-*n*-amylmagnesium free of solvation. The amyl reagent was found to be a viscous liquid which was at least partially miscible in benzene. A freezing point depression suggested that this reagent was dimeric in benzene; however, the high viscosity of the mixture, 0.17 *M* in reagent, indicates a higher order of association. Previous investigators[2] have not been able to prepare secondary and tertiary dialkylmagnesium reagents by direct reaction of alkyl halides with magnesium in the absence of basic solvents, and we have confirmed this observation. The smaller normal dialkylmagnesium reagents (C_1–C_4) and one branched reagent (diisopropylmagnesium) have been prepared by indirect methods and have been found to be solids and to be essentially insoluble in both aromatic and aliphatic hydrocarbons.[3] Such properties are rational on the basis of a polymeric (self-associated) structure of these reagents when they are unsolvated, *i.e.*, free of complexation by Lewis bases.

In a preliminary report[4] we have described the preparation of several alkylmagnesium reagents in ethereal or mixed ether–hydrocarbon solvents (*i.e.*, in the presence of Lewis bases) by reaction of the corresponding Grignard and alkyllithium reagents (eq 1). The present report is to illustrate details of that

$$RMgCl + RLi \rightarrow R_2Mg + LiCl \qquad (1)$$

preparation with di-*sec*-butylmagnesium and to report a new method for obtaining this reagent directly in hydrocarbon solvents in the absence of Lewis bases. The di-*sec*-butylmagnesium obtained has been found to be a mobile liquid, *miscible in hydrocarbon solvents in all proportions*, in contrast to all previously known magnesium alkyls. Our initial effort to obtain a hydrocarbon-soluble magnesium reagent was stimulated by the knowledge that basic solvation of organometallic reagents can profoundly modify their reactivity but that reactions of magnesium alkyls in the absence of solvation had never been studied.

Preparation of Di-*sec*-butylmagnesium.—The direct reaction of magnesium metal with *sec*-butyl chloride alone or in hydrocarbon solvents could not be caused to take place even at elevated temperatures. Addition of a limited amount of an ether to these mixtures allowed the direct reaction to proceed in a hydrocarbon and good yields of product to be obtained (eq 2). Di-*sec*-butylmagnesium obtained in this manner was desolvated (freed of ether) by codistillation with hydrocarbon solvents such as benzene or cyclohexane. A particularly reactive form of magnesium was needed for this direct reaction of secondary halides in hydrocarbon with a limited amount of ether, as well as for reaction of primary halides in hydrocarbon alone, and was obtained by stirring commercially available magnesium powder with *n*-butyllithium in hexane overnight.

$$2sec\text{-}BuCl + 2Mg \xrightarrow[10\%\ CH_3OCH_3]{\text{hexane}} (sec\text{-}Bu)_2Mg + MgCl_2\downarrow \qquad (2)$$

When the limited amount of ether in the direct synthesis was diethyl ether, only a relatively small portion of magnesium chloride precipitated. However, precipitation of the chloride could be forced by removal of ether through codistillation with a hydrocarbon solvent or by vacuum stripping to dryness and redissolving the di-*sec*-butylmagnesium in hydrocarbon. Alternatively chloride could be removed by precipitation as LiCl as in eq 1. If, instead of diethyl ether, dimethyl ether was employed, $MgCl_2$ did precipitate almost completely (*ca.* 90%) during the reaction (eq 2). The remaining soluble portion of the chloride could be precipitated as $MgCl_2$ during a distillative desolvation step. Thus, it appears that ethers other than dioxane may cause reversible formation (and precipitation) of $MgCl_2$ from RMgCl solutions. Characteristic experimental details about the direct synthesis are given in Table I.

The principal synthesis used in this work to obtain unsolvated di-*sec*-butylmagnesium in hydrocarbon solvents involved the reaction of *sec*-butyllithium in hexane solution with various "activated" forms of magnesium chloride (eq 3). A variety of processes were

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[1] W. H. Glaze and C. M. Selman, *J. Organometal. Chem.*, **5**, 477 (1966).

[2] (a) L. I. Zakharkin, O. Yu Okhlobystin, and B. N. Strunin, *Dok. Akad. Nauk. SSSR*, **147**, 108 (1962); (b) D. Brycesmith and G. F. Cox, *J. Chem. Soc.*, 1175 (1961).

[3] (a) W. Strohmeier, *Ber.*, **88**, 1218 (1955); W. Strohmeier and F. Seifert, *Ber.*, **94**, 2356 (1961); (b) G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. I, Methuen and Co. Ltd., London, 1967, pp 97–102.

[4] C. W. Kamienski and J. F. Eastham, *J. Organometal. Chem.*, **8**, 452 (1967).

