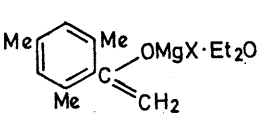
Structure of Grignard Compound Derived from Mesityl Methyl Ketone

By A. G. PINKUS,* JAMES G. LINDBERG, and AN-BANG WU
(*Department of Chemistry, Baylor University, Waco, Texas* 76703)

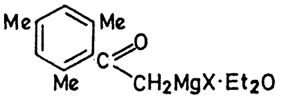
Summary The bromo Grignard compound derived from mesityl methyl ketone is not the presently accepted enolate (I); on the basis of cryoscopic, i.r., and ^{1}H n.m.r. studies the dimeric structure (III) is indicated.

STRUCTURES of derived Grignard compounds as well as ordinary Grignard reagents have been subjects of recent investigations[1] which have early origins. Although Klages[2] first recorded a reaction between mesityl methyl ketone and a Grignard reagent, Kohler and his co-workers[3] clarified the 1 : 1 stoicheiometry and showed that 1 equiv. of alkane was evolved from the reaction. Using Klages' observation that only 1 equiv. of ether was present in the product, Kohler and his co-workers formulated the structure as a mono-etherate enolate (I). Similar enolate structures were postulated for other Grignard compounds derivable from hindered ketones.[4] Although derived Grignard compounds from mesityl ketones underwent substitution on carbonyl oxygen[5] or at carbon α to the carbonyl[6] and gave a positive test[7] for a carbon-to-metal bond with Michler's ketone, the enolic-type structure (I) was considered to be correct[5–7] rather than the alternative keto-structure (II). Nesmeyanov and his co-workers[8] conducted an extensive re-investigation of Grignard compounds derived from Kohler's mesityl ketones,[3–5] eliminated additional tautomeric and mesomeric anionic possibilities, and considered that they had definitely established the monoetherate enolate type structure (I). Enolate structures of type (I) are generally accepted and used at the present time.[9]

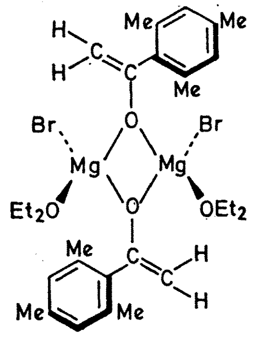
Structures of derived Grignard compounds were important in the present work in connection with studies on various alkyl mesityl ketones.[10] Since enolate structures (I) as formulated at present would be the first authentic tri-co-ordinate magnesium compounds[11d] it was of further importance either to confirm or disprove these structures since compounds containing tri-co-ordinate magnesium have only been recently reported[11] and in addition correct structures are important for mechanistic considerations of Grignard reactions.[1] The Grignard compound derived from mesityl methyl ketone and ethylmagnesium bromide was studied as a representative example. The product was insoluble in ether but soluble in benzene. It was recrystallized from benzene as colourless crystals which gave the correct analysis† for $C_{15}H_{23}O_2BrMg$ as a monoetherate. The molecular weight‡ showed a dimeric structure, $(C_{15}H_{23}O_2BrMg)_2$. The i.r. spectrum§ (mineral oil mull) showed the absence of a carbonyl stretching band, and the presence of a C=C (enolic) stretching doublet at 6·0 and 6·08 μm and a C=C (aromatic) stretching band at 6·24 μm. The ^{1}H n.m.r. spectrum§ (δ in p.p.m.) in benzene showed the co-ordinated ether as a triplet–quartet combination at 0·92 (CH_3) and 3·33 (CH_2), respectively (J 7·1 and 7·0 c./sec., respectively). Integrated areas of co-ordinated ether peaks relative to areas of ring methyl groups confirmed the presence of only one co-ordinated ether molecule. The remaining ^{1}H n.m.r. bands were identified as follows: 2·61 (*o*-CH_3); 2·10 (*p*-CH_3); 6·76 (arom-H); 4·59 (vinylic H *cis* to enolic O) (J 1·0 c./sec.); 4·10 (vinylic H *trans* to enolic O) (J 1·0 c./sec.). The data are in accord with structure (III); the *cis*-form is indicated on the following basis. The n.m.r. signal for the *ortho*-methyl group showed some line broadening which in the case of the iodo-derivative split into two signals. This is interpreted in terms of restricted rotation about the mesityl-to-carbon bond which results in magnetically nonequivalent environments for the two *ortho*-methyl groups in each mesityl ring for a *cis*- but not for a *trans*-arrangement. The restriction of rotation would be expected to be greater for the iodo- than the bromo-derivative.



(I)



(II)



(III)

A four-membered ring with alternating magnesium and oxygen atoms was recently suggested by Coates and Ridley[11b] for a product obtained from condensation of acetone and methylmagnesium bromide; the structure was recently confirmed by *X*-ray crystallographic studies by Moseley and Shearer.[12] Bromine-bridging in a four-membered ring, as found in an *X*-ray crystallographic study of $(Et_2Mg{\cdot}Et_3N)_2$ by Toney and Stucky,[13] is ruled out on the basis of the n.m.r. results.§

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† This particular compound has not previously been characterized with respect to elemental analysis. A quantitative analysis of hydrolysis products was also carried out.

‡ Cryoscopic in benzene and modified Rast method in naphthalene.

§ A more detailed analysis and justification of i.r. and n.m.r. spectra will be given in a more complete account of this work dealing with a series of Grignard compounds derived from various alkyl mesityl ketones and using various halogens. A more complete study with respect to analytical characterization and state of aggregation was carried out on the bromo Grignard derivative of mesityl methyl ketone reported in the present paper than with the other derivatives.

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