Tetrahedron Letters No. 12, pp. 767-773, 1963. Pergamon Press Ltd.
Printed in Great Britain.

STRUCTURE OF GRIGNARD REAGENTS AND ORGANOLITHIUM COMPOUNDS

Gideon Fraenkel, David G. Adams, and James Williams

Department of Chemistry, The Ohio State University
Columbus, Ohio

(Received 11 January 1963; in revised form 11 February 1963)

Several problems concerning the structure of Grignard reagents and organolithium compounds have been studied with the aid of nuclear magnetic resonance spectroscopy, NMR; they are: the ionic character of the carbon metal bonds, the rates of carbanion inversion, the rates of carbon metal exchange and the electron hybridization in the C-H bond in RCHM.

The NMR spectra of several organolithium and organo magnesium reagents have been determined. Table I lists the chemical shifts and coupling constants for the different species studied together with several examples from the literature. The spectra were determined on the Varian HR 60 NMR spectrometer at 60 Mc and 35°C. Calibrations were accomplished by the method of audio side band modulation. Complex spectra were analyzed by means of published procedures.[1]

We have found that there is a remarkable similarity in the appearance of the NMR spectra of the Grignard reagent, organomagnesium compound and organolithium compound obtained from any particular halide RX. When R - ethyl, methyl, allyl

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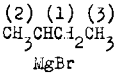
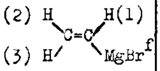
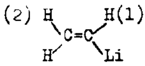
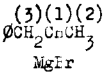
[1] J. A. Pople, W. G. Schneider and H. J. Bernstein, High Resolution Nuclear Magnetic Resonance, McGraw-Hill Book Co., Inc., New York, 1959, Chap. 6.

Table I

NMR Parameters for organolithium compounds and Grignard reagents [a,b]

Compound	Solvent	Conc.				$J_{1,2}$	$J_{1,3}$	$J_{2,3}$
			δH_1	δH_2	δH_3			
CH_3MgI	ether	5%	11.3					
$(CH_3)_2Mg$	ether	1%	11.3					
CH_3CH_2MgBr	ether	5%	10.62			8.96		
(2) CH_3CH_2Li	ether	5%	10.99			8.90		
 $\overset{(2)}{CH_3}\underset{MgBr}{\overset{(1)}{CH}}\overset{(3)}{CH_2}CH_3$	ether	5%	10.20		8.5	6.8		6.8
$CH_2=CH-CH_2MgBr$[c]	ether	3%	7.53	3.72	7.53	10.7		10.7
$CH_2=CH-CH_2Li$[d]	THF	5%	7.53	3.36	7.53	12.0		12.0
 [f]	THF	5%	3.52	4.02	4.34	17.2	22.1	7.4
 [d]	THF	5%	.0[e]	.51[e]	1.19[e]	19.3	23.9	7.3
$CH_3CH\phi CH_2MgBr$[g]	ether	8%	10.00	7.06	8.77	6.6		6.5
 $\phi \overset{(3)}{CH_2}\underset{MgBr}{\overset{(1)}{CH}}\overset{(2)}{CH_3}$	ether	5%	9.81	8.75	7.33	7.4	7.4	
CH_3Li	ether	5%	11.3					

a) Chemical shifts in tau units.
b) Hydrogens are numbered away from C-M bond except where numbered in table.
c) J.E. Nordlander and J.D. Roberts, J. Amer. Chem. Soc. **81**, 1769 (1959).
d) C.S. Johnson, M.A. Weiner, J.S. Waugh and D. Seyferth, ibid. **83**, 1306 (1961).
e) Shifts relative to H_1.
f) Method of H. Normant, Compt. Rend. **239**, 1510, 1811 (1954)
g) Parent bromide was prepared by shaking a mixture of allyl bromide, benzene and sulfuric acid for 24 hours at 28°C., b.p. 96°/10mm.

and vinyl the NMR spectra of the Grignard reagents and organolithium compounds are nearly identical. In the case of the aromatic reagents the hydrogens *ortho* to C...M have slightly different chemical shifts[2] but in all other details including the fine structure of the multiplets the spectra were the same.

