the proposed bond cleavage. The energy corresponding to 320 mμ radiation (90 kcal./mole) is substantially greater than the maximum energy required for bond dissociation in cyclopropane itself (53.4 kcal./mole)[9] and this in turn is probably higher than that required for bond rupture in IIa or IIb.[10]

Particular interest is attached to the problem of the mode of energy transfer from the activated carbonyl chromophore to the beta bond. It remains to be established whether the cleavage process leading to isomerization involves an electronically excited species (perhaps in a high vibrational level)[11] or is a thermal reaction of the molecule in the ground state requiring prior conversion of electronic energy to vibrational energy.[12] A study of the pressure dependence of the gas phase isomerization of 1,2-diacetylcyclopropane, which is in progress, should provide information on this matter. Internal conversion of electronic energy to thermal energy has recently been invoked to explain the conversion of 1,3,5-cycloheptatriene to toluene in the gas phase.[13] In the case at hand, it seems unusual that collisional deactivation of the electronically excited species would not compete efficiently with internal conversion since the reaction is effected in the condensed phase.

The isomerization reaction described herein is undoubtedly related to the irreversible photochemical conversion of the ketone VI to 2,3-diphenylphenol (VII). A vibrationally excited ground state (thermal) mechanism for this reaction was excluded on the basis
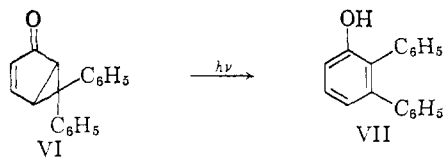
that n,π^* photochemical reactions do not in general parallel thermal reactions.[14]

Classical, radical and ionic structures such as VIII and IX which allow delocalization of the electrons in the beta bond may be invoked to explain the isomerization.[15] Although such representations appear to be functional it is questionable whether they accurately represent the excited state.[16]
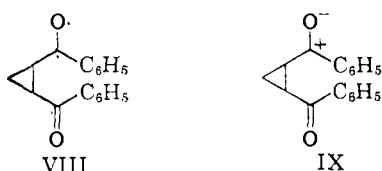
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THE STRUCTURE OF PHENYLMAGNESIUM BROMIDE DIETHERATE AND THE NATURE OF GRIGNARD REAGENTS

Sir:

Since their discovery over sixty years ago,[1] the nature of the Grignard reagents has been the subject of continuous investigation and speculation.[2,3] We report here the structure of phenylmagnesium bromide dietherate and certain other observations which have a strong bearing on this problem and seem to require a major modification of some current interpretations.

Phenylmagnesium bromide was prepared by the action of phenyl bromide and magnesium in diethyl ether. Upon concentration of the reagent by removing ether under reduced pressure, crystals of empirical formula $C_6H_5MgBr \cdot 2(C_4H_{10}O)$ can be obtained upon cooling and rewarming, confirming observations of Schlenk.[4] The composition of the crystals does not depend upon concentration so long as the ratio of ether to phenylmagnesium bromide is greater than two. At the stoichiometric composition the entire solution may be crystallized at 15–20°. Further removal of ether is possible only at higher temperatures and/or lower pressures. At lower ether content an amorphous polymer forms, and the entire reagent polymerizes if all the ether is removed. The polymer redissolves in ether.

Crystals of $C_6H_5MgBr \cdot 2(C_4H_{10}O)$ are orthorhombic, $a = 12.25$, $b = 12.81$, $c = 11.02$ Å, space group $P2_12_12_1$, $Z = 4$. The crystals give a positive color test for active organometallic compounds, such as the Grignard reagent.[5] A three-dimensional Patterson map yielded bromine and oxygen positions. The structure determination has proceeded far enough that the phenyl group has been well resolved, rough ethyl positions of the ethers have been found, and $R = 17.8\%$ for three-dimensional data. The structure consists of phenylmagnesium bromide dietherate monomers (Fig. 1) with the phenyl group, a bromine atom and two ether molecules bonded tetrahedrally to a single magnesium atom.

A preliminary study of diphenylmagnesium crystallized from diethyl ether shows that it is also a dietherate consisting of monomers, undoubtedly with tetrahedral coördination of phenyls and ethers to magnesium. It is well known that $MgBr_2$ forms etherates soluble in ether. We have obtained crystals of an etherate, but have not yet examined them by X-rays.

