

On the properties of the Grignard Magnesium species;  
by Wilhelm Schlenk and Wilhelm Schlenk junior.



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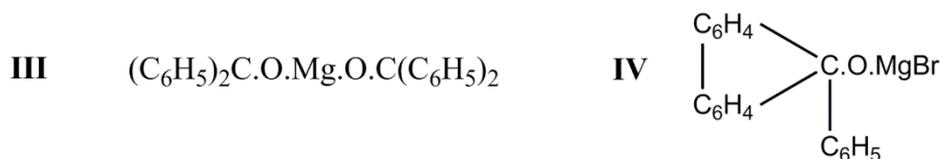
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With regard to the nature of the Grignard organomagnesium compounds, two different viewpoints have been shown with the main difference being in their structural formulas:

- I.** R.Mg.Hlg + nMol. ether and
- II.** (R)<sub>2</sub>Mg, Mg(Hlg)<sub>2</sub> + xMol. ether

If a minor and seemingly simple problem like that of the form of the organomagnesium compounds has remained unresolved in spite of many efforts over many years, only novel experimental work promises to provide the intellectual means for final clarification. If one wanted to, for example, determine the likelihood of each of formulas **I** and **II**, here's how it is often performed in other cases with great success: by determining the reactive behaviour and product formations of the disputed species, which can be done by the right choice of compound that is reacted with the Grignard reagent. It is shown dramatically by a comparison of the outcomes of reacting phenylmagnesium bromide with either benzophenone or fluorenone. We contend that—under the same reaction conditions—in the first case the major product is **III**, whereas in the second case the major product is **IV**. The first result speaks to the formula **II**, while the latter explained only by formula **I**.



Our newly designed experiment takes and addresses the old problem of the use of dioxane and the diether glycols, O(CH<sub>2</sub>.CH<sub>2</sub>)<sub>2</sub>O. This compound has the surprising and in our view very important property of precipitating not only all existing inorganic magnesium, but it also quantitatively precipitates halogen-containing organomagnesium compounds present in the Grignard solution. The precipitates, which are compounds that have co-crystallized with dioxane, are always crystalline and therefore easy to isolate. The stability of the

corresponding ether-dioxane crystallites are not actually discrete reaction products that change the nature of the organomagnesium: because the precipitations go with compounds whose reactivity is known towards the Grignard reagents, e.g., acid esters, ketones, etc., in exactly the same manner as the reactions previously discussed.

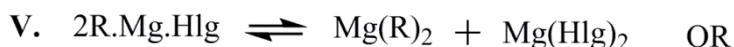
The first success is not brought about the investigations of the precipitates generated by dioxane, but those of the ethereal filtrates. It was shown specifically that, these filtrate species which were thought to be alkyl or aryl halides, were in fact 'pure' organomagnesium compounds, i.e., magnesium dialkyls or diaryls, contained in solution. So in all Grignard solutions, among other organomagnesium compounds, ones of the type  $Mg(R)_2$  are present.

In regards to the dioxane-precipitate species, it was taken from the outset to observe whether or not they were uniform. On one hand it is a known fact that the Grignard compounds resulting from organomagnesium products do react (in varying degree) with unreacted hydrocarbon halide to form the hydrocarbon and magnesium. For this reason, had the dioxane precipitate species partially consisted of an inorganic magnesium halide, it now gave further security to conclude the presence of such a to conclude as such, because in the formation of  $Mg(R)_2$  the same number of molecules are required as for  $Mg(Hlg)_2$ .

In order to capitalize on this and reach some definitive conclusions on the composition of the precipitates generated by dioxane, it was necessary to start from pure solutions of crystallized Grignard compounds. Meeting this requirement enabled us to observe that most not-too-dilute Grignard solutions, when cooled by a  $CO_2$ /acetone mixture, deposit their 'Grignard compound' as large crystalline etherates that melt away again at room temperature. By repeated freezing, decanting and dissolving with ether we arrived easily at solutions that were free from extraneous admixtures and each also had exactly 1 atom of magnesium per atom of halogen.

Where such pure solutions precipitated with dioxane, the filtrates are, in all cases, either a dialkyl or diaryl magnesium species. These compounds therefore under these conditions spontaneously formed uniform crystalline organomagnesium halides. Accordingly, the dioxane-precipitates always contain partly-inorganic magnesium-halides, and therefore magnesium and halogen in atomic ratio  $Mg : Hlg < I$ .

From these observations an equilibrium has been observed:



is most likely formed; as was proven by the results of the fractional precipitates formed by dioxane, ie those produced by successive additions of quite small amounts of dioxane. The atomic ratio of magnesium to halogen was always considerably smaller in the first case of precipitate formation than in the second; In the following precipitation stage it approached an increase in the values of  $I$ .

From the fractional precipitation of an ethereal solution of pure  $\alpha$ -naphthyl magnesium bromide the following ratios—cited by the large number of our individual—were revealed:

1. **Precipitant Mg : Br = 1:1.70**
2. **Precipitant Mg : Br = 1:1.60**
3. **Precipitant Mg : Br = 1:1.51**
4. **Precipitant Mg : Br = 1:1**

After this key finding, there remained the final problem of the question over whether the 'mixed' organomagnesium compounds with the Grignard compounds is correctly described by formula **I** or formula **II**.

This question could be settled by a simple experiment. If formula **I** is right, this corresponds to a prevailing disproportionation of equilibrium in equation **V**, and so the equilibrium position must be independent of the concentration of the solution. If formula **II** is valid, we have a situation where the equilibrium dissociation of equation **V** must—according to the law of mass action—increase as dilution increases. In the latter case dioxane must therefore bind with the magnesium when in a dilute solution of a mixture organo-magnesium-halogen-compound, but not in a more concentrated mixture; In the former case, the composition of the mixture of the two 'precipitated-with-dioxane halogen compounds' must be independent of concentration. The experiment has pointed towards formula **I**, as indeed did the precipitations from a concentrated solution of ethyl magnesium iodide, which when obtained after dilution to 8x the volume were practically identical.