The NMR spectra of dimethyl magnesium and methyl magnesium bromide are identical; in fact among all the reagents we have studied there is almost no difference between the NMR spectrum for any particular Grignard reagent and that for the corresponding dialkyl magnesium compound.

In the aliphatic series it is interesting that the chemical shift for CHM occurs at unusually high fields decreasing in the order CH_3-M, CH_3CH_2-M   CH-M. We suggest that negative charge on the carbon atom bonded to magnesium or lithium will repel electron density out of the C-H bond on to the H *1s* orbital thereby increasing the shielding at H. A similar effect of negative charge on the chemical shift of hydrogen has been found for aromatic systems.[3] The coupling constants in these reagents, $J_{CH,CHM}$ are noticably different from those in the parent halides.

The spectrum of vinyl magnesium bromide is of the ABC type and was analyzed by the methods of Castellano and Waugh.[4,5] Our spectrum of vinyl magnesium bromide is almost identical to that obtained for vinyl lithium. Since the resonance pattern in the

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[2] G. Fraenkel and D. G. Adams, *J. Amer. Chem. Soc.* Submitted for Publication.

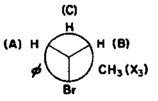
[3] G. Fraenkel, R. B. Carter, A. McLachlan and J. H. Richards, *ibid.* **82**, 5846 (1960).

[4] S. Castellano and J. S. Waugh, *J. Chem. Phys.* **34**, 295 (1961).

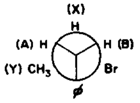
[5] Preparation described in Table I, footnote f.

Grignard reagent is ABC rather than A_2B we conclude that electron inversion at CHM is slow in accordance with the chemical observation that *cis* and *trans* isomers of vinyl Grignard reagents equilibrate slowly.[6]

Grignard reagents have been prepared from 1-bromo-2-phenyl-propane I, and 2-bromo-1-phenylpropane, II, both bromides being racemic. Newman projections of one of the three rotamers of each bromide are shown below.



I



II

The NMR spectra of the aliphatic parts of these molecules consist of $ABCX_3$ and $ABXY_3$ patterns for I and II respectively.[7] Chemical shifts and coupling constants for the two compounds are listed in Table II. The principal facts to be learned from

TABLE II

NMR PARAMETERS FOR ASYMMETRIC BROMIDES

δ in tau units, J in cps

2-bromo-1-phenylpropane	$\delta_A = 6.950$	$J_{AB} = 14.0$
	$\delta_B = 7.070$	$J_{AX} = 7.0$
	$\delta_X = 5.870$	$J_{BX} = 7.0$
	$\delta_Y = 8.490$	$J_{XY} = 6.9$
1-bromo-2-phenylpropane	$\delta_A = 6.627$	$J_{AB} = 11.7$
	$\delta_B = 6.736$	$J_{AC} = 6.6$
	$\delta_C = 6.942$	$J_{BC} = 6.6$
	$\delta_X = 8.723$	$J_{CX} = 6.4$

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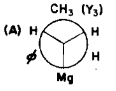
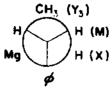
[6] F. G. Bordwell and P. S. Landis, *J. Amer. Chem. Soc.* *74*, 1593 (1957), D. Y. Curtin and J. W. Crump, *ibid.* *80*, 1922 (1958).

[7] Formalism of Pople *et al.*

these spectra are that the methylene hydrogens adjacent to the asymmetric carbon atoms are magnetically non-equivalent and that there is rapid rotation about the bonds CH_2-CABC in these molecules. Magnetic asymmetry at CH_2 has been ascribed to three factors: 1) There may be unequal populations of rotamers about the CH_2-CABC bonds.[8] 2) The second group attached to CH_2, Br in I and phenyl in II, induces extra magnetic asymmetry at CH_2.[9] 3) The hydrogens H_A and H_B are staggered between different groups attached to the asymmetric carbon atom and the averaged magnetic environments for the two hydrogens will always be different regardless as to the rate of rotation about CH_2-C (asymmetric), unless H_A exchanges places with H_B by inversion at the asymmetric carbon atom.[9, 10] Such a process cannot occur in the bromides but it might take place in the corresponding Grignard reagents, III and IV.