Though the structural work reported here has validity only for the solid state, the following conclusions concerning this Grignard in ether solution seem warranted:

(1) The often suggested species, such as $(C_6H_5)_2\text{-}Mg \cdot MgBr_2 \cdot n(C_4H_{10}O)$, are unlikely because they would most probably have an ether/Mg ratio of less than two. For example, a probable structure, based on known structures of organometallic compounds and metal halides such as Al_2Br_6, etc., would be

$$(I)$$
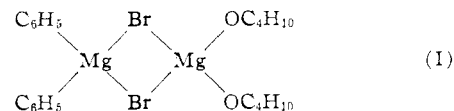
Higher complexes should contain even lower ether/magnesium ratios. The observed fact that removing ether until the ether/magnesium ratio is less than two

(1) V. Grignard, Compt. rend., **130**, 1322 (1900).
(2) See G. E. Coates, "Organometallic Compounds," 2nd Ed., John Wiley and Sons, New York, N. Y., 1960, and older reviews listed therein.
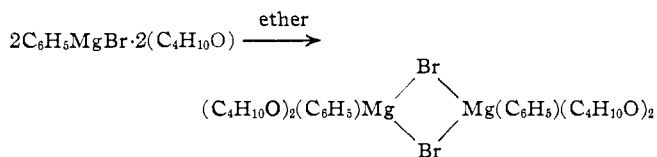(3) R. E. Dessy and G. S. Handler, J. Am. Chem. Soc., **80**, 5824 (1958); R. E. Dessy, G. S. Handler, J. H. Wotiz and C. A. Hollingsworth, ibid., **79**, 3476 (1957).
(4) W. Schlenk, Thesis, Univ. of Charlottenburg, 1929.
(5) H. Gilman and F. Schulze, J. Am. Chem. Soc., **47**, 2002 (1925).

causes polymerization and precipitation tends to confirm that polymerization involves loss of ethers of solvation.

(2) Alternatives which require dimerization without loss of ether, but with higher coördination numbers in solution, such as

$$2C_6H_5MgBr\cdot2(C_4H_{10}O) \xrightarrow{\text{ether}}$$

$$(C_4H_{10}O)_2(C_6H_5)Mg \underset{Br}{\overset{Br}{\diamond}} Mg(C_6H_5)(C_4H_{10}O)_2$$

are contrary to entropy and thermodynamic data below, and seem unlikely.
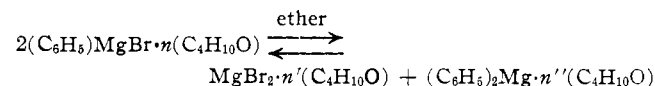
(3) The Mg–O bond to ether in this Grignard is among the strongest Mg–O bonds known (2.06 Å. *vs.* 2.10 in MgO, 2.09 in $Mg(OH)_2{}^6$ and 2.14 in $Mg(H_2O)_6$-$(ClO_4)_2{}^7$). The bond energies of Mg–O bonds are expected to be greater than those of Mg–Br bonds, and this is supported by thermodynamic data, including $\Delta H^0{}_{25} = -44.5$ kcal./mole for solution of crystalline $MgBr_2$ in water.[8] The high Madelung energy of $MgBr_2$ along with the relative low heat of hydration of the bromide ion, and octahedral coördination of magnesium in both crystal and solution, all are factors consistent with increased bond energies in the hydrated solution. Also, for $MgBr_2(s) + 6H_2O(l) = Mg(OH_2)_6Br_2(s)\ \Delta H^0{}_{25} = -104.9$ kcal./mole.[9] In this reaction bromide ions are displaced by water in the coördination polyhedron about magnesium, and again competing effects do not seem to be large enough to alter the conclusion that increased bond energy in the product is a key factor in the heat of reaction.

(4) $C_6H_5MgBr\cdot2(C_4H_{10}O)$ forms molecular crystals with normal van der Waals packing and nothing to suggest an unusual lattice energy.

These points make it very unlikely that dimagnesium species such as (I) predominate in ether solution. Higher complexes are even less likely.

The crystal structure does not exclude the possibility that in solution the Grignard consists of $(C_6H_5)_2Mg\cdot$ $n(C_4H_{10}O)$ plus $Br_2Mg\cdot n'(C_4H_{10}O)$. This possibility is, however, eliminated by n.m.r. examination of diphenylmagnesium in ether solution and phenylmagnesium bromide in ether solution. In both solutions there is evidence for only one type of phenyl group. In both cases resonances of *ortho*-hydrogens of the phenyl group are well separated from the combined *meta–para resonances*, both are found at low fields. But the separation of *ortho* and *meta–para* resonances for diphenylmagnesium is about 0.1 p.p.m. greater than for phenylmagnesium bromide. This difference in internal chemical shifts persists unchanged over a considerable concentration range.

