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THE DIPHENYLMAGNESIUM/ALKALI METAL ALKOXIDE SYSTEM. HYDROCARBON-SOLUBLE ORGANOALKALI METAL REAGENTS

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Summary

Unsolvated diphenylmagnesium is solubilized in aromatic hydrocarbon solvents by an alkali metal 2-ethoxyethoxide. The mode of interaction between Ph_2Mg and $MOCH_2CH_2OEt$ ($M = Li, Na, K$) varies with M. For $M = Li$ the complex formed has an Mg/Li ratio equal to 1.3/1.0, and is evidently different from the $PhLi/Mg(OCH_2CH_2OEt)_2$ complex. For $M = Na$, the metal–metal interchange apparently leads to a complex identical to that derived from PhNa and $Mg(OCH_2CH_2OEt)$. For $M = K$ the results are not conclusive. The width of the resonance ^{13}C from the *ipso*-carbon, increases with increasing ionic radius, and for $M = K$ the signal is too broad to be clearly observed. The *ipso*-carbon in the NMR spectrum of the $PhNa/Mg(OCH_2CH_2OEt)$ complex has now been shown to give rise to resonance at 175.95 ppm. Metalation experiments involving Ph_2Mg along with two equivalents of $MOCH_2CH_2OEt$ indicated that reactivity increases in the order $Li < Na < K$.

Organosodium and organopotassium reagents which can be stored and used as homogeneous alkylating or metalating agents are obviously desirable. One such type of reagent was reported in a recent publication [1], this type of reagent resulted from the solubilizing effect of certain magnesium alkoxides on unsolvated arylalkali metal compounds. Thus, possibly contrary to expectation, PhNa and PhK for example form benzene-soluble complexes with $Mg(OCH_2CH_2OEt)_2$ rather than undergoing metal–metal interchange. Phenylsodium was shown to form the complex $[Na_2Mg(Ph)_2(OCH_2CH_2OEt)_2]_n$ which exhibits normal organometallic reactivity toward electrophiles such as CO_2 and benzophenone, and metalates such as thioanisole, for example, to give $PhSCH_2Na$, just as do ordinary organosodium reagents under heterogeneous conditions [2]. It is probable [3] that n is > 1 and in this case the complex $[Na_2Mg(Ph)_2(OCH_2CH_2OEt)_2]_n$ could be viewed as a bimetallic pleiad or cluster, and this class of organometallic compounds may be of even greater importance than was initially evident [4].

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It appeared of interest to investigate the behaviour of the system $Ph_2Mg/MOCH_2CH_2OEt$, where M is an alkali metal, because it could possibly give the same complexes as are formed from PhM and $Mg(OCH_2CH_2OEt)_2$ [1].

The following modes of interaction between diphenylmagnesium and an alkali metal alkoxide can be envisaged: (a) metal–metal exchange (eq. 1), (b) complex formation (eq. 2), and (c) mixed mode, involving partial metal–metal exchange and complex formation among the species shown on both sides of eq. 1.

$$Ph_2Mg + MOCH_2CH_2OEt \rightarrow PhMgOCH_2CH_2OEt + PhM \qquad (1)$$

$$nPh_2Mg + mMOCH_2CH_2OEt \rightarrow (Ph_2Mg)_n(MOCH_2CH_2OEt)_m \qquad (2)$$

The mode shown in eq. 1 appears more likely to occur in the light of the analogy with the system $Bu^tOK/BuLi$, which involves metal–metal interchange and formation of the organometallic product of the more electropositive metal [5,6].

Diphenylmagnesium forms almost water-clear solutions in tetrahydrofuran (THF). Under this condition Ph_2Mg is a very poor metalating agent, it does not, for example, metalate triphenylmethane at an appreciable rate. If sodium 2-ethoxyethoxide is also present, however, the red color of the Ph_3C^- anion appears instantly. Even the characteristic color due to $PhCH_2^-$ forms when a potassium alkoxide is added to a solution of Ph_2Mg in THF and toluene. In the absence of a substrate capable of being metalated, addition of an alkali metal alkoxide to Ph_2Mg in THF produces a brownish solution reminiscent of concentrated solutions of PhLi in ether. There is no doubt that diphenylmagnesium in THF is coordinationally saturated, i.e., $Ph_2Mg(THF)_2$ [7], and in such a case would seem more probable that the observed enhanced reactivity of Ph_2Mg in the presence of an alkali metal alkoxide is due to metal–metal interchange, i.e., eq. 1. The alternative, complex formation, requires ligand displacement from $Ph_2Mg(THF)_2$, and the question arises of whether this is possible. In order to clarify this point we employed a mixture of $KOCH_2CH_2OEt$ and Ph_2Mg in THF and toluene. We assumed that if a 'simple' displacement reaction occurred the organometallic species PhK and the metalation product $PhCH_2K$ would not survive long in the presence of the readily cleaved THF. However, after carbonation we isolated ca. 60% yield of phenylacetic acid and obviously, some type of interaction, probably complex formation, between the reactant and/or organometallic product and the respective alkoxides makes both PhK and $PhCH_2K$ less reactive toward THF. Of course, complexation requires that the alkoxide is a more effective ligand than THF, and it is noteworthy that interaction between organometallic compounds and metal alkoxides is not uncommon [1,5,6,8].

