Journal of Organometallic Chemistry, 292 (1985) 325–333
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

PREPARATION OF SOLVATED AND/OR UNSOLVATED SIMPLE AND MIXED DIARYLMAGNESIUMS

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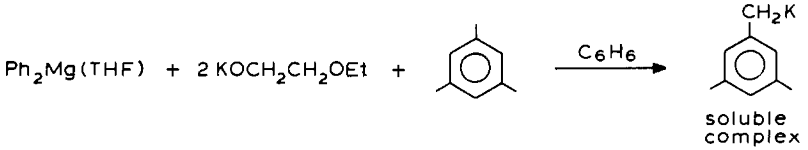
(Received February 14th, 1985)

Summary

Arylation of arylmagnesium halides or magnesium halide etherates by aryllithium provides a convenient method of preparing $Ar_2Mg(Et_2O)_2$ or $Ar_2Mg(THF)_2$. The ether complexes can be completely desolvated but the THF complexes cannot. Mixed diarylmagnesium tetrahydrofuranates, $Ar^1Ar^2Mg(THF)_2$, although coordinationally saturated, have ^1H and ^{13}C NMR spectra which suggest that they are fluxional.

We have been involved for some time in the development of soluble as well as storable organometallic reagents of the heavier alkali metals [1,2]. We recently observed that dialkyl- and diaryl-magnesiums form complexes with alkali metal alkoxides, and that with certain alkoxides, such as $MOCH_2CH_2OEt$, these complexes are soluble in hydrocarbon media [3]. These soluble complexes exhibit normal organometallic reactivity, i.e., they function both as alkylating or arylating agents, and as metalating reagents. For example, potassiation of mesitylene can be carried out in a selective and homogeneous reaction with these reagents, as can the sodiation of thioanisole, eq. 1 and 2, respectively.



(1)

$$Ph_2Mg + 2\,NaOCH_2CH_2OEt + PhSCH_3 \xrightarrow{C_6H_6} \underset{\text{soluble complex}}{PhSCH_2Na} \qquad (2)$$

Obviously, the ready preparation of these reagents depends on the existence of a convenient method of preparing diphenylmagnesium free from halide ions. This prompted us to examine some of the existing methods [4] of preparing diarylmag-

0022-328X/85/$03.30

nesiums and to search for new ones. In this paper we describe convenient methods of preparation of both solvated and unsolvated, as well as simple and mixed diarylmagnesiums, and report the ^{13}C spectra of their tetrahydrofuranates.

The use of the organomercurial route for the synthesis of Ph_2Mg quarantees a product free of halide ion but unfortunately, this method involves use of a Carius bomb [5]. In our attempts to avoid the use of a Carius bomb, we were unsuccessful in trying to make diphenylmercury react with magnesium metal in boiling diethyl ether; dialkylmercury compounds in contrast do react with magnesium metal in boiling Et_2O. Even in refluxing tetrahydrofuran (THF) diphenylmercury reacts with magnesium very sluggishly, and to complete the reaction requires about one week even after activation of the metal with mercuric chloride. The completeness of the conversion of Ph_2Hg to Ph_2Mg can be confirmed by hydrolysing an aliquot of the solution. Any solid material or cloudiness in the hydrolysate indicates absence of unreacted Ph_2Hg; solutions of diphenylmagnesium in THF prepared by the organomercurial route were almost water-clear. Several attempts to desolvate $Ph_2Mg(THF)_2$, the coordinationally saturated solvate [6], were unsuccessful. Upon heating solid $Ph_2Mg(THF)_2$ up to 100°C under vacuum (ca. 0.04 mbar) for 24 h, we obtained the monosolvate $Ph_2Mg(THF)$, as a glassy material soluble in aromatic hydrocarbons.

Alkylation of magnesium chloride and alkylmagnesium chlorides by organolithium reagents has been reported [7] to lead to simple and mixed dialkylmagnesiums, respectively. This method gives halide-free products which can be desolvated from their etherates. A very interesting result from the same work [7] is that a hydrocarbon-soluble unsolvated dialkylmagnesium, Bu^s_2Mg solubilizes dialkylmagnesiums, such as Bu^i_2Mg, which are normally insoluble apparently as a result of a conproportionation (eq. 3).

$$\underset{\text{soluble}}{\frac{n}{2}(Bu^s_2Mg)} + \underset{\text{insoluble}}{\frac{n}{2}(Bu^i_2Mg)} \rightarrow \underset{\text{soluble}}{(Bu^sMgBu^i)_n} \qquad (3)$$

Magnesium bromide has been used as a trapping agent for carbanions generated in situ by the action of a naphthalenesodium radical anion on alkyl halides [8]. Monoarylation of magnesium bromide etherate has recently become of importance in certain synthetic strategies involving lithiated aromatic compounds [9].