TABLE I

DIRECT PREPARATION OF DI-*sec*-BUTYLMAGNESIUM FROM *sec*-BUTYL CHLORIDE

Reactants		Solvents		Reaction	Reaction	Final concn of	
sec-BuCl, mol	Mg, g-atom	Hydrocarbon	Ether	time, hr	temp, °C	$(sec\text{-Bu})_2Mg$, *M*	% yield[a]
0.10	0.10	Cyclohexane[b]	DME	48	25	0.39[c]	80
0.39	0.42	Benzene[d]	Et_2O	3	77	0.30[e]	78
0.40	0.40	Benzene[f]	Et_2O	4	35	0.85[g]	79

[a] Yields were based on analyses of aliquots of filtered solutions for active alkyl, magnesium, and chlorine. [b] Reaction initiated at −30° in 100 ml of DME, which was then largely displaced by 100 ml of cyclohexane so that the final solution contained *ca.* 2 molar equiv of DME/mol of $(sec\text{-Bu})_2Mg$. [c] Active alkyl/chloride ion ratio, 9; addition of an amount of *sec*-BuLi equivalent to the chloride ion caused precipitation of LiCl and increased the active alkyl/chloride ion ratio to >100. [d] Amount of ether, 0.48 mol; *ca.* 800 ml of benzene. [e] Molar ratio of ether/magnesium reagent was 2 after distillation of 50% of the solvent; active alkyl/chloride ion ratio was 11. [f] Reaction carried to completion in ether, which was then removed by distillation, finally under vacuum. The residue was stirred with 50 ml of benzene which dissolved the magnesium reagent. [g] Active alkyl/chloride ion ratio was >100.

TABLE II

PREPARATION OF DI-*sec*-BUTYLMAGNESIUM FROM SYNTHETIC MAGNESIUM CHLORIDE

Reactants						
$MgCl_2$		*sec*-BuLi		Reaction	Reaction	% yield[a] of
Mol	Solvent	Mol	Solvent	time, hr	temp, °C	$(sec\text{-Bu})_2Mg$
0.25[b]	Benzene	0.40	Cyclohexane	2	25–35	90[c]
0.05[d]	Benzene	0.026	Cyclohexane	0.25	25–35	95[c]
0.09[e]	Benzene	0.026	Cyclohexane	0.25	25–35	95[c]
0.60[f]	Cyclohexane	0.89	*n*-Hexane	5	40	83

[a] Yields were based on analyses of aliquots of supernatant solutions for total base, active alkyl, and magnesium. These are recovered yields of product; lithium was not found in the solutions. [b] Washed solid by-product from direct reaction of *sec*-BuCl and Mg in benzene–DME. [c] Ether of complexation, present in quantities equivalent to $(sec\text{-Bu})_2Mg$ removed by distillative desolvation. [d] Washed solid by-product from direct reaction of *n*-AmCl and Mg in benzene. [e] Washed solids from distillation under vacuum of ether from *sec*-BuMgCl in ether. [f] Desolvated solid product from reaction of *sec*-BuMgCl with benzyl chloride.

TABLE III

PREPARATION OF DI-*sec*-BUTYLMAGNESIUM FROM COMMERCIAL MAGNESIUM CHLORIDE

Reactants and catalyst							
$MgCl_2$		RLi		DME,	Reaction	Reaction	% yield of
Mol	Solvent	Mol	Solvent	mol	time, hr	temp, °C	$(sec\text{-Bu})_2Mg$
0.22[a]	None	0.36	*n*-Hexane	0.44	16	10	87[b]
0.59[a]	None	0.80	*n*-Hexane	0.9	27	25–35	85[b]
1.16[a]	None	1.94	*n*-Hexane	2.1	22	0–25	85[b]
0.15[c]	Cyclohexane	0.11	Cyclohexane	None	16[d]	25	21[e]
0.5[f]	Benzene	0.026	Cyclohexane	None	16	25	61[e]
0.07[g]	Toluene	0.11	*n*-Hexane	None	4	30	76[e]
0.2[h]	Tetralin	0.12	*n*-Hexane	None	20	25	77[e]

[a] Anhydrous powdered $MgCl_2$ from Alfa Inorganics, Inc. [b] Yields were based on analyses of aliquots of supernatant reaction solutions for total base, active alkyl, and magnesium. Unless otherwise noted, there are recovered yields of product when lithium was not found in the solutions. [c] Anhydrous lump $MgCl_2$ (from Dow Chemical Co.) ball-milled in 100-ml of cyclohexane. [d] High speed stirring employed. [e] Per cent of total alkalinity represented by magnesium-containing compounds; lithium was still present in solution. [f] Anhydrous powdered $MgCl_2$ (Alfa) stirred vigorously overnight with ethyl ether, than desolvated with benzene. [g] Ball-milled lumps treated with isopropyl alcohol, then desolvated with toluene. [h] $MgCl_2 \cdot 6H_2O$ (from J. T. Baker Co.) dehydrated with isoamyl alcohol and then desolvated with tetralin.

used to obtain activated forms of magnesium chloride

$$2RLi + MgCl_2 \xrightarrow[\text{hexane}]{\text{benzene or}} R_2Mg + LiCl\downarrow \qquad (3)$$

which were used with varying degrees of success in this synthesis; *cf.* Tables II and III. No other activating process produced a salt which was as active or which reacted as completely with *sec*-butyllithium as that magnesium chloride obtained as a solid by-product from reaction of *sec*-butylmagnesium chloride with benzyl chloride (eq 4). Another of the processes which produced a magnesium chloride structure with relatively superior activity was reaction of *sec*-butylmagnesium chloride with chlorine in ether, followed by desolvation of the precipitated salt (eq 5). During the reaction with chlorine intermittent flashes of light were given off, indicative of a chemiluminescent reaction. Less successful processes involved desolvation

$$sec\text{-BuMgCl} + PhCH_2Cl \rightarrow MgCl_2 + \text{organic products} \qquad (4)$$

$$sec\text{-BuMgCl} + Cl_2 \rightarrow MgCl_2 + \text{organic products} \qquad (5)$$

of hydrated or alcohol-treated magnesium chloride. However, any of these activated salts[5] were a great improvement over ordinary anhydrous (commercially available) magnesium chloride; the ordinary reagent in hydrocarbons gave low conversions of *sec*-butyllithium to di-*sec*-butylmagnesium even in the presence of a large excess of the finely powdered salt.