Unsolvated diphenylmagnesium, which is insoluble in benzene [9], when brought into contact with a benzene solution of $NaOCH_2CH_2OEt$ interacts exothermically with the alkoxide and dissolves. The dissolution of Ph_2Mg is accompanied by the development of a brownish color, which is again reminiscent of solutions of phenyllithium in ether. Formation of 'free' PhNa can be ruled out because phenylsodium is insoluble in benzene [10], no precipitation was observed even after a few days at room temperature. In order to prepare the soluble species with the minimum amount of alkoxide unsolvated diphenylmagnesium was dissolved completely in benzene containing two equivalents of the alkali metal alkoxide. An aliquot of the solution was added to a large excess of unsolvated Ph_2Mg. Surprisingly this method failed with $NaOCH_2CH_2OEt$, the soluble species reacting with the solid Ph_2Mg to form insoluble products. When the method was used for the system $LiOCH_2CH_2OEt/Ph_2Mg$, it gave a benzene-soluble species with a Li/ Mg ratio of 1/1.3. Potassium 2-ethoxyethoxide has only a low solubility (< 0.2 *M*) in benzene at room temperature, and only becomes very soluble at temperatures above 50°C. When diphenylmagnesium and two equivalents of $KOCH_2CH_2OEt$ are mixed in benzene heat is evolved and both species dissolve to give a brownish solution. On standing the color changes to purple, the solution becomes viscous, and some precipitation takes place. Use of the monosolvate $Ph_2Mg(THF)$ gave a more stable solution without significant loss of organometallic activity even at higher temperatures (60–70°C), evaporation of this solution under vacuum at room temperature resulted in loss of THF. In contrast in the absence of alkoxide complete desolvation of $Ph_2Mg(THF)_2$ did not take place even at 100°C for 24 h under a vacuum of ca. 0.04 mbar [11]. The results indicate that alkoxides are better ligands toward Ph_2Mg than THF. Thus complex formation between $Ph_2Mg(THF)_2$ and $MOCH_2CH_2OEt$ is realistic.

In order to obtain some information about the structure of these organometallic species in solution we recorded their proton and ^{13}C NMR spectra in benzene-d_6, along with those for the relevant alkali metal alkoxides. The ^1H NMR spectrum of the soluble species from diphenylmagnesium and lithium 2-ethoxyethoxide with the lowest possible Li/Mg ratio, of 1/ 1.3, is shown in Fig. 1a. It will be seen that in the aliphatic region of the spectrum, relative to lithium alkoxide (Fig. 1b), the signals have lost their fine structure and, more importantly, the spectrum shown in Fig. 1a is more complex. Integration indicated a Ph/OCH_2CH_2OEt ratio of 2.66/1.00, which agrees very closely to the ratio 2.6/1.0, inferred from the Li/Mg ratio. If any exchange of the type shown in eq. 1 occurs, a species such as $PhMgOCH_2CH_2OEt$ should be present in solution, and a question arises of whether the resonances in the aliphatic region of the spectrum shown in Fig. 1a are due to $PhMgOCH_2CH_2OEt$. Figure 1c shows the spectrum of an equimolar solution of Ph_2Mg and $Mg(OCH_2CH_2OEt)_2$. On the basis of the assumption that the two species disproportionate to form "$PhMgOCH_2CH_2OEt$", we can conclude that in the $Ph_2Mg/LiOCH_2CH_2OEt$ system no, or very little "free" $PhMgOCH_2CH_2OEt$ is present. Figure 1d shows the NMR spectrum of Ph_2Mg solubilized by about two equivalents of $LiOCH_2CH_2OEt$, in this case the spectrum is much simpler and more alkoxide-like than that shown in Fig. 1b, but more diffuse. This is taken to indicate the existence of a dynamic process, involving rapid (on the NMR time scale) exchange of $LiOCH_2CH_2OEt$ between complexed and uncomplexed sites. An indication of the possible sites of coordination of Ph_2Mg with the alkoxide can be derived from the ^{13}C NMR spectra.

The spectra shown in Fig. 2a and 2b are those of the soluble species with a Li/Mg ratio of 1/1.3 and lithium 2-ethoxyethoxide, respectively. It will be seen that the C(1) signal of the alkoxide in the soluble species has shifted to higher fields by 4.55 ppm. The resonances from C(3) and C(4) were similarly shifted by 2.22 and 1.37 ppm, respectively, but the C(2) signal was not shifted. In the case of the spectrum shown in Fig. 2c, which corresponds to the soluble species from $Ph_2Mg/2LiOCH_2OH_2OEt$, the respective shifts are 2.73, 2.07 and 0.48 ppm, i.e., considerably smaller. This, again, agrees with the conclusion drawn from the respective ^1H NMR spectra, namely that there is a dynamic exchange between free

