MAGNESIUM

ANNUAL SURVEY COVERING THE YEAR 1975

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Contents

Magnesium, Annual Survey covering the year 1974 see J. Organometal. Chem., Vol. 106(1976)1-114.

1. INTRODUCTION

At the occasion of the appearance of Volume 100 of this Journal a number of renowned organometallic chemists have contributed to this volume with articles surveying their own field of specialisation. In the field of organomagnesium chemistry Professor Henry Gilman contributed with a review on Synthesis of some perfluoro organometallic compounds [1] (among which many organomagnesium compounds can be found), whereas Professor Henri Normant reviewed the preparation of α-Halo-enolates [2].

Trofimov and Korostova reviewed The cleavage of the Carbon-Oxygen Bond by Organomagnesium Compounds, a field of research in which the russian group has been working for almost 15 years now [3].

A review on Reactions of 1,3-enyne and 1,3,5-dienyne hydrocarbons and their derivatives with organic compounds of Group II metals appeared from Cherkasov, Pis'mennaya, Radchenko and Bal'yan [4].

The Stereochemistry of organometallic compounds addition to ketones (for a large part dealing with organomagnesium compounds) was written by Ashby and Laemmle [5].

Rearrangements in organomagnesium chemistry were reviewed by E.A. Hill [6].

An up-to-date subject i.e. Activation of Grignard reagents by transition metal compounds was reviewed by Felkin and Swierczewski [7].

Another subject of recently grown interest i.e. Reactions of organomagnesium compounds with thiocarbonyl compounds, was reviewed by Paquer [8].

In his review on the Organic Chemistry of Metal Vapors Klabunde also briefly mentions the possibilities with this new techniques in the field of organomagnesium chemistry [9].

Hursthouse reviewed X-ray diffraction studies of compounds of Li, Be, Mg and other alkali-metal and alkaline earth elements [10].

Kartsova presented a biography of Francois August Victor Grignard [11].

Ioganson, Anisimov and Kolobova presented a 90 pages review, containing 565 references in the field of organomagnesium chemistry [12].

An 18 pages review with 146 references appeared from Wardell on Group II, Alkaline earths and zinc and its congeners [13].

Bell reviewed Organo derivatives of magnesium; 23 pages with 151 references [14].

The following dissertations were reported to have appeared: Reactions between nitrosyl chloride and phenylmagnesium bromide by Marsh [15]; Asymmetric induction in Grignard reactions in a chiral solvent by Davis [16]; Cleavage of cyclic ethers with magnesium bromide and acetic anhydride. Ortho vs para cyclization of m-alkoxyphenyl substituted epoxides. Use of tert-butyloxy to sterically direct a cyclization, by Campbell [17]; Grignard synthesis of some vinyl germanes by Hammon Jr. [18]; Preparation of organomagnesium fluorides by organometallic exchange reactions and the composition in solution of alkoxy(methyl)magnesium and dialkylamino(methyl)magnesium compounds by Nackashi [19]; Solution composition of some organomagnesium reagents as inferred from spectroscopic and colligative property studies by Parris [20]; Addition of dichlorosilane to conjugated dienes. Intramolecular cyclization of allylic dichlorosilanes. Reversible Grignard reaction by Roche [21]; Infrared and Raman studies of A.) Tetrafluorodiphosphine, B.) Silicon tetraisocyanate and germanium tetraisocyanate, C.) Tetrachloroallene and Tetraiodoallene, D.) Methylmagnesium iodide and ethylmagnesium bromide in diethyl ether by Snider Jr. [22]; A study of the Wurtz reaction by Hart [23].

2. PREPARATION OF GRIGNARD COMPOUNDS

Introduction

In view of the recently increasing knowledge of the influence of transition metal impurities in magnesium on the course of the reaction of Grignard compounds, prepared from low quality magnesium the publication of Revel, Pastol and Rouchaud on the purification of this metal by sublimation in vacuo requires special attention [24]. When about 50 g of magnesium were purified 70-90% of the metal were recovered in about 12 hours. Only zinc could be detected as the major contaminant (about 1 ppm). Analysis of the impurities was performed with the aid of neutron activation.

X-ray fluorescence spectroscopy was applied by Yamamoto, Yamagishi and Ueda for trace analysis of copper, zinc, iron and nickel in magnesium metal [25].

In an American patent Blackmar, Wight and Smith report the continuous production of a Grignard reagent in a newly developed vessel; the reaction proceeded in the presence of excess of magnesium, constantly maintained [26].

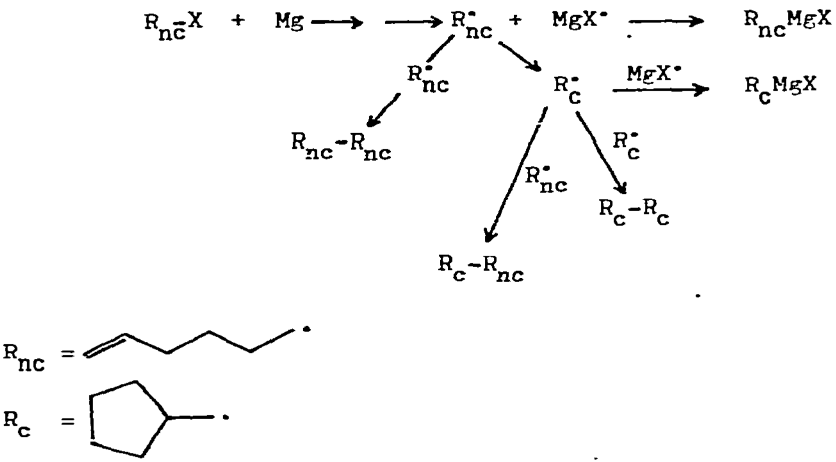
In a Japanese patent Kato and Hirayama applied less than one molar equivalent of ethereal solvents such as tetrahydrofuran or mixed alkyl ethers for the production of phenylmagnesium chloride [27]; at temperatures as high as 90° yields were higher than 95%.

