SHORT COMMUNICATION

The preparation and properties of organomagnesium compounds in benzene solvent

I. *n*-Amylmagnesium compounds

The reaction of powdered magnesium metal with *n*-amyl chloride, bromide, or iodide yields benzene-soluble organomagnesium compounds whose halogen content increases in the order Cl < Br < I. Unlike the analogous complexes studied by Bryce-Smith[1], who observed the same trend if the alkyl group was either ethyl or *n*-butyl, *n*-amylmagnesium compounds are soluble in benzene *in the absence of magnesium halide*. "Chloride" preparations, in fact, result in solutions which are essentially halide free, as Table 1 shows. In view of the rather low solubility reported for di-*n* alkylmagnesium compounds in hydrocarbon media[1,2], we were surprised by this result, and have prepared di-*n*-amylmagnesium by an alternate route, *viz.* through the exchange reaction between magnesium metal and the corresponding dialkylmercury compound. Although the reaction is slow in benzene solvent (70% yield after one month), solutions were obtained in which the concentration of $(n\text{-}C_5H_{11})_2Mg$ was > 0.2 *M*, and whose properties were essentially the same as those which resulted from the alkylmagnesium chloride reaction.

Table 1 also shows the results of molecular weight measurements on these solutions. Although the bromide solutions yielded rather scattered data, which may reflect the presence of small amounts of alkoxide impurities, it appears that the presence of halide substantially increases the degree of association of these species. Whereas di-*n*-amylmagnesium appears to be dimeric at the temperature of freezing benzene solutions, the incorporation of halides, of which iodide is the most soluble, results in larger *i* values. Presumably this is due to the ability of the halide to cause polymerization of the organomagnesium compound by the formation of bridge bonds as shown in (I)[1]. The higher concentration of iodide, observed in this work and by

$$\left[{<}\frac{R}{R}{>}Mg{<}\frac{X}{X}{>}Mg{<}\frac{R}{R}{>}Mg{<}\right]_x$$

(I)

Bryce-Smith[1], and the molecular association data of Table 1, may indicate that magnesium iodide is a more effective bridging agent than the bromide or chloride, although the association of Grignard reagents in diethyl ether[3] and the heats of dimerization of aluminum halides[4] would seem to indicate the opposite trend.

An alternate explanation of our data in terms of the solubility of complexes such as (I) seems preferable. During the preparation, insoluble complexes of the type $(RMgX)_x$, where x is large, may be formed at the metal surface (1). Disproportionation into complexes of lower halide content follows. In the case of the iodide, disproportionation stops at the empirical formula R_5Mg_3I, presumably a soluble species,

TABLE 1

PROPERTIES OF *n*-AMYLMAGNESIUM COMPOUNDS IN BENZENE

n-Amyl halide used	*Alkyl concentration (moles/l)*	*Halide concentration (moles/l)*	$[R]/[X]$	*Association factor*
Chloride	0.434	[a]		1.8
	0.348	0.003	116	2.1
	0.130	[a]		2.2
Bromide	0.255	0.015	16.1	5.1
	0.513	0.035	14.1	4.5
	0.320	0.026	12.3	7.7
	0.290	0.023	12.6	8.4
	0.185	0.015	12.3	8.3
	0.360	0.0200	18.0	5.2
	0.244	0.0136	17.9	4.8
	0.153	0.0084	18.2	4.1
Iodide	0.438	0.095[c]	4.6	[b]
	0.208	0.041[c]	5.1	[b]
	0.077	0.015	5.1	[b]

[a] Not measured; each of the chloride solutions reported here were from the same original preparation and presumably contained the same halide concentration. [b] Molecular weights were too large to measure by the method employed. [c] These solutions showed evidence of minute precipitation upon dilution. The amount of material was too small to identify, however.

whereas in the case of the chloride it has proceeded to virtual completion, driven by the low solubility of chloride complexes analogous to (I), the larger crystal energy

$$x\,\mathrm{RX} + x\,\mathrm{Mg} \rightarrow (\mathrm{RMgX})_x \tag{1}$$

$$(\mathrm{RMgX})_x \rightarrow \mathrm{R_2Mg} + \mathrm{MgX_2} \tag{2}$$

of $MgCl_2$, and the solubility of R_2Mg. It is the latter which distinguishes the behavior of di-*n*-amylmagnesium compounds from ethyl- and *n*-butylmagnesium complexes[1].