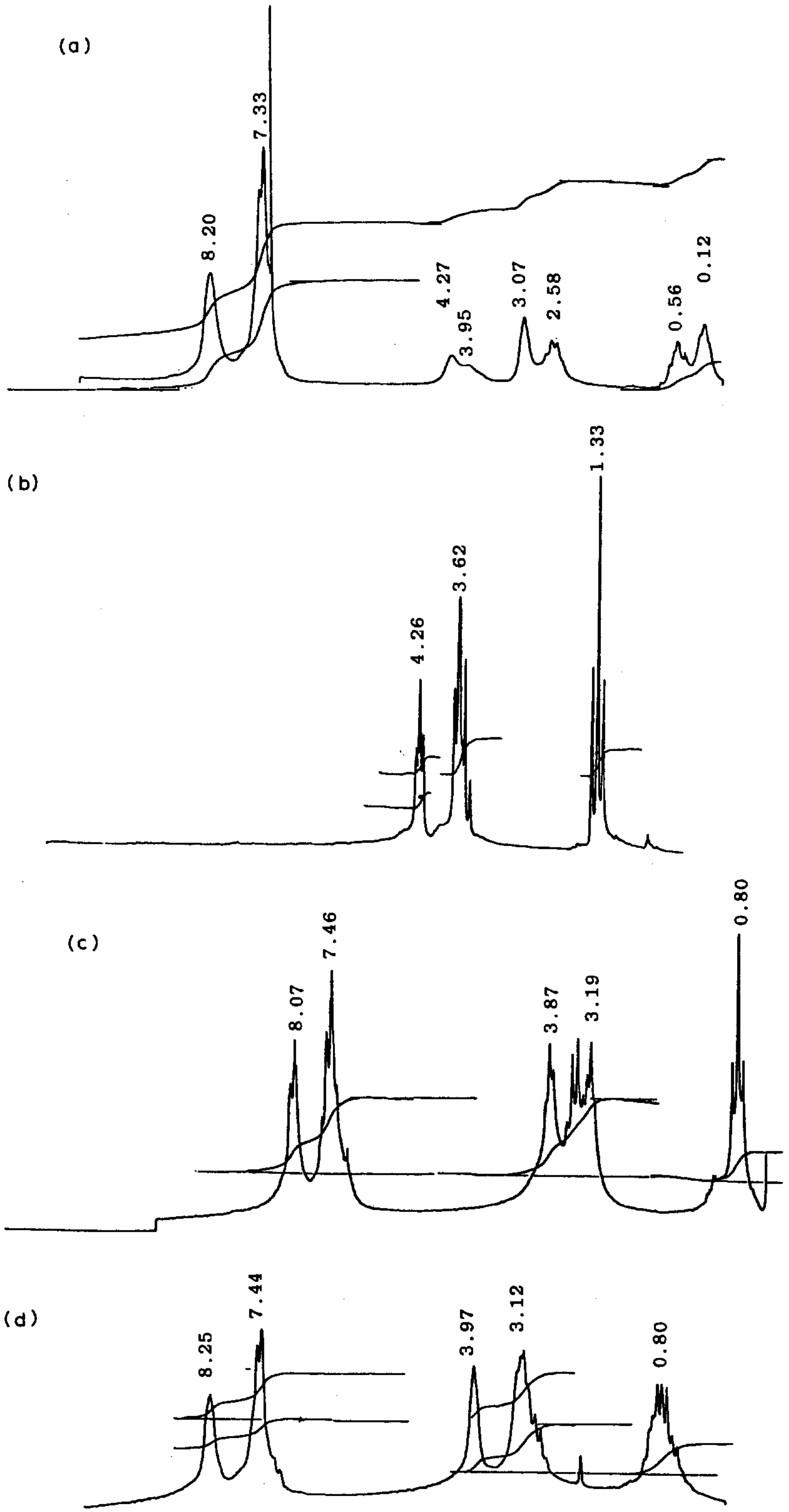


Fig. 1. ^{1}H NMR spectra (80 MHz) of (a) $Ph_2Mg/LiOCH_2CH_2OEt$ with Mg/Li ratio 1.3/1.0, (b) $LiOCH_2CH_2OEt$, (c) $PhMgOCH_2CH_2OEt$, (d) Ph_2Mg in the presence of two equivalents of $LiOCH_2CH_2OEt$ (solvent C_6D_6).

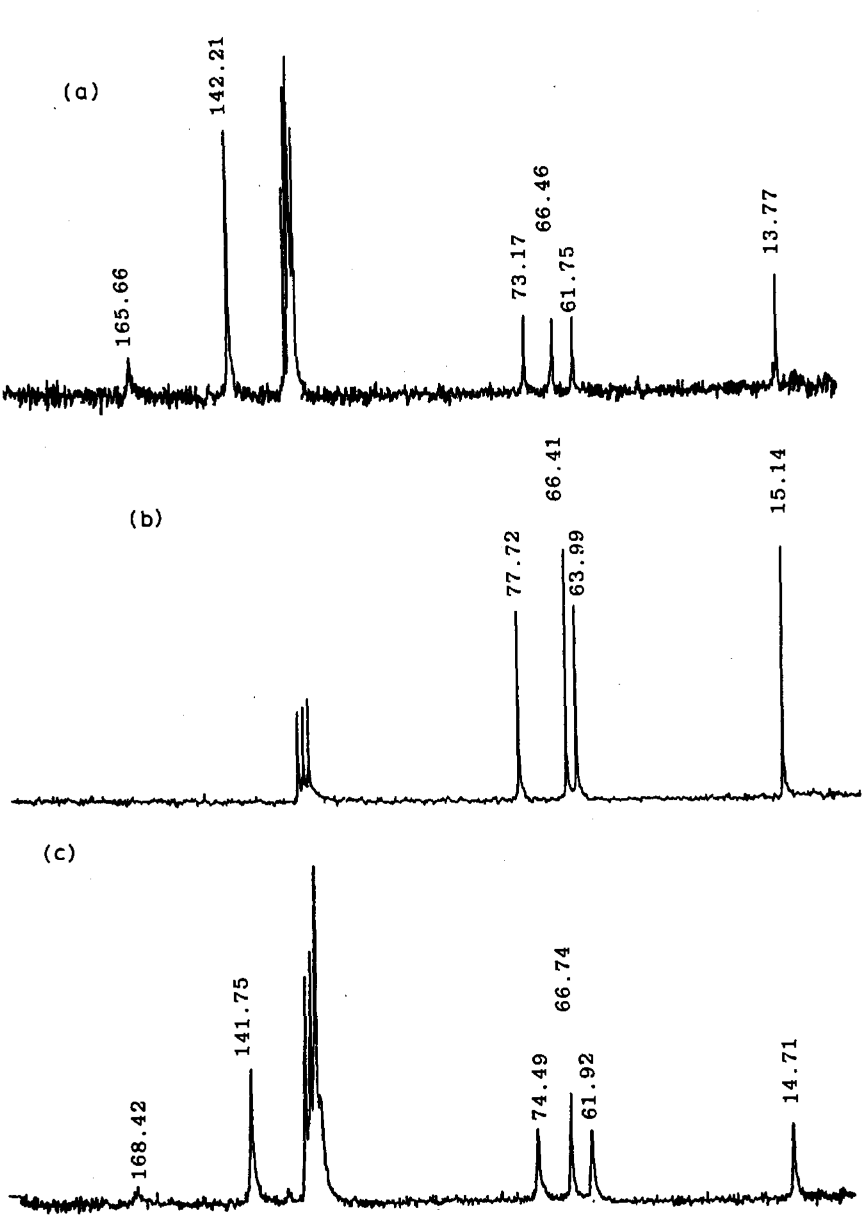


Fig. 2. ^{13}C NMR spectra of (a) $Ph_2Mg/LiOCH_2CH_2OEt$ with Mg/Li ratio = 1.3/1.0, (b) $LiOCH_2CH_2OEt$, (c) Ph_2Mg in the presence of ca. two equivalents of $LiOCH_2CH_2OEt$ (solvent C_6D_6).