Although magnesium metal does not dissolve in liquid ammonia in the presence of ethyne it does so when about 10% by weight of metallic sodium is present at the same time. Gardner reports the utilisation of this solution for reactions with carbonyl compounds [28].

Greaves, Landor and Lwanga mentioned the facile reaction of 1-halogeno-allenes with magnesium in diethyl ether or in THF to form the expected Grignard reagents despite previous reports by other groups concerning the lack of reactivity [29].

2A. Discussion of reactions leading to the formation of organomagnesium compounds

With the aid of NMR techniques Bodewitz, Blomberg and Bickelhaupt were able to observe the initial formation of RMgX in the reaction of R-X with Mg, followed by disproportionation of the Grignard reagent formed to R_2Mg and MgX_2 [30]. When tert-butyl chloride was used ^1H-NMR spectra indicated the formation of $t\text{-}C_4H_9MgCl$ as the primary product, with C_6F_5-Br the ^{19}F-NMR spectrum of the para fluoro atom proved the initial formation of the Grignard compound.
Using 6-bromohexene in its reactions with magnesium the same workers studied the influence of the solvent on the product formation and thus on the mechanism involved [31]. In the scheme given



the basicity of the solvent plays a role in the solvation of the MgX$^{\bullet}$ species and of the formed Grignard reagent. The more basic the solvent the more rapidly the solvation occurs, the less probable is the cyclization of the hexenyl radical. If Grignard formation is retarded radicals $R^{\bullet}_{nc}$ and $R^{\bullet}_{c}$ can escape from the site of formation to form coupling products. This process however is influenced also by the viscosity of the solvent. Also the CIDNP signals, observed by NMR, are indicative for the mechanisms involved.

Horak and Palm, together with Soogenbits continued publication of experimental data first started in 1960. More precise and cc - plete data on reaction rates of formation of organomagnesium compounds from the reaction of organic halides with magnesium with the aid of a thermographic method are given. These authors suggest the formation of two free radicals:

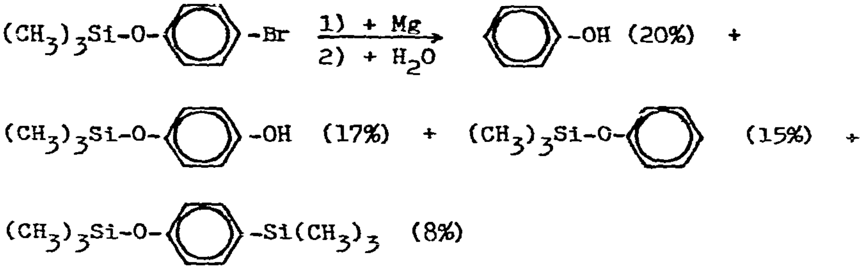
$$R\text{-}Br \; + \; Mg \xrightarrow{k_1} RMg^{\bullet} \; + \; MgBr^{\bullet}$$

each of which may react in two different reaction chains in which the solvent plays an important role. In the first of their three publications the order of the reaction was determined [32]. It seemed to be first order in [R-X], first order in [solvent] and also first order in S_{Mg}, being the effective surface of magnesium. Solvation of the radicals leads to species such as $RMg^{\bullet}$:S and $MgBr^{\bullet}$:S which may react with RBr to yield RMgBr:S and either $R^{\bullet}$ or $Br^{\bullet}$. Interruption of the radical chain only takes place with the unsolvated radicals.

In their second paper the authors investigated the kinetics of the Grignard formation reaction in different solvents [33]; in weakly basic solvents such as diethyl ether and di-n-butyl ether the radical chain mechanism involving the species $RMg^{\bullet}$ predominates, in tetrahydrofuran the chain including $MgBr^{\bullet}$ is the more important one. It was found that the reaction rate was practically independent of the structure of the alkyl group in the organic halide with tetrahydrofuran as the solvent contrary to the results obtained in the less basic solvents.

In their third report finally the authors studied the influence of the presence of impurities such as peroxides, water and oxides on the metal surface on the length of the induction period, often observed in the start of a Grignard reaction. As in the previous publication only in weakly basic solvents the induction periods depend on the structure of the alkyl halide whereas in tetrahydrofuran no dependence on the structure was observed. The induction periods are ascribed to interruption reactions in the radical reaction chains [34].

The reaction of trimethylsilyloxy substituted bromobenzenes with magnesium was studied by Razuvaev, Vasileiskaya and Khrzhanovskaya [35]; rearrangements seem to take place:



In a Japanese Patent Ikeno utilized the same silyloxy bromide to produce the Grignard reagent [36].

