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PREPARATION OF ORGANOMAGNESIUM REAGENTS IN HYDROCARBON SOLVENTS WITHOUT ORGANIC BASES

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Summary

A detailed investigation of the formation of n-R_2Mg compounds in hydrocarbon solvents in the absence of organic base is reported, including information on the nature of the solutions formed and by-products, the effect of the alkyl halide, the hydrocarbon solvent and temperature of formation. The colorless product solutions had relatively high R_2Mg/MgX_2 ratios ranging from about 4 for preparations from alkyl iodides to almost 30 for those from alkyl chlorides. sec-Butyl bromide reacted only in the presence of a stoichiometric amount of diethyl ether in hexane to form solutions of $[s\text{-BuMgBr}\cdot Et_2O]_x$. The reactions of the n-R_2Mg compounds in hydrocarbon solutions were also examined. Possible implications are discussed regarding the nature of these compounds.

Introduction

In the course of a research program dealing with organomagnesium chemistry, it was desirable to prepare Grignard reagents in hydrocarbon solvents without the presence of any organic base [1]. There are a number of reports describing the use of hydrocarbon solvents and the organic halides, themselves, as solvents for the preparation of a "Grignard" reagent [2 - 21]. Frequently organic bases were required as initiators. For reviews of the preparation of Grignard reagents in hydrocarbon solvents, see refs. 8, 22 - 25. In the papers through 1950, the solutions and the precipitates were analyzed together, if at all.

A renewed interest in the preparation of Grignards in hydrocarbon solvents began with Bryce-Smith [26 - 30] and Zakharkin [31 - 34], when aliphatic and aryl "Grignards" were prepared in alkyl aromatic and aliphatic hydrocarbons, respectively. The products of these preparations, although term-

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TABLE 1

DIALKYLMAGNESIUM/MAGNESIUM HALIDE RATIOS FROM REACTIONS OF PRIMARY n-ALKYL HALIDES WITH MAGNESIUM IN HYDROCARBON SOLVENTS[a]

Solvent	No. of carbons in R												
	n-RI					n-RBr						n-RCl	
	8	5	4	3	2	8	7	6	5	4	3	8	5
Isopentane	6.5		5.9			11.1[b]				12.6[c]			
n-Pentane	6.6		6.7			17.2							
n-Hexane	6.0		6.1			15.6	14.9	15.4	14.6	13.0			
n-Heptane	5.1_2	6.1	5.8_2			12.4_3				10.0_2		32.3_3	32.6
n-Octane	5.3_2					8.6						27.9	
2,2,4-Trimethyl-pentane	5.1					12.0						28.6	
Cyclohexane	5.0_2					12.3						28.4_2	
Benzene	3.9		4.8_2	2.7[d]	1.3[e]	11.3				9.0	8.5[f]	23.9	
Toluene						6.9							

[a] These values are listed only for solutions greater than 0.02 *M* except where the concentrations have been given. The numerical subscript given after the ratio indicates the number of determinations made for that value and averaged together. The values are estimated to be good to ±4%. [b] 0.006 *M* final conc. [c] 0.018 *M* final conc. [d] 0.007 *M* final conc. [e] 0.002 *M* final conc. [f] 0.0043 *M* final conc.

ed "Grignard" reagents, were recognized as being "different" in properties and reactivity from the usual Grignard reagents in ethers.

Glaze and Selman [35] prepared the n-pentylmagnesium compounds in benzene from the corresponding chloride, bromide and iodide in the manner described by Bryce-Smith, and found considerably more Mg—C bonds than Mg—X bonds in the product solutions.

Preparation of sec-R_2Mg compounds in hydrocarbons has been reported by Kamienski and Eastham [36 - 38], by an indirect approach utilizing the reaction of sec-RLi and $MgCl_2$. The sec-R_2Mg products reported by them had lower solution viscosities, lower halide content and higher solubilities than reported by this work and other workers in the field. Their indirect approach avoided the presence of MgX_2 during the formation of the sec-R_2Mg compound which may account for the different results observed. Another explanation might be the presence of contaminating organic base or lithium cation, in spite of their determined efforts to prevent such contamination. The results reported in this paper will aid in further delineation of the nature of the organomagnesium reagent in hydrocarbon solvents.

Results

The direct reaction of RX with Mg metal was investigated in greater detail than previously reported, with the expected stoichiometry of reaction (1) found.

$$2\,RX + 2\,Mg \rightarrow 2\,[RMgX]? \rightarrow R_2Mg + MgX_2 \qquad (1)$$

The detailed optimum preparative conditions are given in the experimental section while the specific reaction results including solution composition are given in Table 9. The preparations described were very reproducible.

A. Reaction of primary halides and analysis of product solutions

The ratio of base to halide was always found to be much greater than one for organomagnesium reagents in the centrifuged solutions prepared from n-RX and Mg in hydrocarbon solvents, in agreement with other workers. Since the total Mg concentration found was equal to one-half the base concentration plus half of the halide ion concentration, within 3%, it is more convenient to express the base/halide ratio as the ratio of n-R_2Mg to magnesium halide (MgX_2) in the hydrocarbon solvent, with the understanding that the halide is present as complexed or bonded MgX_2. Magnesium halides are normally insoluble in these solvents.

The n-R_2Mg/MgX_2 ratios found in the clear, centrifuged solutions are listed in Table 1, Included also in this table are a few n-R_2Mg compounds which were too insoluble or unreactive to obtain any solutions greater in concentration than 0.020 *M*. The ratios listed were determined from solutions varying from 0.020 to 0.190 *M* in n-R_2Mg unless otherwise stated, and seemed to be little affected by concentration.

These ratios indicate that of the halides, $MgCl_2$ bonds or complexes least readily to n-R_2Mg in the hydrocarbon solvents. This may be because $MgCl_2$ is the most ionic MgX_2 excepting MgF_2. The ratios found for $MgBr_2$ and MgI_2 also correlate with this explanation.