The exchange reaction with ordinary anhydrous salt in hydrocarbons could be promoted by the addition of

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(5) Additional information and experimental details on activation of $MgCl_2$ and on other points discussed in this paper are given in the Ph.D. Dissertation of C. W. Kamienski, The University of Tennessee, 1967.

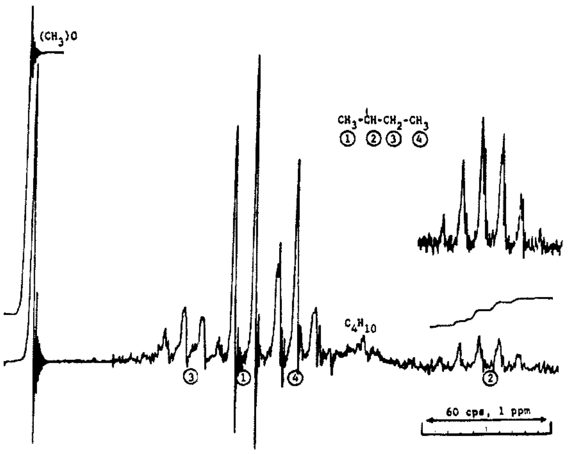

Figure 1.—Nmr spectrum from benzene solution of di-*sec*-butylmagnesium containing *ca.* 3 mol equiv of dimethyl ether.

2 equiv of ethyl ether to the reaction mixtures. To gain this activation the ether had to be present during the exchange; stirring the salt with the ether, but then removing it, did not facilitate the exchange. Since all reagents are commercially available, ethereal promotion of the exchange with ordinary anhydrous magnesium chloride is the most convenient preparation of solvated di-*sec*-butylmagnesium. Ether could then be removed by desolvation (codistillation with a hydrocarbon solvent), but this technique for obtaining unsolvated reagent is not so desirable as the reaction between *sec*-butyllithium and activated anhydrous $MgCl_2$ in pure hydrocarbons. The desolvation technique is a slow process and can lead to some cracking of the reagent.

The solutions of di-*sec*-butylmagnesium reagent prepared were characterized by a variety of analytical techniques. Active alkyl determinations were done in some cases by gas chromatographic analysis (vpc) of *sec*-butyl alcohol from air oxidation (eq 6) of the solutions, in some cases by vpc of the organic solutions

$$(sec\text{-Bu})_2Mg \xrightarrow[2.\ H_2O]{1.\ O_2} 2sec\text{-BuOH} \qquad (6)$$

before and after hydrolysis, and in all cases by use of a phenanthroline indicator and direct titration of the solutions themselves.[6] Nmr spectroscopy was also used to analyze the solutions directly, primarily for ether/organometallic ratios (*cf.* Figure 1); vpc also indicated this ratio. Hydrolysates of the solutions were used to determine total base, chlorine, and magnesium concentrations by conventional titrations and to determine lithium concentrations by flame photometry.

Each of the magnesium reagent preparations (eq 1, 2, and 3) could be carried out so that the final solution contained an amount of active alkyl equivalent to the total base within experimental error. This active alkyl was also the same as the equivalents of metal present minus the chloride ion. The chloride ion concentration in the solutions was essentially negligible in all cases except those involving the direct preparation (eq 2) in solvents containing some ether; in those preparations the chloride ion/active alkyl ratio approached 0.1. Addition of 1 equiv of *sec*-BuLi to such ethereal solutions reduced this ratio to <0.05. Chloride was then equivalent to the lithium present, *i.e.*, was soluble to the extent that LiCl is soluble in ethereal media. The chloride ion/active alkyl ratio was too small to measure, as was the lithium/magnesium ratio, when $MgCl_2$–*sec*-BuLi exchanges (eq 3) were carried out with an excess of unsolvated magnesium salt using a pure hydrocarbon solvent.

Properties of Di-*sec*-butylmagnesium.—Vacuum distillation of the hydrocarbon solvent from di-*sec*-butylmagnesium left it as a very light yellow, mobile liquid. In our hands the reagent could not be distilled without decomposition and, in the absence of complexing bases, could not be induced to crystallize. The liquid reagent was miscible in all proportions in hexane, benzene, cyclohexane, and mixtures of these solvents. The solutions were also quite mobile, having a viscosity approximately the same as the solvents alone. These properties are unusual in that all previously prepared unsolvated, *i.e.*, Lewis base free, dialkylmagnesium reagents are reported either to be infusible solid products which possess a very low order of solubility in hydrocarbon solvents[2,3] or to form viscous mixtures therein.[1]

A solid complex could be quantitatively precipitated from hydrocarbon solutions of di-*sec*-butylmagnesium by the addition of triethylenediamine (TED). Methyltriethylenediamine (MTED) also yielded a crystalline complex. While the TED derivative was extremely insoluble in hydrocarbon solvents, the MTED derivative was moderately soluble and could be recrystallized from cyclohexane. These complexes melt with decomposition at 201–203° and 160°, respectively. Analyses of the complexes showed that they contain a 1:1 ratio of magnesium reagent/amine, *e.g.*, $(sec\text{-Bu})_2Mg \cdot TED$.