Contrary to allyl bromide the γ-triphenylsilyl homologue is rather unreactive and yields the corresponding Grignard reagent in very good yields, according to Corriu, Masse and Samate [37]:

$$(C_6H_5)_3Si\text{-}CH{=}CH\text{-}CH_2\text{-}Br \ + \ Mg \xrightarrow[\text{ether}]{\text{diethyl}} (C_6H_5)_3Si\text{-}CH{=}CH\text{-}CH_2\text{-}MgBr$$

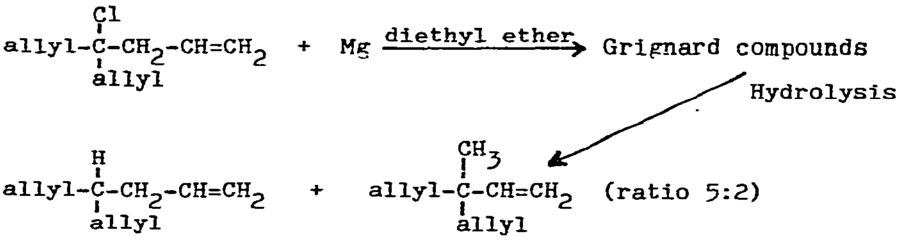
good yields

The bimetal derivatives of phenylacetic acid were investigated by Blagoev, Mladenova and Kurtev [38]; on reaction with benzaldehyde a mixture of diastereomers was obtained under thermodynamically or kinetically controled conditions. The results obtained indicated that these bimetal derivatives (Ivanov reagents) , obtained by different methods have the same behavior.

According to Grim and Barth 2-chlorodiphenylphosphynylethane reacts with magnesium in THF under the formation of ethene and of substantial amounts of "diphos" [39]:

$$(C_6H_5)_2P\text{-}CH_2\text{-}CH_2\text{-}Cl \ + \ Mg \xrightarrow{THF} CH_2{=}CH_2 \ + \ MgCl^{\oplus} + \ (C_6H_5)_2P^{\ominus}$$

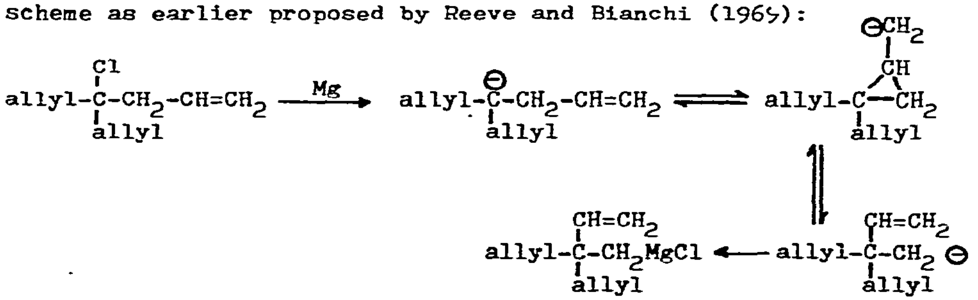
The following rearrangement occured in the reaction of triallylmethyl chloride with magnesium as studied by Lindgren and Adolfsson [40];



$$\text{allyl-}\overset{\text{Cl}}{\underset{\text{allyl}}{\text{C}}}\text{-CH}_2\text{-CH=CH}_2 \ + \ \text{Mg} \xrightarrow{\text{diethyl ether}} \text{Grignard compounds}$$

$$\text{allyl-}\overset{\text{H}}{\underset{\text{allyl}}{\text{C}}}\text{-CH}_2\text{-CH=CH}_2 \ + \ \text{allyl-}\overset{\text{CH}_3}{\underset{\text{allyl}}{\text{C}}}\text{-CH=CH}_2 \quad \text{(ratio 5:2)}$$

The formation of the rearranged product is given in the following scheme as earlier proposed by Reeve and Bianchi (1969):

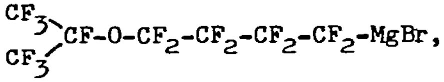


2B. Preparation of organomagnesium compounds

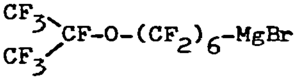
2Bi. Halide substituted organomagnesium compounds

A surprising number of reports on the preparation and utilisation of fluoro substituted Grignard reagents has appeared in 1975. In Chapter 1 Gilmans review article on this subject has been mentioned [1]. Together with Dua and Howells Gilman (in 1974! unfortunately not mentioned in that year's annual survey) reported the formation of some perfluoroalkyl Grignard reagents by halogen-metal exchange reactions [41]; the following reagents were prepared:

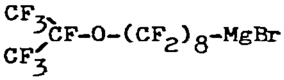
$n\text{-}C_{10}F_{21}MgBr$,



$(CF_3)_2CF\text{-}O\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}MgBr$,



$(CF_3)_2CF\text{-}O\text{-}(CF_2)_6\text{-}MgBr$ and



$(CF_3)_2CF\text{-}O\text{-}(CF_2)_8\text{-}MgBr$

Howells and Gilman, in order to study the thermal decomposition of perfluoroalkyl magnesium halides prepared $n\text{-}C_{10}F_{21}\text{-}Mg\text{-}X$, $n\text{-}C_8F_{17}\text{-}Mg\text{-}X$ and $n\text{-}C_6F_{13}\text{-}Mg\text{-}X$, with X = Cl, Br or I [42].

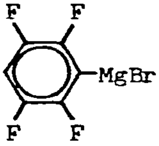
Moreau, Dalverny and Commeyras reported the preparation of $n\text{-}C_4F_9\text{-}MgBr$, $C_6F_{13}\text{-}MgBr$ and $C_8F_{17}\text{-}MgBr$ [43].

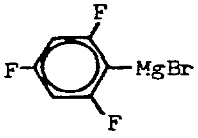
Nguyen Thoai [44] and Ngyuen Thoai together with Wakselman [45] prepared $C_2F_5\text{-}MgBr$, $n\text{-}C_6F_{13}\text{-}MgBr$ and $n\text{-}C_8F_{17}\text{-}MgBr$.

