

from kinetics and equilibrium studies,^{2,4} but only about one-tenth as large as might have been predicted from chemical studies^{2,4,13,14} on the basis of the sensitivity of the F¹⁹ method for alkyl substituents.⁶

The present results, based on the well-established F¹⁹ technique of Taft, indicate that $\Delta\sigma_1$ is zero and $\Delta\sigma_R^\circ$ is smaller than expected for the change in substituent $\text{CH}_3 \rightarrow \text{CD}_3$. This points to a need for additional critical examination of the applicability of the language of ordinary substituent effects to the subject of secondary deuterium isotope effects.

(13) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **79**, 1913 (1957).

(14) E. S. Lewis and G. M. Coppinger, *ibid.*, **76**, 4495 (1954).

Gary E. Maciel

Department of Chemistry, University of California
Davis, California

Daniel D. Traficante

The Frank J. Seiler Research Laboratory
Office of Aerospace Research
United States Air Force Academy, Colorado Springs, Colorado

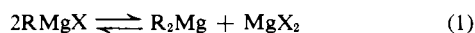
Received March 4, 1965

Proof for the RMgX Composition of Grignard Compounds in Diethyl Ether. RMgX, the Initial Species Formed in the Reaction of RX and Mg

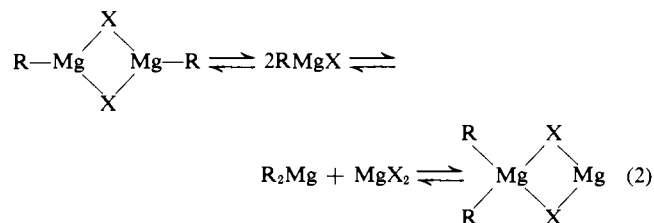
Sir:

The composition of Grignard compounds in diethyl ether solution has been assumed to be described adequately by the unsymmetrical dimeric species $\text{R}_2\text{Mg} \cdot \text{MgX}_2$.¹⁻⁴ The acceptance of this composition is based on the reported dimeric nature of Grignard compounds in diethyl ether solution and the lack of alkyl group exchange in a mixture of $(\text{C}_2\text{H}_5)_2\text{Mg}$ and $^{28}\text{MgBr}_2$.¹

We have reported evidence to support the description of Grignard compounds in tetrahydrofuran by the equilibrium⁵



More recently we have cited⁶ circumstantial evidence in favor of the existence of RMgX species in diethyl ether solution. The composition in diethyl ether was described by equilibria 2.



Two other recent reports have contributed importantly to eliminating the confusion in this area. First, Dessy and co-workers⁷ have repeated previously reported ^{28}Mg experiments and now find exchange with

(1) R. E. Dessy, G. S. Handler, J. H. Wotiz, and C. A. Hollingsworth, *J. Am. Chem. Soc.*, **79**, 3476 (1957).

(2) J. Miller, G. Grigoriou, and H. S. Mosher, *ibid.*, **83**, 3966 (1961).

(3) N. M. Bikales and E. I. Becker, *Can. J. Chem.*, **41**, 1329 (1962).

(4) H. O. House and D. O. Traficante, *J. Org. Chem.*, **28**, 355 (1963).

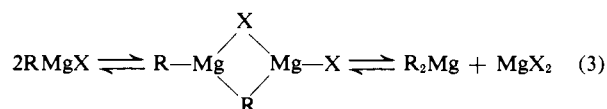
(5) E. C. Ashby and W. E. Becker, *J. Am. Chem. Soc.*, **85**, 118 (1963).

(6) E. C. Ashby and M. B. Smith, *ibid.*, **86**, 4363 (1964).

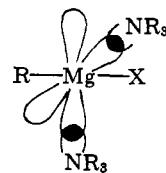
(7) R. E. Dessy, S. Green, and R. M. Salinger, *Tetrahedron Letters*, 1369 (1964).

certain, but not all, grades of magnesium. Similar results using ^{25}Mg have been recently reported by Cowan.⁸ Second, Rundel and co-workers^{9,10} have reported $\text{RMgX} \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$ structures for phenyl and ethylmagnesium bromide in the solid state based on X-ray diffraction, although whether a single solid state structure can be equated to species in solution is questionable. We report now (1) proof establishing RMgX as the initial species formed when RX and Mg react, and (2) proof for the existence of RMgX species in diethyl ether solution.