We obtained diphenylmagnesium etherate with very low halide ion content from the reaction of strictly equivalent amounts of phenyllithium and phenylmagnesium bromide in diethyl ether (eq. 4)

$$PhLi + PhMgBr \xrightarrow{Et_2O} Ph_2Mg(Et_2O)_2 + LiBr \qquad (4)$$

The reaction is rapid and exothermic. The diphenylmagnesium etherate thus produced can be taken up in toluene after removal of the ether solvent. The total alkalinity should correspond to the magnesium content and halide ion must be absent to obtain diphenylmagnesium as the only species in solution. (Analysis indicated that these conditions were met). In this way a substantial amount of diphenylmagnesium etherate can be prepared rapidly and conveniently in a relatively short time. Thus, we prepared ca. 1 mole of $Ph_2Mg(Et_2O)_2$ in one day as a 1.0 *N* solution in toluene, with an Mg/Br ratio of 100/1. Evidently the more accurately the PhLi and the PhMgBr solutions are standardized and the more accurately the volumes are measured the lower the halide content. The same method was employed for the preparation of mixed diarylmagnesiums, as e.g., in eq. 5.

$$p\text{-CH}_3\text{C}_6\text{H}_4\text{Li} + o\text{-CH}_3\text{C}_6\text{H}_4\text{MgBr} \xrightarrow{\text{Et}_2\text{O}} (o,p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{Mg(Et}_2\text{O)}_2 + \text{LiBr} \quad (5)$$

Simple diarylmagnesium can be prepared by treating aryllithium reagents with magnesium bromide or chloride. The active form of magnesium halide required for the reaction was prepared from magnesium and the appropriate 1,2-dihaloethane [10], (eq. 6)

$$\text{Mg} + \text{XCH}_2\text{CH}_2\text{X} \xrightarrow{\text{Et}_2\text{O or THF}} \text{MgX}_2(\text{R}_2\text{O})_2 + \text{CH}_2=\text{CH}_2 \quad (6)$$

The THF-solvated $MgBr_2$ and $MgCl_2$, after being kept under vacuum (ca. 0.05 mbar) for 24 h gave analyses corresponding with $MgBr_2(THF)_2$ and $MgCl_2(THF)_{1.5}$, respectively. It is likely that $MgCl_2(THF)_2$ undergoes partial desolvation under these conditions. The diethyl ether complex of $MgBr_2$ under these conditions was almost completely desolvated, and this may be a good way of making anhydrous $MgBr_2$. The THF complexes of $MgCl_2$ and $MgBr_2$ both reacted readily with aryllithium reagents, e.g. eq. 7.

$$2\ o\text{-CH}_3\text{C}_6\text{H}_4\text{Li} + \text{MgBr}_2(\text{THF})_2 \rightarrow (o\text{-CH}_3\text{C}_6\text{H}_4)_2\text{Mg(THF)}_2 \quad (7)$$

It should be emphasized that the use of THF-complexed magnesium halides leads to THF solvated diarylmagnesiums even though diethyl ether is the reaction medium. Evidently, Ar_2Mg competes successfully with LiBr for the stronger Lewis base · THF. Lithium bromide solvated with THF has considerable solubility in toluene, viz. 0.39 *M*, and so solutions of $Ar_2Mg(THF)_2$ prepared according to eq. 7 have rather low Mg/Br ratios, usually about 3/1. If this method is used for the preparation of unsolvated Ar_2Mg then magnesium bromide etherate should be employed. Diphenylmagnesium etherate can be desolvated completely by heating under vacuum at 60–80°C for 24 h. Unsolvated diphenylmagnesium is insoluble in aromatic hydrocarbons.