TABLE 2

A COMPARISON OF SOME OF THE PROPERTIES OF THE REACTIONS OF PRIMARY n-ALKYL HALIDES WITH MAGNESIUM IN ALIPHATIC HYDROCARBON SOLVENTS

n-Alkyl halide	Reflux time[a] after the reaction started (h)	Coupling (%)	Yield (%)
Iodide	3	3 - 6[b]	65 - 100
Bromide	5 - 8	15 - 30	55 - 70
Chloride	6 - 12	15 - 35	35 - 60

[a] The reflux time is varied according to how rapidly the solution appeared to be reacting. [b] The coupling for the n-alkyl iodide goes up to 12% in n-pentane and isopentane.

The ratios also decreased as the length of the carbon chain of the solvent increased, as from n-pentane to n-octane. The aromatic solvents, benzene and toluene, gave lower ratios than the aliphatic solvents. Only low concentrations of the more-insoluble n-R_2Mg compounds, Et_2Mg and n-Pr_2Mg, could be obtained, even in benzene. The low solubilities of Et_2Mg and Ph_2Mg in n-heptane and benzene were measured by Strohmeier [40], who also found that benzene was the better solvent.

In addition to wet chemical analyses, the n-R_2Mg solutions after centrifugation were hydrolyzed, and the resulting hydrocarbon layer analyzed by GLC. These hydrocarbon solutions from the hydrolysis contained the resulting n-alkane from the n-R_2Mg, coupling product, and in the solvents that boil at a higher temperature than n-hexane, small amounts of olefin corresponding to the RX used. The reactions in benzene also yielded small amounts of alkylated benzenes. Table 2 lists the average results. (Specific results are in the Table 9). The coupling was considerably less for the n-RI (5% in n-heptane) than for the n-RBr or n-RCl. In general, the reflux temperature of the solvent affected the rate of reaction, and therefore the yield of n-R_2Mg. Coupling increased with a slower rate of reaction of the n-RX. The unreacted n-RX did not react with the n-R_2Mg in solution after the solution had been centrifuged and stored, even after several weeks. The coupling, therefore, must occur in the presence of the Mg during the reaction. In addition, no post-precipitation was observed in the centrifuged solutions if sealed from air except when BuBr and lower alkyl halides were used. Small amounts of olefin found were probably formed by decomposition of the n-RX caused by the Lewis acid properties of the MgX_2 present or by the decomposition of the n-R_2Mg. The former explanation is more consistent with the known stabilities of n-R_2Mg reagents and the Lewis acid properties of MgX_2 described in the work of Bryce-Smith [28]. Three material balances using the n-octyl system are listed in Table 3.

In order to determine if the presence of excess $MgBr_2$ would cause any decrease in the ratios, a clear, centrifuged solution of $(n\text{-}C_5H_{11})_2Mg$ in n-heptane prepared from n-$C_5H_{11}Br$ was mixed with 1.3 mole equivalents of anhydrous $MgBr_2$ and heated at 95° for ½ h with intermittent shaking. The n-R_2Mg/MgX_2 only changed from 15.3 to 15.9 and not in the expected direction. This slight change can be explained by the accidental admission of a small amount of oxygen. Excess MgX_2 therefore has no effect on the ratios in n-R_2Mg solutions.

TABLE 3

A SAMPLE MATERIAL BALANCE OF THE ALKYL GROUPS AFTER REACTING n-OCTYL HALIDES WITH MAGNESIUM IN n-HEPTANE

	n-Octyl iodide	n-Octyl bromide	n-Octyl chloride
Di-n-octylmagnesium[a]	87.7	60.3	50.5
Coupling (hexadecane)[b]	5.6	28.2	33.0
n-Octyl halide[b]	0.5	11.7	5.0
Octene from decomposition	0.5	0.5	0.5
Alkyl group balance (%)	94.3	100.7	89.0

[a]Measured by titration. [b]This amount is calculated from areas on GLC traces. A factor of two is included for hexadecane. [c]The octene was estimated after its detection and calculation in several other runs.

Several observations were made about the viscosity dependence of the hydrocarbon solutions of n-R_2Mg compounds. The maximum concentrations in n-heptane that could readily be handled and centrifuged at 1800 rpm were approximately 0.125 *M* for $(n\text{-}C_8H_{17})_2Mg$ and 0.200 *M* for Bu_2Mg. The reaction would proceed at higher concentrations, but the viscosity increased dramatically. The viscosity appeared slightly greater in a higher n-alkane solvent like n-octane than in a lower n-alkane like n-hexane. The MgX_2 present caused the viscosity to increase in the order: I < Br < Cl. The greatest effect on increasing viscosity was due to increased concentration, and increased length of the n-alkyl group present in the n-R_2Mg. No quantitative viscosity measurements were made.

B. n-Butyl halides and lower primary halides

The preparation of Bu_2Mg from BuI was accomplished without any difficulty. When BuBr was used, the concentrations of Bu_2Mg varied from nearly zero to 0.15 *M* and a large amount of precipitate formed. Even when the concentrations of Bu_2Mg (formed from BuCl or BuBr) in solution were negligible, the heavy precipitate could be carbonated to valeric acid. This precipitate also reacted violently with water. Good reaction but no soluble base was always obtained from BuCl. Prolonged reflux of the Bu_2Mg preparation from BuBr gave low solution concentrations of Bu_2Mg; and preparations that went very rapidly and were not refluxed for a long time gave relatively high concentrations. This sporadic behavior was only noted for BuBr and to a lesser extent with PrI, PrBr and i-$C_5H_{11}Br$. It appears that this must be some type of supersaturation or rearrangement effect occurring, for the solution after centrifugation was stable to precipitation for short periods of time before use. The BuBr preparations of Bu_2Mg must be at a transition point in solubility between the soluble and insoluble preparations of n-R_2Mg compounds containing MgX_2. None of these solubility effects were observed with n-$C_5H_{11}X$.

