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SHORT COMMUNICATIONS

Preparation of hydrocarbon solutions of unsolvated dialkylmagnesium reagents

Review of the literature on the subject reveals a general belief that unsolvated dialkylmagnesium reagents constitute a class of compounds which are insoluble in hydrocarbons, presumably as a consequence of their polymeric state of association[1-3]. Now, however, Glaze and Selman[4] have prepared di-n-amylmagnesium in benzene solution, and by cryoscopic measurements, found the reagent to be dimerically associated. To prepare their solution, these authors directly reacted n-amyl chloride and magnesium powder at 85° and extracted the semisolid product with refluxing benzene for two hours.

We have found that di-sec-butylmagnesium is conveniently prepared in ether by reaction of the corresponding Grignard reagent with sec-butyllithium (1). Removal of the ether can be effected at 80° by addition of a hydrocarbon and distillation of this solution, both in a continuous manner. The desolvated di-sec-butylmagnesium is quite miscible with hydrocarbons, *e.g.*, hexane or benzene. Diisobutylmagnesium prepared and desolvated in a similar manner, is less soluble, about 0.1 moles/liter in benzene. Surprisingly, addition of approximately an equivalent of di-sec-butylmagnesium in hexane to the dry, white solid diisobutylmagnesium caused it to dissolve completely, yielding a solution containing approximately 0.8 moles/liter of the dialkylmagnesium mixture. We expect di-sec-butylmagnesium will solubilize other of the alkyls which may be relatively insoluble, even the smallest dialkylmagnesium compounds, presumably by formation of mixed sec-butylalkylmagnesium reagents. We have prepared another dialkylmagnesium mixture, "iso-butylmethylmagnesium", via reaction (1) of isobutylmagnesium chloride in ether with an equivalent of methyllithium. When desolvated of ethyl ether by continuous distillation with benzene, the isobutyl-methyl reagent is unexpectedly soluble in benzene, *ca.* 0.7 moles/liter at 25°.

$$\mathrm{RLi+RMgCl} \xrightarrow{\text{ether}} \mathrm{R_2Mg+LiCl}\downarrow \qquad (1)$$

It should be stressed that our preparations of the magnesium alkyls in ethereal solution contain little halogen, *i.e.*, a halide/base ratio of *ca.* 0.02, and in hydrocarbon solution contain essentially no halogen. We have also observed that a solution containing a halide/base ratio of about 0.1 can be produced directly by reaction of magnesium with sec-butyl chloride in a cyclohexane/dimethyl ether (95:5) solvent. This reaction course (2) appears to follow the normal pattern observed during direct preparation of alkyllithium compounds[5]. After reaction (2), added sec-butyllithium will react (1) to remove that halide which remains in solution, and in fact, will react with the precipitated $MgCl_2$ *in situ* to form another equivalent of di-sec-butylmagnesium. Even with dimethyl ether, if desolvation is desired a period of continuous distillation with hydrocarbon is still required. We were unsuccessful in removing all

$$\mathrm{2\,Mg+2\,RCl} \xrightarrow[\text{in cyclohexane}]{\text{5\% dimethyl ether}} \mathrm{R_2Mg+MgCl_2}\downarrow \qquad (2)$$

dimethyl ether from the dialkylmagnesium solutions by simple vacuum stripping at 50°.

Di-tert-butylmagnesium was readily prepared (1) in diethyl ether from tert-butylmagnesium chloride and tert-butyllithium. However, in this case attempted desolvation by continuous distillation with benzene at 80° caused thermal decomposition to MgH_2 and 1-butene. Apparently rearrangement occurs during pyrolysis for no isobutylene was obtained from the decomposition. Desolvation under milder conditions (possibly from a dimethyl ether/cyclohexane solution) is indicated in this case.