The difference between the composition of Grignard compounds in tetrahydrofuran (1) and diethyl ether (2) is explained by the difference in basicity of the two solvents. Ebullioscopic measurements show a monomer-dimer equilibrium in diethyl ether, but only monomeric species present in tetrahydrofuran. Thus tetrahydrofuran coordinates with magnesium more strongly than diethyl ether, and a stable halogen bridge compound is not formed. The exchange of alkyl groups in either tetrahydrofuran or diethyl ether can be explained by an intermediate mixed alkyl-halogen bridge structure.



Grignard compounds coordinated to a much more basic solvent than diethyl ether or tetrahydrofuran might not form such intermediates if the magnesium orbitals are strongly bonded to the basic solvent. Thus dispor-



portionation is prevented and the initial species formed by reaction of RX and Mg is isolated.

Ethylmagnesium bromide was prepared from ethyl bromide and Mg in triethylamine. The reaction product was fractionally crystallized into seven fractions. Each fraction has a Mg:Br:N ratio of 1.0:1.0:1.0¹¹ within experimental error. Molecular association measurements of the crystallized fractions in triethylamine at 35° showed the presence of only monomeric species over a wide concentration range. Because of the highly insoluble nature of MgBr_2 in triethylamine and the soluble nature of $(\text{C}_2\text{H}_5)_2\text{Mg}$, precipitation of MgBr_2 from solution would have occurred if an unassociated mixture of these two products were present. These data prove that the reaction product is a single species and not a mixture. The product, $\text{C}_2\text{H}_5\text{MgBr} \cdot (\text{C}_2\text{H}_5)_3\text{N}$, does not disproportionate in boiling triethylamine over 24 hr., nor is it formed by redistribution of $(\text{C}_2\text{H}_5)_2\text{Mg}$ and MgBr_2 in triethylamine. Thus it is proved that $\text{C}_2\text{H}_5\text{MgBr}$ is the initial product from the reaction of $\text{C}_2\text{H}_5\text{Br}$

(8) D. O. Cowan, J. Hsu, and J. D. Roberts, *J. Org. Chem.*, **29**, 3688 (1964).

(9) G. D. Stucky and R. E. Rundel, *J. Am. Chem. Soc.*, **85**, 1002 (1963).

(10) L. J. Guggenberger and R. E. Rundel, *ibid.*, **86**, 5344 (1964).

(11) Although EtMgBr crystallizes from triethylamine as the bisolvate, the monosolvate is isolated on drying under high vacuum.

and Mg and in triethylamine solution the composition can be represented by this single structure.

Similarly, the existence of RMgX in diethyl ether solution was established. When a diethyl ether solution of ethylmagnesium bromide, prepared from C_2H_5Br and Mg in diethyl ether, was added slowly to a large rapidly stirred volume of triethylamine, $C_2H_5MgBr \cdot (C_2H_5)_3N$ was isolated in over 90% yield by fractional crystallization. The fact that no $MgBr_2 \cdot (C_2H_5)_3N$ was isolated, although it is the most insoluble of the possible products, leads to the conclusion that the rate of solvation is greater than the rate of equilibration and therefore in diethyl ether solution ethylmagnesium bromide consists mainly, if not entirely, of RMgX species (as monomer or dimer).

Reaction of Ethyl Bromide and Magnesium in Triethylamine. To 16.0 g. (0.65 g.-atom) of triply sublimed magnesium metal was added 54.5 g. (0.50 mole) of ethyl bromide (distilled in a nitrogen atmosphere) dissolved in 400 ml. of triethylamine (freshly distilled over $NaAlH_4$ in a nitrogen atmosphere). The reaction was very exothermic; however, the temperature was not allowed to exceed 50° . The reaction produced a white solid suspended in a colorless liquid. The solid was filtered, dried under vacuum, and dissolved in 300 ml. of benzene (distilled over $NaAlH_4$ in a nitrogen atmosphere) in order to remove the unreacted magnesium. Fractional crystallization of the clear benzene solution was effected by slow removal of the benzene under vacuum. Four fractions were collected (fractions 1-4 in Table I), weighing 69.4 g. The triethylamine filtrate from the initial separation was fractionally crystallized into three fractions weighing 31.8 g. These fractions are labeled 5-7 in Table I. The deviation in analyses from one fraction to another is due to the extent of drying the fractions under vacuum. A better indication of fraction comparison can be obtained from consideration of the Mg:Br:N ratio.