C. Secondary halides

Many attempts were made to obtain sec-R_2Mg compounds in hydrocarbon solvents using the direct reaction of sec-RX and Mg, but only very low concentrations were ever obtained and these were with sec-RI in benzene. Table 4 lists these results. A small amount of precipitate always formed. A

TABLE 4

DI-sec-ALKYLMAGNESIUM/MAGNESIUM IODIDE RATIOS FROM THE REACTIONS OF SECONDARY IODIDES WITH MAGNESIUM IN AROMATIC SOLVENTS

Secondary Iodide	Solvent	Concn. [R_2Mg]	Concn.[MgI_2]	Ratio[a]
Cyclohexyl iodide	Benzene	0.00205	0.00206	1.00
sec-Octyl iodide	Benzene	0.00303	0.00209	1.45
Phenyl iodide	Xylene	0.00860	0.00500	1.72

[a] These values are estimated to be good to ±6%.

slight reaction was also found with PhI in refluxing xylene which on carbonation produced a small amount of benzoic acid. The low R_2Mg/MgX_2 ratios obtained indicated that a 1/1 complex tended to dissolve, but the low MgX_2 complexes analogous to the primary alkyl cases did not form. The reactions of the sec-RI could not be forced even when initiated by adding n-RI to refluxing toluene, and then adding the sec-RI. The small amount of precipitate formed in the reaction of sec-$C_8H_{17}I$ and Mg in refluxing xylene was carbonated and a trace of 2-methylcaprylic acid isolated. The clear hydrocarbon product solution contained no base.

The effect of adding a small amount of an organic base to the hydrocarbon solvent is well known in preparing Grignard reagents in these media. When small amounts of Et_2O were added to the reaction of s-BuBr and Mg turnings in hexane, and the reaction brought to a gentle reflux while stirring, a solution of a Grignard reagent formed (only a small amount of precipitate formed). The recent work of Ashby and Reed [41] used a related system consisting of Et_3N and benzene with similar results, but with the n-butyl and the ethyl systems. The analyses of the solutions that were obtained containing the sec-butyl Grignard reagent and small amounts of Et_2O are listed in Table 5. The results show the formation of [s-BuMgBr·$Et_2O]_x$ in n-hexane solutions is linearly dependent on the amount of Et_2O.

D. Other halides

No observable reactions with sublimed Mg turnings were obtained at reflux from benzyl bromide or chloride in toluene, crotyl chloride in benzene, 1,2-dibromoethane in n-octane, 1,2-diiodopropane in benzene, 1,10-dibromodecane in toluene or n-$C_8H_{17}F$ in xylene. A freshly distilled, colorless sample of tert-pentyl iodide also failed to react in refluxing benzene. The extreme insolubility of the resulting organomagnesium compound might be the reason for the lack of reactions of these halides.

TABLE 5

THE EFFECT OF SMALL AMOUNTS OF DIETHYL ETHER ON THE PREPARATION OF THE GRIGNARD REAGENT OF sec-BUTYL BROMIDE IN HEXANE

Run	Initial concn. [s-BuBr] added	Concn. [Et_2O]	Concn. [s-Bu_2Mg] found	Concn. [$MgBr_2$] found	Yield(%) [s-Bu_2Mg]	[s-Bu_2Mg] / [$MgBr_2$]	[Et_2O] / [s-Bu_2Mg]
1	0.400	0.286	0.145	0.122	72.5	1.19	1.98
2	0.350	0.191	0.0925	0.0870	53.1	1.06	2.06
3	0.453	0.0419	0.0201	0.0158	8.8	1.27	2.08

TABLE 6

THE EFFECT OF THE ADDITION OF SMALL AMOUNTS OF OXYGEN ON THE DI-n-PENTYLMAGNESIUM/MAGNESIUM BROMIDE RATIO IN n-HEPTANE SOLUTION

Determination	Concn. $[(n\text{-}C_5H_{11})_2Mg]$	Concn. $[MgBr_2]$	$[(n\text{-}C_5H_{11})_2Mg]/[MgBr_2]$	Concn. $[Mg^{++}]$	$([(n\text{-}C_5H_{11})_2Mg]+[MgBr_2])/[Mg^{++}]$ agreement (%)
Initial	0.0837	0.00711	11.78	0.0916	99.1
1	0.0828	0.00699	11.85	0.0914	97.2
2	0.0822	0.00665	12.35	[a]	
3	0.0812	0.00641	12.66	[a]	
4	0.0739	0.00561	13.77	0.0807	98.5
5	0.0524	0.00232	22.58	0.0554	99.0
6	0.0303	0.00191	15.83[b]	[a]	

[a] The magnesium ion concentration was not checked. [b] The lower ratio may result in the difficulty of equilibrating the gelatinous precipitate with the supernatant since the precipitate was quite heavy in this case.

E. Effect of oxygen

The solutions of n-R_2Mg reacted instantly with air, forming a white gelatinous precipitate at the interface. These solutions are as air-sensitive as R_3Al, R_2Zn or RLi compounds, in contrast to the relatively very low reactivity of the usual Et_2O solutions of Grignards. The absence of organic base and MgX_2 obviously enhances the reaction with air several orders of magnitude. A 60% yield of n-octanol was obtained by the reaction of $(n\text{-}C_8H_{17})_2Mg$ in n-heptane with air for 10 min. $(n\text{-}C_8H_{17})_2Mg$, isolated as a white powder, reacted vigorously with air but did not ignite.

The n-R_2Mg/MgX_2 ratios in the hydrocarbon solvents could be moderately increased by the addition of small amounts of oxygen to the solutions of n-R_2Mg and thereby forming $Mg(OR)_2$ which separates as a gelatinous precipitate as previously mentioned. Table 6 lists these results. The MgX_2 complexes preferentially to the insoluble alkoxide [42].