In summary, due to our unique experimental results we can now make the following statement: The so-called: Grignard-specific solutions represent equilibria of the type:



As for the role of the ether in the formation of Grignard solutions, the above result now provides a simple explanation. For the creation of a Grignard solution, the magnesium metal must react in the presence of a solvent that can not only dissolve the metal-organic compounds, but also the inorganic magnesium halides. Hydrocarbons are therefore unsuitable, as is dioxane—even though it is an ether. These ether-insertion compounds that in our case follow the type  $R.Mg[C_4H_{10}O]Cl$  are often distinguished by particularly good responsiveness, as shown by multiple observations. The presence of an ether group is not very likely to be of crucial importance for the Grignard reaction.

The knowledge of the existence of equilibria in Grignard solutions conjures three main questions:

1. What are the principles of equilibria in the individual Grignard reagents?
2. Are the pure magnesium compounds or organomagnesium halides the actual carrier of Grignard syntheses?
3. If the adjustment of equilibrium is at the speed of adjustment of ion equilibria, ie unmeasurable speed, or concerning the reaction-time?

A comprehensive answer to the first question requires greater experimental resources than we have available at present. But some interesting conclusions can be made as of now: The

equilibrium position expected depends upon the nature of the hydrocarbon halides from which the Grignard solutions are made up.

In the case of ethyl magnesium iodides it was found that the dioxane precipitates produced at room temperature contained magnesium and iodine in an atomic ratio 1:1.4. This value corresponds to the composition  $6 \text{ C}_2\text{H}_5\text{MgI} + 4 \text{ Mg}(\text{C}_2\text{H}_5)_2 + 4 \text{ MgI}_2$ . The whole of the magnesium is therefore in solution: 43% as ethyl magnesium iodide, and 28.5% as each of diethyl magnesium and magnesium iodide.

With phenyl-magnesium bromide the analytical results could be calculated so give the relative composition as: 1 mol.  $\text{C}_6\text{H}_5\text{MgBr} + 0.115 \text{ mol Mg}(\text{C}_6\text{H}_5)_2 + 0.115 \text{ mol MgBr}_2$ , or in percentages: around 81% of magnesium was present as phenyl magnesium bromide, and 9.5% each of diphenyl magnesium and magnesium bromide.

In response to the second question we draw on the earlier mentioned observation that exposure of benzophenone to a phenyl-magnesium bromide solution gave a carbinolate  $\text{R.OMg.O.R.}$ . It can be seen that when the same experiment is carried out using fluorenone an intermediate with the formula  $\text{R.O.Mg.Br}$  is easily isolable from reaction mixture (Since we have limited ourselves to the study of convenient crystallizable constituents, it is on no way claimed by this statement that benzophenone might not produce  $\text{R.O.Mg.Br}$ , but with fluorenone a halogen-free carbinolate arises). It is thus clear that both types of organomagnesium compounds are reactive.

With regard to the rate of disproportionation in the molecules  $\text{R.Mg.Hlg}$  we can say that it is to do with the reaction time, because when we disturbed the equilibrium on an ethyl magnesium iodide solution by addition of a little dioxane that gave a small amount of precipitate that we quickly filtered off, the filtrate part immediately after filtration, the remainder of the contents of the flask gave, after several hours of further treatment with dioxane, more of the latter precipitate but with more  $\text{MgBr}_2$  in the second poorer in than the first. When the experiment was carried out analogously using phenyl magnesium bromide however, the two precipitates were identical in their composition; an indication that the short period of the first filtration had been long enough ( $\sim 10 \text{ min}$ ) to readjust the equilibrium.

It feels necessary to clarify another point. Although magnesium iodide etherate is considerably soluble in ether; the etherates of magnesium chloride are much less soluble. Under these circumstances it should be expected that the halides, given the amounts in which they must exist because of their equilibrium (determined by us) will simply excrete in presenting reasonably-concentrated Grignard-solutions, but this is not what was seen by us to happen when we tried this out. There is no doubt that this explains why a relatively small amount of the magnesium halides crystallite etherates tend to form metastable supersaturated solutions\*. Even in ether relatively little magnesium chloride can be dissolved and as far as we could identify, this is true without exception.

\* After formation of the etherate  $\text{MgBr}_2 \cdot \text{C}_8\text{H}_{10}\text{O}$  in absolute ether gave a metastable solution with 17.9% salt content (Landolt-Bornstein).

A solution of 35 g benzyl chloride in 150 mL of ether was used to prepare a Grignard solution and after its filtration remained clear for two days and then eliminated (without dioxane addition!) a large amount of fine crystals. Upon analysis these crystals were shown to be nearly two thirds magnesium chloride etherate.

The ability to precipitate the halogen compounds by means of dioxane-Grignard solutions without loss gives us a way forward so that, henceforth, the previously unknown etherates 'pure organomagnesiums' [ie the compounds of the type  $Mg(R)_2$ ] can be isolated and studied. The results of these experiments will be communicated later.

From having carried out the experiments/reactions in this paper we share some further thoughts: Although the organomagnesium species were not air-sensitive to the extent of organic alkalis, it was still necessary to carry out all of the reactions/experiments undertaken in the above with rigorous exclusion of both air and moisture. We therefore used an apparatus as described in the Houben-Weyls handbook (z. Ed., Vol. IV, pp 959ff) that is recommended for reactions involving organic alkali compounds.

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