III



IV

Grignard reagents may be considered to be highly associated salts of carbanions, and carbanions have always been assumed to be tetrahedral. If the rate of inversion at the carbon atoms bonded to magnesium in the above reagents were fast, the methylene hydrogens would become magnetically equivalent. This is indeed the

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[8] P. M. Nair and J. D. Roberts, J. Amer. Chem. Soc. 79, 4565 (1957), G. Whitesides, F. Kaplan, K. Nagarajan and J. D. Roberts, Proc. Nat. Acad. Sci. 000 (1962).

[9] H. S. Gutowsky, J. Chem. Phys., In Press.

[10] J. A. Pople, Mol. Phys. 1, 1 (1958).

case, the NMR spectra for III and IV consist of A_2XY_3 patterns, see Table I, the methylene hydrogens are magnetically equivalent and *carbanion inversion is fast.*

If Dessy's formulation for the Grignard reagent[11] is correct it would be expected that the reagents III and IV would exist in diastereomeric forms and that two A_2XY_3 patterns of differing intensities would appear in the NMR spectrum of each reagent. Actually in the examples studied only one pattern was found for each spectrum. Since it was unlikely that only one diastereomer was present each time our spectra must have represented two diastereomers in a time averaged environment,[12] and hence the rate at which the group R exchanged between diastereomers $R_2Mg.MgX_2$ was fast. We will describe this phenomenon as intermolecular carbon magnesium exchange.

Finally we have obtained the NMR spectrum of methyl-C^{13}-magnesium iodide. It has been found experimentally[13,14] and explained theoretically[15] that for C^{13}-H bonds in which the electron hybridization is $\underline{sp}^2$ or $\underline{sp}^3$ the magnitude of $J_{C^{13}, H}$ is a linear function of the $\underline{s}$ character in the C^{13}-H bond. In $C^{13}H_3MgBr$ $J_{C^{13}H}$ is 107.7 cps corresponding to 20.4% $\underline{s}$ character for the C-H bond and the electron hybridization is $\underline{s}^{0.61}\,\underline{p}^{2.39}$ leaving for the pair of electrons bonded to magnesium 39% s character and $\underline{s}^{0.78}\,\underline{p}^{1.22}$ hybridization.

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[11] R. E. Dessy, G. S. Handler, J. H. Wotiz and C. A. Hollingsworth, *J. Amer. Chem. Soc.* **79**, 3476 (1957), R. E. Dessy and G. S. Handler, *ibid.* **80**, 5824 (1958).

[12] Ref. 1 Chap. 10.

[13] N. Muller and D. E. Pritchard, *J. Chem. Phys.* **31**, 768 (1959).

[14] N. Muller and D. E. Pritchard, *ibid.* **31**, 1471 (1959).

From the chemical shift of the methyl hydrogens in methyl magnesium iodide we estimate about 21% ionic character for the carbon magnesium bond[3] and the same value applies to the carbon lithium bond in methyl lithium. It is thus reasonable that the hybridization for the C-H bonds in methyl magnesium iodide should lie between sp^3 for CH_4 and p for CH_3^- by analogy to amines.[16]

From these experiments we have established that for Grignard reagents in ether solution at 33° both carbanion inversion and intermolecular carbon magnesium exchange are fast. On the basis of the chemical shift data given for the magnesium and lithium reagents and of electron hybridization measured for $C^{13}H_3MgI$ we suggest that all these materials are best considered as highly associated salts of carbanions. That the reagents produced from these two metals should have such similar properties is expected from the diagonal relationship of lithium and magnesium in the periodic table.[17]

This research was supported by the Petroleum Research Fund of the American Chemical Society and the National Institutes of Health, USA.

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[15] H. S. Gutowsky and C. Juan, *Discussions of the Faraday Society*, In Press.

[16] G. Herzberg, "*Infrared and Raman Spectra of Polyatomic Molecules*", D. van Nostrand Co., Inc., Princeton, N.J. 1945, p. 257.

[17] An expanded version of this work will appear in another place.