The addition of a 5/1 mole ratio of anhydrous MgO to a n-heptane solution of $(n\text{-}C_5H_{11})_2Mg$ caused no significant change in the ratio.

F. Effect of the addition of dioxane

A solution of $(n\text{-}C_8H_{17})_2Mg$ in n-heptane prepared from n-$C_8H_{17}Cl$ showed an increase of the n-R_2Mg/MgX_2 ratio from 24 to 84 with the addition of very small amounts of dioxane, and only a slight decrease in $(n\text{-}C_8H_{17})_2Mg$. These results are listed in Table 7. Evidently dioxane has the same complexing effect on MgX_2 in hydrocarbon solvents as in ether.

TABLE 7

THE EFFECT OF THE ADDITION OF DIOXANE ON THE DI-n-OCTYLMAGNESIUM/MAGNESIUM CHLORIDE RATIO OF A n-HEPTANE SOLUTION OF DI-n-OCTYLMAGNESIUM

Detn.	Volume (ml)	Concn. $[(n\text{-}C_8H_{17})_2Mg]$	Concn. $[MgCl_2]$	$MgCl_2$[a] (moles)	Dioxane (moles added)	$[(n\text{-}C_8H_{17})_2Mg]/[MgCl_2]$
Initial	164	0.0835	0.00353	0.00058		23.6[b]
1	154	0.0800	0.00193	0.00037	0.00028	41.5
2	149	0.0799	0.00094	0.00015	0.00039	83.7

[a] Present in solution after centrifugation. [b] This solution of di-n-octylmagnesium had been stored in a bottle and had reacted with some oxygen, but the resulting precipitate had not been mixed or equilibrated with the rest of the solution. The solution was removed by syringe without disturbing the precipitate. The original base titration had gone down a significant amount leaving a lower dialkylmagnesium:magnesium chloride ratio than is usually found in n-heptane.

TABLE 8

REACTIONS OF DI-n-ALKYLMAGNESIUM IN n-HEPTANE[a]

Reagent	n-R_2Mg	MgX_2	Product	Yield (%)
Carbon dioxide[b]	Octyl	Br	Pelargonic acid	56
Oxygen[c]	Octyl	Br	1-Octanol	60
Propylene oxide[b]	Pentyl	Cl	2-Octanol	27
Mercuric bromide[b]	Pentyl	Br	n-Pentylmercuric bromide	75
Pyrrole (Et chloroformate)[c]	Pentyl	Cl	Ethyl 1-pyrrolecarboxylate 43% Ethyl 2-pyrrolecarboxylate 57%	50
1-Phenyl-2-buten-2-one[b]	Pentyl	Br	1,2-Addition 37% 1,4-Addition 63%	95
Acetyl chloride[b,d]	Pentyl	Cl	2-Heptanone	Trace

[a] Runs at 0° with the n-R_2Mg in heptane added to a solution or slurry of the reagent for inverse addition, and the organic to the n-R_2Mg solution for normal addition. [b] Inverse addition. [c] Normal addition. [d] Essentially the same results were obtained with EtOAc and CH_3CN, main product was a mixture of alcohols and condensation products.

G. Reactions of the di-n-alkylmagnesium solutions

Some typical Grignard reactions were carried out by adding the hydrocarbon solutions of n-R_2Mg to various reagents containing specific functional groups normally reactive to Grignard reagents at 0°. It was expected that there would be some difference in the reaction, due to solvent effects and the absence of MgX_2. However, this was not the case. The results are listed in Table 8. Reduction of the ketone formed appeared to occur whenever it was formed initially as in the case of acetyl chloride. The selectivity of 1,4-addition over 1,2-addition with 4-phenyl-3-buten-2-one showed no differences from the results of Kohler [43], who found 60% 1,4-addition with the EtMgBr Grignard and 4-phenyl-3-buten-2-one. Various hydrocarbon solutions of n-R_2Mg were carbonated with yields of 56—95% of the distilled acid. The (n-C_8H_{17})$_2$Mg compounds in n-heptane prepared from n-C_8H_{17}I, n-C_8H_{17}Br and n-C_8H_{17}-Cl_2 were carbonated and the methyl esters of the resulting samples of pelargonic acid were found free of rearranged isomers by GLC.

The n-R_2Mg reagnets did not add to 1,1-diphenylethylene at room temperature. RLi reagents do add to this reagent [44]. Higher pressures and temperatures are reported to cause the polymerization of ethylene with (n-C_5H_{11})$_2$-Mg in benzene [45].

The reaction of propylene oxide gave a 27% yield of the secondary alcohol with no precipitate forming during the 22 h of reaction. This result is quite close to that reported by Evans and Huston who obtained 24% yield of 2-heptanol in 18 h from BuMgI Grignard and propylene oxide [46].

H. Comparison with organozinc compounds

Bu_2Zn was prepared from reagent grade Zn dust and BuI in refluxing n-heptane by the same procedure used for n-R_2Mg compounds. The Bu_2-Zn/ZnI_2 ratio obtained was 48.4 with a yield of 50%. Similarly s-Bu_2Zn was prepared from s-BuBr with a yield of 50% and a sec-R_2Zn/$ZnBr_2$ ratio of 1.16.

Discussion

This investigation has described the direct formation of R_2Mg compounds in hydrocarbon solvents, properties of their solutions and their chemical reactivity. The high n-R_2Mg/MgX_2 ratios previously observed have been confirmed. In addition the limitations on the preparation of these reagents have been examined.

The difficulty experienced by workers in the past in preparing Grignard reagents in hydrocarbon solvents without an organic base can possibly be explained by their frequent use of the relatively inactive lower n-RX compounds, or their use of any of the secondary halides because of solubility effects, in addition to the sensitivity of the reaction to impurities. The reactions of the n-RX are particularly sensitive to small amounts of sec-RX. This is especially a problem with the higher boiling n-RX because the removal of small amounts of sec-RX is not readily accomplished. The preparations of n-R_2Mg as described here in hydrocarbon solvents have been reproducible, and the only exceptions to this have been the reactions of BuBr in hydrocarbon solvents because of supersaturation effects, or cases of slow reaction and resultant coupling in n-pentane and isopentane.

