adjusted to 250 ml., and to the thoroughly nitrogen purged solution was added 12.0 g. (0.05 mole) of $CrSO_4 \cdot 5H_2O$ under nitrogen. The deep blue solution was allowed to stir overnight. The acetylene (1.0 g., 0.014 mole) was added. An aliquot after 2 days indicated $\sim 6\%$ of the Cr(II) had been consumed. The reaction solution was saturated with K_2CO_3 and extracted with ether. The extracts were dried over K_2CO_3, filtered, concentrated, and subjected to gas chromatographic analysis on a Carbowax–$AgNO_3$ column. The oil contained $\sim 90\%$ of unreacted acetylene. Of the small amount of products, the distribution was *trans*-crotyl alcohol $\sim 1-2\%$, *cis*-crotyl alcohol $\sim 60\%$, and 3-buten-1-ol $\sim 40\%$.

2-Butyne-1,4-diol.—The acetylene (9.0 g., 0.105 mole) in 25 ml. of water was treated with 450 ml. of 0.483 N $CrSO_4$ (0.218 mole). The reaction was 90% complete in 30 min. After 2 hr. the green solution was basified with sodium hydroxide, filtered from $Cr(OH)_3$, and the filtrate stripped of water on a rotary evaporator at room temperature. The pasty residue was extracted with ether, dried over Na_2SO_4, and treated with 17 g. (0.106 mole) of bromine. The resulting solution was washed with dilute Na_2SO_4 and concentrated, thereby yielding 22.2 g. (0.0925 mole) of *meso*-1,4-dihydroxy-2,3-dibromobutane, m.p. 131° (lit.[33] m.p. 131°).

A sample of *cis*-2-butene-1,4-diol, prepared by the Raney nickel catalyzed hydrogenation of 2-butyne-1,4-diol, when bro-

minated under these conditions gave *dl*-1,4-dihydroxy-2,3-dibromobutane, m.p. 86–87° (lit.[34] 87°).

2-Carboxydiphenylacetylene.—The acetylene (0.15 g., 6.8 $\times 10^{-4}$ mole) in 10 ml. of DMF was treated with a solution of 0.43 g. (18 $\times 10^{-4}$ mole) of $CrSO_4 \cdot 5H_2O$ in 30 ml. of water and 50 ml. of DMF. Upon mixing, the reaction solution became red. The red color gradually dissipated. At 2 days the reaction solution was green. After 3 days the solution was diluted with 200 ml. of water and extracted thrice with ether. The ether extracts were extracted with $NaHCO_3$. The basic aqueous extracts were washed with ether and acidified with 6 N H_2SO_4. The acidic aqueous solution was extracted with ether and dried over Na_2SO_4. Concentration of the ether solution afforded 0.138 g. (85%) of white crystals of *trans*-2-carboxydiphenylethylene, m.p. 158–160° (lit.[35] 158–160°). The infrared and ultraviolet spectra were identical with that reported.[35]

Attempted Reduction of 4-Carboxydiphenylacetylene.—The acetylene, 0.15 g., was exposed to $CrSO_4$ under conditions identical with those for the *ortho* isomer. After 1 week, 0.14 g. of starting material was isolated.

(33) G. W. Kilmer and H. McKennis, Jr., *J. Biol. Chem.*, **152**, 106 (1944).

(34) A. Valette, *Ann. Chim.* [12] **3**, 644 (1948); *Chem. Abstr.*, **43**, 2578 (1949).

(35) D. F. Detar and L. A. Caprino, *J. Am. Chem. Soc.*, **78**, 475 (1956).

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Concerning the Structure of the Grignard Reagent. II.[1]   In Diethyl Ether.   Relevance of Grignard Composition to the Mechanism of Addition to Ketones

BY EUGENE C. ASHBY[2] AND MARTIN B. SMITH[3]

Grignard compounds in diethyl ether solution have been assumed for many years to consist of the dimeric species $R_2Mg \cdot MgX_2$. Molecular weight measurements are reported which indicate that many Grignard compounds in diethyl ether contain essentially monomeric species at low concentrations (0.05 M) and essentially dimeric species at higher concentrations (0.5–1.0 M).[4] Of the compounds studied, the alkyl- and arylmagnesium bromides and iodides follow this pattern, whereas the alkylmagnesium chlorides are essentially dimeric, even at low concentrations. Evidence is presented to support the conclusion that the composition of Grignard compounds in diethyl ether best represented by equilibria containing both monomeric and dimeric species: $(RMgX)_2 \rightleftarrows 2RMgX \rightleftarrows R_2Mg + MgX_2 \rightleftarrows R_2Mg \cdot MgX_2$, with the position of the equilibria being a function of the nature of the R group, the halogen, and the solvent as well as the concentration. Re-evaluation of data from several publications, with respect to the newly accumulated association–concentration data, leads to the conclusion that the RMgX species definitely exists in solution to a considerable degree and that the dimeric species in solution can be described as the symmetrical species $(RMgX)_2$, as well as the unsymmetrical species $R_2Mg \cdot MgX_2$. It is also shown that an equimolar mixture of $(C_2H_5)_2Mg$ and $MgBr_2$ in diethyl ether solution need not necessarily be equivalent to the corresponding Grignard solution. Mechanisms for the reaction of R_2Mg and MgX_2 to form $2RMgX$ are discussed. The mechanism describing Grignard compound addition to ketones in terms of an attacking unsymmetrical dimer, $R_2Mg \cdot MgX_2$, is questioned. It would appear in the light of the discussion presented herein that this mechanism is more accurately described in terms of RMgX species, either monomeric or dimeric. A possible pathway involving ionic species is also presented.

Introduction

The composition of Grignard compounds has been the subject of much study and controversy since Grignard's[5] first report in 1900 that alkyl halides react with magnesium in ether solution to produce this highly versatile reagent. Although many suggestions have been made concerning the composition of Grignard compounds, only two of these have received much attention. The first suggestion made by Grignard,[6]

(1) Part I: *J. Am. Chem. Soc.*, **85**, 118 (1963).

(2) To whom all inquiries should be addressed: Chemistry Department, Georgia Institute of Technology, Atlanta, Ga. 30332.

(3) Ethyl Corporation, Baton Rouge, La.

(4) Monomeric species are referred to as those species containing one magnesium atom per molecule, such as R_2Mg, MgX_2, and RMgX. Dimeric species are referred to as those species containing two magnesium atoms per molecule, such as $R_2Mg \cdot MgX_2$ and $(RMgX)_2$.

(5) V. Grignard, *Compt. rend.*, **130**, 1322 (1900).

