321. *The Effect of Metallic Impurities in Magnesium on the Formation of Grignard Compounds.*

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Magnesium alloyed with various amounts of aluminium, copper, and manganese has been used in preparing ethylmagnesium iodide under quantitatively controlled conditions. The percentages of each of three main reactions which take place were determined, *viz.*,

Grignard reaction :

$$C_2H_5I + Mg \longrightarrow C_2H_5{\cdot}MgI$$

Wurtz reaction :

$$2C_2H_5I + Mg \longrightarrow C_4H_{10} + MgI_2$$

Disproportionation reaction :

$$2C_2H_5I + Mg \longrightarrow C_2H_6 + C_2H_4 + MgI_2$$

Compared with very pure magnesium, alloys containing up to 50% of aluminium do not substantially increase the Wurtz and the disproportionation reaction. Alkylaluminium compounds are formed as well as alkylmagnesium compounds. A 50% Mg : 50% Al alloy has been used successfully in a Grignard synthesis.

Alloys containing up to about 2% of copper or manganese increase the Wurtz and especially the disproportionation reaction very markedly. A preliminary investigation has been made of the mechanisms proposed to explain this increase.

THE effect of metallic impurities on the formation of Grignard compounds is of considerable practical and theoretical interest. From the practical standpoint, it has been reported (Johnson and Adkins, *J. Amer. Chem. Soc.*, 1931, **53**, 1520) that 12% of copper in magnesium lowers the yield of Grignard reagent and increases the combined Wurtz and disproportionation reactions (cf. also Cusa and Kipping, *J. Soc. Chem. Ind.*, 1934, **53**, 213). It was of interest to test whether on reducing impurities down to the limits in a sample of specially pure distilled magnesium (Fe, 0·0004%; Zn, 0·003%; Pb, 0·002%; Si, Ni, Sn, Cd, <0·005%) these side reactions might be completely suppressed.

A further practical point refers to the possible use of alloys of magnesium containing substantial amounts of other metals, such as aluminium, to form mixed alkyl reagents. Apart from economic considerations, this might facilitate the preparation of mixed-metal Grignard reagents of controlled reactivity, which could be used in certain syntheses where more than one reactive grouping is attacked by alkylmagnesium compounds. Although the formation of alkylaluminium halides from pure aluminium is a comparatively sluggish process which has not been much investigated (Hnizda and Kraus, *J. Amer. Chem. Soc.*, 1938, **60**, 2276; Grosse and Mavity, *J. Org. Chem.*, 1940, **5**, 106), the results described below show that when, for example, a 50 : 50 Mg–Al alloy is used, the dissolution of the magnesium in an ethereal solution of alkyl halide appears to leave the aluminium in such a finely divided active state that it likewise dissolves. This opens up the possibility of forming other metal alkyls by using suitable alloys of the metal with magnesium. A synthesis carried out with the magnesium aluminium alkyl mixture is described below.

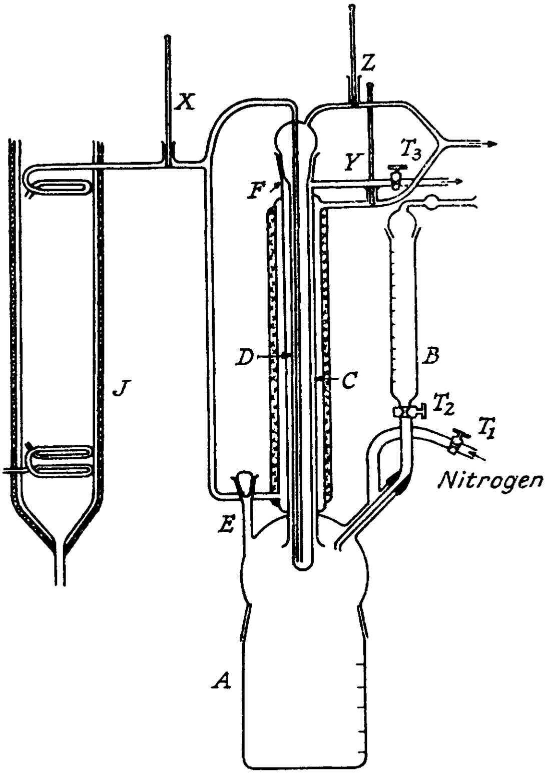
From the theoretical standpoint, the effect of metallic impurities in magnesium is of interest in view of the results obtained by adding halides of the transitional elements to solutions of Grignard reagents (cf. Hey, *Ann. Reports*, 1944, **41**, 195, who gives a number of references). Small amounts of metallic impurities alloyed with the magnesium would be left in a finely divided condition when the magnesium dissolves, and might be expected to form reactive intermediates, similar to those obtained when the corresponding halides are added to the solution of Grignard reagents.