Reactions of n-RX with Mg in refluxing hydrocarbon solvents were only slightly exothermic in contrast to the usual Grignard reactions in ethers. This would indicate that the reaction in ethers uses as its driving force the heat of solvation of MgX_2 by the ether, and the maintaining of a clean surface on the Mg metal by the solubility of the products in the ether. The usual Grignard reactivity order is observed in hydrocarbons: n-RI > n-RBr > n-RCl. Except with oxygen, reactions of n-R_2Mg in hydrocarbon solvents were surprisingly similar to those of the normal Grignards. The reacting organic molecule containing the functional group must act as the strongest organic base toward the magnesium compound in solution whether in Et_2O or hydrocarbon, giving the same products in both cases.

The inability to obtain hydrocarbon solutions of sec-R_2Mg without organic bases is puzzling especially in the light of published reports of such solubility. The formation of the exact stoichiometric amount of sec-$RMgBr \cdot Et_2O$ on addition of small amounts of Et_2O to hexane solutions indicates that this non-reactivity was not simply failure to obtain the correct reaction conditions.

In this direct reaction of sec-RX and Mg to form sec-R_2Mg, MgX_2 is always present and available for coordination. It appears that the interaction of sec-R_2Mg with MgX_2 is much stronger than in the case of n-R_2Mg so that the same association of $(R_2Mg)_x$ cannot form with the sec-R_2Mg systems. Apparently, $[\text{s-BuMgBr} \cdot Et_2O]_x$ is the more soluble and stable species in hydrocarbon solvents in the direct formation reaction, and stoichiometric amounts of Et_2O bring about solution of s-Bu_2Mg as the $MgBr_2 \cdot Et_2O$ complex. The markedly different ratios for secondary and primary R_2Zn reagents in n-heptane, 1.2 and 48.4, respectively, agree with the stronger bonding noted for the sec-R_2Mg compounds with MgX_2, compared to n-R_2Mg compounds.

Experimental

Materials

The aliphatic hydrocarbons were all 99 mole % except the n-pentane which was 95 mole % and were obtained from Phillips Pet. Co. They were washed with concd. H_2SO_4 until the washings were colorless, washed with water once, and distilled from P_2O_5 with a liberal forerun. Benzene and toluene were distilled directly from P_2O_5. The hydrocarbons after purification were all 99.5%+ by GLC. Dow triply sublimed grade Mg, cut into shavings under argon and stored under argon, was used.

·The alkyl halides were from 3 sources: Columbia Organic Chem , Eastman Organic Chem., and Matheson, Coleman and Bell. Both the RBr and RCl were fractionally distilled from P_2O_5, with reduced pressure if the atmospheric b.p. was higher than 125°. The primary RI were dried over $CaCl_2$ and distilled under reduced pressure from CaH_2. If the RI to be purified was colored, it was initially washed with aq. $Na_2S_2O_3$. The secondary RI were distilled from Cu wire under reduced pressure. The RI were stored in brown bottles over Cu wire. Nitrogen and argon having a low oxygen content were passed through silica gel, KOH and, finally, Linde 4A Molecular Sieves to remove traces of CO_2 and H_2O. All GLC analyses were on a 10-ft. DEGS on Chromasorb W col.

General reactivity of n-alkyl halides

A variety of n-RX were reacted with a 20% excess of sublimed Mg turnings under argon or nitrogen in many of the common aliphaitc and aromatic hydrocarbons. The conditions used for each run were standardized as closely as possible except for the length of reflux which depended on the particular halide. A typical run is described later, but it should be noted that all of the reacting n-RX was added at one time before bringing the solvent to reflux. The reactivity was such that a mildly exothermic reaction began which was readily controlled. The ground-glass joints were lubricated with Apiezon T as silicone grease was considered an organic base and might be washed into the reaction mixture. No initiators of any type were added. (In the few instances noted, a n-RI was used as an initiator.) After the reaction was complete, the heat was removed from the reaction mixture and the reaction allowed to cool to room temperature, and then centrifuged free of precipitate. The clear, colorless solution was analyzed for total base, halide ion and magnesium ion. All solutions were handled under argon or nitrogen until after hydrolysis for the analysis.

These reactions, once started, clouded up the solution with the precipitating MgX_2 so that the reacition could be followed visually. Induction periods for BuX or higher n-RX in refluxing n-heptane ranged as follows: iodides began to react before reflux was reached; bromides, in 5 - 15 min; chlorides, in 15 - 45 min. The induction period increased as the reflux temperature of the solvent was lowered. Once the reaction had begun, the mixtures were run at reflux for varying lengths of time depending on the apparent rate of reaction: iodides, 1½ - 3 h; bromides, 2 - 8 h; and chlorides, 4 - 12 h. The induction periods were shorter in the larger runs. The use of commercial Grignard grade Mg turnings in the reaction with n-C_8H_{17}Br in n-heptane had about the same induction period, yield and amount of coupling as the sublimed grade Mg. The regular Grignard grade Mg was less reactive toward n-C_8H_{17}Br in refluxing n-hexane, and no reaction occurred with n-C_8H_{17}Cl in refluxing n-heptane. This may be due to a thicker oxide coating or increased coupling due to traces of transition metal, providing a thicker MgX_2 coating.

The reactions of BuBr and n-C_8H_{17}Br were quite slow in n-pentane and isopentane, with induction periods up to 12 h, so that yields from n-RBr were always low in these solvents because of the competing coupling reaction. n-$C_8H_{17}Cl$ reacted normally in refluxing benzene and cyclohexane, but needed a few drops of a n-RI to initiate the reaction in refluxing n-hexane. The reaction of n-$C_8H_{17}Cl$ failed in refluxing n-pentane.