Nmr chemical shifts for α hydrogen (the methine proton) in the *sec*-butyl group of magnesium, Grignard, and lithium reagents are shown in Table IV. The spread in these values, about 1.5 ppm, and the effect of solvent on them show that one cannot interpret such shifts simply in terms of the relative electro-

Table IV

Chemical Shift of the Methine Proton in the *sec*-Butyl Group of Magnesium and Lithium Reagents

Reagent[a]	Solvent	Additional base[b] (mol equiv)	Chemical shift[c]
R_2Mg	C_6H_6	Et_2O (1)	9.57
RMgCl	C_6H_6	Et_2O (1)	9.64
R_2Mg	C_6H_6	None	9.80
R_2Mg	C_6H_6	$(CH_3)_2O$ (2)	10.02
R_2Mg	C_6H_{12}	None	10.06
R_2Mg	C_6H_{12}	$(CH_3)_2O$ (2)	10.15
R_2Mg	C_6H_{12}	TMEDA[d] (2)	10.31
R_2Mg	C_6H_{12}	THF[e] (2)	10.35
RLi	C_6H_{12}	None	10.97
RLi	C_6H_6	None	11.01

[a] In every case R is *sec*-butyl. [b] Amount of base is in moles of base per gram atom of metal in solution. [c] Shift in τ of proton on carbon attached to metal. [d] Tetramethylethylenediamine. [e] Tetrahydrofuran.

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(6) S. C. Watson and J. F. Eastham, *J. Organometal. Chem.*, **9**, 1965 (1967).

negativity of the metal, *i.e.*, in terms of how the electronegativity of the metal determines "carbanion character" in the α position.[7] An α hydrogen in a self-associated lithium alkyl shifts upfield (becomes more shielded) as a consequence of solvation of the reagent by Lewis base, but, because such solvation does not dissociate the lithium alkyl to a monomeric structure, the shift is small.[8] Somewhat larger solvent effects can be seen (Table IV) in chemical shifts measured for the α hydrogen in di-*sec*-butylmagnesium. These effects will bear further study, but they probably are, in part, a consequence of solvation causing changes in the associated state of the magnesium alkyl. Preliminary colligative property measurements of di-*sec*-butylmagnesium in cyclopentane indicate that the reagent is self-associated in the hydrocarbon. Data are shown in Table V.

TABLE V

APPARENT DEGREE OF ASSOCIATION OF DI-*sec*-BUTYLMAGNESIUM IN CYCLOPENTANE MEASURED BY OSMOMETRY

Formula concn, *M*	Measured concn, *M*	Degree of assocn
0.36	0.171	2.10
0.36	0.175	2.05
0.18	0.087	2.07
0.18	0.092	1.96
0.09	0.040	2.25
0.09	0.042	2.08

Structure of Di-*sec*-butylmagnesium.—Variation in the degree of self-association can influence the nature of the physical state as well as the solubility characteristics of metal alkyls. Weiss[9] studied the crystal structure of solid magnesium alkyls by X-ray crystallography and described them as infinite chains. In the case of dimethylmagnesium, the unit cell is orthorhombic with an Mg–Mg distance of 2.73 Å; the metal atoms are connected by pairs of methyl bridges (Mg–C distance of 2.24 Å) with an almost tetrahedral arrangement of four methyl groups around each metal atom. These solid, insoluble associated structures of magnesium alkyls can be classed as typical electron-deficient polymers. Lithium alkyls associate only up to the hexameric state[10] and are appropriately classed as electron-deficient oligomers;[8,11] both *n*-butyllithium and *sec*-butyllithium are liquids at room temperature and are completely miscible with hydrocarbon solvents.[12] In contrast, the *n*-butylmagnesium reagent is an infusible solid at room temperature and possesses a low order of solubility in hydrocarbon solvents, while, as the present study has shown, the *sec*-butylmagnesium reagent is a liquid and is, like *sec*-butyllithium, miscible in all proportions with hydrocarbon solvents.

