

Barbier-Grignard: explosive reaction

Tadeusz Urbański

The early paper by P. Barbier (1898) and the thesis of V. Grignard (1901) led to the foundation of the 'Grignard reaction'. It follows, however, from existing documents, the discussion between Barbier and Grignard (1910) and a letter of Grignard (1912) that the reaction should more correctly be called 'Barbier-Grignard reaction' but that the reagent should be named the familiar 'Grignard reagent.'

There is no doubt that Grignard is one of the best known names of great chemist-founders of present day chemistry. It obviously is due to the fact that every organic chemist has carried out the Grignard-reaction at least once in their lifetime. For a long time the use of the reaction was limited to laboratory *ie* small scale work. However, in the late 30s and after World War 2 it penetrated into chemical factories thanks to

(i) improvement in the design of air-tight reactors and (ii) introduction of less volatile and relatively high boiling point solvents with an ether function such as tetrahydrofuran and dioxane.

The Grignard reaction is now used in chemical industry in the production of some fine chemicals, drugs, scents *etc.*

The increasing importance of the reaction compels us to look into the history of this remarkable achievement which in 1912 brought the Nobel Prize to Victor Grignard, professor at the University of Nancy. He shared it with another French chemist—Paul Sabatier, professor at the University of Toulouse who received the Nobel Prize for his catalytic hydrogenation of organic compounds which he developed with Senderens.

On 9 December 1912 the French journal *Salut Public* published a note *L'oeuvre d'un savant* giving information on Victor Grignard's Nobel Prize.

The note invoked a strong reaction from P. Barbier, professor at the University of Lyon, where

Grignard studied chemistry under Barbier and received in 1901 his degree of *Docteur ès sciences* on the basis of his thesis where he investigated the use of magnesium for organic synthesis on the suggestion of Barbier. A few days later Barbier sent a letter to the editor of *Salut Public*. The letter contains some statements important to the history of the reaction. Here are main parts of the text:

Monsieur le rédacteur en chef du
Salut Public

J'ai lu un peu tardivement dans le *Salut Public* du lundi 9 décembre l'article intitulé: 'L'oeuvre d'un savant.' Cet article relatif aux travaux de M. Grignard, exact dans son ensemble, renferme néanmoins une affirmation erronée évidemment involontaire qu'il m'est impossible de ne pas vous signaler. Je fais allusion à la phrase: 'La méthode nouvelle découverte par le jeune docteur . . . qui attribue à M. Grignard un travail qui ne lui appartient aucunement.'

C'est moi qui, dans le courant de l'année 1899, ai institué cette nouvelle méthode de synthèse des matières organiques basée sur l'emploi du magnésium ainsi que le prouve mon mémoire aux *Comptes rendus de l'Académie des Sciences*, tome CXXXVIII, page 110 année 1899.

L'oeuvre de Grignard a consisté à développer les conséquences normales de cette découverte qui m'appartient intégralement. Ce travail exécuté très brillamment a valu à son auteur les récompenses et les faveurs que vous savez, ce dont j'ai été très heureux.

Il n'entre pas dans mes vues de diminuer la valeur des recherches d'un de mes meilleurs élèves, mais la justice et la vérité exigent qu'il soit rendu à chacun ce que lui appartient. . .

. . . Je tiens à votre disposition les pièces qui en justifient la légitimité.

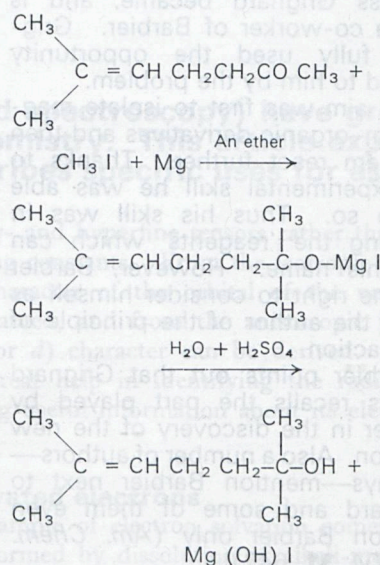
Veillez agréer, . . .