To test this possibility, alloys of magnesium were used which contained up to 2% of manganese and 2·5% of copper, severally. As is described below, these impurities have a substantial influence on the course of the reactions. Experiments were also carried out in which the magnesium was plated with thin films of nickel, copper, iron, and manganese before addition of the alkyl iodide. However, except in an isolated experiment with nickel, metals added in this way were not found to influence the course of the reaction. The significance of this observation is discussed below.

EXPERIMENTAL.

Experimental Details.—The apparatus used (see Fig.) for the preparation incorporated (*a*) a method of drawing off aliquot portions of the Grignard reagent for analysis, (*b*) facilities for the collection of the evolved gases, (*c*) an efficient condenser to condense most of the ether out of the gas before gas analysis.

The reaction vessel *A* has a calibrated scale attached so that the total volume of liquid could be observed with the aid of a cathetometer to ± 0·1 c.c. This vessel is joined to the upright condenser *C* which has an inner condensing surface *D* fitted inside it by means of the ground-glass join *F*. The gases and ether vapour evolved in the reaction vessel *A* ascend the space between these condensing surfaces, pass out through the Tap *T*3, and are collected over a saturated sodium chloride solution in a gasometer. Water circulating through the condenser is cooled to 3° in the insulated cooler *J*, where it circulates through a copper spiral round which is packed a mixture of ice and salt. This condensation at 3° serves to remove as much ether vapour as possible, without unduly retaining butane. Ethyl iodide is added from the burette *B*. For the purposes of analysis samples of the solution of the Grignard reagent may be drawn off in a pipette through the outlet *E*, using counter-currents of dry oxygen-free nitrogen to protect the contents of the vessel.



Before the preparation was carried out the apparatus was thoroughly cleaned and dried by means of hot air and swilling with pure dry ether. All taps were lubricated with petroleum jelly.

2 G. of magnesium in the form of turnings were rinsed in alcohol and ether and placed in the vessel *A*. 25 C.c. of pure ether and a crystal of iodine were added. Pure dry nitrogen was passed through the apparatus for 15 minutes to expel all the air. A solution of 6·9 g. of ethyl iodide in ether was put in the burette *B*. About 1·5 g. of ethyl iodide were added to the magnesium, and the vessel gently heated till the reaction started. The remaining ethyl iodide was added slowly as recommended by Gilman and Meyers (*J. Amer. Chem. Soc.*, 1923, **45**, 159). When all the ethyl iodide had been added (35 mins.), the reaction mixture was refluxed for 20 minutes to drive over the evolved hydrocarbons. The solution was then diluted to 60 c.c. and again refluxed. A current of nitrogen was then passed to take all the evolved hydrocarbons into the gasometer.

The nitrogen and ether were carefully purified (see Mackle and Ubbelohde, this vol., p. 1161).

