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ALKOXYMAGNESIUM HALIDES

N. Ya. TUROVA and E. P. TUREVSKAYA
Chemical Department, M.V. Lomonosov State University, Moscow (U.S.S.R.)

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SUMMARY

Possible synthetic routes to alkoxymagnesium halides HalMgOR have been studied indicating that the halides may be formed by the thermolysis of cements [solidified equimolar mixtures of $Mg(OR)_2$ with $MgHal_2$] or from the alcoholysis of solutions of Grignard reagents in ether. The products have been characterised by the use of X-ray and IR techniques. $Mg(OR)_2$ reacts with $MgHal_2$ in alcohol to form metastable alkoxymagnesium halides whose composition may be expressed as $3Mg(OR)_2 \cdot MgHal_2 \cdot n ROH$ and not as HalMgOR.

INTRODUCTION

Alkoxymagnesium halides are well known as intermediates in most important organic syntheses, as catalysts in the reduction of carbonyl-containing compounds and in polymerisation reactions[1,2]. The formation of HalMgOR has been suggested (*i*) in the alcoholysis of Grignard reagents, (*ii*) in the addition of Grignard reagents to carbonyl groups (the Grignard synthesis), (*iii*) in the oxidation of Grignard reagents and (*iv*) in the formation of a complex between an alkoxide and a halide dissolved in alcohol. In most cases, however, the formation of HalMgOR has been suggested merely on the basis of the hydrolysis products, *i.e.* alcohols. No physical or chemical characteristics verifying the existence of alkoxymagnesium halides have ever been reported in the literature.

RESULTS AND DISCUSSION

We have examined thoroughly, possible synthetic routes to the formation of HalMgOR and the identification of the products.

Four $Mg(OR)_2/MgHal_2/ROH$ systems (where R is Me, Et; Hal is Cl, I) have been subjected to physical and chemical analysis to reveal $Mg(OR)_2$ and $MgHal_2 \cdot 6ROH$ as the solid phase (Fig. 1, Tables 1–4). The kinetics of the dissolution of solid alkoxides in solutions of halides have been studied indicating that the solutions become supersaturated in alkoxide within several minutes or hours (depending on the concentration of the $MgHal_2$ solution) after a run has been started, Fig. 2. This indicates that a metastable phase is formed during the first stage of the alkoxide/halide interaction, this phase slowly decomposing to give the stable alkoxide and halide. The transformation of the stable to the unstable phase is the basis of the solidification

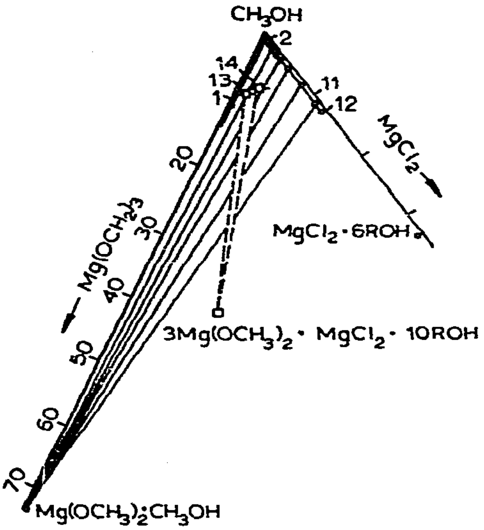

Fig. 1. Solubility characteristics of the $Mg(OMe)_2/MgCl_2/MeOH$ system at 20° (weight per cent).

TABLE 1

SOLUBILITY CHARACTERISTICS OF THE $Mg(OMe)_2/MgCl_2/MeOH$ SYSTEM AT 20°, (WEIGHT PER CENT)