The origin of the mistaken belief that unsolvated halogen-free magnesium alkyls are insoluble can probably be attributed to problems in their preparation. Thus it has been difficult to free the reagent of the ethereal solvation introduced in the common dioxane-precipitation method[2]. The mercury exchange method is extremely slow in ether-free hydrocarbons and will leave the magnesium reagent contaminated with mercury. Direct reaction of alkyl halide and magnesium can produce reagents with various halide/base ratios, *i.e.*, m/n in the empirical formulation (I)[1]. The interrelation of this ratio, reagent solubility, and the rate of establishment

$$\frac{n}{2}\,R_2Mg + \frac{m}{2}\,MgX_2 \rightleftarrows R_nMg_{0.5(n+m)}X_m \quad \text{(I)} \qquad (3)$$

of the many equilibria represented by (3), will determine what is or is not found in solution after reaction under particular conditions of solvent, time and temperature. Direct reaction conditions can be found to prepare magnesium reagents in solution with negligible or low halide/base ratios, *cf.* Glaze's preparation[4] and our preparation (2), respectively, but for the time being we find it most convenient to prepare dialkylmagnesium reagents by precipitation of the halide as LiCl, preparation (1).

With the availability of hydrocarbon solutions of unsolvated magnesium reagents, it should be possible to analyze their structures and the structures of their solvates by modern physical techniques, particularly by the techniques recently used with lithium reagents*. Analogies between these two types of electron deficient reagents can already be seen. Ethereal solvation can increase the solubility of both magnesium and lithium reagents. Choice of the branched chain magnesium alkyls for our initial solubility study was based on previously obtained solubility information on organic lithium compounds in hydrocarbons[9]. Formation of specific mixed-alkylmagnesium reagents, suggested by our solubility data, finds analogies with both mixed lithium alkyls[10] and mixed aluminum alkyls[11]. Dimeric association of diamylmagnesium observed by Glaze[4] can be considered analogous to tetrameric association of a lithium alkyl[6-8], *i.e.*, R_4Mg_2 can be compared to R_4Li_4.

Perhaps the most interesting analogy is the influence of the corresponding metal halide on each reagent. Reactivity of unsolvated lithium reagents has been extensively studied and attenuation of their reactivity by lithium halide is well established[12,13], but there have been no studies of the relative reactivity of unsolvated magnesium reagents *without* halide. Results which we will report subsequently show a striking increase in the reactivity of a dialkylmagnesium reagent over a Grignard reagent [or species like (I)] in some reactions.

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* For a recent review see ref. 6; *cf.* also refs. 7 and 8.

TABLE 1

DATA ON R_2Mg SOLUTION PREPARATIONS

R_2Mg prepared	*Reactants*								*Orig. conc. ethereal R_2Mg*	*Final conc. R_2Mg*	*Final solvent*
	RMgCl				*RLi*						
	R	*Solvent*	*Amount*	*Conc.*	*R*	*Solvent*	*Amount*	*Conc.*			
$(n\text{-}Bu)_2Mg$	n-Bu	Bu_2O	29 g	40 wt.%	n-Bu	heptane	40 ml	2.4 *M*	0.84 *M*	1.0 *M*	benzene[a]
(iso-Bu)MeMg	iso-Bu	Et_2O	72 ml	1.12 *M*	Me	Et_2O	48 ml	1.7 *M*	0.76 *M*	0.72 *M*	benzene
$(sec\text{-}Bu)_2Mg$	sec-Bu	Et_2O	87 ml	1.03 *M*	sec-Bu	C_6H_{12}	30 g	19 wt.%	0.78 *M*	0.92 *M*	cyclohexane
$(sec\text{-}Bu)_2Mg$	sec-Bu	Me_2O[b]	130 ml	0.77 *M*	sec-Bu	hexane	57 g	11 wt.%	0.46 *M*	0.68 *M*	hexane/ cyclohexane[c]
$(iso\text{-}Bu)_2Mg$	iso-Bu	Et_2O	89 ml	0.88 *M*	iso-Bu	Et_2O	80 ml	0.96 *M*	0.42 *M*	0.1 *M*[d]	cyclohexane
$(tert\text{-}Bu)_2Mg$	tert-Bu	Et_2O	53 ml	0.91 *M*	tert-Bu	pentane	55 ml[e]	1.44 *M*	0.82 *M*	—	benzene[f]

[a] Solution contained di-n-Bu_2O. [b] Solvent was 5% dimethyl ether in cyclohexane. [c] From this solution there was obtained a 1.35 *M* $(sec\text{-}Bu)_2Mg$ solution in benzene by vacuum distilling the hexane/cyclohexane and redissolving the residual viscous liquid in benzene. [d] White precipitate formed; N.E., 66; calcd. for $(iso\text{-}Bu)_2Mg$, 69. [e] This volume of tert-butyllithium added to react with tert-BuMgCl and with solid by-product $MgCl_2$ present. [f] Solution contained ethyl ether. Heating to 80° caused thermal decomposition with the formation of a black precipitate.