These comparisons in properties, as well as the data from colligative measurements (Table V) are rationalized with a dimeric structure for di-*sec*-butylmagnesium (Figure 2).[13] Using the C–Mg and Mg–Mg bond distances reported by Weiss[9] and using tetrahedral configurations around each Mg atom, it is possible to construct unstrained models of polymeric di-*n*-butylmagnesium, but it is not possible to construct associated forms of the *sec*-butyl reagent beyond the dimer state. This restricted ability to self-associate is due to the steric hindrance imposed by the presence of both an α- and a β-methyl group. Three α-methyl groups would also afford hindrance to polymerization, so that di-*t*-butylmagnesium can be expected to be dimeric.[14] Dimeric magnesium alkyls (R_4Mg_2) correspond in molecular size to the tetrameric oligomers (R_4Li_4) previously found for *sec*-butyllithium[15] and *t*-butyllithium.[16]

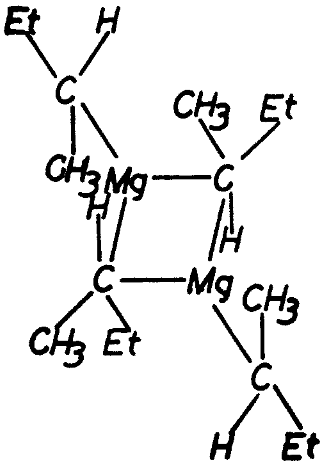

Figure 2.—Di-*sec*-butylmagnesium, a dimer.

Experimental Section[5]

Reagents.—*sec*-Butyllithium in *n*-hexane and cyclohexane solutions was obtained from Foote Mineral Co. Anhydrous triethylenediamine, mp 158–160°, and methyl triethylenediamine, a liquid, were obtained from Houdry Process and Chemical Co. Hydrocarbons used for ordinary solvent purposes were reagent grade and before use were dried with activated alumina and stored over Linde Molecular Sieves 4-A. Benzene and cyclohexane used for desolvation of di-*sec*-butylmagnesium and for active alkyl analyses were refluxed for at least 8 hr over anhydrous barium oxide and distilled into bottles (previously dried at 125°) containing 4-A sieves and sodium metal. Ethereal solvents were refluxed over lithium aluminum hydride and distilled into amber bottles containing 4-A sieves and sodium.

Analytical Techniques.—Total base and inorganic ion analyses were carried out on hydrolyzed samples of organometallic solutions. Magnesium was determined using a conventional complexometric titration involving an ethylenediamine tetraacetic acid disodium salt solution as titrant and "calmagite" obtained from the G. F. Smith Chemical Co. as indicator. Lithium was determined by flame photometry. Chloride ion was determined

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(7) G. Fraenkel, D. G. Adams, and J. Williams, *Tetrahedron Lett.*, 729 (1963).

(8) (a) Z. K. Cheema, G. W. Gibson, and J. F. Eastham, *J. Amer. Chem. Soc.*, **85**, 3517 (1963); (b) F. A. Settle, M. Haggerty, and J. F. Eastham, *ibid.*, **86**, 2076 (1964).

(9) E. Weiss, *J. Organometal. Chem.*, **2**, 314 (1964); *Ber.*, **98**, 2805 (1965).

(10) T. L. Brown, *Advan. Organometal. Chem.*, **3**, 365 (1966); D. Margerison and J. P. Newport, *Trans. Faraday Soc.*, **59**, 2058 (1963).

(11) J. F. Eastham, *J. Amer. Chem. Soc.*, **89**, 2237 (1967).

(12) D. H. Lewis, W. S. Leonhardt, and C. W. Kamienski, *Chimia* (Aarau), **18**, 134 (1964).

(13) It is assumed that the bridging and terminal *s*-butyl groups of the dimer shown in Figure 2 can exchange rapidly and give rise to an average nmr signal (*cf.* Figure 1) just as do the bridging and terminal groups of a dimeric aluminum alkyl.

(14) Work in progress with unsolvated di-*t*-butylmagnesium has now established that it too is miscible with hydrocarbons.

(15) W. H. Glaze, J. Lin, and E. Felton, *J. Org. Chem.*, **30**, 1258 (1965); W. H. Glaze, G. Adams, and J. Lin, Paper Presented at 22nd International Symposium on Organometallic Chemistry, Madison, Wis., Aug 1965.

(16) M. Weiner, G. Vogel, and R. West, *Inorg. Chem.*, **1**, 654 (1962).

by the standard Mohr procedure. Total alkalinity analyses were carried out by adding a known amount of acid and back-titrating with standard base. Active alkyl analyses were done directly on organometallic solution samples by titration with *sec*-butyl alcohol in xylene using a 9,10-phenanthroline indicator.

For vpc analyses of an organometallic solution, 0.5–1.0 ml of the solution was syringed slowly into a cooled conical test tube fitted with a rubber septum and containing *ca.* 1 ml of isopropyl or isoamyl alcohol. The tube was shaken thoroughly and a few drops of 6 N HCl was added to clarify the solution. The tube was centrifuged and 3–5 μl of the clear solution were syringed into the chromatograph for analysis. A similar technique was employed to determine the amount of ether or alcohol remaining in a desolvated slurry of anhydrous $MgCl_2$ mixed with hydrocarbon.