Bifunctional perfluoroalkyl Grignard reagents were reported by Smith Jr. and Gilman [46] who prepared $BrMg\text{-}(CF_2)_6\text{-}MgBr$; the same perfluoroalkyl diGrignard was reported by Denson, Moore and Tamborski [47].

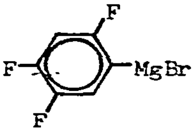
Brewer, Heaney, Ley and Ward [48] as well as Filler, Beaucaire and Kang [49] investigated reactions of $C_6F_5\text{-}MgBr$.

Deacon and Vince utilized the following tetra- and trifluorophenylmagnesium bromides [50]:

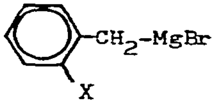




and

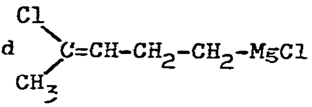


Jacob, Thiele, Keilberg and Niebuhr prepared the following ortho-halobenzylmagnesium bromides [51]:



with X = F, Cl or Br

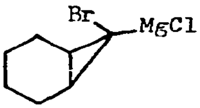
Myrsina and Kuznetsov reported the preparation of the monofunctional Grignard compound prepared from 2,5-dichloro-2-pentene [52]:

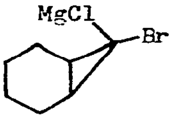


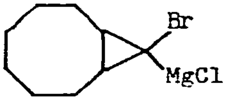
$$(Cl)(CH_3)C{=}CH\text{-}CH_2\text{-}CH_2\text{-}MgCl$$

Santini, Le Blanc and Riess investigated reactions of $n\text{-}C_6F_{13}\text{-}C{\equiv}C\text{-}MgBr$ and $C_8F_{17}\text{-}C{\equiv}C\text{-}MgBr$ [53].

By halogen-metal exchange reactions at lower temperatures Seyferth, and Lambert Jr. prepared the following α-bromo-Grignard reagents [54]:







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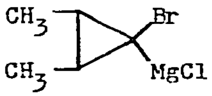


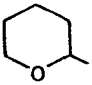
Finally in this chapter attention is drawn to Normant's review article, already mentioned in Chapter 1 dealing with synthesis and properties of α-halo-enolates [2].

2Bii Alkoxy substituted organomagnesium compounds.

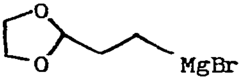
The introduction of the tetrahydropyryl group as functional protection in Grignard reagents has been used several times:

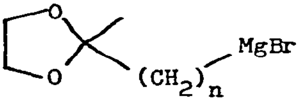
THP-O-(C_6H_{12})-MgBr ; Mori [55]; THP-O--MgBr ; Lednicer [56];

THP-O-CH_2-$C\equiv C$-MgBr; Anderson [57], [58] and [59].

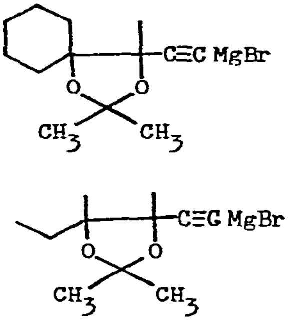
THP = tetrahydropyryl- 

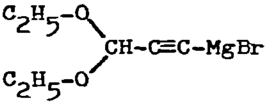
Other acetal functionalization in Grignard reagents was reported by

Loozen [60]: 

Kuznetsov and Myrsina [61]:  (n = 3, 4 or 5)

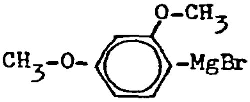
Vereshchagin, Kirillova, Buzilova, Bol'shedvorskaya and Chernysheva [62]



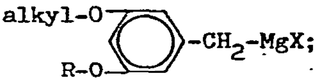
Frangin and Gaudemar [63]: 

$$(C_2H_5\text{-}O)_2CH\text{-}C\equiv C\text{-}MgBr$$

Other bifunctional alkoxy substituted Grignard compounds reported are:



; Soos, Fogassy, Palinkas, Hernadi and Gressay [64]



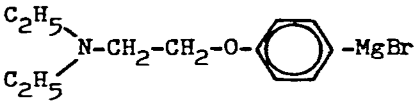
; Saito, Yamaguchi and Ishimoto [65].

R = alkyl or benzyl

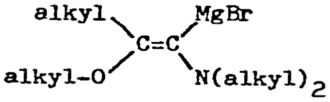
De Botton continued his investigations on the synthetic utility of the α-ethoxy Grignard compound derived from chloromethyl ethers [66]:

C_2H_5-O-CH_2-MgCl

In a US patent Griot reports the preparation of an alkoxy dialkylamino substituted Grignard reagent [67]:



By the addition to the carbon-carbon triple bond in substituted alkynes Mornet and Gouin prepared Grignard reagents of the following types [68]:



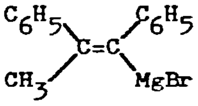
2Biii Unsaturated organomagnesium compounds

Vinylic organomagnesium compounds:

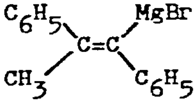
Zembayashi, Tamao and Kumada studied the cis-trans isomerization of the following β-substituted vinylmagnesium bromides [69]:

CH_3-CH=CH-MgBr (cis/trans ratio 96/4); n-C_3H_7-CH=CH-MgBr (cis/trans ratio 100/0); i-C_3H_7-CH=CH-MgBr (cis/trans ratio 94/6) and C_6H_5-CH=CH-MgBr (cis/trans ratio 71/29).