The presence of dissolved oxygen and apparently moisture, too, also appeared to inhibit the reaction. If the solvent or the n-RX to be used were accidently left open to the atmosphere, the induction period increased considerably when the reagents were used again.

A. Determination of halide, magnesium and base in solution

A 5-ml sample of the R_2Mg solution was pipetted into a known excess of standard 0.1 *N* aq. HNO_3 and back-titrated with stand. 0.1 *N* aq. NaOH using phenolphthalein. For very low concn. of R_2Mg, the soln. was added directly to H_2O, titrated with acid. After the base analysis, the light pink soln. was made slightly acidic and then analyzed for halide ion using 0.05 *M* aq. $AgNO_3$ soln. and dichlorofluorescein.

Another 5-ml sample of the same R_2Mg soln. was added to a slight excess of 0.1 *N* aq. HCl solution and a few ml of pH 10 buffer solution (NH_4Cl/NH_4OH) were then added. 0.3 g of UniVer-1 (Hach Chem. Co., Ames, Iowa) was then added, and the light pink soln. was titrated for Mg ion concn. with standard 0.1 *N* versene soln. (Base titrations of the organozinc compounds were performed with cresol purple as the indicator.)

B. Preparation of di-n-octylmagnesium (general procedure)

A 250-ml, 3-necked round-bottomed flask was equipped with a reflux condenser and a Tru-bore stirrer with teflon paddle. The joints were lubricated with Apiezon T. After 1.75 g (0.072 mole) of Mg turnings was added, the flask was flushed out with argon and heated by direct flame with the inert gas still flowing. Upon cooling under the gas flow, 150 ml of n-heptane and 10.4 ml (0.060 mole) n-$C_8H_{17}Br$ were added with a syringe. The soln. was heated to reflux as rapidly as possible (100°) with stirring. The soln. began to cloud in 5 - 10 min, and was refluxed for 7½ h after this point. The soln. was cooled and transferred to a 200-ml centrifuge bottle under argon and centrifuged for 1.5 h at about 1500 rpm yielding 150 ml of a clear, colorless soln. The yield by base titration was 60% as a 0.121 *M* solution of R_2Mg with a halide concn. of 0.0186 *M*. The $(n\text{-}C_8H_{17})_2Mg/MgBr_2$ was 12.96. GLC analysis of the hydrolyzed soln. showed 28% coupling and 12% n-$C_8H_{17}Br$ left. This procedure just described was used in all preparations.

C. Preparation of sec-butyl Grignard in hexane

The procedure and apparatus were the same. 200 ml hexane was added to 5.9 g (0.205 mole) of Mg turnings, and then 11.0 ml (0.102 mole) of s-BuBr was added. 1 ml (0.00954 mole) of Et_2O was added, and the soln. brought to reflux with stirring. The soln. became slightly clouded after 15 min. After 2 h the heat was turned off and the soln. allowed to cool. A small amount of ppt. had formed. The base concn. of the clear soln. was 0.041 *M*, and the halide concn. was 0.0316 *M* for a ratio of 1.27. The yield of s-Bu_2Mg was 8.8%

(continued on p. 38)

TABLE 9

PREPARATION OF GRIGNARD REAGENTS IN HYDROCARBONS

Run	RX	Solvent	Induction period, (h)	Reflux time, (h)	Calcd. Init. [RMg]	Concn. [R—Mg] found	Concn. [X$^-$] found	R_2Mg/MgX_2	R—R formed (%)	Yield (%)	RX final (%)
1	n-Octyl Cl	n-Heptane	1.00	3.0	0.392	0.1930	0.00596	32.38	33.0	50.5	5.0
2	n-Octyl Cl	n-Heptane	0.50	3.5	0.392	0.1950	0.00610	32.00		51.5	
3	n-Octyl Br	n-Heptane	0.10	3.7	0.300	0.1910	0.01564	12.21		66.0	
4	n-Octyl Br	n-Heptane	0.03	5.8	0.205	0.1510	0.0124	12.18	18.6	73.7	8.0
5	n-Octyl I	n-Heptane	0.00	5.8	0.205	0.1960	0.0382	5.13	4.1	81.7	4.3
6	n-Octyl Br	n-Heptane	0.08	7.9	0.400	0.2410	0.0186	12.96	28.2	60.3	11.7
7	n-Octyl I	n-Heptane	0.00	8.0	0.400	0.3760	0.0743	5.07	5.6	87.7	0.5
8	n-Octyl Br	n-Heptane	0.10	16.0	1.000	0.5390	a	a	25.9	54.6	4.6
9	n-Octyl Cl	n-Heptane	0.00	10.5	0.392	0.1480	0.00454	32.68	25.1	39.3	11.6
10	n-Octyl Br	n-Hexane	0.75	8.0	0.400	0.2090	0.0134	15.61	27.9	53.3	5.0
11	n-Octyl I	n-Hexane	0.00	9.0	0.400	0.3460	0.0581	5.96	9.8	87.7	1.5
12	n-Octyl Br	n-Pentane	2.75	9.0	0.400	0.0480	0.00277	17.31	20.0	8.4	39.8
13	n-Octyl Cl	Cyclohexane	0.50	7.5	0.400	0.1390	0.00494	28.18	21.9	34.5	9.8
14	n-Octyl Br	Cyclohexane	0.10	8.0	0.400	0.1700	0.0139	12.25	37.0	50.0	0.5
15	n-Octyl Br	n-Octane	0.00	4.1	0.400	0.2530	0.02948	8.59	21.1	64.5	0.0
16	n-Octyl Br	2,4,4-Trimethylpentane	0.00	4.2	0.400	0.1836	0.0153	11.96	22.4	59.6	0.0
17	n-Octyl Cl	Benzene	0.16	7.0	0.400	0.0573	0.0024	23.86	7.1	15.2	
18	n-Octyl Cl	n-Octane	0.16	6.8	0.400	0.1560	0.00544	27.90	23.0	61.5	0.9
19	n-Octyl Br	n-Octane	0.08	7.0	0.400	0.2100	0.0244	8.62	17.5	63.7	2.0
20	n-Octyl Br	Benzene	0.88	7.0	0.400	0.2278	0.02013	11.32	17.2	56.2	0.5
21	n-Propyl I	n-Hexane	0.30	7.5	0.400	0.0026					
22	n-Propyl Br	n-Heptane	0.00	5.5	0.300	0.0006					
23	n-Octyl Br	n-Pentane	7.30	2.3	0.400	0.0764	0.00442	17.28	33.3	19.8	
24	n-Butyl Br	n-Hexane	0.33	1.5	0.400	0.0895	0.00689	13.00	19.8	22.8	2.0
25	n-Butyl Br	n-Pentane	1.00	3.5	0.400	0.0838	0.00487	17.21		21.6	
26	n-Propyl I	n-Heptane	0.05	1.8	0.300	0.0030	0.00073	4.11	13.8	6.8	25.6
27	n-Pentyl Br	n-Hexane	0.30	1.5	0.400	0.2070	0.01420	14.58	1.9	52.8	18.5
28	n-Octyl I	Isopentane	0.30	2.0	0.400	0.2000	0.0307	6.52	8.2	47.7	25.4
29	n-Octyl I	n-Pentane	0.25	2.0	0.400	0.2440	0.0372	6.56	9.1	57.5	
30	n-Octyl I	Benzene	0.17	12.0	0.400	0.1900	0.0488	3.90	47.6	50.4	
31	Phenyl I	Xylene	0.17	4.0	0.300	0.0172	0.00999	1.72		5.7	