(6) V. Grignard, *Ann. Chim. Phys.*, [7] **24**, 433 (1901).

and later supported by Meisenheimer,[7] was that Grignard compounds are best represented by the formula RMgX. The second suggestion which received acceptance was made by Jolibois[8] and involved the representation of Grignard compounds by the formula $R_2Mg \cdot MgX_2$. Since this time, there has been much discussion and speculation as to which of these two formulations best describes the composition. The first convincing evidence permitting a clear-cut choice between these formulations was presented, in 1957, by Dessy and co-workers.[9] They found no exchange between $Mg^{28}Br_2$ and $(C_2H_5)_2Mg$ and presented evidence that an equimolar mixture of $MgBr_2$ and $(C_2H_5)_2Mg$ has the same characteristics as the Grignard reagent prepared from

(7) J. Meisenheimer and J. Casper, *Ber.*, **54B**, 1655 (1921).

(8) P. Jolibois. *Compt. rend.*, **155**, 353 (1912).

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

C_2H_5Br and Mg. Thus it was concluded that alkyl exchange does not take place in diethyl ether solution, that the RMgX species does not exist in solution, and therefore Grignard compounds are best represented by the structure first suggested by Jolibois, namely $R_2Mg \cdot MgX_2$.

Since this work by Dessy, the representation $R_2Mg \cdot MgX_2$ for Grignard compounds has been widely accepted. Thus, Mosher,[10] Becker,[11] and others have postulated that the reaction of Grignard compounds with ketones involves a six-membered transition state in which the Grignard compound exists in the dimeric form supported by Dessy. Although there has been much difficulty in rationalizing all of the kinetic data in terms of reaction order and reaction mechanism with respect to an attacking dimeric species, certainly the postulates presented were the most logical at the time and well accepted.

Recently we reported results which show clearly that in tetrahydrofuran alkyl exchange in Grignard compounds does take place and that the species RMgX does indeed exist in solution.[1] These conclusions were based on two observations: (1) Grignard compounds are monomeric in tetrahydrofuran and (2) crystallization of Grignard compounds produced the species RMg_2X_3 and R_2Mg in quantitative yield. Thus the composition of Grignard compounds in tetrahydrofuran was then concluded to be best described by the formulation first reported by Schlenk,[12] namely

$$2RMgX \rightleftharpoons R_2Mg + MgX_2 \qquad (1)$$
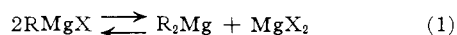
with the equilibrium mixture containing a significant concentration of RMgX. At the same time it was suggested, on the basis of the isolation of RMg_2X_3 compounds from diethyl ether solution, that alkyl exchange may also take place in diethyl ether. The molecular association study of "C_2H_5MgCl" in diethyl ether over a wide concentration range indicated a dimeric structure. This fact complicated the simple equilibrium proposed for Grignard compounds in tetrahydrofuran solution, in that, for diethyl ether solution, dimeric species would have to be included; hence, the equilibria

$$(RMgX)_2 \rightleftharpoons 2RMgX \rightleftharpoons R_2Mg + MgX_2 \rightleftharpoons$$
$$R_2Mg \cdot MgX_2 \quad (2)$$
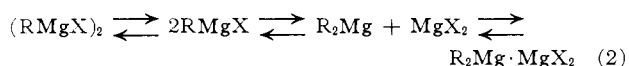
Although the possibility of alkyl exchange in diethyl ether was suggested, we could not definitely establish exchange based on RMg_2X_3 isolation since the molecular association of these compounds could not be established. In tetrahydrofuran, $C_2H_5Mg_2Cl_3$ is soluble and its molecular association was determined to be 0.5. This association factor indicates essentially complete dissociation in solution thereby establishing alkyl exchange in tetrahydrofuran solution of the "C_2H_5MgCl" Grignard.

$$C_2H_5Mg_2Cl_3 \longrightarrow C_2H_5MgCl + MgCl_2$$

Unfortunately, in diethyl ether, $CH_3Mg_2Cl_3$, $C_2H_5Mg_2Br_3$, and $C_6H_5Mg_2Br_3$ were not soluble and therefore their molecular weights could not be determined. For this reason the possibility of these compounds being represented by the general formula A *does* exist and

hence the isolation of RMg_2X_3 compounds without accompanying association data cannot be used to establish alkyl exchange in diethyl ether solution. Although this complication exists, structure B would appear more likely than structure A.
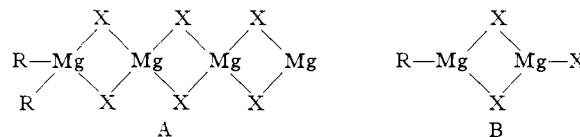
More data have now been accumulated which lead us to the conclusion that alkyl exchange in Grignard compounds does take place, that the RMgX species does exist in diethyl ether solution as well as in tetrahydrofuran, and that the composition of Grignard compounds in diethyl ether is best described by the equilibria 2. Our conclusions are based on molecular association data and reinterpretation of existing data in the literature reported by other authors.

The molecular association data for Grignard compounds in diethyl ether which are presented are certainly not the first data of this type to be found in the literature. Association studies involving Grignard compounds in diethyl ether were first reported by Terentjev[13] and later on by Meisenheimer and Schlichenmaier.[14] More recently (1955), Slough and Ubbelohde[15] cast doubt on the reliability of the association studies reported previously owing to their findings relating the effect of atmospheric oxygen to the degree of association of Grignard compounds. Slough and Ubbelohde determined the molecular association factors of several Grignard compounds in the complete absence of oxygen and found that the species varied from monomeric (p-methoxyphenylmagnesium bromide) to tetrameric (cyclohexylmagnesium bromide) with most of the compounds being essentially dimeric. In the many publications attempting to establish the composition of Grignard compounds or the mechanism of their reactions with ketones, it has been tacitly assumed that these compounds are dimeric.[10,11]

Vreugdenhil and Blomberg[16] reported recently that "C_2H_5MgBr"[1] is monomeric at 10^{-2} to 10^{-3} M concentration. Although this report represents an important contribution, it has added to the confusion in deciding just what is the molecular association of Grignard compounds in diethyl ether. We have felt for some time that much of the controversy concerning Grignard compound association and composition could be resolved if there existed a dependence of the association on concentration. We have studied this effect and report the results and their interpretation here.

Experimental

Grignard Solutions.—The Grignard reagents in diethyl ether were prepared by conventional methods from purified alkyl or aryl halides and triply sublimed magnesium. Diethyl ether freshly distilled over $LiAlH_4$ in a nitrogen atmosphere was used as the solvent. An atmosphere of argon was maintained throughout the preparation and isolation of the resulting clear and colorless Grignard solutions. The compositions of the resulting solu-

(10) J. Miller, G. Grigoriou, and H. S. Mosher, J. Am. Chem. Soc., **83**, 3966 (1961).

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

(12) W. Schlenk and W. Schlenk, Jr., Ber., **62**, 920 (1929).

(13) A. P. Terentjev, Z. anorg. allgem. Chem., **156**, 73 (1936).