These n.m.r. data do not eliminate an equilibrium

$$2(C_6H_5)MgBr\cdot n(C_4H_{10}O) \xrightleftharpoons{\text{ether}}$$
$$MgBr_2\cdot n'(C_4H_{10}O) + (C_6H_5)_2Mg\cdot n''(C_4H_{10}O)$$

with a rapid phenyl exchange. (Rapid phenyl exchange is to be expected.[10,11]) In any case our results strongly imply that $C_6H_5MgBr\cdot2(C_4H_{10}O)$, or possibly

(6) W. G. Wyckoff, "Crystal Structures." Interscience Publishers. Inc., New York, N. Y., 1948.

(7) C. D. West, *Z. Krist.*, **91**, 480 (1935).

(8) Data from W. M. Latimer, "Oxidation Potentials." 2nd Ed., Prentice-Hall, Inc.. New York, N. Y., 1952.

(9) Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

(10) A. L. Allred and C. R. McCoy, *Tetrahedron Letters*, **27**, 25 (1960).

(11) E. N. Sinotova, Y. Vobetski, Y. N. Logniov and V. N. Evikheev, *Radiochemica*, 1, 687 (1959).

a higher etherate of the monomer, is a significant feature of this Grignard reagent prepared in the traditional way.

At this time there seems to be no certain evidence that mixing diphenylmagnesium and magnesium bromides in ether leads rapidly to the traditional Grignard
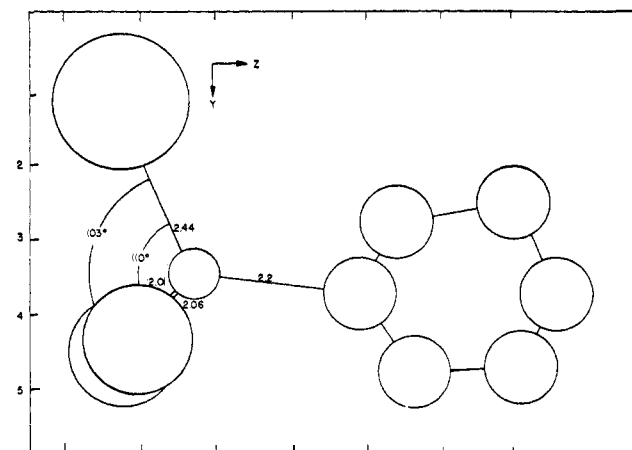

Fig. 1.—Molecular structure of $(C_6H_5)MgBr\cdot2C_4H_{10}O$ in the crystal. Ether carbons are omitted for clarity.

reagent, though this is frequently assumed. It is possible that phenyl–bromine exchange is very slow, although phenyl–phenyl exchange is rapid, since quite different mechanisms may be involved. Until there is evidence to the contrary slow phenyl–bromine exchange offers the simplest explanation of the lack of exchange of magnesium between diphenylmagnesium and magnesium bromides when the two are dissolved together in ether.[3]

The literature on Grignard reagents is confusing and often inconsistent. Generalizations to other groups and to other ethers are not yet justified.

The full report of the structure of phenylmagnesium bromide dietherate and other studies of Grignard reagents now underway will be published in due course.

The authors are indebted to Dr. R. W. King for the n.m.r. spectra, and to Dr. King and to Profs. H. Gilman and O. Chapman for helpful discussions.

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THE REACTION OF SODIUM BOROHYDRIDE WITH NICKEL ACETATE IN AQUEOUS SOLUTION—A CONVENIENT SYNTHESIS OF AN ACTIVE NICKEL HYDROGENATION CATALYST OF LOW ISOMERIZING TENDENCY

Sir:

The reaction of sodium borohydride with nickel salts in aqueous solution produces a granular black material which is an active catalyst for the hydrolysis of borohydride ion.[1,2] This material, which has been considered to be a nickel boride, Ni_2B,[1,3] is a hydrogenation catalyst which has been reported to approach Raney nickel in activity.[3]

In the course of investigating the effect of olefin structure upon the rate of hydrogenation over various

(1) J. I. Schlesinger, H. C. Brown, A. E. Finholt, J. R. Gilbreath, H. R. Hoekstra and E. K. Hyde, *J. Am. Chem. Soc.*, **75**, 215 (1953).

(2) H. C. Brown and C. A. Brown, *ibid.*, **84**, 1493 (1962).

(3) R. Paul, P. Buisson and N. Joseph, *Ind. Eng. Chem.*, **44**, 1006 (1952).