The ^1H NMR spectra of the simple and mixed diarylmagnesium tetrahydrofuranates were recorded and used mainly for determining the Mg/THF ratio in the complex e.g. Fig. 1. This ratio was found to range between 1/1.4 and 1/2.0. In cases where the Mg/THF ratio deviates markedly from the expected value of 1/2.0, such as entries 1 and 3, Table 1, the THF used in the preparation was sufficient only to solvate the diarylmagnesium. It seems, therefore, that the LiBr formed competes with Ar_2Mg for the THF. Partial desolvation during sample preparation seems also to be a possible explanation of the deviation of the Mg/THF ratio from 1/2.0

Table 1 also shows the positions of the ^1H NMR signals from the methyl protons of the tolyl groups in simple and mixed diarylmagnesiums, shielding increases in the order p-CH_3, m-CH_3, o-CH_3, and the shifts depend very little on whether the tolyl group is present in a simple or a mixed diarylmagnesium. For example, the p-CH_3 protons resonate at 2.40 ± 0.01 ppm in both $(o,p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{Mg}$ and $(m,p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{Mg}$, entires 5 and 6, the small variation observed in the chemical shift may well be due to concentration-difference effects in the samples. The variations in the chemical shifts of H(α) and H(β) of the THF ligand are more pronounced. It is noteworthy that the PMR spectrum of $(o,p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{Mg (THF)}_2$ and the spec-

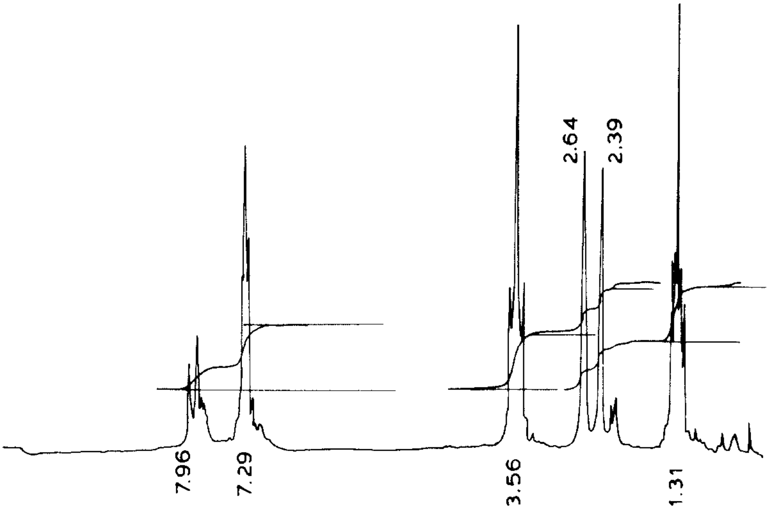


Fig 1. The 80 MHz ^1H NMR spectrum of *o,p*-ditolylmagnesium tetrahydrofuranate (Solvent C_6D_6)

trum of an equimolar mixture of $(o\text{-}CH_3C_6H_4)_2Mg(THF)_2$ and $(p\text{-}CH_3C_6H_4)_2\text{-}Mg(THF)_2$ are almost identical (compare entries 5 and 5a).

The ^{13}C spectra, which are summarized in Table 2, and shown e.g. in Fig. 2, exhibit a similar insensitivity to composition. For example, the positions of the C(*o*-) resonances in di-*o*-tolylmagnesium and the *o,p*-ditolylmagnesium are almost identical, viz., 28.37 and 28.46. Again, the C(*p*-) resonance is at 21.84 in the di-*p*-tolylmagnesium and 21.87 in *m,p*-ditolylmagnesium; the small difference, is probably due to concentration differences for the two samples. The C(α) and C(β) resonances, which appear in the range 69.11–69.75 and 25.02–24.34, respectively, reflect, amongst other effects, small differences in the Mg-THF coordination bond strengths. Unfortunately, the concentration of the $Ar_2Mg(THF)_2$ in the NMR samples, as well

TABLE 1

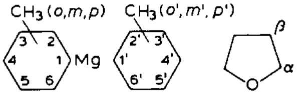
SELECTED ^1H NMR SHIFTS IN DIARYLMAGNESIUM TETRAHYDROFURANATES [e]