Estimation of the Grignard Reaction.—Gilman's acid titration method (*J. Amer. Chem. Soc.*, 1927, **49**, 3181) was used for the estimation of the Grignard reaction, phenolphthalein being used as indicator. Magnesium hydroxide is sufficiently alkaline to give satisfactory titrations, but when aluminium is also present its evaluation by this method is not complete. In this case aluminium and magnesium in the solution were estimated by precipitation with 8-hydroxyquinoline (Vogel, "Quantitative Analysis", 1939).

Estimation of Side Reactions.—The Wurtz and the disproportionation side reaction were estimated by measuring the amount of ethylene, ethane, and butane evolved during the reaction. These hydrocarbons are contained in a gasometer together with ether vapour and nitrogen. The total volume of gas was observed, and a portion analysed in a type of gas analysis apparatus in which the gases were absorbed by " fountains " of the various reagents. The ether vapour was absorbed with 10% sulphuric acid, and the ethylene with bromine water. The ethane and butane were determined simultaneously by sparking with excess of oxygen and measurement.

Ethane and ethylene, formed from the disproportionation reaction, should be evolved in equal volume. In practice there is always rather more ethane than ethylene. In spite of rigorous precautions it was not possible to exclude water altogether, and some hydrolysis of ethylmagnesium iodide occurs during its formation. To avoid confusion from this effect, the amount of disproportionation in Tables I—III was always calculated from the volume of *ethylene* evolved. The volume of butane gives a measure of the amount of Wurtz reaction. The probable error in the gas volumes was ± 1·5% and in the estimation of Grignard reagents ± 0·25%.

Analysis of the Sediment from Mg/Mn 98/2.—The black slurry was dissolved in warm concentrated sulphuric acid and diluted. The ether was boiled off, and the solution analysed for iodine with silver nitrate and for manganese by the bismuthate method.

Methods and Results.—Throughout the experiments, ethyl iodide was used as the alkyl halide. It was allowed to react with magnesium in the calibrated vessel *A* (see Fig.). Specially purified ether was used as solvent. During the reaction and also during transfer of ethereal solutions from one vessel to another, all solutions were protected from oxygen and water vapour by an atmosphere of oxygen-free nitrogen (Mackle and Ubbelohde, *loc. cit.*). The contents of the vessel *A* were allowed to settle and aliquot parts of the solution were removed for analysis, so as to evaluate the extent of the Grignard reaction. Gaseous products of reaction passed up the double-surface condenser *C,D* which is specially designed to permit easy cleaning and rigorous drying. They were then collected for gas analysis, so as to evaluate the extent of the Wurtz and disproportionation reactions. Typical results are given in Table I.

TABLE I.

Reactions with pure magnesium.

		Reaction, %.		
Expt.	Mg, g.	Grignard.	Wurtz.	Disproportionation.
A	2·0	90·0	4·4	3·7
B	2·0	90·6	5·9	2·3
C	2·0	90·8	4·15	3·5
D	2·0	90·1	4·2	3·8

In these reactions the magnesium theoretically required by the ethyl iodide used was 1·09 g. Percentage reactions are calculated from the amounts of the various products relative to the total ethyl iodide consumed.

The data illustrate the sort of variation observed under conditions which were kept as constant as possible. Side reactions account for about 8% of the ethyl iodide, and together with the Grignard reaction they account for at least 98% of the ethyl iodide. It is not yet clear whether the remaining 2% is due to further reactions, or to difficulties in the analyses. Experiments made in another connection (Mackle and Ubbelohde, *loc. cit.*) indicate that attack of the ether solvent during the formation of the Grignard reagent can be neglected under the above conditions.

TABLE II.

Reactions with Mg/Al *alloys.*

			Reaction, %.		
Expt.	Alloy.	G.	Grignard (apparent).	Wurtz.	Disproportionation.
I	100% Mg	2·0	(See below)	4·2	3·8
A	5% Al	2·1	75·7	4·3	3·4
B	,,	,,	74·3	4·7	4·1
C	,,	,,	75·4	4·9	4·55
D	,,	,,	72·6	4·4	4·0
E	50% Al	4·0	77·0	3·4	1·6
F	,,	—	80·0	3·8	2·5
G	,,	—	76·4	3·15	3·2

In experiments recorded in Table II the total amount of alloy used was such as to contain 2·0 g. of magnesium, to compare with Table I. Comparison of these data with those of Table I shows that the amount of ethyl iodide consumed in side reactions is not increased by alloying the magnesium with aluminium.