and complexed $LiOCH_2CH_2OEt$. From the relative shifts of the carbon resonances in the complex it can reasonably be assumed that complexation takes place both through Li metal and the ether linkage in the alkoxide. The same conclusion was reached for the $PhM/Mg(OCH_2CH_2OEt)_2$ system [1]. On the basis of the data we can exclude the mode of interaction between Ph_2Mg and $LiOCH_2CH_2OEt$ which corresponds to eq. 1. Provided that there is a single species in solution, the Li/Mg ratio of 1/1.3 could indicate a stoichiometry of $4(Ph_2Mg)/3(LiOCH_2CH_2OEt)$. We can now conclude with confidence that the systems: $Ph_2Mg/LiOCH_2CH_2OEt$ and

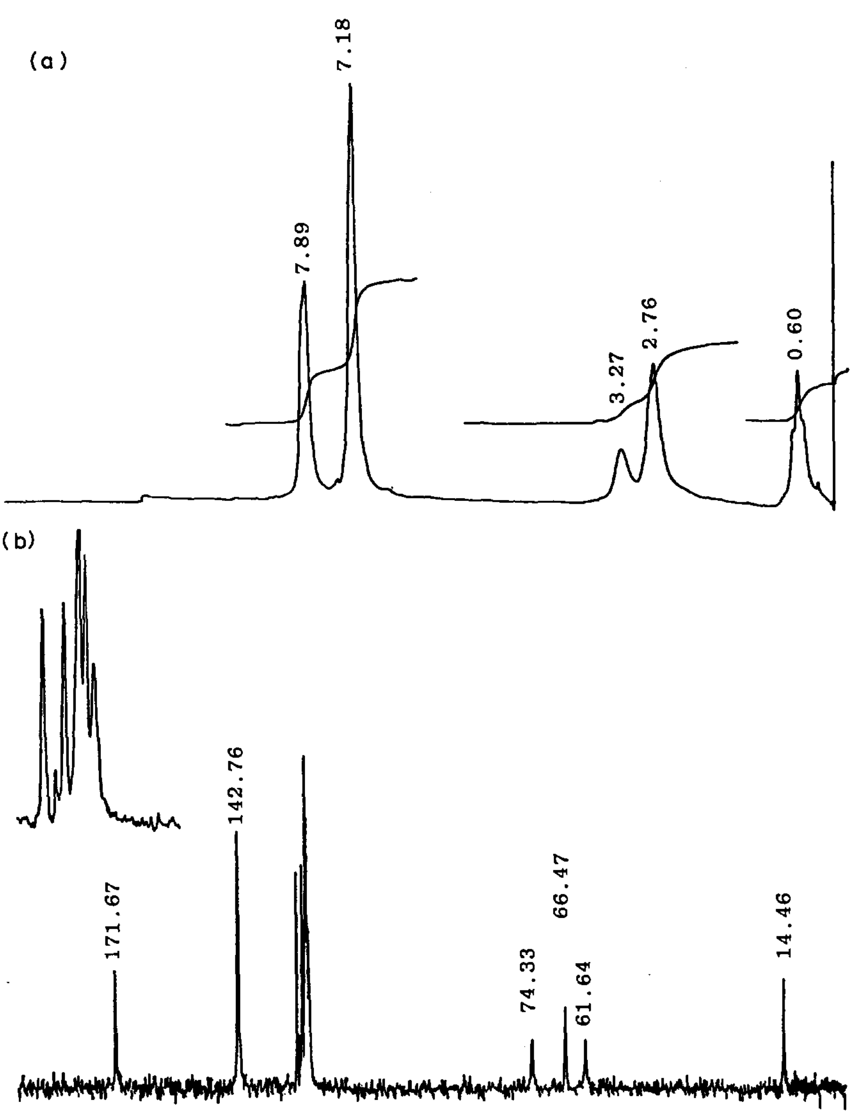


Fig. 3. ^1H NMR spectrum (80 MHz) of $PhLi/Mg(OCH_2CH_2OEt)_2$ (a) and ^{13}C NMR spectrum of $PhLi/Mg(OCH_2CH_2OEt)_2$ (b) with Mg/ Li ratio 1.0/6.0 (solvent C_6D_6).

$PhLi/Mg(OCH_2CH_2OEt)_2$ do not lead to the same soluble species. This is obvious when the NMR spectrum as seen in Fig. 1a and 2a are compared with those of the soluble species derived from PhLi and $Mg(OCH_2CH_2OEt)_2$ (Fig. 3a,b).

Figure 4a shows the spectrum of Ph_2Mg solubilized in benzene-d_6 by two equivalents of $NaOCH_2CH_2OEt$. We notice again that interaction between the organometallic and the alkoxide components causes broadening of the signals in the aliphatic region of the spectrum. In addition, the signals are shifted to higher field compared with those from the relevant alkoxide alone (Fig. 4b); thus the $MgOCH_2$, CH_2OCH_2 and CH_3 proton bands became more shielded by 0.56, 0.35 and 0.38 ppm, respectively . Of course, the corresponding ^{13}C shifts are more pronounced:

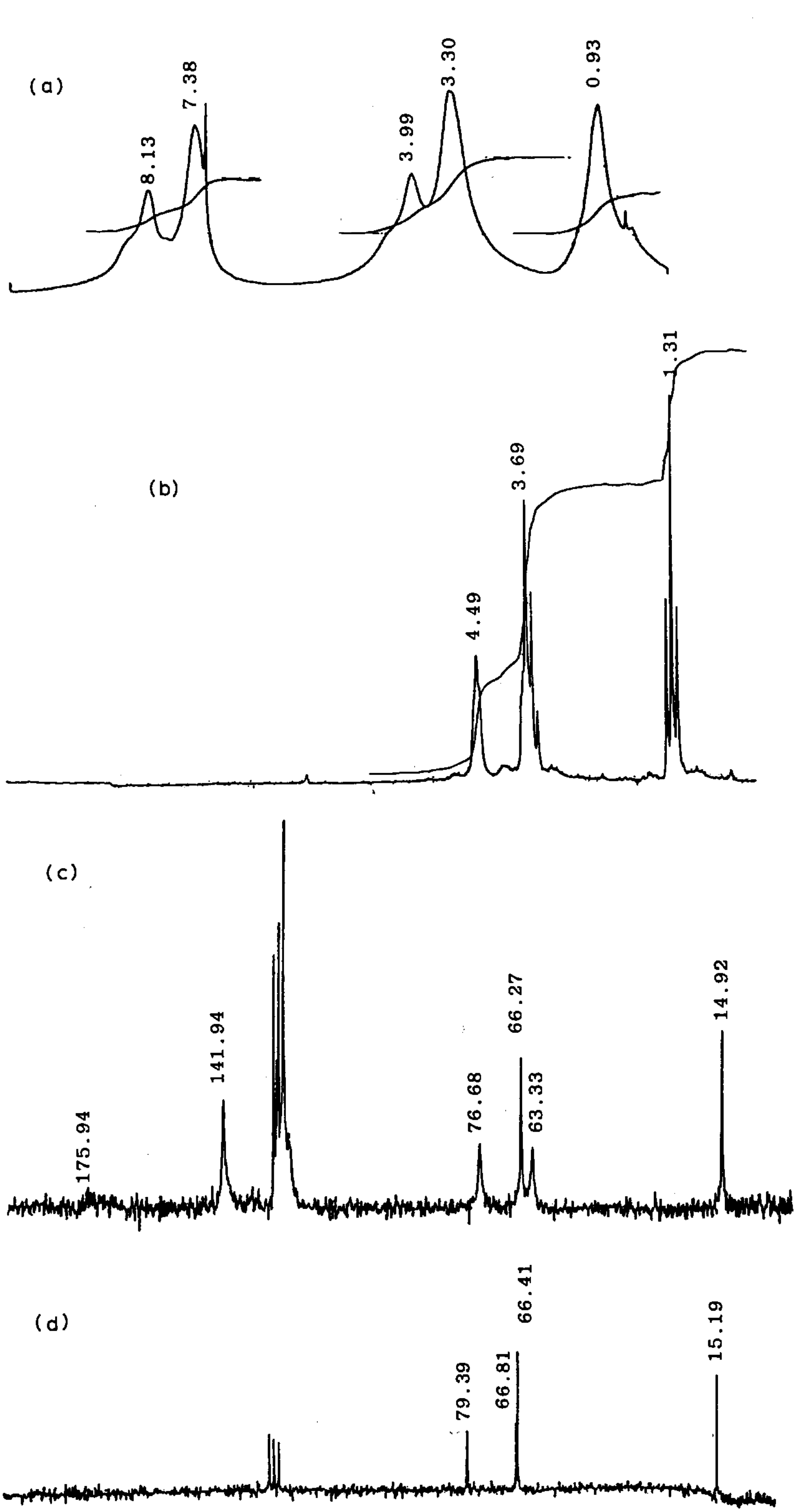


Fig. 4. ^{1}H and ^{13}C NMR spectra (80 MHz) of (a,c) Ph_2Mg in the presence of ca. two equivalents of $NaOCH_2CH_2OEt$, (b,d) $NaOCH_2CH_2OEt$ (solvent C_6D_6).

2.71, 0.54, 3.08 and 0.27 ppm for the C(1)–C(4), respectively, all to higher fields (Fig. 4c,4d). On comparing the ^{1}H and ^{13}C NMR spectra of the combination $Ph_2Mg/2NaOCH_2CH_2OEt$ with those of the soluble species derived from PhNa and $Mg(OCH_2CH_2OEt)_2$ [1], it can be seen that the proton and ^{13}C NMR spectra are almost identical; the differences in the chemical shifts in the two sets of ^{13}C spectra are $< 0.3\%$, and this small difference might well be due to effects of concentration. It was found possible to observe the signal from the *ipso*-carbon, which is very broad and tends to be buried in the noise of the spectrum; and it appeared at 175.94 ppm , and so the signal at 141.76 ppm, which was previously assigned to the *ipso*-carbon of $[Na_2Mg(Ph)_2(OCH_2CHOEt)_2]_n$ [1] , can now be reassigned correctly to the *ortho*-carbons of the phenyl group. Again, the resonances of the *ortho*-carbons in the $Ph_2Mg/NaOCH_2CH_2OEt$ and $PhNa/Mg(OCH_2CH_2OEt)_2$ differ by less than 0.2%. We therefore suggest that the $PhNa/Mg(OCH_2CH_2OEt)_2$ and the $Ph_2Mg/NaOCH_2CH_2OEt$ systems form the same soluble species. The spectral feature which appears to depend strongly on the alkali metal are the band widths. In the system $Ph_2Mg/MOCH_2CH_2OEt$ both the ^{1}H and ^{13}C signals exhibit widths which increase in the order of M = Li, Na, K, i.e., in the order of increasing ionic radius, or in the order of increasing ionicity in the carbon–metal and/or oxygen–metal bond. Thus, the system $Ph_2Mg/KOCH_2CH_2OEt$ exhibits very broad proton and ^{13}C NMR spectral signals (Fig. 5a,5d).