Point No.	*Composition*				*Solid phase*
	Solution		*"Residue"*		
	$Mg(OMe)_2$	*$MgCl_2$*	*$Mg(OMe)_2$*	*$MgCl_2$*	
1	Above 10.5				
2	0.15	0.12	11.1	0.66	$Mg(OMe)_2 \cdot MeOH$
3	0.61	0.35			
4	0.24	1.35	10.3	1.08	
5	0.27	1.95			
6	0.24	2.56	8.50	1.43	
7	0.42	3.09	15.4	1.08	
8	0.82	3.80	7.20	4.50	
9	0.18	5.65			
10	0.03	7.55	13.5	5.45	
11	0.05	12.2			$Mg(OMe)_2 \cdot MeOH + MgCl_2 \cdot 6MeOH$
12		12.2			$MgCl_2 \cdot 6MeOH$
13	6.54	2.02			$3Mg(OMe)_2 \cdot MgCl_2 \cdot 10MeOH$
14	7.70	2.10			

of "cements" (these systems being similar to Sorel's magnesial cements[3,4]). Methanol solutions of $Mg(OMe)_2$ and $MgCl_2$ give metastable tetragonal crystals of composition $3Mg(OMe)_2 \cdot MgCl_2 \cdot 10MeOH$. The crystals are extremely unstable and decompose to give the components even when ground in a mortar. X-ray analysis (space group $D^4_{2d}-P42_1c$) reveals that the methoxymagnesium chloride lattice contains the cations $[Mg_4(MeO)_6 \cdot (MeOH)_{10}]^{2+}$ comprising four closely packed octahedra with Cl^- anions in between[5].

TABLE 2

SOLUBILITY CHARACTERISTICS OF THE $Mg(OEt)_2/MgCl_2/EtOH$ SYSTEM AT 20°, (WEIGHT PER CENT)

Point No.	*Solution composition*		*Solid phase*
	$Mg(OEt)_2$	*$MgCl_2$*	
1	0.20		$Mg(OEt)_2$
2	0.43	1.61	$MgCl_2 \cdot 6EtOH$
3	0.43	2.74	
4	0.70–0.16	4.42	
5		6.50	

TABLE 3

SOLUBILITY CHARACTERISTICS OF THE $Mg(OMe)_2/MgI_2/MeOH$ SYSTEM AT 20° (WEIGHT PER CENT)

Point No.	*Solution composition*		*Solid phase*
	$Mg(OMe)_2$	*MgI_2*	
1	Above 10.5		$Mg(OMe)_2 \cdot MeOH$
2	5.61	0.79	
3	2.32	1.49	
4	0.63	3.64	
5	0.58	7.95	
6	0.75	14.8	
7	0.04	21.6	
8	0.05	27.2	
9	0.03	30.9	$Mg(OMe)_2 \cdot MeOH + MgI_2 \cdot 6MeOH$
10		30.9	$MgI_2 \cdot 6MeOH$

TABLE 4

SOLUBILITY CHARACTERISTICS OF THE $Mg(OEt)_2/MgI_2/EtOH$ SYSTEM AT 20°, (WEIGHT PER CENT)

Point No.	*Solution composition*		*Solid phase*
	$Mg(OEt)_2$	*MgI_2*	
1	0.20		$Mg(OEt)_2$
2	0.08	3.9	
3	0.05	9.1	
4	0.25	12.1	
5	0.03	17.5	$Mg(OEt)_2 + MgI_2 \cdot 6EtOH$
6		17.5	$MgI_2 \cdot 6EtOH$

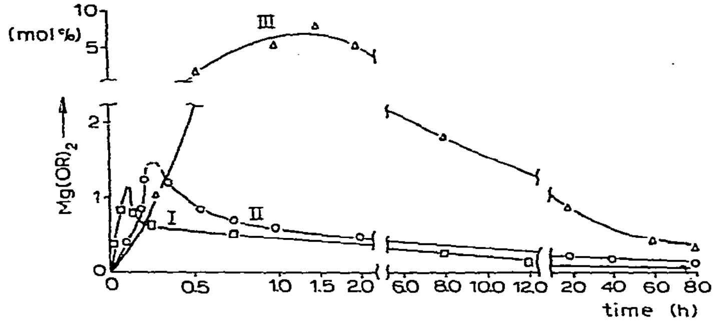

Fig. 2. Kinetics of the equilibration of solid $Mg(OR)_2$ with solutions of $MgHal_2$ in alcohols; I, $Mg(OMe)_2$ + a 3.3% solution of $MgCl_2$ in MeOH; II, $Mg(OEt)_2$ +a 2.0% solution of MgI_2 in EtOH; III, $Mg(OEt)_2$ +a 16% solution of MgI_2 in EtOH.