The figures in the column under " Grignard (apparent) " do not allow for the simultaneous formation of alkylaluminium compounds. It was found that these do not respond to the Gilman method of acid–alkali analysis. The presence of these aluminium alkyls was, however, verified as follows: (1) Qualitative tests showed that aluminium compounds were formed which were soluble in ether. (2) In special experiments the total magnesium and aluminium in ethereal solution were estimated by using 8-hydroxyquinoline, with the following results, in experiments under similar conditions to those in Tables I and II.

Alloy.	Mg dissolved, g.	Al dissolved, g.
Pure Mg	0·970	—
Mg 95, Al 5	0·839	0·037
Mg 50, Al 50	0·727	0·161

Although the analytical separation is not fully satisfactory owing to various complications, the figures show that the amount of soluble aluminium compounds formed roughly accounts for the ethyl iodide not accounted for in the figures of Table II, having regard to the higher valency of the aluminium. It seems likely that compounds are formed according to the reaction $3C_2H_5I + 2Al \longrightarrow AlIEt_2 + AlI_2Et$, since Hnizda and Kraus (*loc. cit.*) did not observe any triethylaluminium in their experiments. Further investigation is, however, required to establish this point in detail. The fact that the Mg : Al ratio in solution is greater than 50/50 in the above experiments is probably due to the use of excess of alloy (see Table II), with preferential dissolution of the magnesium.

In certain circumstances it may be more economic to use an alloy such as 50/50 Mg/Al in place of pure magnesium. In order to obtain a preliminary idea of the possibilities, two Grignard syntheses were attempted. For these the recommended amount of magnesium was taken (cf. *Org. Synth.*) and the same amount of 50/50 Mg/Al was used in the comparison experiment.

In the preparation of phenylethylcarbinol from benzaldehyde, the yield of crude product was 17·1 g. when pure magnesium was used and 16·8 g. with the 50/50 alloy. In this case the mixed alkyls can be used successfully. On the other hand, in the preparation of triethylcarbinol from ethyl carbonate, no appreciable yield was obtained from the mixed alkyls. The reason for this is under further investigation.

TABLE III.

Reactions with magnesium alloyed with transitional elements.

			Reaction, %.		
Exp.	Alloy.	G. used.	Grignard.	Wurtz.	Disproportionation.
A	0·5% Mn	2·01	75·7	7·7	13·85
B	,,	,,	76·6	6·5	16·45
C	2·0% Mn	2·04	68·8	8·5	23·0
D	,,	,,	66·7	6·9	24·5
E	,,	,,	59·0	10·5	30·35
F	0·5% Cu	2·01	78·8	8·85	11·2
G	,,	,,	80·5	7·65	11·6
H	2·5% Cu	2·05	70·3	11·9	16·2
I	,,	,,	68·7	12·25	17·2
J	,,	,,	68·1	11·2	18·35

In these experiments the amounts of alloy used contained 2·0 g. of magnesium, in order to give data comparable with Tables I and II.

Unlike aluminium, both copper and manganese when alloyed with magnesium increase the side reactions, particularly the disproportionation reaction. Two further items of experimental evidence have a bearing on these observations :

(1) It was of interest to see whether the transitional metals formed any *soluble* alkyl compounds, like those formed from Mg/Al. To economise labour, tests were restricted to the experiments with Mg 98%, Mn 2·0%. During the dissolution of this alloy in ethereal ethyl iodide, a fine black powder filled the vessel. This was allowed to settle, together with any unreacted alloy, before carrying out the usual analyses on the clear supernatant solution. Qualitative tests showed only traces of manganese in this clear solution. The weight of manganese present in the black sediment was almost equal to the weight originally present in the weight of alloy taken. The black sediment also contained very substantial amounts of combined iodine.