The questions raised earlier concerning (i) whether the two systems, $PhM/Mg(OCH_2CH_2OEt)_2$ and $Ph_2Mg/MOCH_2CH_2OEt$, lead to the same soluble species and (ii) the mode of interaction between the organometallic reagent and the alkoxide component can be answered with different degrees of certainty on the basis of the NMR information. It is certain that in the case where M = Li the two systems do not lead to the same soluble species, but for M = Na , the two systems do appear to give the same soluble product. For M = K the results are inconclusive because the K/Mg ratio was not kept constant in the two sets of experiments. As far as (ii) is concerned, the two systems appear to result in complex formation in all cases, with or without metal–metal exchange. Obviously, metal–metal interchange must take place in one of the two systems, $PhNa/Mg(OCH_2CH_2OEt)_2$ and $Ph_2Mg/NaOCH_2CH_2OEt$, otherwise they could not give the same soluble species. We suggest that metal–metal interchange probably occurs in $Ph_2Mg/NaOCH_2CH_2OEt$, on the basis of the behavior of the potassium alkoxide/butyllithium system which leads to the formation of the organometallic product of the more electropositive metal [5,6].

The metalating ability of a combination of unsolvated Ph_2Mg and two equivalents of an alkali metal 2-ethoxyethoxide was studied briefly. When the alkali metal was Li and the substrate anisole only traces of products resulting from metalation were observed. Under the same conditions the combination $Ph_2Mg/2\ NaOCH_2CH_2OEt$ gave a 36% yield of *o*-methoxybenzoic acid after carbonation, along with a 30% yield of benzoic acid (entries 1,2, Table 1) . When a temperature of 65°C for 5.5 h was employed for the metalation of 1,3-dimethoxybenzene, a 66% yield of 2,6-dimethoxybenzoic acid was obtained (entry 3, Tab 1). However, despite the fact that 1,3-dimethoxybenzene is much more susceptible to metalation than anisole, a small percentage of the metalating reagent remained unreacted. Greater metalating ability was exhibited by the combination $Ph_2Mg/KOCH_2CH_2OEt$, but in this case in order to ensure solubility in benzene of both the reactant and the organometallic product it was necessary to use the monosolvate $Ph_2Mg(THF)$; with

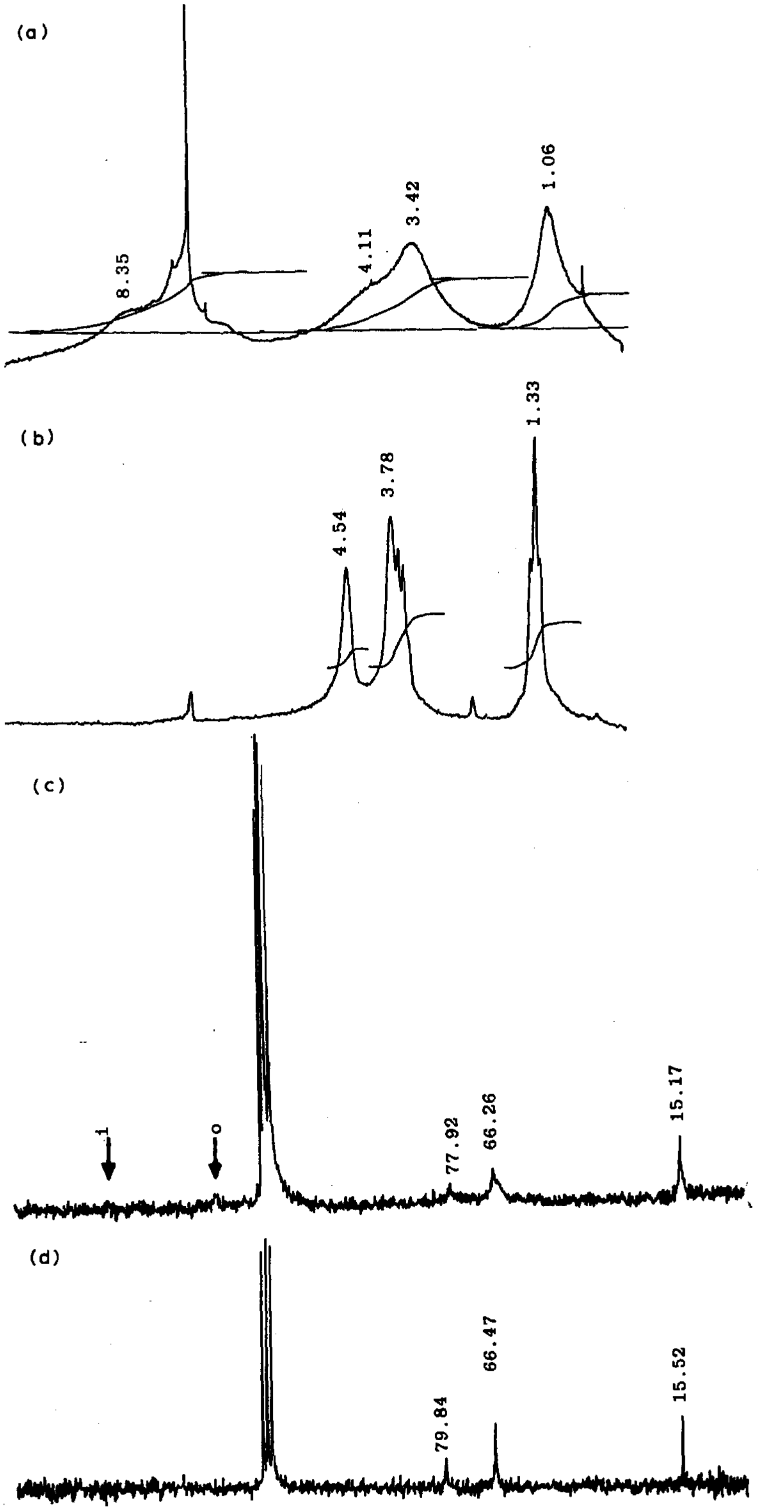


Fig. 5. The ^{1}H and ^{13}C NMR (80 MHz) spectra of (a,c) Ph_2Mg in the presence of ca. 1.5 equivalents of $KOCH_2CH_2OEt$, (b,d) potassium 2-ethoxyethoxide (solvent C_6D_6). Arrows indicate the positions of the signals from the *ortho*- and *ipso*-carbons (*o*, *i*, respectively).