Entry	Ar^1	Ar^2	*o*-CH_3	*m*-CH_3	*p*-CH_3	H(α)	H(β)	Mg/THF ratio
1	Phenyl	*p*-tolyl			2.38	3.47	1.21	1/1.50
2	*o*-tolyl	*o*-tolyl [a]	2.66			3.59	1.43	1/2.0
2a	*o*-tolyl	*o*-tolyl [b]	2.68			3.60	1.35	1/2.0
3	*m*-tolyl	*m*-tolyl		2.45		3.41	1.14	1/1.40
4	*p*-tolyl	*p*-tolyl [a]			2.39	3.51	1.19	1/1.60
4a	*p*-tolyl	*p*-tolyl [b]			2.41	3.57	1.26	1/2.0
5	*o*-tolyl	*p*-tolyl [c]	2.64		2.39	3.56	1.31	1/2.0
5a	*o*-tolyl	*p*-tolyl [d]	2.70		2.41	3.60	1.33	1/2.0
6	*m*-tolyl	*p*-tolyl		2.48	2.39	3.56	1.25	1/1.70
7	*o*-tolyl	*m*-tolyl	2.65	2.43		3.53	1.24	1/2.0
8	Phenyl	Phenyl				3.65	1.38	1/1.00

[a] From $2ArLi + MgX_2$. [b] From $ArLi + ArMgBr$. [c] Prepared from $Ar^1Li + Ar^2MgBr$. [d] Prepared from $Ar^1_2Mg(THF)_2 + Ar^2_2Mg(THF)_2$. [e] The concentration of the diarylmagnesiums in the samples was estimated to be in the range 0.2–0.5 *M*.

TABLE 2

^{13}C NMR SPECTRA OF DIARYLMAGNESIUM TETRAHYDROFURANATES

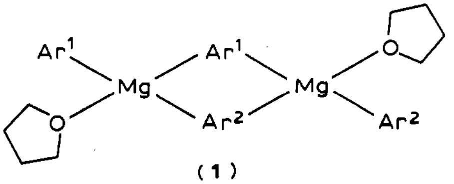


Entry no	Ar^1	Ar^2	
1	Phenyl	*p*-tolyl	C(1) 165.34; C(2, 6) 142.00; C(3.5) 126.76; C(4) 125.99; C(1′) 157.10; C(2′, 6′) 143.07; C(3′, 5′) 127.93; C(4′) 04135.56; C(α) 69.44; C(β) 25.10
2	*o*-tolyl	*o*-tolyl [a]	C(*o*) 28.37; C(1) 169.18; C(2) 147.84; C(3) 126.41; C(4) 125.05; C(5) 123.28; C(6) 140.81; C(α) 69.11; C(β) 25.34
2a	*o*-tolyl	*o*-tolyl [b]	C(*o*) 28.42; C(1) 168.40; C(2) 147.82; C(3) 126.62; C(4) 125.34; C(5) 123.44; C(6) 140.76; C(α) 69.29; C(β) 25.25
3	*m*-tolyl	*m*-tolyl	C(*m*) 22.12; C(1) 162.26; C(2) 143.94; C(3) 135.03; C(4) 126.85; C(5) 127.84; C(6) 139.99; C(α) 69.44; C(β) 25.02
4	*p*-tolyl	*p*-tolyl [a]	C(*p*) 21.84; C(1) 158.06; C(2,6) 143.03; C(3,5) 127.95; C(4) 135.62; C(α) 69.49; C(β) 25.06
4a	*p*-tolyl	*p*-tolyl [b]	C(*p*) 21.83; C(1) 160.95; C(2,6) 142.04; C(3,5) 127.66; C(4) 134.28; C(α) 69.35; C(β) 25.15
5	*o*-tolyl	*p*-tolyl [c]	C(*o*) 28.46; C(1) 167.57; C(2) 148.06; C(3) 126.67; C(4) 125.57; C(5) 123.46; C(6) 141.01; C(*p*′) 21.84; C(1′) 161.78; C(2′, 6′) 142.24; C(3′, 5′) 127.72; C(4′) 134.39; C(α) 69.43; C(β) 25.21
5a	*o*-tolyl	*p*-tolyl [d]	C(*o*) 28.53; C(1) 168.12; C(2) 147.85; C(3) 126.59; C(4) 125.35; C(5) 123.40; C(6) 140.81; C(*p*′) 21.83; C(1′) 162.88; C(2′, 6′) 141.59; C(3′, 5′) 127.54; C(4′) 133.61; C(α) 69.28; C(β) 25.25
6	*m*-tolyl	*p*-tolyl	C(*m*) 22.28; C(1) 165.58; C(2) 142.79; C(3) 134.58; C(4, 5) 126.58; C(6) 138.89; C(*p*′) 21.87; C(1′) 160.14; C(2′, 6′) 142.37; C(3′,5′) 127.79; C(4′) 134.70; C(α) 69.51; C(β) 25.16
7	*o*-tolyl	*m*-tolyl	C(*o*) 28.56; C(1) 166.66; C(2) 147.91; C(3) 126.47; C(4) 126.21; C(5) 123.48; C(6) 140.88; C(*m*′) 22.27; C(1′) 162.02; C(2′) 142.42; C(3′) 134.42; C(4′, 5′) 126.67; C(6′) 138.50; C(α) 69.29; C(β) 25.20
8	Phenyl	Phenyl	C(1) 166.40; C(2, 6) 141.91; C(3,5) 126.83; C(4) 125.88; C(α) 69.75; C(β) 25.31