(14) J. Meisenheimer and W. Schlichenmaier, Ber., **61**, 720 (1928).

(15) W. Slough and A. R. Ubbelohde, J. Chem. Soc., 108 (1955).

(16) A. D. Vreugdenhil and C. Blomberg, Rec. trav. chim., **82**, 453 (1963).

(17) The quotation marks, as in "RMgX," will be used not to indicate the RMgX species, but merely the Grignard compound formed from RX and Mg.

tions, usually about 2 M, were established by Mg and halogen analyses. The Mg–halogen ratio in all cases was 1.00:1.00 (± 0.04).

Molecular Weight Measurements.—The molecular weights were determined ebullioscopically in diethyl ether at 760.0 mm. pressure with a standard Cottrell boiling-point apparatus. The condenser, which was cooled with ice–water, was connected through a manifold to a Wallace–Tiernan precision manometer, a surge tank, a source of dry nitrogen, and a vacuum pump. The diethyl ether charged to the unit was always freshly distilled over $LiAlH_4$. The sample was added as small, accurately weighed portions of concentrated solution. Four or five additions were usually made in order to cover the desired concentration range (about 0.04–0.3 M). Precautions were taken at all times to avoid exposure of the materials to oxygen or moisture.

Results and Discussion

The results of the molecular weight determinations are listed in Table I and plotted as degree of associa-

TABLE I

ASSOCIATION FACTORS FOR GRIGNARD COMPOUNDS IN DIETHYL ETHER

Mg compd.	M, moles RMgX per l. soln.	i, mol. wt./ formula wt.	Mg compd.	M, moles RMgX per l. soln.	i, mol. wt./ formula wt.
C_2H_5MgCl	0.086	1.87	C_6H_5MgBr	0.042	1.07
	0.143	1.86		0.111	1.17
	0.196	1.92		0.179	1.31
i-C_3H_7MgCl	0.042	1.85		0.241	1.50
	0.080	1.90		0.326	1.71
	0.144	1.93	Mesityl MgBr	0.059	1.06
	0.201	2.00		0.172	1.41
	0.260	2.02		0.275	1.77
C_2H_5MgBr	0.035	1.00	CH_3MgI	0.037	1.09
	0.102	1.04		0.084	1.17
	0.150	1.16		0.140	1.36
	0.200	1.26		0.245	1.59
	0.249	1.37	C_2H_5MgI	0.055	1.00
				0.108	1.12
				0.158	1.27
				0.204	1.36

tion *vs.* concentration in Fig. 1. Figure 1 shows that the degree of association for the bromides and iodides increases uniformly with concentration, going from monomeric species at low concentrations ($\sim 0.05\ M$) and approaching a dimeric species at the higher concentrations (0.5–1.0 M). Figure 1 also shows that the chlorides are essentially dimeric even at the low concentrations. This difference between chlorides and bromides–iodides can be explained easily in terms of inductive and steric effects. Since Grignard compounds are normally employed in solution between 0.1 and 1 M, it would appear that both monomeric and dimeric species are available for reaction. The above results establish without question that in diethyl ether solution the composition $R_2Mg \cdot MgX_2$ is not adequate in describing Grignard compounds. The substantial difference in association of the chlorides as compared to the bromides and iodides also suggests possible differences to be expected in reactions of "RMgCl" compounds as compared to "RMgBr" and "RMgI" compounds in relation to reaction rates as well as reaction mechanisms.

The monomeric species which exist in a Grignard solution in diethyl ether are (I) RMgX, (II) a mixture of R_2Mg and MgX_2, or (III) an equilibrium mixture of I and II. The dimeric species which are present include the symmetrical dimer IV and the unsymmetrical

Figure 1.

dimer V. Each of these species is complexed with ether which, for the sake of simplicity, is not shown. These possibilities are represented by the equilibria

$$R-Mg \underset{X}{\overset{X}{\diamondsuit}} Mg-R \rightleftarrows 2RMgX \rightleftarrows R_2Mg + MgX_2 \rightleftarrows$$

$$\text{IV} \qquad\qquad \text{I} \qquad\qquad \text{II}$$

$$\underset{R}{\overset{R}{\diamondsuit}} \underset{X}{\overset{X}{\diamondsuit}} Mg \underset{X}{\overset{Mg}{\diamondsuit}} \quad (3)$$

$$\text{V}$$

The symmetrical dimeric structure IV was suggested by Ashby and Becker,[1] among others, while the unsymmetrical structure V has been supported by Dessy[18] and others.

The knowledge of concentration dependence on the degree of association of Grignard compounds in diethyl ether has turned out to be an important factor in defining the compositions of these compounds. For example, Evans and Maher,[19] on the basis of n.m.r. studies of $(CH_3)_2Mg$ and "CH_3MgI" in ether, suggested that the complex $(CH_3)_2Mg \cdot MgI_2$, a dimeric species, is stable in highly dilute solution. The molecular weight studies (Fig. 1), however, indicate that "CH_3MgI" is largely monomeric at these concentrations (0.06 M). Since, according to Evans and Maher, interaction between $(CH_3)_2Mg$ and MgI_2 occurs, the product of this interaction must be CH_3MgI. The τ-values reported by Evans and Maher for dimethylmagnesium in diethyl ether show an appreciable concentration dependence whereas the concentration dependence for methylmagnesium iodide is very small over a considerable concentration range. These authors attribute this difference to the dissociation of polymeric dimethylmagnesium species on dilution. This appears unlikely since diethylmagnesium is monomeric at this concentration.[16] It would appear that these data support the conclusion that "CH_3MgI" does not contain an appreciable amount of $(CH_3)_2Mg$ rather than the opposite conclusion drawn by the authors.

Other studies by Evans and Maher in diethyl ether showed that the proton resonance spectra of "C_2H_5-

(18) R. E. Dessy and G. S. Handler, *J. Am. Chem. Soc.*, **80**, 5824 (1958).

(19) D. F. Evans and J. P. Maher, *J. Chem. Soc.*, 5125 (1962).

MgBr" closely resemble those of $(C_2H_5)_2Mg$ for the concentration range 0.040 to 0.296 M (with respect to the ethyl group). They interpreted this as indicating the absence of a significant amount of C_2H_5MgBr and supporting the representation of Grignard compounds in solution as $R_2Mg \cdot MgX_2$. However, the molecular weight studies indicate that at the highest concentration studied (0.296 M), about 64% of the "C_2H_5MgBr" exists as dimeric species, either IV or V, or both; n.m.r. was therefore unable to distinguish between $(C_2H_5)_2Mg$ and structures IV and V. Since each of these structures contains Mg bonded to both carbon and halogen, it follows that n.m.r. could not be expected to distinguish between $(C_2H_5)_2Mg$ and C_2H_5-MgBr. This apparent inability of n.m.r. to distinguish between $(C_2H_5)_2Mg$ and C_2H_5MgBr may be due to the shielding effects of the strongly complexed ether molecules attached to the magnesium atoms.