Experimental

Preparation of organomagnesium compounds. The following method, which is basically an adaptation of that described by Bryce-Smith[1], was used. Magnesium metal, in powder form was heated to approximately 85° and stirred at a rate of approximately one half revolution per second in a 500-ml three-necked flask fitted with dropping funnel, Friedrich condenser and a Nichrom wire stirrer. A slight nitrogen pressure was applied to the system. The reaction was initiated by the addition of 5–10% of the *n*-amyl halide. After smoking and refluxing of the excess *n*-amyl halide was noted as visual evidence of reaction, the remaining halide was added dropwise, over a period of three to four hours. As the reaction neared completion, the contents of the reaction vessel formed a "muddy" consistency. At this point heating was continued and the stirring increased to a vigorous rate for an additional hour. Dry benzene was then introduced from a dropping funnel which was stacked on the condenser, and the heating controlled to gain a slow reflux of the solvent for another two hours. The yield of organomagnesium compound at this point was approximately 80 %, based on derivatization with 2-butanone. The reaction product consisted of a very viscous liquid phase and a solid "mud" phase. Separation of these two phases was accomplished by centrifuging the mixture at *ca.* 2100 rpm, after which the mixture was taken into the dry box and filtered through a medium frit to obtain a clear, viscous solution. In order to remove the coupling product, decane, the solution was evaporated to dryness under vacuum. Benzene was readded to bring the solid *n*-amylmagnesium compound back into solution. Without exception, only traces of solid did not redissolve, and alkyl/halide values were unchanged after redissolving the solid. These and all other *n*-amylmagnesium solutions remained clear and colorless for indefinite periods in the dry box.

Analytical methods. Total hydroxide concentration produced upon hydrolysis of an aliquot of the solution was determined by the standard volumetric method using phenolphthalein indicator. A VPC analysis of the hydrocarbon (*n*-pentane) from another hydrolyzed aliquot of the solution was used to determine the concentration of carbon-bound magnesium. A 15-foot, ¼-inch diameter silicone column (SE-30) at a temperature of 120° (helium carrier gas flow rate: one milliter per second) was used for the hydrocarbon analysis. Standard solutions of pentane/benzene were used to calibrate the VPC technique. No other peaks were detectable in those solutions used for molecular weight measurements. A determination of the concentration of the halide species was made from a hydrolyzed aliquot of the solution by a potentiometric titration utilizing a silver/silver halide and calomel electrode system.

Alternate preparation of di-n-amylmagnesium. The method employed for the synthesis of di-*n*-amylmercury was that described by Gilman[5]. Synthesis of the di-*n*-amylmagnesium consisted of stirring a solution of di-*n*-amylmercury and benzene with triply-sublimed magnesium turnings, with a trace of anhydrous $HgCl_2$. The exchange reaction was carried out in a dry box at *ca.* 40°. After one month of stirring, a solution of the di-*n*-amylmagnesium (70 % yield) was obtained by filtering the viscous reaction mixture which contained a magnesium amalgam suspension. A Varian A60 nuclear magnetic resonance spectrometer was used to monitor the reaction, utilizing the α-methylene triplet of di-*n*-amylmercury at $\delta = 1.35$ ppm with respect to TMS. The yield of the exchange reaction was determined by two methods. The amount of di-*n*-amylmagnesium was determined by the same methods used in the analysis of the *n*-amylmagnesium halide solutions described above. In addition, the mercury content remaining in solution was measured by a spectrographic procedure utilizing the emission of sparked mercury at 2536 Å.

Molecular weight measurements. Molecular weights of the benzene solutions were obtained cryoscopically, utilizing a thermistor thermometer. Freezing point determinations were made outside the dry box under argon or nitrogen atmospheres in a cell of glass construction[6]. A Leeds and Northrup 10 mV recorder served as a null-point indicator for the thermistor bridge, and had a sensitivity corresponding to 0.001°. Solvent freezing points could be duplicated to ± 0.006°. Sample freezing points could be duplicated to ± 0.01°. The thermistor was calibrated with a previously calibrated Philadelphia Thermometer.

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The interaction of tricarbonyltoluenechromium with Lewis acids

Unlike bisarenechromium compounds, the arenetricarbonylchromium compounds readily undergo the standard electrophilic substitution reactions characteristic of an aromatic nucleus. The arene ring in the latter compounds, in this respect, resembles the cyclopentadienyl moiety in ferrocene. In contrast to bisarenechromium compounds and ferrocene and its derivatives, no stable cationic derivatives of arenetricarbonylchromium compounds have been reported, suggesting that the latter are more difficult to oxidize than are the bisarenechromium compounds. These observations and the reported oxidation potentials for dibenzenechromium[1] and ferrocene[2] suggest that the order of oxidative stability for these compounds is $ArCr(CO)_3 >$ $(C_5H_5)_2Fe > Ar_2Cr$. Since both dibenzenechromium[3] and the metallocenes[4,5] react with strong π acids to form compounds which can be formulated as salts of radical anions, it was of interest to investigate the interaction of arenetricarbonylchromium compounds with π acids.

Experimental

Mixtures of tricarbonyltoluenechromium and Lewis acids were manipulated under an inert atmosphere using standard techniques in an attempt to isolate complex compounds from these systems and to show that some interaction occurs in solution.

Electron spin resonance spectra were determined with the equipment described previously[4].

Tricarbonyltoluenechromium was prepared by the method of Nicholls and Whiting[6], using the apparatus described by Strohmeier[7]. In a typical preparation, hexacarbonylchromium (6.0 g, 0.027 mole), toluene (8.67 g, 0.0942 mole), and 100 ml of diethylene glycol dimethyl ether ("diglyme") were heated at 180° for 5 h with stirring. The mixture was cooled, filtered, and the solvent and unreacted hexacarbonylchromium removed *in vacuo*. The residue was taken up in benzene, placed on an