32	n-Propyl I	Benzene	0.10	1.0	0.400	0.0146	0.00544	2.69	6.5	3.8	4.6
33	n-Butyl I	Isopentane	0.33	2.0	0.400	0.1546	0.0262	5.90	11.8	40.5	19.7
34	n-Butyl I	n-Pentane	0.03	1.3	0.400	0.1830	0.0274	6.68	8.8	45.8	7.2
35	n-Octyl I	2,4,4-Trimethylpentane	0.00	1.3	0.400	0.2280	0.0448	5.09	9.6	69.6	5.0
36	n-Octyl I	n-Octane	0.00	1.3	0.400	0.2130	0.0400	5.33	2.2	65.1	
37	n-Butyl I	n-Heptane	0.00	1.8	0.400	0.3564	0.0672	5.32	1.3	88.4	
38	n-Butyl I	n-Hexane	0.00	1.8	0.400	0.3326	0.0544	6.12	2.9	88.4	2.1
39	n-Octyl I	Cyclohexane	0.00	1.0	0.400	0.1890	0.03825	4.94	17.6	74.2	
40	n-Hexyl Br	n-Hexane	0.10	1.5	0.400	0.1946	0.01268	15.36	3.1	50.0	12.7
41	2-Octyl I	Benzene	0.17	1.5	0.200	0.0061	0.00417	1.45	1.4	3.0	
42	Cyclohexyl I	Benzene	0.00	1.5	0.200	0.0041	0.00412	1.00	5.0	2.2	
43	n-Propyl Br	Benzene	1.25	2.0	0.300	0.0086	0.00101	8.49	5.5	3.0	73.7
44	Ethyl I	Benzene	0.10	1.5	0.200	0.0043	0.00324	1.33		2.1	
45	n-Octyl Cl	2,4,4-Trimethylpentane	1.00	3.0	0.400	0.1388	0.00484	28.64		35.0	
46	n-Butyl I	Benzene	0.00	1.2	0.400	0.3370	0.0686	4.92		89.0	
47	n-Octyl Br	n-Octane	0.00	2.0	0.400	0.1473	0.0170	8.66		58.3	
48	n-Butyl Br	Benzene	0.17	2.0	0.400	0.2092	0.02025	10.32		51.5	
49	n-Octyl Br	Toluene	0.08	1.7	0.400	0.1300	0.01872	6.94		43.0	
50	n-Octyl Br	n-Pentane	4.00	7.0	0.400	0.0488	0.00286	17.06		11.0	
51	n-Heptyl Br	n-Hexane	0.67	6.0	0.400	0.1214	0.00817	14.88		35.4	
52	n-Butyl I	Benzene	0.00	1.5	0.400	0.3600	0.0729	4.62		87.6	
53	n-Butyl Br	Benzene	0.17	4.0	0.400	0.0520	0.00649	8.02		13.0	
54	n-Butyl I	n-Hexane	0.00	3.5	0.400	0.3758	0.0596	6.34		98.5	
55	n-Butyl Br	n-Hexane	0.05	6.0	0.400	0.0016	heavy precipitate present				
56	n-Butyl Cl	n-Hexane	0.05	10.0	0.400	0.0002	heavy precipitate present				
57	n-Pentyl Cl	n-Hexane	0.25	11.5	0.400	0.1454	0.00406	32.58		47.9	
58	n-Pentyl Br	n-Hexane	0.25	7.0	0.400	0.2083	0.01369	15.25		59.0	
59	n-Pentyl I	n-Hexane	0.00	2.0	0.400	0.3018	0.04970	6.07		89.5	
60	n-Pentyl Br	n-Heptane	0.00	5.0	0.250	0.1673	0.01421	11.78		67.7	
61	n-Butyl I	n-Heptane[b]	0.33	4.5	0.400	0.2308	0.00478	48.4		56.0	ZnR_2
62	sec-BuBr	n-Heptane[b]	0.30	6.0	0.400	0.1710	0.1498	1.16		50.0	ZnR_2

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[a] Too viscous to centrifuge. [b] Zinc powder was used in place of magnesium as a comparison under these conditions.

(0.00954 mole) according the base titration, and the ratio of Et_2O to s-Bu_2Mg was 2.08.