In tetrahydrofuran we found that "C_2H_5MgCl" and $(C_2H_5)_2Mg$ exhibited essentially identical n.m.r. spectra, yet we know that in tetrahydrofuran the RMgX species is present in solution. Although it is true that THF should provide a greater shielding effect than diethyl ether, nevertheless n.m.r. was not able to distinguish between $(C_2H_5)_2Mg$ and C_2H_5MgCl in solution.

Recently Fraenkel, Adams, and Williams[20] reported little if any difference between the n.m.r. spectra of "CH_3MgI" and CH_3Li. Once again this points out the inability of n.m.r. in certain cases to differentiate between two different chemical species.

As a second example, Dessy[21] reported dielectric constants for 0.139 M $MgBr_2$ in $(C_2H_5)_2O$ to which was added varying amounts of $(C_2H_5)_2Mg$. The plot of dielectric constant vs. $(C_2H_5)_2Mg–MgBr_2$ ratio showed a distinct break at the 1:1 ratio, indicating compound formation. The dielectric constant for the 1:1 mixture was identical with that measured for "C_2H_5MgBr" at the equivalent concentration, indicating that the mixture and the "C_2H_5MgBr" contained the same species. According to Fig. 1 the i-value for "C_2H_5MgBr" (at $M = 0.278$) is 1.43, so that about 60 wt. % of the "C_2H_5MgBr" is present as monomeric species. Since this monomeric "C_2H_5MgBr" is a compound rather than a mixture of $(C_2H_5)_2Mg$ and $MgBr_2$, it must consist of the species C_2H_5MgBr. This indicates that the "Schlenk equilibrium," $2RMgX \rightarrow R_2 + MgMgX_2$, lies considerably to the left for 0.278 M "C_2H_5MgBr" in $(C_2H_5)O$.

The existence of the species C_2H_5MgBr in dilute ether solution is also indicated by the data of Vreugdenhil and Blomberg[16] who reported the following association factors at concentrations of 10^{-3} to 10^{-2} M: $(C_2H_5)_2Mg$, 1.00 ± 0.02; $MgBr_2$, 1.13 ± 0.04; "C_2H_5-MgBr," 1.00 ± 0.02; $(C_2H_5)_2Mg + MgBr_2$, 1.05–1.06. If the "C_2H_5MgBr" had consisted of $(C_2H_5)_2Mg + MgBr_2$, it should have had an i-value of 1.06 (calculated from the i-values for $(C_2H_5)_2Mg$ and $MgBr_2$), as was actually found for the mixture. The i-value of 1.00 determined for "C_2H_5MgBr" did not change within 72 hr., indicating that the monomeric Grignard compound must have consisted of C_2H_5MgBr and that the latter had no measurable tendency to disproportionate to

$^1/_2(C_2H_5)_2Mg + {}^1/_2MgBr_2$. The i-value of 1.05–1.06 for $(C_2H_5)_2Mg + MgBr_2$ indicates that very little reaction to produce C_2H_5MgBr took place. Perhaps this reaction is quite slow, *particularly at these low concentrations*, unless a suitable catalyst is present.

The dimeric structure one would expect to find in equilibrium with "C_2H_5MgBr" is the symmetrical dimer IV. Preference for structure IV over structure V in the equilibria 3 is suggested, as least, for "mesitylmagnesium bromide" since this compound in diethyl ether solution showed at least as much association as "C_6H_5-MgBr" (Fig. 1). If the dimeric species in diethyl ether solution exists as the unsymmetrical dimer, it would seem that "mesitylmagnesium bromide" should be more dissociated than "C_6H_5MgBr" over a wide concentration range because of its greater steric requirement. Since "mesitylmagnesium bromide" shows approximately the same degree of association over the same concentration range as "C_6H_5MgBr," it would seem that the dimer formed would be predominantly the symmetrical one which could only originate from monomeric RMgX species.

The molecular weight determinations indicate that many of the "RMgX" compounds are almost completely dimeric in ether at concentrations in the neighborhood of 1.0 M. The question arises as to what might be expected to happen if equimolar quantities of R_2Mg and MgX_2 are mixed at this concentration. From the equilibria 3 one would expect that $R_2Mg + MgX_2$ would react almost quantitatively to form either I, $2RMgX$ (which would then dimerize to IV $(RMgX)_2$), or V $(R_2Mg \cdot MgX_2)$; or both possibilities could happen simultaneously to form a mixture of IV and V. The composition of the end products may thus depend on the relative rates of the two reactions. Since the reaction rates may be influenced differently by the presence of impurities acting as catalysts or inhibitors, the composition of the end products may vary from one experiment to another and may not necessarily be the same as the composition of "RMgX.[22] For example, Dessy and Jones[23] found the specific conductance of the equimolar mixture of $(C_2H_5)_2Mg$ and $MgBr_2$ in ether to be 2.26×10^{-4} ohm^{-1} cm.$^{-1}$. The corresponding figure obtained for the equivalent concentration (1.0 M) of "C_2H_5MgBr" was only 0.61×10^{-4} ohm^{-1} cm.$^{-1}$.

As another example, Dessy and co-workers[9,18] described experiments in which equimolar amounts of $MgBr_2$ (labeled with radioactive magnesium) and $(C_2H_5)_2Mg$ were dissolved in ether to give a solution 1.0 M in Mg. In all the experiments in which Mg^{25} was used as the tracer, complete exchange occurred between $(C_2H_5)_2Mg$ and Mg^*Br_2. Evidently the $(C_2H_5)_2Mg$ and $Mg^{25}Br_2$ reacted according to the Schlenk equilibrium to form $C_2H_5MgBr + C_2H_5Mg^{25}Br$, which then dimerized to the IV structure. On the other hand, when Mg^{28} was used as the tracer, only 6–10% exchange occurred, even after contact times as long as 36 hr. It is clear that in the Mg^{28} experiment, C_2H_5MgBr was formed in only limited quantities, if at all. Instead, the $(C_2H_5)_2Mg$ and $Mg^{28}Br_2$ probably reacted to form the unsymmetrical dimer $(C_2H_5)_2Mg \cdot Mg^{28}Br_2$, which,

(20) C. Fraenkel, D. Adams, and J. Williams, *Tetrahedron Letters*, **12**, 767 (1963).

(21) J. E. Dessy, *J. Org. Chem.*, **25**, 2260 (1960).

(22) Private communication with R. E. Dessy reveals agreement on this point. Concepts similar to the ones expressed will be contained in a forthcoming publication by R. E. Dessy.