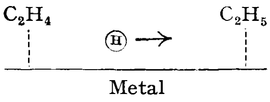
(2) A second line of investigation was to test if layers of metals such as copper and manganese deposited on the outer surface of the magnesium filings, so as to form magnesium–metal couples, produced a similar change in the extent of the side reactions to that when the metals are alloyed with the magnesium. Chips of pure magnesium were washed with aqueous solutions of a salt of copper, manganese, nickel, or iron, severally, until tests showed all the metal had been deposited on the surface of the magnesium. Various degrees of plating were investigated with each metal, using amounts ranging from 0·0005% to 1·0% of the magnesium. The magnesium–metal couples were then washed with ether and placed in ethereal magnesium iodide. Whereas pure magnesium and the various alloys gave induction periods of much the same duration, before dissolving actively in the ethereal ethyl iodide, the plated magnesium chips gave long induction periods except when the plating was very thin. In most cases couples prepared in this way gave reaction ratios very similar to those with pure magnesium. One isolated observation with Mg–Ni couple, with a prolonged induction period, subsequently gave a reaction with 43·5% disproportionation, but the conditions for obtaining this result could not be repeated.

DISCUSSION.

Reference has been made above to the practical significance of this investigation. Brief mention may also be made of some theoretical considerations on the mechanism of the Grignard reaction, and of side reactions.

Two main types of mechanism may be proposed to explain the formation of the Grignard reagent and of the simultaneous occurrence of side reactions. These may be described as the " heterogeneous " and the " homogeneous " mechanism. According to the " heterogeneous " mechanism, the alkyl iodide adsorbed on the magnesium becomes split by activation into ethyl radicals and iodine atoms, which then weaken the attraction of a magnesium atom to the remaining parts of the metal sufficiently to permit its being dissolved as the alkylmagnesium iodide. With less reactive metals such as aluminium, a high temperature is required for effective attack of the surface atoms in this way, unless the aluminium is left in a finely divided state, as in our experiments, by prior dissolution of the magnesium in the alloy.

The essential feature about the heterogeneous mechanism is that the disproportionation reaction would involve a heterogeneous migration of hydrogen atoms from one alkyl radical to a neighbouring alkyl radical. Metals which are effective hydrogenation and dehydrogenation catalysts would be expected to favour the side reaction involving disproportionation, by facilitating such transfers. This would explain the distinction of behaviour between aluminium, on the one hand, and metals such as copper and manganese on the other Objections to the heterogeneous mechanism are the fact that metal couples were not found to be effective, and that the " heterogeneous " mechanism does not offer any simple explanation of the increased Wurtz reaction due to such impurities.



According to the " homogeneous " mechanism, the impurities in the magnesium dissolve in the first instance in the ether. The molecules produced may perhaps have the structures suggested by Kharasch (Hey, *loc. cit.*) though the evidence does not exclude other soluble intermediates.

The essential feature of the explanation proposed by Kharasch is that free radicals are formed *in solution,* by some such scheme as (in our examples)

$$C_2H_5{\cdot}MgI + MnI_2 \longrightarrow C_2H_5{\cdot}MnI + MgI_2$$

$$2C_2H_5{\cdot}MnI \longrightarrow C_4H_{10} + 2MnI{\cdot}$$

$$MnI{\cdot} + C_2H_5I \longrightarrow C_2H_5{\cdot} + MnI_2$$

The alkyl radical then either disproportionates with other radicals or dimerises. This explanation fits a number of facts, but does not readily accord with the relative increases of the Wurtz and the disproportionation reaction as the amount of the manganese is increased. Further work seems required to decide whether the catalytic effect of the impurities in the magnesium acts in a heterogeneous or a homogeneous manner to increase the side reactions.

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