Table I

Fractions	Sample wt., g.	Mg, %	Br, %	N, %	Mg:Br:N
1	15.0	11.2	36.6	6.55	1.00:0.99:1.02
2	10.1	11.5	39.2	6.71	1.00:1.04:1.01
3	32.4	13.4	41.8	7.47	1.00:0.93:0.95
4	11.7	12.3	37.9	7.10	1.00:0.94:1.00
5	9.1	10.6	34.8	5.87	1.00:1.00:0.94
6	12.0	10.8	35.1	6.12	1.00:0.99:0.98
7	10.7	12.2	38.2	6.98	1.00:0.95:0.99
Calcd. for $C_2H_5MgBr \cdot N(C_2H_5)_3$		10.4	34.1	5.97	1.00:1.00:1.00

Molecular Weight Measurements. The molecular weight of $C_2H_5MgBr \cdot N(C_2H_5)_3$ was determined ebullioscopically in triethylamine at 150 mm. The results are given in Table II.

Quenching of a Diethyl Ether Solution of Ethylmagnesium Bromide in Triethylamine. To 1 l. of freshly distilled triethylamine was added slowly at room temperature with rapid stirring 100 ml. of a 1.95 M solution of ethylmagnesium bromide in diethyl ether. The solvent was then removed under vacuum in order to remove all traces of diethyl ether, and the resulting

Table II

Concn., <i>m</i>	Δt , $^\circ C$.	Solvent, g.	Solute, g.	Mol. wt. ^a
0.086	0.163	46.75	0.943	232
0.148	0.272	53.33	1.854	242
0.198	0.350	59.95	2.775	247

^a Calculated value for $C_2H_5MgBr \cdot N(C_2H_5)_3$ as a monomer is 234.2.

solid was redissolved in triethylamine. Fractional crystallization produced three fractions with the analyses shown in Table III.

Table III

Fractions	Sample wt., g.	Mg, %	Br, %	N, %	Mg:Br:N
1	10.2	10.9	35.8	6.12	1.00:1.00:0.97
2	11.6	11.2	39.0	6.62	1.00:1.06:1.03
3	Residue 23.7	11.8	43.9	6.91	1.00:1.11:1.02

Acknowledgment. The author acknowledges with appreciation the assistance of the Petroleum Research Fund for their support of this work.

E. C. Ashby

Georgia Institute of Technology
Atlanta, Georgia 30332

Received December 8, 1964

A Novel Rearrangement of Ethylenimine Ketones

Sir:

The epimerization of ethylenimine ketones under the influence of sodium alkoxides has been reported recently,^{1,2} the *cis*-ethylenimine ketones (I) being formed in good yields from the *trans* isomer (II). In a further study of the effect of basic reagents on ethylenimine ketones, we have found that N-methylanilinolithium effects a novel rearrangement of *cis*-1-cyclohexyl-2-phenyl-3-benzoylethylenimine (I) to 2-cyclohexylamino-3-phenylindanone (IIIa). Thus treatment of 4 g. (0.0066 mole) of I in 20 ml. of anhydrous ether with 0.04 mole of N-methylanilinolithium in ether (prepared from N-methylaniline and butyllithium), followed by hydrolysis with methanol, leads to the formation of 0.78 g. (19.5%) of IIIa as a deep purple solid, m.p. $119-120^\circ$. *Anal.* Calcd. for $C_{21}H_{22}NO$: C, 82.86; H, 7.28; N, 4.60. Found: C, 83.09; H, 7.16; N, 4.62.

The structure of IIIa was established by consideration of its spectral data and hydrolysis to 3-phenylindandione (IIIb). The infrared spectrum of IIIa in CCl_4 shows characteristic NH absorption at 3370 cm^{-1} and a strong carbonyl band at 1720 cm^{-1} . The mass spectrum yields a molecular weight of 303 for the parent ion and exhibits a cracking pattern fully consistent with structure IIIa. These data exclude structure IV, which has a molecular weight of 305 and would be expected to exhibit carbonyl absorption in the infrared below 1700 cm^{-1} .³

(1) A. B. Turner, H. W. Heine, J. Irving, and J. B. Bush, Jr., *J. Am. Chem. Soc.*, **87**, 1050 (1965).

(2) R. C. Badger, Ph.D. Thesis, The University of Nebraska, Nov. 1963.