D. Addition of oxygen in small amounts to di-n-pentylmagnesium

Several 30-ml samples of 0.0837 *M* (n-$C_5H_{11})_2Mg$ (n-$C_5H_{11}Br$) in n-heptane were added to small flasks and allowed to react briefly with varying amounts of air. The flasks were capped, shaken thoroughly in the presence of the gelatinous ppt. formed, and allowed to stand for 3 h. The clear supernatant was analyzed for base, halide and Mg ion (results in Table 6).

E. Addition of magnesium bromide to di-n-pentylmagnesium in n-heptane

115 ml (0.0122 mole) of 0.106 *M* (n-$C_5H_{11})_2Mg$ (n-$C_5H_{11}Br$) in n-heptane was added to a centrifuge bottle. Anhydrous $MgBr_2$, 3.0 g (0.017 mole), dried under vacuum for 12 h at 120°, was added to this soln. (The $MgBr_2$ was prepared from the reaction of sublimed Mg and $BrCH_2CH_2Br$ in Et_2O and dried under high heat and vacuum.) The mixture of $MgBr_2$ and (n-$C_5H_{11})_2Mg$ in n-heptane was shaken intermittently while being heated at 95° for ½ h. The soln. was allowed to cool for 3 h and then centrifuged. The clear supernatant was analyzed. The n-R_2Mg/MgX_2 ratio changed from 15.3 to 15.9 with only a 3% decrease in (n-$C_5H_{11})_2Mg$.

F. Addition of dioxane to di-n-octylmagnesium in n-heptane

To 164 ml (0.0127 mole) of 0.0835 *M* (n-$C_8H_{17})_2Mg$ (n-$C_8H_{17}Cl$) in n-heptane was added 0.024 ml (0.00028 mole) of dioxane. The soln. was shaken, centrifuged and the clear supernatant analyzed for base and halide. Additional dioxane 0.033 ml (0.00039 mole), was added to the soln., shaken, centrifuged and analyzed (results in Table 7).

G. Reactions of R_2Mg compounds in heptane

All reactions were run under argon atmosphere unless otherwise stated.

1. Carbon dioxide. 170 ml (0.0155 mole) of 0.092 *M* (n-$C_8H_{17})_2Mg$ (n-$C_8H_{17}Br$) in 2,4,4-trimethylpentane was poured over an excess of crushed Dry Ice in a large beaker. After warming to r.t. and working up with aq. HCl and CH_2Cl_2, the yield of distilled pelargonic acid was 2.77 g, 56%; b.p. 101 - 102° (1.6 mm); lit. [47] b.p. 150° (20 mm).

2. Oxygen. 125 ml (0.0239 mole) of 0.096 *M* (n-$C_8H_{17})_2Mg$ (n-$C_8H_{17}Br$) in n-heptane was reacted with air by stir. in an open dish for 10 min. The reaction was worked up with aq. 1 *M* NH_4Cl and hexane. The yield was 1.87 g distilled 1-octanol, 60%; b.p. 47 - 49° (0.6 mm); lit. [47] b.p. 98° (19 mm).

3. 4-Phenyl-3-buten-2-one. 100 ml (0.0084 mole) of (n-$C_5H_{11})_2Mg$ (n-$C_5H_{11}Br$) in n-heptane was added to 2.34 g (0.016 mole) of 4-phenyl-3-buten-2-one with stirring at 0° over 7 min. The soln. was warmed to r.t., and after 3 h, worked up with aq. 1 *M* NH_4Cl and CH_2Cl_2. After removal of the solvent, the residue was chromatographed over Woelm Act. IV neutral alumina using pet. ether. The total product recovery was 3.34 g, 95%. The amount of saturated ketone or 1,4-addition was 63%, and that of the tertiary alcohol or 1,2-addition was 37% of the isolated product.

4. Propylene oxide. 100 ml (0.0073 mole) of 0.073 *M* $(n\text{-}C_5H_{11})_2Mg$ $(n\text{-}C_5H_{11}Cl)$ in n-heptane was added to 1.0 ml (0.0145 mole) propylene oxide in 20 ml n-heptane at 0° over 15 min with stirring. The soln. was warmed to r.t. and stirred 22 h, and worked up with aq. 1 *M* NH_4Cl and hexane. (No ppt. had formed during the reaction.) The yield of distilled 2-octanol was 0.5 g, 27%, b.p. 60° (4 mm); lit. [47] b.p. 86° (20 mm).

5. Mercuric bromide. 100 ml (0.00836 mole) of 0.0836 *M* $(n\text{-}C_5H_{11})_2Mg$ $(n\text{-}C_5H_{11}Br)$ in n-heptane was added to 9.0 g (0.0247 mole) $HgBr_2$ in 100 ml benzene over 15 min with stirring. The cloudy soln. was poured into 150 ml cold H_2O. The organic layer after extraction 3 times with H_2O was dried over anhydrous Na_2SO_4 and evaporated to product. The n-pentylmercuric bromide after crystallization weighed 4.38 g, 75% yield; m.p. 121.6 - 122.5°; lit. [48] m.p. 122.3°.

6. Pyrrole. 100 ml (0.0073 mole) of $(n\text{-}C_5H_{11})_2Mg$ $(n\text{-}C_5H_{11}Cl)$ in n-heptane was added to 1.0 ml (0.0145 mole) of pyrrole at 0° over 30 min with stirring. A heavy white ppt. formed. The reaction was warmed to r.t. and after 1 h was cooled to 0°, and 2.0 ml (0.021 mole) of ethyl chloroformate added. The reaction was warmed to r.t. after 10 min. After another 6 h, water was added, the pH adjusted to 7.0 - 8.0 and the mixture extracted twice with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4. GLC of this solution showed the product to be 43% ethyl 1- and 57% ethyl 2-pyrrolecarboxylate. The yield of distilled product mixture was 0.9 g, 50%.

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