(23) R. E. Dessy and R. M. Jones, *J. Org. Chem.*, **24**, 1685 (1959).

once formed, was relatively stable. It is unlikely that both the $(C_2H_5)_2Mg-Mg^{25}Br_2$ mixture and the $(C_2H_5)_2-Mg-Mg^{28}Br_2$ mixture are equivalent to "C_2H_5MgBr." Evidence was presented earlier which indicated that the predominant monomeric species present in "C_2H_5-MgBr" solutions in the low-to-moderate concentration range is C_2H_5MgBr. It therefore seems most probable that the predominant dimeric species in 1.0 M "C_2H_5-MgBr" solution is the symmetrical (IV) structure and that, if either mixture is equivalent to "C_2H_5MgBr," it is the $(C_2H_5)_2Mg-Mg^{25}Br_2$ mixture.

The fact that Dessy observed complete exchange between $Mg^{25}Br_2$ and $(C_2H_5)_2Mg$ in diethyl ether appears to have been de-emphasized and largely overlooked. Dessy reconciled the difference in behavior of Mg^{25} and Mg^{28} to impurities in the Mg^{25} which he concluded catalyzed the exchange. The possibility that some trace impurity in the Mg^{28} may have inhibited exchange was not considered. It is important to note that the effect of impurities on the exchange reaction has never been thoroughly investigated.[24]

The reaction between R_2Mg and MgX_2 to form $2RMgX$ (such as apparently occurred between $(C_2H_5)_2-Mg$ and $Mg^{25}Br_2$) may proceed by the mechanism

$$R_2Mg + MgX_2 \rightleftarrows R-Mg \overset{R}{\underset{X}{\diamondsuit}} Mg-X \rightleftarrows 2RMgX \quad (4)$$

II   VI   I

The proposed transition state VI contains an R group in a bridged position. This is not unreasonable since alkyl bridges are well known in the chemistry of related aluminum compounds.[25] The dimeric species VI would not be expected to have more than a transitory existence since dimeric structures containing halogen atoms in both bridging positions are thermodynamically favored. Molecular weight measurements of "C_2H_5-MgBr" have shown that, in highly dilute solutions, even the energetically favored dimeric structures for this compound do not exist in appreciable concentrations. Mechanism 4 therefore seems to be consistent with the data of Vreugdenhil and Blomberg[16] which indicated that the reaction between $(C_2H_5)_2Mg$ and $MgBr_2$ is extremely slow at concentrations of 10^{-3} to 10^{-2} M. The reaction might also occur by an ionic mechanism such as

$$R_2Mg + MgX_2 \rightleftarrows (R^- + MgR^+) + (X^- + MgX^+) \rightleftarrows 2RMgX \quad (5)$$

Since this mechanism would be expected to apply almost as well at low concentrations as at higher concentrations, it does not appear to be consistent with the measurements of Vreugdenhil and Blomberg.[16] Another ionic mechanism which should be considered involves carbanion transfer to MgX_2.

$$R_2Mg + MgX_2 \rightleftarrows RMg^+ + RMgX_2^- \rightleftarrows 2RMgX \quad (6)$$

Here one would expect to find a concentration depend-

ence. Furthermore, as explained in a subsequent paragraph, there is good experimental evidence for the existence of the species $[RMg]^+$ and $[RMgX_2]^-$. Mechanisms 4 and 6 are therefore preferred over mechanism 5.

Recently Stucky and Rundle[26] found by X-ray studies that phenylmagnesium bromide is composed of units containing the phenyl group, a bromine atom, and two diethyl ether molecules bonded tetrahedrally to a single magnesium atom. Although the structure of phenylmagnesium bromide in the solid state cannot be extrapolated to solution without some concern, it does appear that the work of Stucky and Rundle adds to the evidence supporting the existence of RMgX species in Grignard solution.

In any discussion concerning the composition of Grignard compounds, some consideration should be given to the existence of ionic species in solution. Evans and Pearson[27] generated interest in describing Grignard compounds in terms of ionic species by their report of electrolysis studies of Grignard compounds in diethyl ether solution. They reported that in the electrolysis of "n-C_4H_9MgBr," magnesium-containing species migrated to both the anode and the cathode. Dessy and Jones[28] verified this work sometime later and further concluded that the major positive ion involved in the migration was RMg^+. Although the number of possible ionic species described by these workers[27,28] are numerous, it appears that the most prevalent ionic species in solution are RMg^+ and $RMgX_2^-$. Thus the equilibria suggested for Grignard compounds in tetrahydrofuran (1) and diethyl ether (2) could be expanded to include these ionic species (6) and still be consistent with the molecular association data we have reported.

In many ways this system is similar to the ion association systems described by Fuoss and Kraus.[29] The conductivity data of Evans and Lee[30] for "C_2H_5MgBr" at concentrations greater than 0.5 M shows an increase in conductivity with concentration. Thus, the indication is that the system is past the conductivity minimum. This suggests that in the concentration range studied, one is dealing with ion-triplet formations. Applying the Harned–Owen symbolism to this system: (1) RMg^+ and X^- would be simple ions, (2) $RMgX$ would be an ion pair, (3) $RMgX_2^-$ and $(RMg)_2X^+$ would be ion triplets, and (4) $(RMgX)_2$ would be a quadruple ion.[31]

Ionic mobilities would be expected to be reasonably high in a low-viscosity medium such as diethyl ether. If dissociation into ions were extensive, high conductance values would be expected.[32] However, the concentration of ionic species cannot be very great due to the low conductances reported for Grignard compounds in ether solution. Evans and Lee[30] have reported conductivities for several Grignard compounds in diethyl ether and we have recently made conductivity measurements for $MgCl_2$, $Mg(C_2H_5)_2$, and "C_2H_5MgCl" in tetra-

(24) Private communication from R. E. Dessy indicates that the exchange reaction in the $R_2Mg \cdot MgX_2$ system is more complicated than earlier indicated.

(25) For example $(C_2H_5)_3Al$ is known to be dimeric in dilute benzene solution. The accepted structure for the dimer involves ethyl groups in the bridging positions.

(26) G. D. Stucky and R. E. Rundle, J. Am. Chem. Soc., 85, 1002 (1963).

(27) W. V. Evans and R. Pearson, ibid., 64, 2865 (1942).

(28) R. E. Dessy and R. M. Jones, J. Org. Chem., 24, 1685 (1959).

(29) R. M. Fuoss and C. A. Kraus, J. Am. Chem. Soc., 55, 2387 (1933).

(30) W. V. Evans and F. H. Lee, ibid., 55, 1474 (1933).

(31) Consider the way μ varies with C, in the light of Harned and Owens' discussion of ion association[32b]; specifically, see the figure on p. 194.

