Proton Resonance Studies of the Nature of Aryl Grignard Reagents in Solution

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A PREVIOUS paper[1] reported the ^{19}F n.m.r. spectra of a number of fluoroaryl Grignard reagents over a range of temperatures. It was possible to slow down the fluoroaryl exchange and distinguish unambiguously between "RMgX" and "R_2Mg" species. Although proton chemical shifts are normally much smaller than fluorine chemical shifts, we have been able to obtain similar results for a variety of aryl Grignard reagents, using ^1H n.m.r. spectroscopy.

At 35° the resonance due to the *o*-protons of [3,5-$^2H_2$]phenylmagnesium bromide in tetrahydrofuran (THF) is a slightly broadened doublet. As the temperature is lowered, this band broadens, and finally splits into two doublets (Figure). In a solution containing additional bis-([3,5-$^2H_2$]phenyl)-magnesium, the low-field doublet increases in relative intensity. Accordingly this doublet can be assigned to "$(C_6H_3D_2)_2Mg$", and the high-field doublet to "$C_6H_3D_2MgBr$". Similar results are obtained with 2,5-dimethylphenylmagnesium bromide in THF (*o*-methyl resonance) although here aryl exchange is slower presumably because of steric hindrance (Figure). The observed ratios of ["RMgX"]: ["R_2Mg"] are given in the Table, together with those obtained previously.[1] (There is an error in this paper: 2["RMgX"/["R_2Mg"] should read ["RMgX"]/2["R_2Mg"]).

Phenylmagnesium bromide is monomeric in

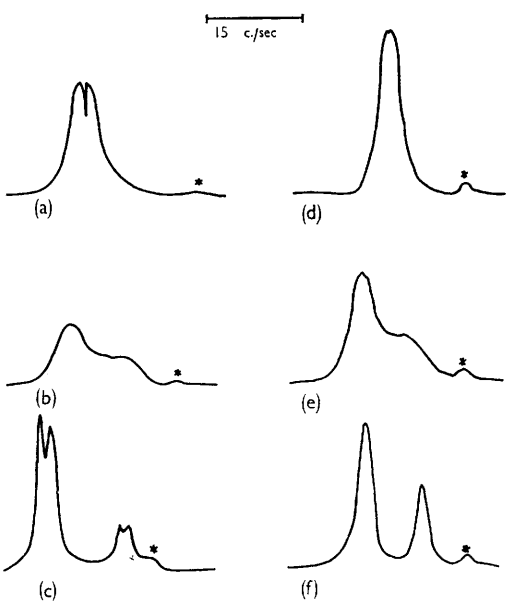

FIGURE. *The proton resonance spectra* (100 *Mc./sec.*) *of* (i) *the* o-*protons of* 0·15M-3,5-$C_6H_3D_2MgBr$ *in tetrahydrofuran at* (a) 35°, (b) −20°, (c) −65° *and* (ii) *the* o-*methyl protons of* 0·4M-2,6-$Me_2C_6H_3MgBr$ *in tetrahydrofuran at* (d) 35°, (e) 0° *and* (f) −40°.

* Impurity peak.

The ratios ["RMgX"]: ["R_2Mg"] *for aryl Grignard reagents*†

Grignard	Solvent	Temperature	$\frac{["RMgX"]}{["R_2Mg"]}$
[3,5-$^2H_2$]PhMgBr	THF	−30°	$1{\cdot}0_6$
		−40°	$1{\cdot}0_4$
		−50°	$0{\cdot}81_3$
		−60°	$0{\cdot}70_9$
		−70°	$0{\cdot}59_6$
		−80°	$0{\cdot}54_1$
2-*$CH_3C_6H_4$·MgBr	THF	−50°	1·5
2-CH_3·CH_2*C_6H_4MgBr	THF	−40°	2·0
	Et_2O	−60°	>20
2,*6-$Me_2C_6H_3$·MgBr	THF	−30°	$4{\cdot}0_6$
		−40°	3·6
		−50°	3·3
		−60°	$2{\cdot}8_4$
	Et_2O	−40°	>20
2,*6-$Me_2C_6H_3$·MgCl	THF	−30°	5·5
2,*4,6-$Me_3C_6H_2$·MgBr	THF	−40°	3·5
2-*CH_3·$C_{10}H_6$·MgBr	THF	0°	3·5
	2-Methyltetrahydrofuran	−20°	18
2-*CF_3·C_6H_4·MgBr	THF	0°	4·0
		−30°	3·8
		−60°	3·9
,,	2-Methyltetrahydrofuran	10°	10·6
		−10°	9·1
		−20°	7·1
		−40°	5·6
,,	Et_2O	−50°	18
C_6F_5MgBr[1]	THF	+22°	1·4
,,	Et_2O	−55 to 22°	2·0
C_6F_5·MgCl[1]	Et_2O	22°	4·0
C_6F_5·MgI[1]	Et_2O	22°	2·8
C_6H_2·Cl_2FMgBr[1]	Et_2O	−63°	~5·0
$C_{10}H_6$·FMgI[1]	Et_2O	−75°	>40
p-FC_6H_4·MgBr[1]	Et_2O	−75°	>40
p-FC_6H_4·MgI[1]	Et_2O	−75°	>40

* This indicates the resonance that was studied.

† EtMgBr in THF was also studied. The two methylene quartets overlapped considerably ($\delta_{R_2Mg} - \delta_{RMgX} =$ 0·03 p.p.m.) but $\frac{["RMgX"]}{["R_2Mg"]}$ at −60° was found to be ~0·7.

tetrahydrofuran,[2] and accordingly values of K for the Schlenk equilibrium

$$(C_6H_3D_2)_2Mg + MgBr_2 \rightleftharpoons 2C_6H_3D_2MgBr \quad (1)$$

can be calculated. From a plot of log K against T^{-1} the extrapolated value of K at 25° is 4·0 ± 0·8 and for reaction (1) ΔH is 3·2 ± 0·5 kcal. and ΔS 13·5 cal. deg.$^{-1}$. These values are in agreement with those obtained for phenylmagnesium bromide by Smith and Becker[2] from measured heats of reaction (3·77, 2·82 kcal. and 12·1 cal. deg.$^{-1}$ respectively). It can be seen from the Table that the position of the Schlenk equilibrium depends very markedly on the aryl group and also upon the solvent. "Conventional" aryl Grignard reagents in diethyl ether are largely "RMgX", but the more strongly co-ordinating the ether, the greater is the proportion of "R_2Mg" species.

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[1] D. F. Evans and M. S. Khan, *J. Chem. Soc.* (*A*), **1967**, **1643**.
[2] M. B. Smith and W. E. Becker, *Tetrahedron*, 1967, **23**, 4215.