Thus, in contrast to the data by Meerwein[6], HalMgOR does not crystallise from alcohol solutions. The systems studied have been shown to be similar to the aqueous system $Mg(OH)_2/MgCl_2/H_2O$[7], thus enabling the synthesis of HalMgOR by the use of techniques similar to those used for the syntheses of the hydroxyl analogues (HalMgOH)[8,9]. The thermolysis of $MgHal_2 \cdot 6ROH$ (Hal=Cl, I; R=Me, Et) has also been studied. Chemical, thermogravimetric and X-ray analyses have shown that thermolysis leads only to IMgOMe (at 130°). In all other cases, solvolysis is not sufficient to produce an alkoxymagnesium halide with a 1/1 composition, desolvation of other $MgHal_2$ systems giving compounds of composition $Cl_{1.75}Mg(OMe)_{0.25}$, $Cl_{1.80}Mg(OEt)_{0.20}$ and $I_{1.50}Mg(OEt)_{0.5}$ respectively. To synthesise the 1/1 species thermolysis of cements having a predetermined alkoxide/halide ratio has been employed. At 160° to 200° ClMgOMe, ClMgOEt and IMgOEt are formed, their X-ray and IR spectra showing that the resulting HalMgOR differs from its components and from the system $Mg(OR)_2/MgHal_2$ (where Hal=Cl, I)[10,4]. This suggests that the material ROMgHal produced by these thermolytic methods is comparable to those products resulting from organomagnesium compounds.

Previously Grignard reagents were thought to react with alcohols according to the equation:

$$RMgX + R'OH \rightarrow R'OMgX + RH\uparrow \qquad (1)$$

The alkoxymagnesium halides presumed to form from RMgHal (where Hal=Br, I) and alcohols were established by means of chemical analysis of the solid products formed in the reaction[11,14]. No physico-chemical proof of the existence of the various compounds involved in the reaction has however been reported.

Recently, the traditional point of view, which presumes that the alcoholysis of Grignard reagents provides a synthetic route to the formation of alkoxymagnesium halides, has been questioned. Bryce-Smith[15] has reported that when alcohol is treated with a two-fold excess of "ether-free" RMgHal in hydrocarbon solvent the result of the reaction is the exchange of an alkoxy group for the halogen group and the formation of soluble RMgOR' which is stable to active hydrogen[16].

Carbon–magnesium bond rupture was not observed, and a precipitate of magnesium chloride was formed.

$$2RMgCl + R'OH \rightarrow R'OMgR + RH\uparrow + MgCl_2 \qquad (2)$$

In our examination of the reaction of RMgHal with alcohols, we have attempted to extend the Bryce-Smith scheme to the alcoholysis of ether solutions of Grignard reagents. If the reaction is terminated by the formation of R'OMgR (eqn. (2)], then gas evolution should cease when ROH/RMgHal = 0.5, whereas if all the Mg–C bonds are broken the solid products of the reaction should be $Mg(OR)_2$ and $MgCl_2$ or (when $MgHal_2$ soluble in ether) just $Mg(OR)_2$ rather than the HalMgOR depicted in eqn. (2).

The evolution of hydrocarbon has been studied relative to the ratio of reactants in the system for ether solutions of MeMgI with various absolute alcohols (MeOH to t-BuOH). In order to effect complete decomposition of the Grignard reagent a 1.5-fold excess of MeOH or a 1.2-fold excess of EtOH have been found to be necessary. For n-PrOH or t-BuOH gas evolution ceases at the stoichiometric ratio of the components (Fig. 3). Thus, the reactivity of the hydroxyl-containing agents towards RMgHal decreases as their acidity increases: t-BuOH $<$ n-PrOH $<$ EtOH $<$ MeOH $<$ H_2O.