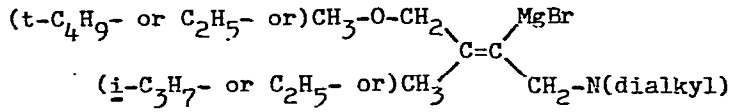
The same type of isomerization of vinylic organomagnesium compounds was studied by Duboudin and Jousseaume [70]; they prepared



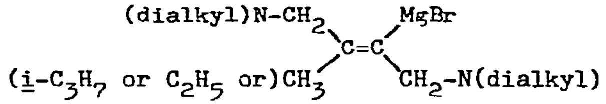
and



Mornet and Gouin prepared alkoxy-/amino substituted vinylic organomagnesium compounds of the following type [68]:



The same authors report the preparation of dialkylamino substituted vinylic organomagnesium compounds of the following type [71]:



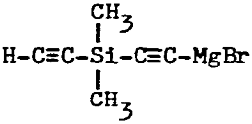
Acetylenic organomagnesium compounds.
Sudweeks and Broadbent [72] as well as Newkome and Martin [73] used the bifunctional acetylenic Grignard reagent

$$\mathrm{Br{-}Mg{-}C{\equiv}C{-}Mg{-}Br}$$

for synthetic purposes.
The preparation of acetalfunctionalized acetylenic organomagnesium halides has been mentioned in chapter 2Bii (references [57], [58], [59], [62] and [63]).
The intermediate preparation of the following acid-functionalized acetylenic Grignard compound was reported by Fryer, N.W. Gilman and Holland [74]:

$$\mathrm{Br{-}Mg{-}C{\equiv}C{-}CH_2{-}CH_2{-}CH_2{-}CO_2H}$$

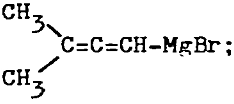
Vinyl- and ethynylsilyl-functionalized acetylenic Grignard reagents were prepared and utilized by Voronkov, Yarosh, Burnashova, Misiunas and Tsvetaeva [75]:

$CH_2=CH-C\equiv C-MgBr$ and 
$H-C\equiv C-\underset{CH_3}{\overset{CH_3}{Si}}-C\equiv C-MgBr$

Moreau and Gaudemar investigated reactions of Grignard reagents, derived from 3-bromo-1-butyne and from 3-bromo-1-hexyne [76]:

$CH_3-CH=C=CH-MgBr$ and $\underline{n}-C_3H_7-CH=C=CH-MgBr$

The same type of Grignard reagents were prepared by Greaves, Landor and Lwanga [29] :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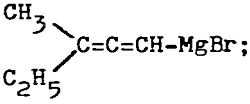
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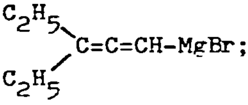
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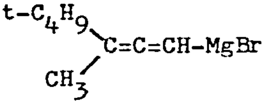

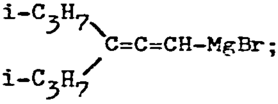
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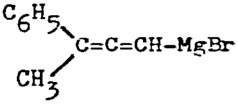
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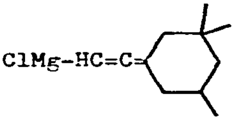
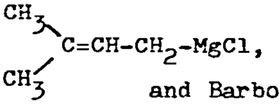
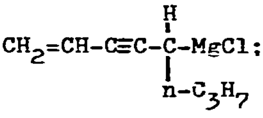
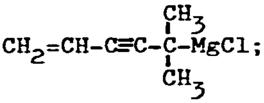
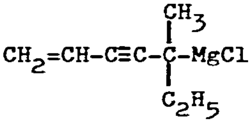


γ,γ'-dimethylallylmagnesium chloride,  was prepared and utilized by Ph. Miginiac and Barbot [77].
A silicon-containing allylic Grignard reagent was prepared by Corriu, Masse and Samate [37]:

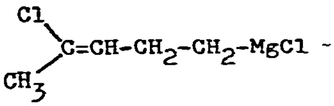
$(C_6H_5)_3Si-CH=CH-CH_2-MgCl$

β-Acetylenic organomagnesium chlorides were reported to be prepared by Voskanyan, Pashayan and Badanyan [78]:


$CH_2=CH-C\equiv C-\underset{n-C_3H_7}{\overset{H}{C}}-MgCl$;

$CH_2=CH-C\equiv C-\underset{CH_3}{\overset{CH_3}{C}}-MgCl$;

$CH_2=CH-C\equiv C-\underset{C_2H_5}{\overset{CH_3}{C}}-MgCl$

The solvent used was a 1:1 mixture of diethyl ether and tetrahydrofuran.

The preparation of the monofunctional Grignard reagent derived from 1,4-dichloro-3-pentene has already been mentioned in chapter 2Bi [52]



Finally the rearrangement in the Grignard reagent, obtained from triallylchloromethane, as reported by Lindgren and Adolfsson [40] requires mention in this chapter :

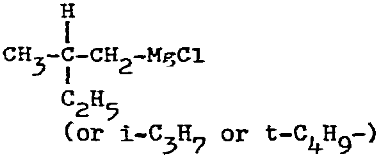
2Biv Some other organomagnesium compounds

Marshall and Engel prepared CD_3-CH_2Mg-I [79].