[a,b,c,d] See relevant footnotes in Table 1.

as the Mg/THF ratio, could not be kept constant, and quantitative comparisons of relative Mg–THF bond strengths could not be made.

From the measured Mg/THF ratios (Table 1) the percentage of the coordinationaly saturated species, $Ar^1Ar^2Mg(THF)_2$ can be calculated. For example, a ratio of 1/1.4 indicates that the sample is composed of 40% $Ar^1Ar^2Mg(THF)_2$ and 60% $Ar^1Ar^2Mg(THF)$. There is no doubt that the monosolvated species must be in the form of a dimer with bridging aryls [11] **1**.



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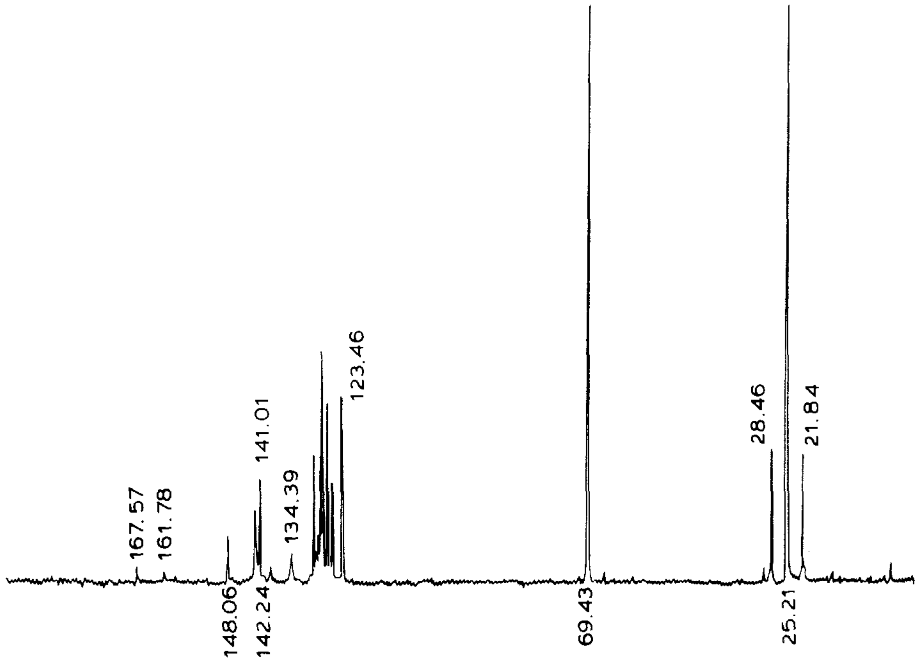
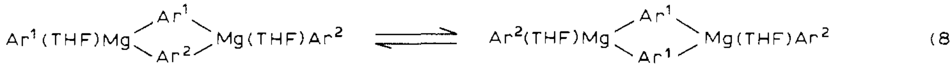


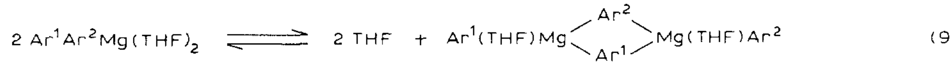
Fig. 2. The ^{13}C NMR spectrum of *o,p*-ditolylmagnesium tetrahydrofuranate (Solvent C_6D_6).