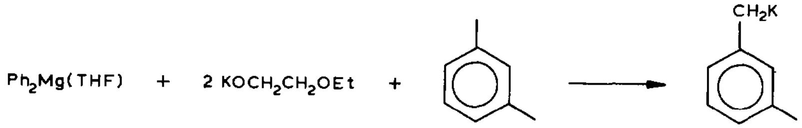
TABLE 1
METALATIONS WITH Ph_2Mg IN THE PRESENCE OF TWO EQUIVALENTS OF AN ALKALI METAL 2-ETHOXYETHOXIDE UNDER HOMOGENEOUS CONDITIONS IN BENZENE

Entry No.	M	Substrate	Products [a]	Yield (%) [c]	Reaction Temperature (°C)	Reaction Time (h)
1	Li	Anisole	o-$CH_3OC_6H_4CO_2H$ $PhCO_2H$	traces 64	r.t.	24
2	Na	Anisole	o-$CH_3OC_6H_4CO_2H$ $PhCO_2H$	36 30	r.t.	24
3	Na	1,3-Dimethoxybenzene	2,6-$(CH_3O)_2C_6H_3CO_2H$ $PhCO_2H$	66 ~3	65	5.5
4	Na	Thioanisole	$PhSCH_2CO_2H$	61	63	24
5	K [b]	*m*-Xylene	*m*-$CH_3C_6H_4CH_2CO_2H$ $PhCO_2H$	0 65	r.t.	24
6	K [b]	*m*-Xylene	*m*-$CH_3C_6H_4CH_2CO_2H$ $PhCO_2H$	40 29	63	3
7	K [b]	Mesitylene	3,5-$(CH_3)_2C_6H_3CH_2CO_2H$ $PhCO_2H$	34 36	70	1

[a] After carbonation. [b] In the presence of one equivalent of THF per Mg. [c] Yields are based on the amount of $Ph_2Mg(Et_2O)_2$ used, before desolvation.

this combination the metalation of *m*-xylene, a substrate which strongly resists metalation, takes place according to eq. 3.

Reaction 3 occurs with very high selectivity. Equally selective is the metalation of mesitylene by the same reagent (entries 6,7 Tab. 1). It is evident that the metalating ability of the reagent combination depends very strongly on the alkali metal in the alkoxide component, and increases in the order Li < Na < K. Thus the reactivities of the combination $Ph_2Mg/2MOCH_2CH_2OEt$ follows the same order as the respective insoluble reagents PhM, but the reactivities of the combination of diphenylmagnesium/alkali metal alkoxide is markedly lower than that of the PhM species. This relatively low reactivity of the combination becomes evident in the case where M = Na. With the soluble reagent only facile metalations can be performed, e.g., metalations of aromatic ethers and the like. Even metalation by $Ph_2Mg/KOCH_2CH_2OEt$ requires higher than room temperatures; it may be that this diminished reactivity is responsible for the high selectivity in metalations by this system. The final conclusion which can be reached is that magnesium alkoxides lower the reactivity of the incipient ArM reagents.



(3)

(Soluble complex)

Experimental

^1H and ^{13}C NMR spectra were recorded on a Varian FT80A NMR spectrometer. Samples of organometallic compounds for NMR analysis were prepared as previously described [1,11]. The compositions of the soluble complexes were determined as described previously [1]. Diphenylmagnesium was prepared as described in an other paper [11]. All operations involving organometallic or alkoxide preparations and reactions were carried out under pure argon. Preparations of alkali metal alkoxides are exemplified by the synthesis of $NaOCH_2CH_2OEt$, below.

Sodium 2-ethoxyethoxide

Sodium metal (6.5 g, 0.28 mol) was dispersed in boiling toluene (200 ml) by the use of a Hershberg stirrer. 2-Ethoxyethanol (23 ml, ca. 0.24 mol), which had been dried over 4A molecular sieves for several days, was added dropwise to the stirred sodium dispersion, initially without heating. When the addition was complete stirring was continued with heating until the yellow color of the $PhCH_2^-$ anion appeared. Excess of sodium was removed as a dilute amalgam by addition of mercury (12 ml), and this also resulted in loss of the yellow color, obviously as a result of scavenging of the metal from $PhCH_2Na$ [12]. Toluene was removed by vacuum evaporation to dryness and the solid alkoxide was redissolved in dry benzene to give an approximately 1.0 *M* solution.

Potassium 2-ethoxyethoxide

This alkoxide is soluble in benzene or toluene at temperatures > 50°C. At lower temperatures $KOCH_2CH_2OEt$ crystallizes out as long white needles. The saturated solution in benzene at room temperature is approximately 0.2 *M*. Solid potassium 2-ethoxyethoxide should be handled in stoppered flasks under argon, since it is destroyed in less than one minute upon exposure to air.

Diphenylmagnesium and potassium 2-ethoxyethoxide in THF/toluene

A solution of $Ph_2Mg(Et_2O)_2$ in toluene (6 ml containing ca. 10 mmol of Ph_2Mg) was added with stirring to a 0.25 *N* solution of $KOCH_2CH_2OEt$ in THF (42 ml, ca. 17 mmol). A brown color immediately appeared. The resulting mixture was stirred for 13 h at room temperature then carbonated. The usual work-up, involving ether extraction, gave 0.8 g (59%) of phenylacetic acid. The recrystallized material (methylcyclohexane) melted at 72°C (lit. [13], m.p. 77°C. NMR ($CDCl_3$): 3.59 (s, 2H, CH_2); 7.25 (s, 5H, aromatic), 8.78, (br,s, 1H acidic).