Chiral Grignard reagents have been reported:

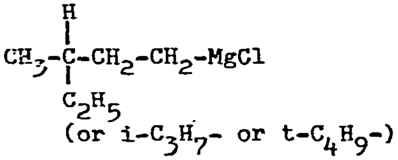
By Vasi and Desai [80]: (S)-(+)-C_2H_5-C(H)CH_3-CH_2-MgBr

Giacomelli, Lardicci and Caporusso prepared the same type of Grignard compounds [81]:



$CH_3-\overset{H}{\underset{C_2H_5}{C}}-CH_2-MgCl$ (or i-C_3H_7 or t-C_4H_9-)

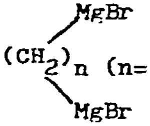
and



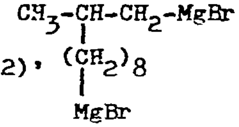
$CH_3-\overset{H}{\underset{C_2H_5}{C}}-CH_2-CH_2-MgCl$ (or i-C_3H_7- or t-C_4H_9-)

Bifunctional Grignard reagents were used by Mazerolles who prepared Br-Mg-CH_2-CH_2-CH_2-CH_2-Mg-Br [82]. The pentamethylene homologue, Cl-Mg-CH_2-CH_2-CH_2-CH_2-CH_2-Mg-Cl was used by Hoye and Hargreaves in an American Patent [83].

For the synthesis of metacyclophanes Tamao, Kodama, Nakatsuka, Kiso and Kumada applied the following bifunctional Grignard reagents [84]:

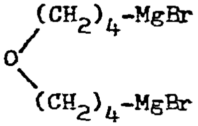


(n= 6, 7, 8, 9, 10 or 12),



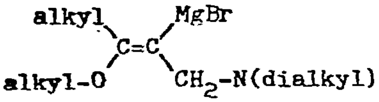
$CH_3-CH(-(CH_2)_8-MgBr)-CH_2-MgBr$

and

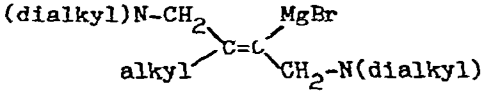


Other substituted organomagnesium compounds reported were:

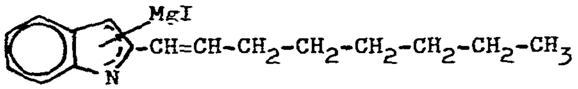
; Bourquin, Schwarb and Waldvogel [85].



as reported in chapter 2Bii [68]

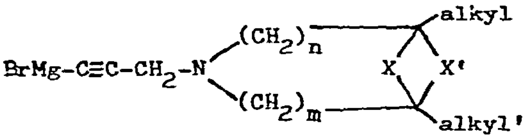


also reported in chapter 2Biii [71].



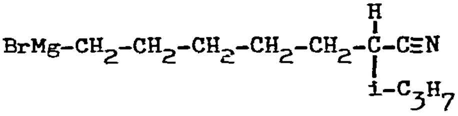
; Avramenko, Levinova, Nazima and Suvorov [86].

In a Japanese patent Katsube, Nakao, Sasajima, Maruyama, Takayama, Ono, Katayama, Tanaka, Yamagihara (et al.!) reported the preparation of a polyfunctional Grignard reagent [87]:



with m and n are 1-4 and with X and X' are O or S or alkylene.

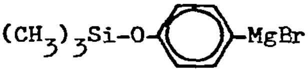
Larchevêque, Debal and Cuvigny report the preparation of a cyanosubstituted Grignard reagent [88]:



$$BrMg\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}\underset{i\text{-}C_3H_7}{\overset{H}{C}}\text{-}C{\equiv}N$$

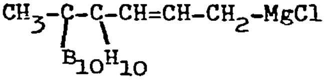
Mention has to be made of the first reported example of a phosphinoalkyl Grignard reagent, $(C_6H_5)_2P\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}MgCl$ by Grim and Barth [39].

The reaction of the corresponding halide with magnesium leads only to small amounts of the following silyloxy substituted Grignard reagent [35] and [36]:

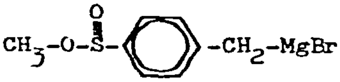


The preparation of $(C_6H_5)_3Si\text{-}CH{=}CH\text{-}CH_2\text{-}MgBr$ has already been reported in chapter 2Biii [37].

Ivanova, Kazantsev and Zakharkin report the preparation of 1-methyl-2-(chloromagnesium allyl)-O-carborane [89]:

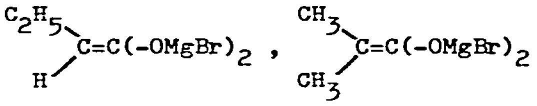


In a American patent Jones Jr. utilizes the following functionalized aromatic Grignard reagent [90]:



McVicker reports the preparation of magnesium compounds containing Mg-transition metal bonds such as $(CpFe(CO)_2)_2Mg$.base, $(Co(CO)_4)_2Mg$.base and others derived from Mo and Co [91].

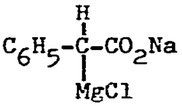
Numerous enolates of magnesium, quite often of still unknown structures have been reported this year. The Ivanov reagent analogue of aliphatic acids has been prepared by Bellassoued, Dardoize, Gaudemar and Goasdoue [92]:



:

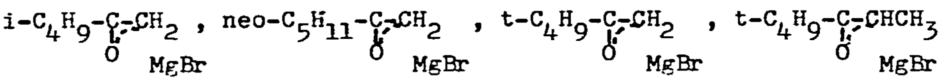
The authors don't claim the reality of the structure given. The same types of derivatives could be prepared from aliphatic acid amides by the authors.

