Grignard Compound Derived from Isopropyl Mesityl Ketone Containing Trico-ordinate Magnesium

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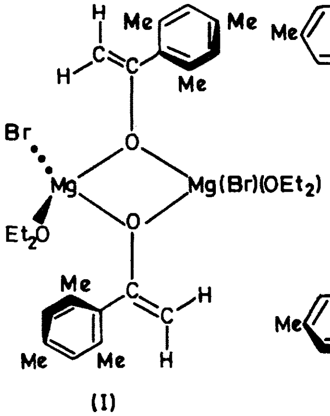
Summary Evidence from cryoscopic determinations in naphthalene and benzene, elemental and hydrolytic analyses, i.r. and ^1H n.m.r. spectra shows that the Grignard compound from isopropyl mesityl ketone originally prepared by Fuson and his co-workers in 1939 is a monomeric enolate (III) containing trico-ordinate magnesium in contrast to the dimeric structure (I) found for the corresponding halogeno-derivatives from methyl mesityl ketone.

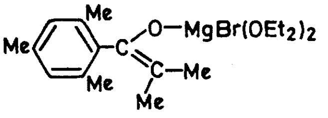
THE first compounds containing trico-ordinate magnesium for which experimental evidence of structure was presented have been reported only in the last few years.[1] The Grignard compound derived from methyl mesityl ketone was recently found[2] to have a dimeric cyclic structure (I). We now report that the Grignard compound from the reaction of isopropyl mesityl ketone and ethylmagnesium bromide is a monomeric enolate in solution and has a trico-ordinate magnesium atom. The compound was prepared and used in condensations by Fuson and his co-workers,[3] but a structure determination was not attempted. To our knowledge this is the first trico-ordinate magnesium compound to be prepared for which there is now conclusive proof of structure.†

The title compound was prepared‡ by treating isopropyl mesityl ketone with an ether solution of ethylmagnesium bromide. The precipitated derivative was recrystallized‡ from dry benzene. The crystal structure was markedly different from that of the corresponding compound from methyl mesityl ketone. Elemental analysis and analysis for isopropyl mesityl ketone from hydrolysis checked accurately for a structure with trico-ordinate magnesium containing the aromatic grouping, bromine, and one co-ordinated ether group and exclude a tetraco-ordinate magnesium dietherate of type (II). Molecular weight determinations by a modified Rast method using naphthalene and by cryoscopy in benzene showed a monomer. [Analysis for Mg and Br correct for $C_{17}H_{27}O_2MgBr$; isopropyl mesityl ketone by hydrolysis, 51·68%; *M* (cryoscopic 2·59, 3·68 wt.-% in naphthalene; 0·735 wt.-% in benzene) 403§ and 377 respectively; $C_{17}H_{27}O_2MgBr$: hydrolysable ketone, 51·76%; *M* 368].

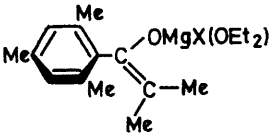
The i.r. spectrum (mineral-oil mull) showed absence of a carbonyl stretching band and presence of a singlet¶ C=C (enolic) stretching band at 6·00 μm. The ^1H n.m.r. spectrum** (δ p.p.m., *J* Hz) in benzene showed the co-ordinated ether as a triplet–quartet combination at 0·96 (CH_3, *J* 6·8) and 3·43 (CH_2, *J* 6·7) respectively. The other ^1H n.m.r. bands (all sharp singlets) were identified as follows: 2·51 (*o*-CH_3), 2·14 (*p*-CH_3), 6·82 (Ar*H*, 2·04 (CH_3 *cis* to enolic O), 1·38 (CH_3 *trans* to enolic O). The data are in accord with structure (III).



(I)



(II)



(III) X= Br or I

The formation of a dimer for the Grignard derivatives of methyl mesityl ketone and a monomer for the corresponding isopropyl mesityl ketone derivatives appears to be due to the additional steric bulk provided by the isopropyl methyl groups which inhibit dimer formation in the latter case; scale molecular models support this idea. The cryoscopic data in naphthalene indicate the possibility that a monomer–dimer equilibrium may be present in both cases;†† the equilibria are toward dimer in the former case and toward monomer in the latter. Although no lines corresponding to the minor components are detectable in the ^1H n.m.r. spectra, the spectra are of benzene solutions; the molecular weight of the isopropyl Grignard checks closely with monomer in this solvent. The configuration of the trico-ordinate magnesium atom is probably planar as would be expected for an atom with six bonded electrons; on this basis the singlet observed for the *ortho*-methyl groups would be

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† Although other compounds of this type were reported earlier (ref. 4) mainly by Kohler *et al.*, analysis was reported for only one of these (ref. 5) and molecular weights were not determined.

‡ Since these types of compounds are extremely sensitive to moisture and oxygen, preparation and handling were all carried out in a dry-box under an oxygen-free dry nitrogen atmosphere.

§ Average of 8 determinations in naphthalene, standard deviation = 19, mean = 16; no significant trend was evident at these concentrations.

¶ Spectra of chloro- and iodo-derivatives also showed singlets at 6·01 and 6·00 μm respectively; spectra of chloro-, bromo-, and iodo-derivatives of methyl mesityl ketone all showed doublets.

** The ^1H n.m.r. spectrum was for the iodo-Grignard derivative of isopropyl mesityl ketone; since the i.r. spectral characteristics of the bromo- and iodo-derivatives correlate closely, similar structures are indicated.

†† *i*-Value = 1·10 for the bromo Grignard of isopropyl mesityl ketone; 1·91 for that from methyl mesityl ketone; both based on cryoscopy in naphthalene. *i*-Value defined as the ratio of the experimentally determined molecular weight to the formula weight: F. W. Walker and E. C. Ashby, *J. Chem. Educ.*, 1968, **45**, 654; also referred to as the degree of association: G. E. Coates and J. A. Heslop, *J. Chem. Soc.* (*A*), 1968, 514.

expected whether mesityl rotation in (III) is restricted or not. Structural considerations apply to solutions and may or may not apply to the solid state.

On the basis of an examination of scale molecular models of *cis*- and *trans*-isomers (bromines or ethers—*cis* or *trans*—with respect to the 4-membered ring) of the dimeric bromo Grignard compound of methyl mesityl ketone,[2] we believe that the line broadening observed for the *ortho*-methyl groups can be adequately explained on the basis of restriction of rotation about the mesityl to carbon bond in a *trans*-(I) structure. In the preferred conformation of the molecule [*trans*-(I)] the two *ortho*-methyl groups are magnetically anisotropic with respect to halogen and ether groups attached to the same magnesium atom. With the iodo-derivative of (I) a doublet appears in the spectrum for the *ortho*- methyl groups; this greater peak separation can be explained as being due to a greater degree of restriction to rotation of the mesityl groups in the *trans*-structure caused by increased steric interference to rotation of the mesityl group from the larger iodine atom. A *cis*-configuration is sterically inhibited; scale models indicate extreme crowding between ether ethyl groups and *ortho*-methyls.

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[2] A. G. Pinkus, J. G. Lindberg, and A. B. Wu, *Chem. Comm.*, 1969, 1350.

[3] R. C. Fuson, C. H. Fisher, G. E. Ullyot, and W. O. Fugate, *J. Org. Chem.*, 1939, **4**, 111.

[4] See refs. listed in ref. 2.

[5] A. N. Nesmeyanov, V. A. Sazonova, and E. B. Landor, *Doklady Akad. Nauk S.S.S.R.*, 1948, **63**, 395 (A. N. Nesmeyanov, "Selected Works in Organic Chemistry," Macmillan, New York, 1963, p. 438).