Unsolvated diphenylmagnesium and sodium 2-ethoxyethoxide in benzene

$Ph_2Mg(Et_2O)_2$ (0.99 *N* solution, 20 ml) in toluene was evaporated to dryness and the solid residue was kept at ca. 70°C (oil bath temperature) and 0.04 mbar for 24 h. A benzene solution of $NaOCH_2CH_2OEt$, (19 ml, 1.025 *N*, ca. 19.5 mmol) was added. On stirring the solids rapidly went into solution with evolution of heat, and the resulting solution rapidly developed a brown color. An aliquot of the solution was transferred into a Schlenk tube to which an NMR tube was fused. The benzene solvent was removed from the Schlenk tube by vacuum evaporation at room temperature for 24 h, then solids were dissolved in C_6D_6, and a portion of the solution was transferred to the attached NMR tube, which was then sealed with a hand torch by usual vacuum line techniques. The solution gave the ^1H and ^{13}C NMR spectra shown in Fig. 4a,4b.

Unsolvated diphenylmagnesium and lithium 2-ethoxyethoxide in toluene

Diphenylmagnesium (20 mmol) was obtained by the desolvation procedure described above and dissolved by adding 8.0 ml of a 2.5 *M* solution of $LiOCH_2CH_2OEt$ in toluene and diluting the mixture with ca. 12 ml of toluene. A 10 ml aliquot of this solution was added to 20 mmol of unsolvated Ph_2Mg and the resulting mixture was stirred for about 11 h. On standing, a clear supernatant was separated from which 1.00 ml was withdrawn for titration. The Mg/Li ratio was found to be 1.3/1.0. A second aliquot was transferred to a Schlenk tube (see previous experimental section) for NMR sample preparation. The integrated proton NMR spectrum of the solution in C_6D_6 indicated a Ph/OCH_2CH_2OEt ratio of 2.66/1.0, which agrees to within 2% with the magnesium and lithium analyses. The ^1H and ^{13}C NMR spectra of the soluble species are shown in Fig. 1a,2a.

Attempted metalation of anisole by $Ph_2Mg/LiOCH_2CH_2OEt$

Desolvated $Ph_2Mg(Et_2O)_2$ (20 mmol) (see previous experiments) was solubilized by adding 16 ml of a 2.5 *M* solution of lithium 2-ethoxyethoxide and 25 ml of degassed argon-saturated benzene. Anisole, (8 ml, ca. 73 mmol) was added and the resulting homogeneous mixture was stirred at room temperature for 24 h. Carbonation followed by the usual work-up gave benzoic acid (3.15 g, ca. 65%). NMR analysis of the crude acid revealed only traces of *o*-methoxybenzoic acid.

Metalation of 1,3-dimethoxybenzene by $Ph_2Mg/NaOCH_2CH_2OEt$

Diphenylmagnesium dietherate (30 ml, 0.99 *N*, ca. 30 mmol) was desolvated as described in the previous paragraphs. The solid Ph_2Mg was dissolved in 20 ml of a 1.7 *M* benzene solution of sodium 2-ethoxyethoxide. 1,3-Dimethoxybenzene (6.0 ml, ca. 46.5 mmol) was added to the homogeneous solution and metalation was carried out at 65°C with stirring for 5.5 h. Carbonation gave 3.7 g of acidic product, which was shown by NMR spectroscopy to be composed of $> 95\%$ of 2,6-dimethoxybenzoic acid and $< 5\%$ benzoic acid. The crude acid melted at 176–180°C. After recrystallization from water the m.p. was 180–182°C (Lit. [14] m.p. 186–187°C). ^1H NMR ($CDCl_3$): 3.79 (s,6H CH_3O); 6.64 (asym. d,(B_2 part of an AB_2 system) 2H (aromatic, *ortho* to CH_3O)); 7.30 (tr, (A part of an AB_2 system), 1H, (aromatic, *para* to CO_2H)).

Metalation of m-xylene by $Ph_2Mg/KOCH_2CH_2OEt$

To ca. 30 mmol of unsolvated diphenylmagnesium was added 15 ml of dry benzene and 1.2 ml (ca. 15 mmol) of freshly distilled $LiAlH_4 \cdot THF$. Solid potassium 2-ethoxyethoxide (3.4 g, 26 mmol) was weighed in a stoppered flask under argon and added to the $Ph_2Mg(THF)$. m-Xylene (5 ml) was then added, and the mixture was stirred at 63°C for 3 h then carbonated; 2.5 g of crystalline acid was isolated, and NMR analysis showed it to be a mixture of *m*-methylphenylacetic acid (58%) and benzoic acid, (42%). Thus, the yield of the metalation product is 40% based on the limiting reagent, i.e., $KOCH_2CH_2OEt$. One recrystallization of the mixture of acids from water gave pure *m*-methylphenylacetic acid, m.p. 60–61°C (lit. [15] m.p. 62°C). ^1H NMR spectrum ($CDCl_3$) (ppm) downfield from TMS: 2.33 (s, 3H, (CH_3)); (3.59 s, 2H (CH_2)) ; 7.11 (peak of a narrow m, 4H (aromatic)); 8.39_5 (br, s , 1H (OH)).

Metalation of mesitylene by Ph_2Mg/ $KOCH_2CH_2OEt$

A mixture of 45 mmol of desolvated Ph_2Mg, 1.8 ml of THF, 6.0 g of solid $KOCH_2CH_2OEt$ (ca. 47 mmol), 30 ml of dry benzene and 6.0 g (ca. 50 mmol) of mesitylene was kept for 1 h at 70°C. After carbonation, 4.5 g of a crystalline product was obtained, and NMR spectroscopy showed it to be a mixture of 3,5-dimethylphenylacetic acid (48% m) and benzoic acid (52%). Thus, the extent of metalation was 34%. After two recrystallizations of the product from water it melted at 96–98°C, (lit. [16], m.p. 101°C). NMR ($CDCl_3$) (ppm): 2.28(s, 6H (two CH_3)); 3.55 (s, 2H (CH_2)) ; 6.89 (s, 3H (aromatic)); 8.65 (s, 1H (acidic).

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