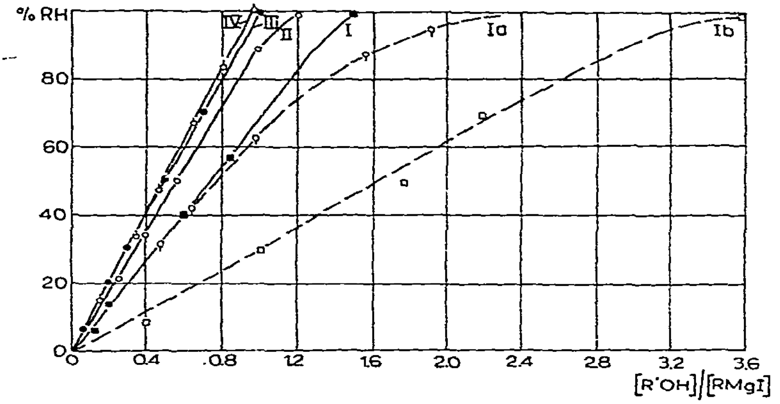

Fig. 3 Amount of methane evolved *vs.* the ROH/MeMgI ratio for the reaction of MeMgI with alcohols in ether solution; I, MeOH; II, EtOH; III, n-PrOH; IV, t-BuOH. Dotted lines denote the curves obtained from the methanolysis of solutions of partially hydrolysed MeMgI after storage, the extent of hydrolysis being: Ia, 16.5%; Ib, 63%.

Stabilisation of Grignard reagents towards reaction with active hydrogen may be explained by assuming that soluble complexes[16] of the type RMgI · *n*R'OMgI are formed, the stability of these complexes decreasing the higher in the homologous series the original alcohol. On the other hand, lower alcohols (or water) being involved in the solvation of R'OMgHal, are thus eliminated from the reaction site.

To synthesise HalMgOR it is necessary to adjust the reactant ratio so that the extent of conversion is as great as possible. The products, after drying *in vacuo*, have compositions corresponding to solvated alkoxymagnesium halides: MeOMgI · MeOH, EtOMgI · 0.2EtOH · $0.3Et_2O$, n-PrOMgI · $0.2Et_2O$ and t-BuOMgI · $0.8Et_2O$.

Ether solutions of BuMgCl react with stoichiometric amounts of the respective alcohols to give MeOMgCl · $0.4Et_2O$ and EtOMgCl · $0.3Et_2O$. X-ray studies of the alkoxymagnesium chlorides (all the iodides are amorphous, except for t-BuOMgI) synthesised through the alcoholysis of Grignard reagents indicate that these compounds exhibit the same lines as halides obtained through the pyrolysis of the cements. The only difference is that the X-ray patterns of the latter halides are much more distinct probably indicating that alkoxymagnesium halides formed at higher temperatures have better formed crystal lattices.

The evidence given above thus agrees with the literature data[11] on the formation of HalMgOR. The interaction of an alcohol with RMgHal in ether may however differ from that in a hydrocarbon solvent. IR and X-ray spectra of HalMgOR obtained from RMgHal and alcohols are quite close to those for the halides obtained by the pyrolysis of the cements which may serve as proof of the individuality of the compounds. Compounds of the type ClMgOR obtained by use of either of the two methods mentioned above are insoluble in ether or benzene, but decompose to give the alkoxide and $MgCl_2 \cdot 6ROH$ when treated with alcohols. When synthesised from cements, however, these compounds disproportionate in THF whereas the products of alcoholysis reactions merely swell. Compounds of the type IMgOR, on the other hand, symmetrise with the loss of MgI_2 when acted upon by THF for a long time. The rate of the reaction of an alkoxymagnesium iodide with an alcohol falls off as the polarity of the alcohol increases, *i.e.* MeOH > EtOH > t-BuOH. Drying compounds of the type IMgOR *in vacuo* (except when R = t-Bu) makes them insoluble in ether[10,4]. $t\text{-}BuOMgI \cdot Et_2O$ has also been synthesised by the interaction of MeMgI and acetone in ether solution. IR spectral studies of the product indicate that it is identical to that obtained from the alcoholysis of the Grignard reagent. The compound is only slightly soluble in ether (ca. 1%) and in benzene (ca. 3%). As with the respective bromide[17], the dimeric compound $(t\text{-}BuOMgI \cdot Et_2O)_2$ may be expected to contain distorted tetrahedra of (MgO_3I), while the compound HalMgOR, when R is an unbranched alkyl group, possesses octahedral coordination around the metal. IR spectral studies of a number of magnesium compounds[18] have shown that compounds of the type HalMgOR and $MgHal \cdot 2Et_2O$ which exhibit tetrahedral coordination inevitably possess bands at 300 to 350 cm^{-1} which are absent in the spectra of $Mg(OR)_2$, HalMgOR (R = Me, Et), $Mg(OH)_2$, $MgCl_2 \cdot 6H_2O$ where octahedral coordination exists around the Mg atom (Fig. 4).