(32) (a) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London, 1959, pp. 51–63, 169; (b) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions," Reinhold Publishing Corp., New York, N. Y., 1950, pp. 480–537.

hydrofuran.[33] We find the specific conductance of "C$_2$H$_5$MgCl" in tetrahydrofuran to be of the same order of magnitude (2.8 × 10^{-5} ohm/cm., 0.051 M, at 25°) as found for "C$_2$H$_5$MgBr" in diethyl ether. In order for Grignard composition to be described in terms of predominantly ionic species in solution, much higher conductances should have been observed.[32] Ionic species of the type described are probably present only to a small extent in solution, so that they are not so important in describing Grignard composition. However, the existence of such species, even in small concentration, could be important in describing the mechanism of Grignard addition to ketones since this process is determined, not by the species in highest concentration, but by the most reactive species.

Mechanism of Grignard Compound Addition to Ketones.—The mechanism of Grignard compound addition to ketones has been interpreted in terms of attack of the dimeric species, R$_2$Mg·MgX$_2$, at the carbonyl group[10,11,34] as represented by 7.
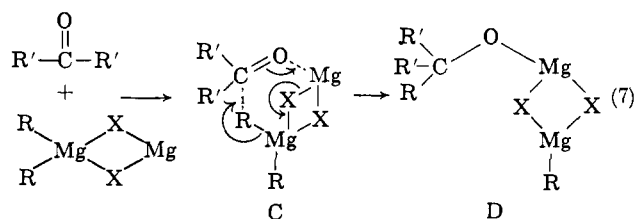
First, it would appear that if the attacking species is dimeric, the symmetrical dimer (RMgX)$_2$ is more likely than the dimeric species R$_2$Mg·MgX$_2$ (8). This
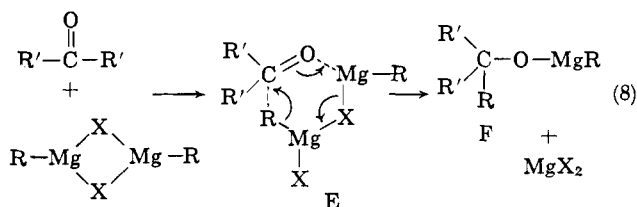
conclusion is based on the fact that mechanism 7 produces product D which would be expected to dissociate according to (9). Since Grignard compounds (bromides and iodides) are considerably dissociated at the concentrations normally employed in addition reactions, product D should be even more dissociated because of
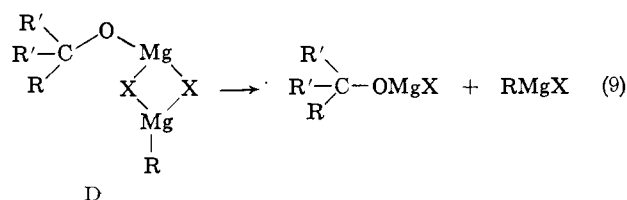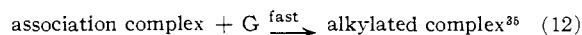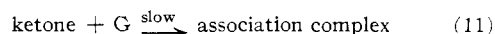

the decreased acidity of the magnesium atom attached to the alkoxy group. The RMgX produced then is rapidly involved in the equilibria 2 and ready for further reaction. The mechanism of Mosher and Becker does not explain the substantial decrease in reaction rate after 50% utilization of the "R" groups in the Grignard reagent. On the other hand, E would be expected to dissociate to F as per eq. 8. Compound F then would be expected to react with another molecule of ketone at a different rate than the Grignard reagent.

(33) Unpublished results, E. C. Ashby and M. B. Smith.
(34) D. O. Cowan and H. S. Mosher, *J. Org. Chem.*, **27**, 1 (1962).

The results of the kinetic studies by Mosher, *et al.*,[10,34] indicate that in order for the proposed mechanism to apply, the resulting Grignard species would have to be dimeric. Yet the molecular association measurements (Fig. 1) indicate that "C$_2$H$_5$MgBr" is essentially monomeric (i = 1.00–1.17) at the concentrations employed (0.02–0.16 M) in these studies. Consequently, unless it is assumed that monomeric Grignard species are unreactive compared to dimeric species, one must consider the possibility of Grignard compound addition to ketones in terms of an attacking monomeric species.

The reluctance of workers[10,11,35] studying the mechanism of Grignard compound addition to ketones to consider the possibility of RMgX as an attacking species is based on two assumptions: (1) Grignard compounds in diethyl ether are dimeric, and (2) RMgX species have been shown not to exist in solution. From the previous presentation we now know that these views are no longer valid. Therefore, it appears quite possible that monomeric species such as RMgX or even RMg$^+$ could be involved in the rate-determining step of the addition reaction. (The proposal of RMg$^+$ as the attacking species is based not on its concentration in solution, which is small, but on its speculated high reactivity.) Contrary to published reports,[10,11] attack by monomeric species is not excluded by the kinetic data. The proposed mechanism is

$$2G \rightleftharpoons G_2 \qquad (10)$$

$$\text{ketone} + G \xrightarrow{\text{slow}} \text{association complex} \qquad (11)$$

$$\text{association complex} + G \xrightarrow{\text{fast}} \text{alkylated complex}^{36} \qquad (12)$$

where G represents monomeric Grignard species (R$_2$Mg, RMgX, RMg$^+$) and G$_2$ represents dimeric Grignard species (R$_2$Mg·MgX$_2$, (RMgX)$_2$). The association complex is represented by ketone–Grignard complexation through the carbonyl oxygen of the ketone and the magnesium atom of the attacking Grignard species. Representing the attacking species by RMgX, the following mechanism appears to be consistent with all available data

$$2RMgX \rightleftharpoons (RMgX)_2 \qquad (13)$$
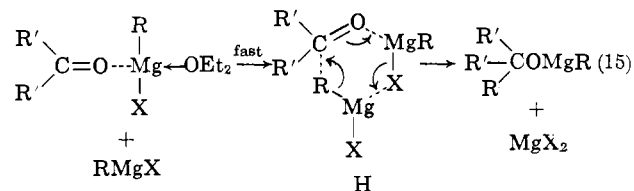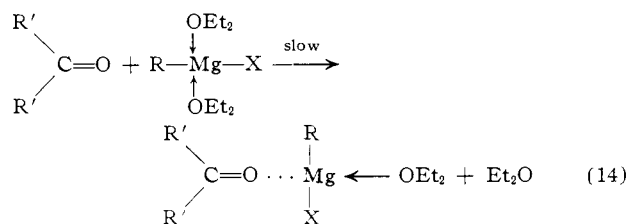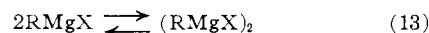
Solvated ether attached to RMgX not shown in the last two steps of eq. 15 for the sake of simplicity

(35) H. O. House and D. O. Traficante, *ibid.*, **28**, 355 (1963).
(36) A similar proposal was made by C. G. Swain, *J. Am. Chem. Soc.*, **69**, 2306 (1947), in which (11) was called the fast step. This mechanism requires third-order kinetics and does not account for the fact that ketone cannot be regenerated by hydrolysis of (11) immediately following the addition of a Grignard reagent to ketone. Both Mosher[10] and Becker[11] have provided valid arguments against the Swain mechanism.