The presence of a bridge structure suggests the possibility of "disproportionation", [12], e.g. via the process shown in eq. 8. Such a process is implied by both the ^1H and



$$\mathrm{Ar^1(THF)Mg}\Big\langle{}^{\mathrm{Ar^1}}_{\mathrm{Ar^2}}\Big\rangle\mathrm{Mg(THF)Ar^2} \rightleftharpoons \mathrm{Ar^2(THF)Mg}\Big\langle{}^{\mathrm{Ar^1}}_{\mathrm{Ar^1}}\Big\rangle\mathrm{Mg(THF)Ar^2} \qquad (8)$$

^{13}C NMR spectra. Moreover, the NMR spectra suggest that even the coordinationally saturated species, such as in entry 5, are fluxional in character. We took special care to record the spectrum of *o,p*-ditolylmagnesium with a Mg/THF ratio of 1/2.0, and observed that the spectrum was almost identical to that obtained for an equimolar mixture of di-*o*-tolylmagnesium and di-*p*-tolymagnesium with a Mg/THF ratio of 1/2.0, see entries 5, 5a, Table 1, 2. Thus it is necessary to consider mechanisms by which a coordinationally saturated mixed diarylmagnesium tetrahydrofuranate "structurally equilibrates", and a reasonable scheme is depicted in eq. 9.



$$2\,\mathrm{Ar^1Ar^2Mg(THF)_2} \rightleftharpoons 2\,\mathrm{THF} + \mathrm{Ar^1(THF)Mg}\Big\langle{}^{\mathrm{Ar^2}}_{\mathrm{Ar^1}}\Big\rangle\mathrm{Mg(THF)Ar^2} \qquad (9)$$

In this it is assumed that the coordinationally saturated species loses one THF ligand to form the monosolvated bridged structure **1**, and as soon as the bridged structure in eq. 9 is formed, the equilibrium as shown in eq. 8 is set up. Obviously both processes in eq. 8 and 9 would have to be rapid on the NMR time scale.

Experimental

Proton and ^{13}C NMR spectra were recorded with a VARIAN FT 80A NMR spectrometer. Samples of $Ar_2Mg(THF)_2$ for NMR analysis were prepared as follows: An aliquot of a toluene solution of the diarylmagnesium tetrahydrofuranate (for preparation see below) containing 3–5 mmol was transferred to a Schlenk tube to which a 5 mm NMR tube was fused. The solution was evaporated to dryness under vacuum for 16–24 h at room temperature, and the residue was dissolved in benzene-d_6 by standard vacuum line techniques. An aliquot of the latter solution was transferred to the NMR tube which was then sealed with a torch. Chemical shifts are reported relative to $(CH_3)_4Si$. The somewhat tentative assignments of the signals from the aromatic carbon nuclei are based on SCS for monosubstituted benzenes [13].

Analytical methods

Total Alkalinity in hydrolysed aliquots was determined by standard acid titration to pH 7. Magnesium was determined complexometrically by EDTA titration [14]. Chloride ion and bromide ion were determined by the Mohr and Volhard procedures, respectively.

Preparation of active magnesium halides

Magnesium chloride and bromide were prepared from magnesium turnings and the apropriate 1,2-dihaloethane in diethyl ether or THF, the reaction being carried out as in an ordinary Grignard preparation. Magnesium bromide etherate thus prepared forms a heavy oily phase, which is approximately 2.8 *M* in $MgBr_2$. Magnesium bromide etherate is readily desolvated to $MgBr_2$, even by being kept under vacuum at room temperature for 24 h. The desolvated material is resolvated very slowly by diethyl ether (several days being required) to reform the two-phase solution. The tetrahydrofuranates of $MgCl_2$ and $MgBr_2$ after being kept under vacuum (ca 0.04 mbar) for 24 h at room temperature gave Mg and halide analyses consistent with the formulae $MgCl_2(THF)_{1.5}$ and $MgBr_2(THF)_2$.