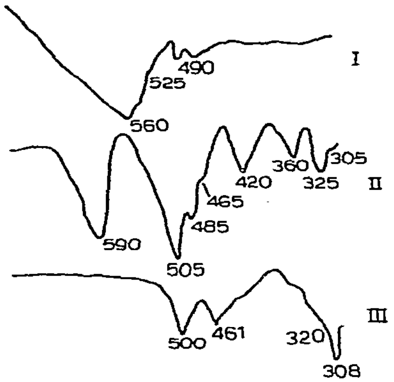

Fig. 4. IR absorption spectra; I, $Mg(OEt)_2$; II, $t\text{-}BuOMgI \cdot Et_2O$; III, $MgI_2 \cdot 2Et_2O$[18].

In summary, therefore, individual alkoxymagnesium halides HalMgOR have been obtained through the pyrolysis of cements or by the reaction of ether solutions of Grignard reagents with alcohols or carbonyl-containing compounds. The properties of HalMgOR are dependent on the nature of the halogen and of the organic group. Lower HalMgOR with unbranched alkyl groups, R, are polymeric and possess octahedral coordination around the metal atom while compounds of the type t-ROMgHal are dimers consisting of two tetrahedra sharing an $(OR)_2$ edge.

EXPERIMENTAL

I. $Mg(OR)_2/MgHal_2/ROH$ systems (R=Me, Et; Hal=Cl, I): Synthesis of $3Mg(OMe)_2\cdot MgCl_2\cdot 10MeOH$

The preparation of the various absolute alcohols and the synthesis and physicochemical characteristics (IR spectra, X-ray and crystal-optical analysis) of the initial alkoxides and of $MgHal_2\cdot 6ROH$ have been described previously[19-21]. The solubility of the compounds was measured by an analytical method while the composition of the solid phases formed was examined using Schreinemaker's technique and tested by X-ray and crystal-optical methods.

Crystalline $3Mg(OMe)_2\cdot MgCl_2\cdot 10MeOH$ was synthesised from solid $MgCl_2\cdot 6CH_3OH$ and a saturated solution of $Mg(OMe)_2$. A solution containing 10.9% $Mg(OMe)_2$ and 2·68% $MgCl_2$ was seeded, or treated with a salting-out agent (Vaseline oil), to give large transparent crystals which readily effloresced in dry air. (Found: C, 26.7, 26.8; H 8.17, 8.51; Cl, 11.7, 11.6; Mg, 14.9, 15.3; Mg/Cl 1.93, 1.95. $3Mg(OMe)_2\cdot MgCl_2\cdot 10MeOH$ calcd.: C, 28.5; H 8.62; Cl, 10.5; Mg, 14.2%; Mg/Cl 2.0.)

The alcohol content was verified roentgenographically[3,5].

II. Synthesis of HalMgOR

1. *Pyrolysis of cements.* Cements prepared from solid $MgHal_2\cdot 6ROH$, $Mg(OR)_2$(Mg/Hal 1/1), and several millilitres of an alcohol were heated *in vacuo* for several hours ($MgCl_2\cdot 6MeOH$ at 200°, $MgCl_2\cdot 6EtOH$ at 160°, $MgI_2\cdot 6EtOH$ at 170°). The composition of the final product was close to that expected for the alkoxymagnesium halides. IMgOMe was formed from $MgI_2\cdot 6MeOH$ at 130°, Table 5.