The equilibrium 13 lies to the left for the concentration range in which Grignard compound addition to ketones is normally effected. Since this equilibrium is quite mobile, the entire reaction could consist in the addition of monomeric RMgX species. The displacement step (14) is slow and rate determining. It involves the displacement by the ketone of one of the strongly solvated ether molecules attached to the magnesium atom. Once complexing or polarization of the carbonyl group is effected, further attack by another RMgX species takes place readily at the activated carbon atom.

The product of the ether displacement step (14) of the mechanism can be represented either by an association complex involving polarization of the carbonyl group (I) or by coordinate covalent bond formation involving an ionic intermediate (J). Structures I and J represent the two extremes describing the transition state of the first step. In either case, the carbonyl group is activated allowing for a fast alkylation by another RMgX species as described in 15.

$$
\begin{array}{c}
\underset{\parallel}{\overset{O}{R'-C-R'}} + \underset{\underset{OEt_2}{\uparrow}}{\overset{OEt_2}{\downarrow}}{RMg-X}
\end{array}
$$

(16)

$$
R'\underset{R'}{\overset{\delta^+ \ \delta^-}{C=O}}\cdots\underset{\underset{X}{\mid}}{\overset{\overset{R}{\mid}}{Mg}}\leftarrow OEt_2 + Et_2O
$$
I

$$
R'\underset{R'}{\overset{}{C-O}}\underset{\underset{X}{\mid}}{\overset{\overset{R}{\mid}}{Mg}}\leftarrow OEt_2 + Et_2O
$$
J
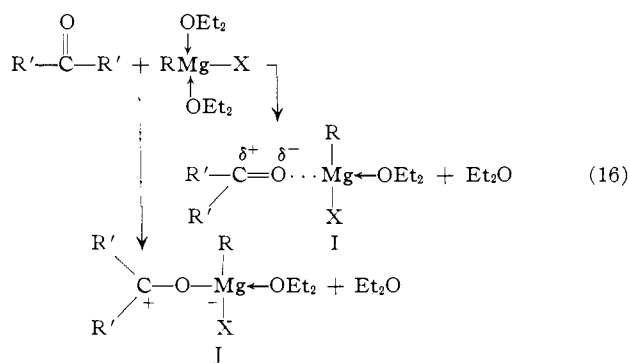
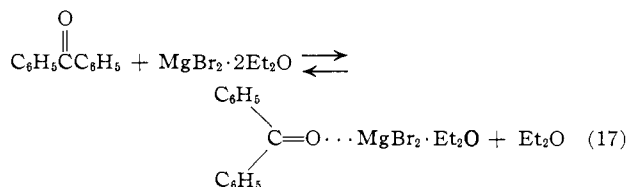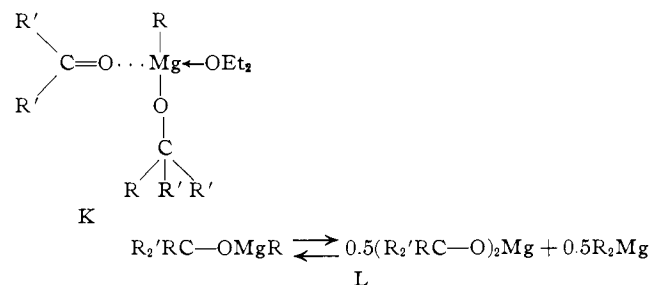The proposed mechanism is in agreement with the results of Becker[37] who reported that the rate of reaction of "C_2H_5MgBr" with benzonitrile (a reaction similar in observed behavior to the reaction of "CH_3MgBr" with benzophenone) decreases as the basicity of the solvent increases. Thus, as the attacking Grignard species is complexed to a more basic ether, the displacement of this ether from the Grignard by ketone becomes more and more difficult. This mechanism also explains why R_2Mg reaction with ketones proceeds at a faster rate than the reaction of "RMgX" with ketones.[11,36,38] The species RMgX is a stronger Lewis acid than R_2Mg and therefore will form stronger bonds with the solvated ether. The ketone in the rate-determining step then displaces the solvated diethyl ether molecules at a slower rate from the stronger acid. If $MgBr_2$ is added to benzophenone, apparently a complex is not formed.[11,35] Magnesium bromide is a stronger acid than either R_2Mg or RMgX and therefore forms an even stronger complex with the solvated ether molecules. The implication is that the equilibrium represented by (17) lies far to the left, even more than would be predicted for R_2Mg or RMgX, if the latter complexation were not followed by rapid and irreversible alkylation.

The proposed mechanism (eq. 13, 14, and 15) explains also the large difference in reactivity after utilization of 50% of the "R" groups in the Grignard reagent. The intermediate $R_2'RC-OMgR$ would be expected to re-

(37) E. I. Becker, *Trans. N. Y. Acad. Sci., Ser. II,* **25,** 513 (1963).
(38) J. H. Wotiz, C. A. Hollingsworth, and R. E. Dessy, *J. Am. Chem. Soc.,* **77,** 103 (1955).

$$
\underset{\parallel}{\overset{O}{C_6H_5CC_6H_5}} + MgBr_2\cdot2Et_2O \rightleftharpoons
$$

$$
\underset{C_6H_5}{\overset{C_6H_5}{\diagdown}}C=O\cdots MgBr_2\cdot Et_2O + Et_2O \quad (17)
$$

act with another molecule of ketone at a considerably different rate from that of RMgX. The mechanism of reaction of this intermediate with another molecule of ketone could be different from the mechanism proposed for the initial stage of the reaction owing to the large difference in steric and electronic environment of this complex as compared to the RMgX or R_2Mg species. Thus, $R_2'RC-OMgR$ could react with another molecule of ketone K or could slowly disproportionate to a more reactive Grignard species L. Alkoxy groups at-

$$
\underset{R'}{\overset{R'}{\diagdown}}C=O\cdots\underset{\underset{\underset{\underset{R \ R'R'}{}}{C}}{\mid}}{\overset{\overset{R}{\mid}}{Mg}}\leftarrow OEt_2
$$
K

$$
R_2'RC-OMgR \rightleftharpoons 0.5(R_2'RC-O)_2Mg + 0.5R_2Mg
$$
L

tached to aluminum are known to decrease the reactivity and mobility of the alkyl groups in aluminum alkyls.[39] A similar effect would be expected in the magnesium alkyls. Thus, further reaction of $R_2'R$-COMgR as represented by either K or L would be expected to proceed at a slower rate than the initial alkylation represented by I.

Since the initial reaction rate falls off after 30% reaction and since the reaction is very rapid, it could be that the concentration of the attacking species is depleted at such a rate that equilibria 13 (or, to be more accurate, equilibria 2) becomes important. This factor would also explain the results of Aston and Bernhard[40] who found that the rate of Grignard reaction with acetone was proportional only to the concentration of Grignard compound, implying that the reaction is so fast with acetone that the rate-determining step is the equilibria 13 or 2. Using ketones that are less and less reactive, the second-order rate (first order with respect to Grignard monomer and first order with respect to ketone) should "taper off" less and less due to the rate of equilibria 2 for exceeding the rate of the reaction.