Preparation of Solvated Di-*sec*-butylmagnesium from *sec*-Butyl Chloride Followed by Desolvation. A. From a Dimethyl Ether–Cyclohexane Solvent.—A weight of 2.43 g (0.1 g-atom) of magnesium turnings and a few crystals of iodine were placed in a 500-ml flask fitted with a thermometer, mechanical stirrer, Dry Ice condenser, and dropping funnel. Enough dimethyl ether (DME), dried by passage over silica gel, was condensed into the flask to cover the turnings and 1–2 ml of *sec*-butyl chloride was added. After addition of a few drops of ethylene dibromide, reaction began. The remainder of 100 ml of DME was condensed into the flask at −25°, the remainder of 9.3 g (0.1 mol) of *sec*-butyl chloride was added, and, finally, 100 ml of cyclohexane was added gradually to the flask. The mixture was allowed to warm slowly to room temperature and stirred at room temperature for 2 days; a white slurry formed during this time. The reaction mixture was heated to 45° for 2 hr and allowed to cool and settle overnight. Analysis of the clear supernatant solution showed 0.77 N total base and 0.085 N chloride ion content. To this solution was added 8.0 mmol of *sec*-butyllithium in hexane. After filtration, analysis of the solution showed it to be 0.86 N in total base, 0.85 N in active alkyl, 0.43 M in Mg, <0.01 N in Li, <0.01 N in Cl, and 0.9 M in DME. After carbonation, air oxidation, and hydrolysis of samples of this solution, the only organic products found were, respectively, α-methylbutyric acid, *sec*-butyl alcohol, and butane. In other words, all of the analytical data indicated that the organometallic reagent in solution was solely di-*sec*-butylmagnesium. Solvent was distilled from a 50-ml portion of this solution for the purpose of removing DME, *i.e.*, for *desolvation.* After distillation of 40 ml of solvent, an equal volume of fresh hexane was added to the distillation flask. Thereafter, four 10-ml fractions of solvent were distilled consecutively. The DME in these four cuts were, respectively, 1.5, 0.83, 0.65, and 0.12%. After dilution with 40 ml of benzene, analysis of the residual solution indicated a molar ratio of di-*sec*-butylmagnesium/DME of 6. Ten milliliters of this solution was further desolvated by distillation from a smaller flask attached to a Vigreux column and fractionating head. During this process, the hexane solvent was completely replaced with benzene. After distillation of about 50 ml of solvent, analysis of the residual solution showed the absence of DME. Nmr chemical shifts (benzene internal standard) from the 1-, 2-, 3-, and 4-position protons of the 2-butyl groups in the organomagnesium reagent were found, respectively, at τ 8.53, 9.79, 7.92, and 8.20.

B. From an Initial Diethyl Ether Solvent.—A solution of Grignard reagent, prepared from 9.7 g (0.4 g-atom) of magnesium and 37 g (0.4 mol) of *sec*-butyl chloride in ethyl ether, showed a total base concentration of 2.20 N and an active alkyl concentration of 2.13 N. Eighty-five milliliters of this solution was transferred to flask equipped with a capillary tube for admitting nitrogen below the liquid level. This flask was heated with an oil bath temperature of 75°. After the residual mixture became quite viscous and only slowly evolved ether, it was further evacuated for 12 hr at 75°. The flask contents were stirred with about 50 ml of benzene at room temperature. The mixture thinned out and a granular white precipitate which settled was separated by centrifugation. The granular solid was washed several times with dry benzene, was found to be pure $MgCl_2$, free of ether, and was subsequently successfully used in an exchange reaction with *sec*-butyllithium as described in the next paragraph. The supernatant benzene solution showed equal total base and active alkyl concentrations, 1.70 N, negligible Cl content, and an ethyl ether/di-*sec*-butylmagnesium molar ratio of 0.7. The ether was not removed from this particular benzene solution, but with other hydrocarbon solutions of di-*sec*-butylmagnesium it was found to be easier to remove diethyl ether than to desolvate of DME (described above). Thus, in one experiment, 50 ml of 0.77 M di-*sec*-butylmagnesium and excess diethyl ether in cyclohexane was distilled through a Vigreux column while cyclohexane was added to maintain the residual volume. All of the ether was removed by and found in 90 ml of distillate.

Preparation of Unsolvated Di-*sec*-butylmagnesium from *sec*-Butyllithium and Active Anhydrous Magnesium Chloride.—Following the procedure of Glaze and Selman,[1] the product mixture from direct reaction of *n*-amyl chloride with magnesium was extracted several times with benzene to leave a solid residue of $MgCl_2$. To 10 ml of a slurry containing 4.8 g (50 mmol) of this $MgCl_2$ in benzene in a centrifuge tube fitted with a rubber septum was added 20 ml of 1.3 N *sec*-butyllithium–cyclohexane. The mixture, which became warm initially and then cooled while it was shaken for 10–15 min, was centrifuged. The supernatant solution showed 1.10 N total base, 1.02 N active alkyl, 0.55 M magnesium, and 0.003 N chloride ion content. Spectroscopic properties of this solution were identical with those of the solutions obtained in the direct syntheses described above. Analysis of a sample of the hydrolyzed product showed no alcoholic impurities and showed *n*-butane as the only hydrocarbon resulting from hydrolysis.