2. *Alcoholysis of ether solutions of MeMgI or BuMgCl.* Solutions of MeMgI or BuMgCl (2 *N* in concentration) in ether were obtained as previously described[22,23]. The

TABLE 5

ELEMENTARY ANALYSES FOR THE COMPOUNDS HalMgOR, FOUND (CALCD.) (%)

Compound	*Mg*	*Hal*	*C*	*H*
ClMgOMe	26.3–26.8 (26.6)	42.9–39.7 (39.3)	14.0–14.4 (13.3)	3.2–3.5 (3.32)
ClMgOEt	23.9–22.8 (24.0)	32.3–34.0 (34.0)	23.1–23.0 (23.0)	4.6–3.9 (4.78)
IMgOMe	13.9–13.5 (13.2)	70.2–70.0 (69.7)		
IMgOEt	13.5–13.0 (12.4)	65.2–65.0 (64.6)		

TABLE 6

REACTION OF A 30.2% SOLUTION OF MeMgI IN ETHER WITH ALCOHOLS[a]

Alcohol	*ROH/RMgI*	*Result*	*Precipitate composition (%)*			*Yield of solid product (%)*
			Found	*Calcd.*	*Formula*	
MeOH	1.77	Precipitate formed after addition of first few drops of alcohol	Mg 11.3, 11.1	11.38	MeOMgI·MeOH	89
			I 58.9, 59.1	59.5		
			C 11.0, 11.4	11.2		
			H 3.30, 3.35	3.27		
EtOH[b]	1.2	Solution divided into layers	Mg 10.5, 10.7	10.7	EtOMgI·0.2EtOH·0.3Et$_2$O	
			I 56.5, 56.7	56.0		
			C 19.6, 19.5	19.0		
			H 4.15, 4.10	4.04		
n-PrOH	1	Colourless solution	Mg 10.8, 10.7	10.8	n-PrOMgI·0.2Et$_2$O	
			I 57.0, 56.8	56.9		
			C 19.9, 19.7	20.3		
			H 3.99, 3.86	4.01		
t-BuOH	1	Precipitate formed after addition first few drops of alcohol	Mg 8.40, 8.52	8.60	t-BuOMgI·0.8Et$_2$O	87
			I 45.0, 45.1	44.9		
			C 30.7, 30.8	30.6		
			H 6.08, 6.06	6.02		

[a] The precipitates were washed with ether and dried *in vacuo*. [b] The solid product was obtained by complete removal of the solvent (from the lower layer in the case of EtOH).

TABLE 7

REACTION OF A 23.4% SOLUTION OF BuMgCl IN ETHER WITH VARIOUS ALCOHOLS[a]

Alcohol	*ROH/RMgCl*	*Precipitate composition (%)*		*Formula*
		Found	*Calcd.*	
MeOH	1	Mg 20.0, 19.8	19.7	MeOMgCl·0.44Et$_2$O
		Cl 28.8, 19.3	28.8	
EtOH	1	Mg 20.2, 20.0	19.1	EtOMgCl·0.3Et$_2$O
		Cl 27.6, 27.5	28.0	

[a] The precipitate formed after addition of the first few drops of alcohol was washed with ether and dried *in vacuo*.

concentration of the Grignard reagents was determined volumetrically for MeMgI and through the use of a double acidimetric titration[24] in the case of BuMgCl.

Gas evolution curves were obtained through the use of an assembly consisting of the reaction flask fitted with a dropping funnel and a gas outlet connected to a gas burette filled with a saturated solution of NaCl in water. The solution was covered by a layer of ether. For each point, the volume of gas evolved was measured after maintaining the mixture at a constant temperature for 3 h. The number of moles of CH_4 evolved was calculated by use of eqn. (3).

$$N_{CH_4} = \frac{V \cdot (P_{atm} - P_{ether\,(at\ 20°)})}{RT} \tag{3}$$

The characteristics of the syntheses of the various HalMgOR compounds and of the reaction products are summarised in Tables 6 and 7.

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