—/— Professeur P. Barbier

Faculté des Sciences de Lyon

Here are a few facts which should make the Barbier-Grignard problem unambiguously clear.

1. The statement of Barbier on his prior use of magnesium for synthesis is well documented by his paper—*Comptes Rendus*, 1899, **128**, 110. Here he described a modification of reaction of Saytzeff (as he pointed out) by replacing zinc with magnesium. Starting from methylheptenone he obtained dimethylheptenol:



In his paper he gives a detailed description of the procedure which is the same as the classical procedure of the Grignard reaction.

Barbier ends his paper with a remark that he was able to carry out a number of synthesis by this method and he intends to report them in the future.

Two more papers of a polemic character are pertinent to the history of the reaction.

2. Barbier published a note 'Sur l'origine de l'introduction du magnésium dans la synthèse organique' in *Bulletin de la Société chimique de France*, 1910, **7**, 206.

The author draws attention to the wrong tendency, which could be seen in the current chemical literature and encyclopaedic publications, in which the discovery of using magnesium in organic synthesis is assigned exclusively to Grignard.

This is not justified as the author had introduced magnesium into chemical technique for the first time

Tadeusz Urbański is emeritus professor in the Chemical Faculty, Technical University, Warsaw, Poland. A member of the Polish Academy of Sciences, he has written over 500 papers, and one of his books *Chemistry and technology of explosives* has been translated into several languages.

for the synthesis of dimethylheptenol. After this introduction Barbier repeated nearly a complete text of his paper published 1899 in *Comptes Rendus*. He adds that by this method he also obtained the secondary methylated alcohol deriving from citronellal. He explains that he has not published the description of it, as at the time he handed the whole problem to Grignard of replacing zinc by magnesium in order to find whether the reaction with magnesium has a general character and whether it is advantageous to replace zinc by magnesium. A detailed description of the reaction can be found (according to Barbier) in the excellent thesis of Grignard presented to the faculty of science in Lyon. Thanks to his success Grignard became, and is still, a co-worker of Barbier. Grignard fully used the opportunity offered to him by the problem.

His aim was first to isolate magnesium-organic derivatives and then let them react further. Thanks to his experimental skill he was able to do so. Thus his skill was in isolating the 'reagents' which can bear his name. However, Barbier has the right to consider himself as being the author of the principle of the reaction.

Barbier points out that Grignard always recalls the part played by Barbier in the discovery of the new reaction. Also a number of authors—he says—mention Barbier next to Grignard and some of them even mention Barbier only (*Am. Chem. J.*, 1904, **31**, 642).

The author finishes his paper with the words:

l'introduction du magnésium dans la synthèse organique est assez féconde pour que chacun de nous ait le droit de revendiquer la part qui lui revient et il me semble qu'en toute équité, il conviendrait désormais d'associer nos deux noms pour désigner cette réaction.

3. V. Grignard reacted to the above paper of Barbier in his note *Sur l'emploi du magnésium on chimie organique* published in *Bulletin de la Société chimique de France*, 1910, **7**, 453.

Grignard says that in November 1909 he left Lyon to Nancy which delayed his reading the paper by Barbier published in the same journal, p 206 on the use of magnesium in organic synthesis.

An insufficiently informed reader may think that Barbier's paper attacked Grignard, and may create a belief that he (Grignard) silently agreed with omitting the name of his highly esteemed master, in the

part which he played in developing the new reaction.

Although Barbier himself does not blame Grignard, it seems worth recalling all the documents which referred to the problem.

Grignard pointed out many times (eg Thesis, *Ann. l'Univ. Lyon, Ann. Chem. Phys.* 1901; *Revue general Science*, 1903) the importance, both theoretical and practical, of the synthesis by Barbier of dimethylheptenol (incidentally Sand and Singer as well as Harries and Weil, *Chemische Berichte*, 1902 and 1904 respectively, described once more this alcohol. Evidently they had no knowledge of the synthesis of Barbier).