Synthesis of Active Anhydrous Magnesium Chloride from Grignard Reagents. A. By Reaction with Benzyl Chloride.—To a Grignard reagent solution, prepared from 0.4 mol of *sec*-butyl chloride and 0.4 g-atom of magnesium in 150 ml of ethyl ether, was added, at reflux and with vigorous stirring, 0.5 mol of benzyl chloride. A precipitate of $MgCl_2$ began to form immediately and copious gas evolution was noted. [Vpc of the gas indicated that it was 1- and 2-butenes and *n*-butane. Products found in the solution (vpc) were 12% toluene, 70% 1,2-diphenylethane, and 18% 2-methylbutylbenzene.] The precipitate of $MgCl_2$ was washed five times with 10-ml portions of benzene, allowing the solids to settle each time before removing the wash. The fifth wash was found to contain *ca.* 5% ethyl ether. The slurry after the fifth wash showed 2.7 M Mg, 6.0 N Cl, and <0.01 N total base content. Continued washing of the solids did not remove all of the ethyl ether. The ether was removed by continuous codistillation with benzene until the residual slurry contained a mole ratio of ether/$MgCl_2$ of <0.01. The slurry was then used as such for reaction with *sec*-butyllithium in hydrocarbon media as described in the preceding paragraph.

B. By Reaction with Chlorine.—A Grignard reagent was prepared from 24.3 g (1.0 g-atom) of magnesium and 92.5 g (1.0 mol) of *sec*-butyl chloride in 500 ml of ethyl ether. Chlorine gas, diluted with argon, was bubbled into the solution for 3 hr. As chlorine passed in to the vigorously stirred mixture, intermittent bright flashes of light appeared (chemiluminescence) every 1–2 sec. The solvent refluxed spontaneously, and, toward the latter part of reaction, a gray-black vapor was noted in the flask and condenser. (Chemiluminescence has been previously observed on reaction of Grignard reagents with oxygen.[17]) Eventually a thick, porridgelike mass formed in the flask, and the chemiluminescence ceased. Analysis of the supernatant solution showed that a 70% consumption of *sec*-butylmagnesium chloride had occurred. After 300 ml of benzene was added to the flask, most of the ether was removed by distillation. The residual mixture was filtered and the solid salt was washed three times with benzene and transferred as a slurry in benzene to a distillation unit where the ether was distilled with the aid of benzene. The slurry was then successfully used for exchange with *sec*-butyllithium as described in the preceding paragraph.

Activation of Commercial Anhydrous $MgCl_2$.—Small lumps, 0.25 in. in diameter, of anhydrous $MgCl_2$ (40 g) were treated with 200 ml of dry isopropyl alcohol; heat was evolved. After about 1 hr of vigorous stirring of the thick mixture, 100 ml of toluene was added and distillation was begun. Successive portions of toluene were added to the residue to replace the solvent distilled. After distilling about 450 ml of toluene, analysis of the residual slurry showed a mole ratio of $MgCl_2$/isopropyl alcohol of 20. Distillation to remove isopropyl alcohol was continued; some reaction of $MgCl_2$ was occurring since HCl

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[17] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., pp 1273, 1274.

appeared in the distillate. After an additional 600 ml of toluene was distilled, analysis showed a mole ratio of the salt/alcohol of *ca.* 50. To 175 ml of the slurry, 6.5 g (68 mmol) of $MgCl_2$, was added 90 ml of 1.24 *N sec*-butyllithium in hexane. The mixture was stirred vigorously, first at 40° for 1.5 hr, then at room temperature overnight. The supernatant solution on analysis showed a 0.31 *N* total base, 0.29 *N* active alkyl, and 0.15 *M* Mg content.

Reaction of *sec*-Butyllithium with Commercial Anhydrous Magnesium Chloride. A. Without Added Ether.—In a 1-qt jar containing smooth milling stones were placed 380 g of lump anhydrous $MgCl_2$ and 400 ml of cyclohexane and the jar was sealed, all under nitrogen. The mixture was rolled overnight on a jar mill. A sample of the slurry of finely ground salt (100 ml, 14 g of $MgCl_2$, 0.15 mol) was added to 85 ml of 1.3 *N sec*-butyllithium (0.11 mol) in cyclohexane. After the mixture was stirred overnight at room temperature, the supernatant solution was 0.53 *N* in total base and 0.055 *M* in Mg. Heating the mixture and further stirring did not bring more Mg into solution.

B. With DME Present.—A second sample of the jar milled $MgCl_2$ (0.22 mol), 360 ml of 1.0 *N sec*-butyllithium (0.36 mol) in *n*-hexane, and 20 g of DME (0.44 mol) were stirred together at 0° for 2 hr and then overnight at room temperature. The supernatant solution was found to be 0.86 *N* in total base, 0.85 *N* in active alkyl, and 0.43 *M* in Mg.

Insoluble Complexes of Di-*sec*-butylmagnesium with Amines. A. With Triethylenediamine (TED).—To 5.0 ml of a 0.85 *N* solution of di-*sec*-butylmagnesium (2.13 mmol) in benzene–cyclohexane in a nitrogen-flushed dry centrifuge tube fitted with a serum cap was added 3.0 ml of an 0.69 *M* solution of TED (2.07 mmol) in cyclohexane. A crystalline precipitate formed immediately. After the mixture was shaken thoroughly, it was centrifuged, the supernatant was withdrawn, and the solids were washed twice with cyclohexane. Nmr analysis of a solution of the washed solid in THF showed a TED/di-*sec*-butylmagnesium mole ratio of 1. In another experiment, 3.2 ml of 0.69 *M* TED (2.2 mmol) in cyclohexane was added to 9.1 ml of 0.98 *N* di-*sec*-butylmagnesium (4.4 mmol) in benzene in a tared centrifuge tube. The fine-grained white crystalline precipitate which formed was centrifuged, washed three times with *n*-pentane, and dried at 80–90° under nitrogen, all in the original centrifuge tube, which was then reweighed to determine a yield of 0.52 g, which is essentially quantitative for a 1:1 $TED \cdot R_2Mg$ complex. The complex melted with decomposition (gas evolution) at 201–203° in a sealed capillary. Active alkyl analysis of the complex showed an equivalent weight of 248 [theory for $(C_4H_9)_2Mg \cdot C_6H_{12}N_2$, 250]. The complex decomposed spontaneously in air.