The possibility that RMgX or R_2Mg is the attacking species represented by a "four-center" transition state is not likely. The postulation of a mechanism repre-

$$
\underset{R'}{\overset{R'-C=O}{\diagup}}\quad\quad \underset{R'}{\overset{R'-C=O}{\diagup}}
$$
$$
R' \quad R-Mg-X \quad\quad R' \quad R-Mg-R
$$
M   N
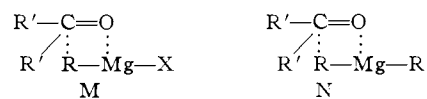
sented by M does not account for the substantial decrease in reaction rate after 50% reaction. The postulation of a mechanism represented by N would imply that Grignard compound and R_2Mg addition to ketones proceed at the same rate. As mentioned earlier, R_2Mg addition to ketones proceeds at a sub-

(39) E. G. Hoffmann, *Trans. Faraday Soc.,* **58,** 642 (1962).
(40) J. G. Aston and S. A. Bernhard, *Nature,* **165,** 485 (1950).

stantially faster rate than Grignard compound addition.

Prior coordination of the ketone by MgX_2 followed by R_2Mg addition to the polarized carbonyl group is not probable on the basis that coordination by MgX_2 in the presence of RMgX and R_2Mg is unlikely (for the reasons discussed previously). Also the intermediate product of such an addition ($R_2'RC$-OMgX) does not explain the reduced reactivity of the Grignard after 50% reaction.

Finally, it appears that Grignard compound addition to ketones can also be explained in terms of attacking ionic species.

$$2RMgX \rightleftarrows R_2Mg + MgX_2 \rightleftarrows RMg^+ + RMgX_2^- \quad (6)$$

$$R'\!-\!\overset{\displaystyle R'}{\underset{\displaystyle }{C}}\!=\!O + RMg^+ \xrightarrow{\text{slow}} R'\!-\!\overset{\displaystyle R'}{\underset{\displaystyle }{C}}\!\oplus\!-\!OMgR \quad (18)$$

$$R'\!-\!\overset{\displaystyle }{\underset{\displaystyle R'}{C}}\!\!\overset{\oplus}{}\!-\!OMgR + RMgX_2^- \xrightarrow{\text{fast}}$$

$$R'\!-\!\overset{R'}{\underset{R)}{C}}\overset{O}{\underset{X}{}}\!\!Mg\!-\!R \longrightarrow R'\!-\!\overset{R'}{\underset{R}{C}}\!-\!OMgR \quad (19)$$
$$\overset{\ominus}{\underset{Mg}{}}$$
$$\underset{X}{} \qquad\qquad + MgX_2$$

The same arguments justifying RMgX addition also hold for attacking ionic species.

In summary, the composition of Grignard compounds in ether solution appears to be a function of the solvent, as well as the nature of the halogen involved. The composition of "EtMgBr" in tetrahydrofuran, for example, is adequately described by the equilibrium

$$2RMgX \rightleftarrows R_2Mg + MgX_2$$

In diethyl ether, however, the composition is expanded to include dimeric species.

$$R\!-\!Mg\overset{X}{\underset{X}{\diamondsuit}}Mg\!-\!R \rightleftarrows 2RMgX \rightleftarrows$$

$$R_2Mg + MgX_2 \rightleftarrows \overset{R \quad X}{\underset{R \quad X}{Mg \quad Mg}}$$

When X = Br and I, association increases with concentration, so that at 0.05 M the species present in solution are predominantly monomeric, whereas at 0.3 M the species present in solution are about one-half monomeric and one-half dimeric. When X = Cl, dimeric species predominate even at 0.05 M.

Conductance data indicate that ionic species such as RMg^+, $RMgX_2^-$, and ion triplets exist in solution, but only to a minor extent.

A new mechanism describing the addition of Grignard compounds to ketones is presented in terms of an attacking monomeric or dimeric RMgX species. All of the pertinent facts reported to date, concerning Grignard compound addition to ketones, can be accounted for in terms of a mechanism involving, in the rate-determining step, ketone displacement of a solvated ether molecule from the attacking Grignard species.

[Contribution from the Department of Chemistry, Whitmore Building, The Pennsylvania State University, University Park, Pennsylvania]

Carbonium Ions. XVII. The Direct Observation of Saturated and Unsaturated Acyl Cations and Their Equilibria with Protonated Acids

By N. C. Deno, Charles U. Pittman, Jr., and Max J. Wisotsky

The equilibria between RCOOH and $RCOOH_2^+$ and between $RCOOH_2^+$ and RCO^+ have been studied in 0–100% aqueous H_2SO_4 and in 0–80% SO_3 in H_2SO_4. The simple aliphatic carboxylic acids have $[RCOOH_2^+]$ equal to $[RCO^-]$ in 10–25% SO_3 and the shift from >90% $RCOOH_2^-$ to >90% RCO^+ occurs within narrow (~4%) ranges of SO_3 concentrations. It is suggested that the equilibrium shifts between RCO^+ and $RCOOH_2^+$ can be used to evaluate changes in the activity of H_2O. The acyl cations, RCO^+, may now be regarded as commonplace and familiar chemical species. Their availability in wide variety will be of synthetic interest.

A representative selection of 11 carboxylic acids have been examined by nuclear magnetic resonance (n.m.r.) spectroscopy in 0–100% aqueous H_2SO_4 and 0–80% SO_3 in H_2SO_4. The shift of equilibria from free acid (RCOOH) to protonated acid ($RCOOH_2^+$) and the further shift from $RCOOH_2^+$ to the acyl cation (RCO^+) were evident. These results, along with the work of Olah, reduce acyl cations to commonplace chemical species and reinforce the current viewpoint that such acyl cations have real existence.

Figure 1 shows the changes in n.m.r. band position for solutions of acetic acid in varying concentrations

of SO_3–H_2SO_4–H_2O. Only the band position shifts, indicating that the changes are entirely confined to the carboxyl group. The downfield shift of 0.56 p.p.m. between 50 and 96% H_2SO_4 is of the magnitude expected for simple protonation. More convincing, the shift is half-completed at 77% H_2SO_4 (35°), agreeing with ultraviolet studies which estimated acetic acid to be half-protonated in 74% H_2SO_4 (25°).[1] Similarly, the n.m.r. data for propionic acid indicate it to be half-protonated in 80% H_2SO_4 (35°) in agreement with the

(1) A. R. Goldfarb, A. Mele, and N. Gutstein, *J. Am. Chem. Soc.*, **77**, 6194 (1955).