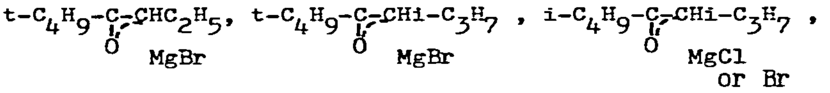
A mixed-metallic enolate derivative of phenylacetic acid was used by Mladenova-Orlinova and Nikolova [93]:



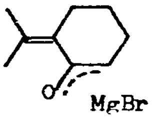
$C_6H_5-\underset{MgCl}{\overset{H}{C}}-CO_2Na$

A series of papers appeared this year again from the laboratory of Mme Maroni on the magnesium derivatives of ketones; the following compounds were reported:

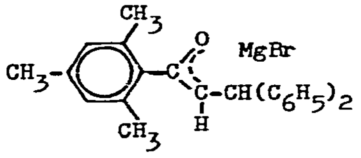




and



[94], [95], [96], [97] and [98].

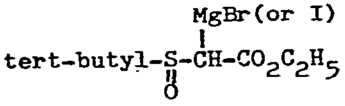


Pinkus and Wu investigated the structure of Grignard compounds derived from 2,2-diphenylethyl-2,4,6-trimethylphenyl ketone [99].

Samusenko, Aleksandrov and Yagupol'skii utilized the following Grignard reagent for synthetic purposes [100]:

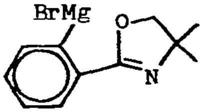
$$CF_3\text{-}SO_2\text{-}CH_2\text{-}MgBr$$

Nokami, Kunieda and Kinoshita applied the new type of Grignard reagent

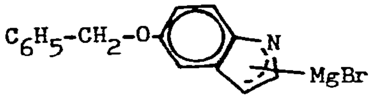


$$\text{tert-butyl-}\underset{\overset{\|}{O}}{S}\text{-}\overset{\overset{\text{MgBr(or I)}}{|}}{CH}\text{-}CO_2C_2H_5$$

to synthesize α,β-unsaturated esters [101]. Marxer, Rodriguez, McKenna and Tsai prepared the oxazoline substituted Grignard reagent [102]:



An indole Grignard compound was used by Friderichs, Back and Mutschler [103]:



Dehnicke and Klopsch [104] investigated complexes of the following types : $[(CH_3)_4N]_2[((CH_3)_2Mg)_2X]_2$ in which X = F,CN, N_3 and NCO. Müller, Schmock, Klopsch and Dehnicke [105] studied the complex $[(CH_3)_4N]_4[(CH_3)_2MgCN]_4$.

Finally Dehnicke and Röder prepared and studied the complex $[(CH_3)_2Al(N_3)_2.MgCH_3][(CH_3)_4N]$ [106].

2C. New or uncommon reactions leading to the formation of organomagnesium compounds

Lang, in an American patent, describes the preparation of phenylmagnesium chloride by reaction of chlorobenzene with highly reactive magnesium obtained with the aid of an electric arc to comminute the metal which reacts as it was formed [107].

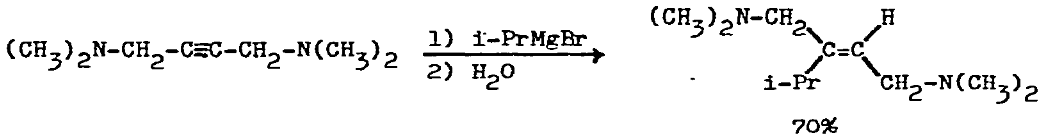
Several reports have appeared in which the preparation of organomagnesium halides was performed by the metal halogen exchange reaction: reaction of gem-dibromocyclopropanes with i-propylmagnesium chloride in tetrahydrofuran at -68° leading to the formation of α-bromoorganomagnesium compounds [54];

reaction of ethyl- or phenylmagnesium bromide with perfluoroalkyl iodides leading to the formation of the corresponding perfluoroalkylmagnesium bromides [41] and [43];

less common is the reaction of (bistrimethylsilyl)perfluoroalkanes with Grignard reagents leading to the corresponding bifunctional organomagnesium compound [46]:

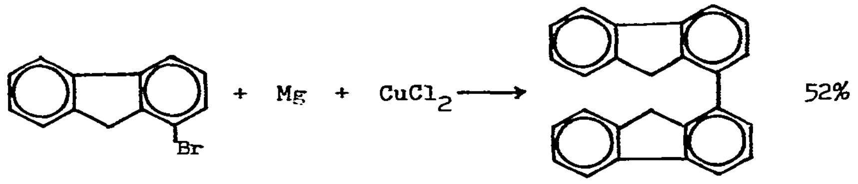
$$(CH_3)_3Si\text{-}(CF_2)_6\text{-}Si(CH_3)_3 + 2RMgBr \longrightarrow BrMg\text{-}(CF_2)_6\text{-}MgBr$$

Finally attention is drawn to the facile addition of methyl-, ethyl- or isopropylmagnesium bromide to the carbon-carbon triple bond in 1,4-diamino- or 1-amino-4-alkoxysubstituted 2-butynes [68] and [71]; as an example the following reaction is given:

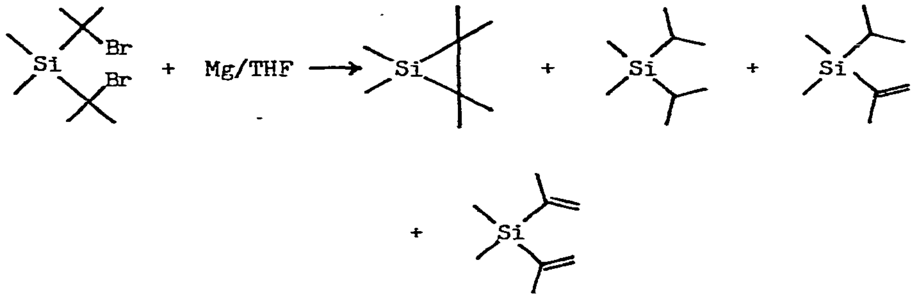


2D. Reactions with "in situ" Grignard compounds

Yukhno and Bikhulov reported aromatic carbon-carbon bond formation in the following reaction [108]:



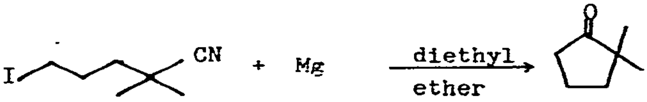
The well-known cyclopropane formation during the reaction of 1,3-dibromoalkanes was utilized by Seyferth and Amarelli for the preparation of hexamethylsilirane [109]; some interesting side-products may require further attention in the elucidation of the mechanism of reactions of this type:



In a Italian patent Moreschini, Delvesco and Carraro claim the preparation of magnesium carboxylates by the reaction of magnesium/amalgam with benzyl halides under CO_2 atmosphere in an inert organic polar solvent (propylene carbonate is given as an example!) in the presence of ammonium salts [110]:

$$C_6H_5CH_2\text{-}Cl \; + \; Mg/Hg + CO_2 \xrightarrow[\text{carbonate}]{\text{propylene}} C_6H_5CH_2CO_2Mg/2$$

A peculiar intramolecular "in situ" reaction was reported by Larchevêque, Debal and Cuvigny when they investigated 1-cyano-4-bromo- and 1-cyano-5- haloalkanes in their interaction with magnesium [88]; in particular iodides give fair yields of cyclic ketones on hydrolysis as is demonstrated by the following example:



Since during the reaction no positive Gilman test for the presence of intermediate organomagnesium compounds was observed the authors propose a one step cyclic mechanism on the metal surface as a possible explanation for the efficient reaction and for the negative results obtained in the more basic tetrahydrofuran. No cyclization is observed with 1-cyano-6-haloalkanes.

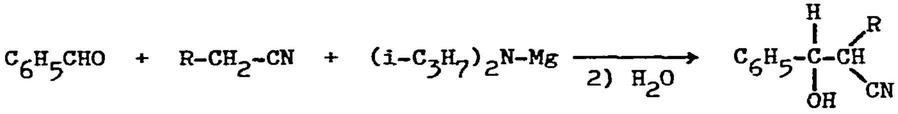
During an attempted coupling of a steroid-22-tosylate with γ,γ-dimethylallyl bromide with the aid of magnesium Dasgupta and Gut observed the formation of the disteroid rather than of the expected desmosterol [111]:

$$\text{R-CH}_2\text{-OSO}_2\text{C}_6\text{H}_4\text{CH}_3 + (\text{CH}_3)_2\text{C=CH-CH}_2\text{-Br} + \text{Mg} \xrightarrow[\text{ether}]{\text{diethyl}} \text{R-CH}_2\text{-CH}_2\text{-R} + \text{R-CH}_3$$

R = 6β-methoxy-3α,5-cyclo-5α-23,24-bisnorcholan-21-yl

Since also the corresponding hydrocarbon was found among the reaction products the authors suppose that the tosylate is first converted to the bromide which then forms a Grignard reagent $\text{R-CH}_2\text{-MgBr}$. This reagent then reacts with a tosylate molecule to form the disteroid. Unreacted $\text{R-CH}_2\text{MgBr}$ yields the hydrocarbon on hydrolysis.

The formation of the so-called Ivanov complex by the reaction of magnesium(bis-isopropyl)amide with alifatic acids or their amides as mentioned in chapter 2Biv fails with aliphatic nitriles [92]; nevertheless the desired products could be obtained by simultaneous addition of an aldehyde and the nitrile to the amide:



$$C_6H_5CHO \;+\; R\text{-}CH_2\text{-}CN \;+\; (i\text{-}C_3H_7)_2N\text{-}Mg \xrightarrow[2)\ H_2O]{} C_6H_5\text{-}\overset{H}{\underset{OH}{C}}\text{-}CH\begin{smallmatrix}R\\CN\end{smallmatrix}$$

Several examples have been reported of carbon-silicon bond formation by in situ reaction of chlorosilanes and organic halides with magnesium:

two reports make use of the reactive couple $(CH_3)_3SiCl/Mg/HMPA$;

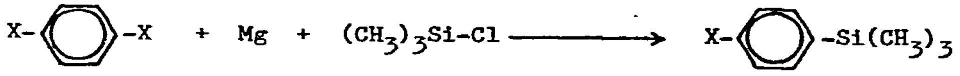
the formation of mono, di- etc. silylation products on reaction with carbon-carbon triple bonds is reported by Dunoguès, Bourgois, Pillot, Merault and Calas [112]. The following reaction is illustrative:

$$Si\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}Si \;+\; \text{reactive couple} \longrightarrow (Si)_3C\text{-}C{\equiv}C\text{-}C(Si)_3$$

$Si = (CH_3)_3Si\text{-}$

One of the possible intermediates in these reactions might be the $(CH_3)_3Si^{\bullet}$ radical. In another report from the same laboratory Biran, Duffaut, Dunoguès and Calas silylated functionalized benzyl and allyl derivatives [113]. In these reactions catalysts play an important role.

Reimann and Langwieler prepared para-trimethylsilyl halobenzenes by reaction of the corresponding para-dihalobenzenes with magnesium in the presence of trimethylchlorosilane [114]:



X = Cl or Br