B. With Methyltriethylenediamine (MTED).—A volume of 5.5 ml of 0.85 *N* di-*sec*-butylmagnesium (2.3 mmol) solution in benzene–cyclohexane was added to a centrifuge tube containing 2.4 mmol of MTED dissolved in 3 ml of benzene. The fine crystalline precipitate which formed slowly was centrifuged and the supernatant solution was drawn off. The solid (0.54 g) was recrystallized from 9 ml of benzene to give monoclinic prisms, which, after washing and drying, melted at 160° dec in a sealed capillary. Nmr analysis of a solution of these crystals in THF showed the presence of a 1:1 mole ratio of di-*sec*-butylmagnesium/MTED.

Additional Characterization of Di-*sec*-butylmagnesium in Hydrocarbon Solution. A. Air Oxidation.—A solution prepared by dilution of 5 ml of 0.81 *N* di-*sec*-butylmagnesium in hexane with 20 ml of hexane was stirred at 0° while dry air was bubbled into it through an 18-gauge needle for 1 hr. After the reaction mixture was hydrolyzed with 5 ml of saturated aqueous ammonium chloride, the organic layer was analyzed by vpc. Only 2-butanol was found under conditions which would have also revealed any other alcohol boiling <250°.

B. Carbonation.—A 10-ml sample of 0.77 *N* di-*sec*-butylmagnesium in hexane–cyclohexane was added to a stirred mixture of crushed Dry Ice and ether. Most of the ether was evaporated on a steam bath and the residual slurry was transferred to a centrifuge tube, where, after centrifugation, the solids were washed with three portions of ether, dried at 100° in a stream of nitrogen, and then dissolved in D_2O. The nmr spectrum of the D_2O solution showed, as the only organic material which could be detected, α-methylbutyrate ion.

C. Addition to Benzophenone.—To a solution of benzophenone (*ca.* 1.5 mmol) in 2 ml of benzene there was added slowly 5 ml of 0.77 *N* di-*sec*-butylmagnesium (1.9 mmol) in hexane–cyclohexane. The reaction mixture was poured into a stirred mixture of ice and 3 *N* aqueous HCl. After the aqueous layer was separated and washed with ether, the combined organic layers were dried and evaporated to leave the product as a residue, which was analyzed both by nmr and vpc. Both analyses indicated that the benzophenone, none of which was recovered, had been converted into a mixture of reduction product, benzhydrol (*ca.* 75%), and addition product, *sec*-butyldiphenylcarbinol (*ca.* 25%).

D. Solubility Properties.—Distillation of the solvent from benzene, hexane, or cyclohexane solutions of di-*sec*-butylmagnesium was carried out numerous times and at no time did phasing occur. In some cases all volatile solvent was removed from solutions leaving the magnesium reagent as a liquid. This liquid dissolved all quantities of benzene or cyclohexane added to it.

E. Colligative Properties.—The liquid di-*sec*-butylmagnesium reagent obtained by removal of solvent from a hydrocarbon solution was a thin oil which could be easily handled at room temperature with a syringe and 20-gauge needle. The reagent could not be induced to crystallize; one attempt to distil it under high vacuum was unsuccessful. One sample of the liquid was prepared by a particularly careful distillation of solvent from a solution which had shown equivalent concentrations of active alkyl, total base, and magnesium. A weighed portion of this sample was diluted with cyclopentane (previously purged with nitrogen) to give a solution 0.36 *M* in magnesium reagent. The state of reagent association in this solution, which is estimated to contain *ca.* 0.01 *M* impurities, was examined by comparison with 0.40 *M* trimethylaluminum in cyclopentane using a Mechrolab, Inc., vapor phase osmometer. To make the comparison the thermistor bridge was first balanced with 1 drop of the aluminum reagent solution on each thermistor, after which magnesium reagent solution was used to replace the drop on one thermistor and the change in resistance of that thermistor measured. Prior to making these comparisons a calibration plot of resistance change *vs.* solution concentration was obtained by similar comparisons of the dimeric aluminum reagent solution with three dilutions of the 0.40 *M* solution. In all comparisons an excess of *ca.* 1 *M* aluminum reagent solution was maintained in the thermistor compartment to provide constant solvent vapor pressure. Resistance changes for several dilutions of the 0.36 *M* magnesium reagent solutions were obtained. The measured concentrations of magnesium reagent, the corresponding molarities, and the ratios of these two values, the degree of association are given in Table V.

Registry No.—Di-*sec*-butylmagnesium, 17589-14-9; di-*sec*-butylmagnesium 1:1 complex with TED, 19190-84-2; di-*sec*-butylmagnesium 1:1 complex with MTED, 19202-57-4.