

Preliminary communication

THE CHEMICAL SHIFT OF EtMgBr AND Et₂Mg AS A QUALITATIVE MEASURE OF THE BASICITY OF ELECTRON-DONATING SOLVENTS

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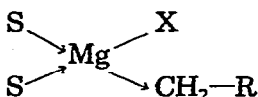
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Summary

The ¹H NMR chemical shift of the protons α to magnesium in EtMgBr and Et₂Mg in various donor solvents provide a measure of the basicity of the solvents.

Several attempts have been reported to determine the electron-donating ability (or the so-called basicity) of solvents towards organomagnesium compounds (cf. e.g. refs. 1–4 and references cited therein), but the methods involve difficult techniques. We now report a simple NMR technique based on the chemical shift of the protons α to magnesium.

The chemical shift of the protons attached to the α carbon atom of organometallic compounds is expected to be an indication of the basicity of the solvent: the more basic the solvent, the larger the negative charge at the α carbon atom and the higher the field at which the protons resonate (see structure I).



(I)

Non-specific medium effects can be eliminated by using TMS as an internal standard, provided that these effects are the same for the organometallic compound as for TMS. As this is not always true (particularly the contribution of the magnetic anisotropy to the chemical shift may be different [5]), the chemical shift may not always parallel the electron donating ability of the solvent. Especially when the solvents contain different heteroatoms (O, N) or aromatic rings (anisol), the results must be treated with caution. Nevertheless, keeping these restrictions in mind, the chemical shift of α-protons in organometallic compounds may provide a useful indication of the basicity of the solvent in which they are dissolved. This has been demonstrated by measuring the chemical

TABLE 1

CHEMICAL SHIFTS ^a OF THE α -METHYLENE PROTONS OF EtMgBr AND Et₂Mg IN SEVERAL ELECTRON DONATING SOLVENTS; TMS WAS USED AS THE INTERNAL STANDARD

Solvent	[EtMgBr] ^b (mol/l)	[Et ₂ Mg] ^b (mol/l)	[MgBr ₂] ^b (mol/l)	- δ (ppm)		
				30.0°C	40.0°C	50.1°C
i-Pr ₂ O	0.05	0.003		0.476, 0.468		
	0.1	0.006		0.473, 0.469, 0.461		
	0.30	0.018		0.470, 0.470		
		0.05		0.441, 0.423		
		0.10		0.416, 0.405, 0.397		
Et ₂ O		0.25		0.397, 0.384		
	0.05		0.001	0.609, 0.616		
	0.10		0.002	0.613, 0.604, 0.601		
	0.28		0.006	0.621, 0.611, 0.604		
		0.05		0.677, 0.676		
THF		0.10		0.671, 0.655, 0.640		
		0.30		0.642, 0.624		
	0.05		0.0004	0.716, 0.702		
	0.10		0.0008	0.714, 0.702, 0.696		
	0.30		0.0025	0.722, 0.712, 0.690		
Et ₃ N ^b		0.065		0.773, 0.767		
		0.129		0.775, 0.771		
		0.258		0.775, 0.769		
	0.05			0.507, 0.500		
	0.10			0.505, 0.501, 0.499		
n-Bu ₂ O	0.17	0.108		0.509, 0.501		
MeCH ₂ CHMeCH ₂ OCH ₂ Me	0.088	0.099		0.559		
DME	0.10	0.005		0.540		
Anisol	0.035	0.013		0.785		
	0.075	0.025		0.115		

^a The measurements were performed on a Varian XL-100 NMR spectrometer using the external lock at a sweep width of 100 Hz, sweep time 50 sec. All values are the mean of six scans (same sample), in the continuous wave mode; the maximum deviation was 0.004 ppm. ^b The solutions of EtMgBr were obtained by reaction of EtBr with Mg in the solvent used. The solutions of Et₂Mg were prepared by precipitating MgBr₂ from a solution of EtMgBr in Et₂O with dioxane; the resulting (clear) solution was decanted and heated under vacuum at 125°C overnight to remove Et₂O and dioxane. The remaining solid was dissolved in the solvent required. All experiments were performed in closed glass apparatus. The concentrations were determined by titration (acid-base and complexometric). If several concentrations were used these were prepared by dilution or concentration of the original sample (except for the highest concentration of Et₃N, which was prepared independently).

shift of the α -methylene protons of CH₃CH₂MgBr and of (CH₃CH₂)₂Mg in different solvents (Table 1).

As can be seen from Table 1, the effect of the temperature and the concentration on the chemical shift is usually not large for EtMgBr, but may be considerable for Et₂Mg. However, for comparison the normal NMR temperature can be used ($\approx 40^\circ\text{C}$ for most NMR spectrometers). The concentration of the organo-magnesium compound should not be too high (especially in the case of Et₂Mg in weakly basic solvents), because at high concentrations association phenomena render the influence of the solvent less pronounced as one or more coordinative bonds of the solvent with magnesium are replaced by alkyl or halogen bridges. Alkylmagnesium halides (RMgX, EtMgBr in our case) mostly contain excess dialkylmagnesium (R₂Mg) or magnesium halide, which exchange rapidly with RMgX. As the resonance of R₂Mg is usually found at higher field than that of RMgX (see however i-Pr₂O) this has to be taken into account if one wants to ob-

tain the true chemical shift of RMgX. Similarly, R_2Mg may be present in solution because of the Schlenk equilibrium:



For the solvents used in the present investigation this is probably only important in the case of THF where the equilibrium constant is $K = 5.1$ at 25°C [6].

From the results presented the following tentative order of basicity of the solvents towards Et_2Mg may be inferred: $\text{THF} > \text{Et}_2\text{O} > i\text{-Pr}_2\text{O}$; towards EtMgBr : $\text{DME} > \text{THF} > \text{Et}_2\text{O} > n\text{-Bu}_2\text{O} > \text{CH}_3\text{CH}_2\text{CHMeCH}_2\text{OCH}_2\text{CH}_3 > \text{Et}_3\text{N} > i\text{-Pr}_2\text{O} > \text{anisol}$.

These results are in good agreement with previous work [1-4].

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