Preparation of diphenylmagnesium

A Grignard solution prepared from 12.5 g of magnesium turnings, 0.50 mol of bromobenzene, and ca 300 ml of anhydrous ether, was found to be 1.50 *N* (total alkalinity), 1.59 *N* by magnesium analysis, and 1.52 *N*, by bromide determination; average, 1.536 *N*. A second solution of PhLi in ether prepared from 7.5 g of lithium chips, 0.50 mol of bromobenzene, and 400 ml of anhydrous ether, was found to have a total alkalinity of 1.075 *N*. Volumes of each of the solutions containing 0.40 mol of PhLi and PhMgBr were measured accurately under argon with the same graduated cylinder, then mixed and stirred magnetically. The mixture, which became warm, was stirred at room temperature for 4.5 h. Titration of an aliquot indicated a total alkalinity of 1.40 *N* and a magnesium content of 1.395 *N*. The ether solution was evaporated to dryness under vacuum and the $Ph_2Mg(Et_2O)_2$ was extracted with 500 ml of anhydrous argon-saturated toluene. Analysis of the toluene solution indicated: Total alkalinity, 0.99 *N*, Magnesium, 1.01 *N*, Bromide ion, 0.005 *N*. Thus, Mg/Br ratio is equal to 100/1.

Desolvation of $Ph_2Mg(Et_2O)_2$

A solution of $Ph_2Mg(Et_2O)_2$ in toluene (20 ml), containing ca. 10 mmol of the reagent, was cooled with a liquid nitrogen bath. After the cooling had been discontinued the stirred mixture was evaporated to dryness. The solid $Ph_2Mg(Et_2O)_2$

was kept at 60–80°C (oil bath temperature) under vacuum for 24 h, and then ca 20 ml of of pure methylcyclohexane was added under argon. The flask containing the suspension of Ph_2Mg in methylcyclohexane was immersed in a Dry Ice and acetone bath and 2.5 ml of isoamyl alcohol was added from a syringe [7]. Cooling was discontinued and the mixture was stirred at room temperature for several hours. GLC analysis of the methylcyclohexane phase indicated the absence of diethyl ether.

Preparation of di-o-tolylmagnesium tetrahydrofuranate

A solution of $MgCl_2$ in THF (33 ml of 0.61 *M*; 20 mmol) was evaporated almost to dryness under vacuum. To the residue under argon was added 31.6 ml of a 0.86 *N* solution of *o*-tollyllithium in ether. The mixture was stirred overnight and then evaporated to dryness. Dry, argon-saturated toluene, 20 ml, was added and the resulting mixture was stirred magnetically for 1 h. Upon standing a clear supernatant solution was formed. The product was characterized by its proton and ^{13}C NMR spectra, see entry no. 2, Table 1 and 2.

Preparation of o,m-ditolylmagnesium etherate

m-Tolyllithium in ether, 35.0 ml, 0.86 *N*, was added to 31.0 ml of a 0.97 *M* solution of *o*-$CH_3C_6H_4MgBr$ in Et_2O. The mixture was stirred overnight and then evaporated to dryness under vacuum. About 15 ml of dry argon-saturated toluene was added under argon and the mixture was stirred magnetically for 14 h. On standing a clear supernatant solution separated, and an aliquot of this was withdrawn for titration. It was found to be 2.45 *N* in total alkalinity, 1.25 *M* in magnesium, and 0.08 *N* in bromide ion. Thus, the Mg/Br ratio is ca. 16/1. For NMR data see entry no. 7, Tables 1 and 2.

Preparation of diphenylmagnesium tetrahydrofuranate by the organomercurial route

A mixture of diphenylmercury (11.0 g, ca. 30 mmol) mercuric chloride (0.2 g), magnesium turnings (0.75 g) and THF (60 ml) were stirred under argon at 55–60°C for 6 days. An aliquot was hydrolysed, to give a clear solution, indicating the absence of uncharged Ph_2Hg. (When aliquots of the solution were hydrolysed after shorter reaction times insoluble material or cloudiness was observed.) The total alkalinity of the solution was found to be 1.05 *N*. An attempt to desolvate the diphenylmagnesium by heating an aliquot at 100°C under vacuum for 24 h gave the monosolvate $Ph_2Mg(THF)$, as a glassy mass soluble in aromatic hydrocarbons. This product was characterized from ^1H proton and ^{13}C NMR spectra. See entry 8, Tables 1, 2.

Acknowledgment

We thank professor John P. Oliver of Wayne State University for a helpful suggestion.

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