Experimental

Analytical methods. Ethereal solutions of magnesium alkyls were obtained clear and colorless typically as described in the following paragraph. After filtration to remove by-product LiCl, hydrolyzed aliquots of the solutions were analyzed for Mg, Li, Cl, total alkalinity and active alkyl content, the latter by VPC for the corresponding alkane. Lithium ion was determined by flame photometry and magnesium and chloride ions by conventional titrimetry. Yields of R_2Mg were essentially quantitative based on starting reactants. During displacement of the ether with hydrocarbons (cyclohexane or benzene) by distillation through an 8 inch Vigreux column (argon atmosphere), the distillate was checked periodically for ethyl ether content by VPC. Distillation was continued to 80° and was discontinued when the ether content of the distillate was below 0.01 wt. % and NMR spectroscopic analysis showed the absence of ether in the residual clear, colorless to light yellow hydrocarbon solutions. After hydrolysis, aliquots of the hydrocarbon solutions were further analyzed for ether and active alkyl content by VPC and for total alkalinity by titration. Active alkyl content has also been determined by direct titration of the magnesium alkyl solution with a standard sec-butanol in xylene solution (0.4 *N*)[14]. The endpoint of this titration is the disappearance of the violet color of a 1,10-phenanthroline–magnesium alkyl complex.

Preparation of di-sec-butylmagnesium

The procedure of Huston and Langham[15] gave a 95% yield of sec-C_4H_9MgCl from reaction of 2.4 g (0.1 mole) of Mg turnings with 9.3 g (0.1 mole) of sec-butyl chloride in 100 ml of anhydrous diethyl ether. A weight of 30.5 g of an 18.9 wt. % solution of sec-C_4H_9Li (0.09 moles) in cyclohexane was added rapidly, with stirring, to 87 ml of a 1.03 *M* solution of the sec-C_4H_9MgCl (0.09 mole) in ether. A small amount of heat was evolved and a gray-white precipitate formed. Reaction appeared to be complete after 30 min as evidenced by cooling of the reaction mixture. The mixture was stirred for an additional 30 min and the solids allowed to settle overnight. At this point Gilman Color Test II (on the supernatant solution) was negative. The clear solution contained 1.56 equivalents of base, 0.77 gram-atom of Mg, and 0.04 gram-atoms each of Li and Cl per liter of solution. The solid residue, after washing with ether, was found to contain Li and Cl in a 1 : 1 molar ratio. VPC of the organic layer obtained on hydrolysis of a sample of the solution showed the presence of 12.6 wt. % n-butane, corresponding to 1.61 equivalents/liter of sec-butyl groups in the original solution.

Fifty ml of the 0.77 *M* di-sec-butylmagnesium solution was distilled under argon through a Vigreux Column while cyclohexane was added to maintain the residual volume. All of the ether in the original solution was removed by and found in 90 ml of distillate. Analysis for alkalinity showed that the 50 ml of clear residual cyclohexane solution was still 0.76 *M* in the desolvated di-sec-butylmagnesium. Removal of cyclohexane from the solution by further distillation (b.p. 80°) increased this concentration to 1.0 *M*. VPC analysis indicated no detectable amount of ether present in the hydrocarbon or water layers after hydrolysis of a sample of this solution in a sealed vial at -10 to $-20°$. The active alkyl content was determined by VPC analysis of the n-butane in the organic layer obtained on hydrolysis of a weighed sample of the solution. No peaks other than n-butane and cyclohexane were found.

Data on some of the other magnesium alkyl preparations by the above techniques are listed in Table 1. Except for di-tert-butylmagnesium, which decomposed to form a black precipitate of MgH_2 on heating, and for di-n-butylmagnesium, which still contained some di-n-butyl ether (present in the original Grignard reagent), all of the magnesium alkyls in Table 1 were desolvated by codistillation with a hydrocarbon to 80°.

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