A number of authors describing the use of magnesium in organic chemistry also gave the true picture, eg: Valeur, *Bulletin des Sciences Pharmaceutiques*, 1902; Klages, *Chemiker Zeitung*, 1905; Waters, *American Chemical Journal*, 1905; Schmidt, *Ahrens' Sammlung*, 1905; *Die organische Magnesium Verbindungen und ihre Anwendung zu Synthesen*, vol 2, Stuttgart, 1905 and 1908; Moissan, *Comptes Rendus*, 1906; MacKenzie, *Chemical News*, 1907; Meyer-Jacobson, *Lehrbuch der organische Chemie*, 1907, and certainly other authors of which Grignard was not aware.

It would be difficult now to ask chemists to change the name of the reaction which has been accepted for nearly 10 years.

Furthermore Grignard draws attention to the fact that a few methods exist for using magnesium in organic synthesis. He mentioned two of them.

The first is similar to Saytzeff reaction but of a much wider scope, it combines two different compounds in the presence of magnesium. This is the method of Barbier. It was applied and perfected by a number of authors such as Houben, Lespieu, Jaworsky, Pariselle, numerous chemists of the school of Reformatsky. Here allyl halogenides were used. Zelinsky and Gutt, Schroeter, Darzens, Rassow and Bauer, Ferrazio used esters of halogenated acids and Sommelet used chloromethylic ethers, etc.

The second method derived from the work of Frankland, Wanklyn and Wagner. It is based on discovery of combination of mixed magnesium-organic compounds (*combinaisons organomagnésiennes mixtes*) and application.

Grignard said that he could accept the honour given to him by chemists of calling only the second reaction with his name (*c'est pour celle-ci seulement que je puis accepter*

l'honneur que m'ont fait les chemists en attachant mon nom).

Grignard also pointed out that the development of mixed magnesium organic compounds produced a great impact upon the development of mixed zinc organic compounds according to Bewad and particularly to Blaise and his school.

4. The last important document is a hand-written letter of V. Grignard to his friend Meunier (13 November 1912).

... A vrai dire et entre nous, j'aurais préféré, quitte à attendre encore un peu, voir partager le prix entre Sabatier et Senderens et le partager ensuite—moi même avec Barbier. Mais que puis-je contre un tel verdict sinon m'en féliciter!

Tu sera bien aimable de me donner aussitôt que tu le pourras quelques renseignements sur l'état de la santé et sur l'état d'esprit de M. Barbier,

Je me demande comment il va prendre la chose. Mais s'il se considère comme frustré, je ne pense pas qu'il puisse m'en rendre responsable. ...

Thus speak the documents.

It should be pointed out that the case Sabatier-Senderens is not identical to this of Grignard-Barbier. Sabatier carried out his work with Senderens and the whole idea and trend of the research derived from Sabatier. In short—Senderens was experimenting under the guidance of Sabatier. In contrast, in the case of Grignard-Barbier, the original idea and first experiments belonged to Barbier. Subsequently Barbier could claim much more rights for participating in the prize than Senderens. (Senderens, a humble catholic priest, never claimed such a right, although his friend used to raise it and Sabatier always loyally stressed the great contribution of Senderens to the work.)

Looking back at the problem Grignard-Barbier one could say that the reaction should from the beginning be called Barbier-Grignard Reaction, but the magnesium organic reagent can be called Grignard reagent because it was isolated and analysed by Grignard.

So much can be said on the basis of official documents. There are, however, some undocumented stories by co-workers and students of Grignard and Barbier. It seems that Barbier underestimated his discovery and importance of the reaction he described 1899.

Acknowledgements

The author is much indebted to Professor Jacques Dreux, Université Claude Bernard, Lyon, for supplying him with documents quoted in this present article.