MAGNESIUM

ANNUAL SURVEY COVERING THE YEAR 1972

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Contents

1. INTRODUCTION

Again the number of publications dealing with the chemistry of organomagnesium compounds has increased in 1972 with approximately 20%, compared with the previous year. Fortunately, excellent reviews on special topics in organomagnesium chemistry continue to appear each year. Elsom, Hunt and McKillop reviewed the cobalt(II)-catalyzed reactions of organomagnesium compounds with organic halides [1]; J.C. Powers, in a review of the chemistry of indole and its derivatives, discussed the physical and spectroscopic properties of the organometallic indole compounds [2]; Razuvaev, Shushunov, Dodonov and Brilkina discussed the reactions of organic peroxides with organometallic compounds in one of the chapters of a book dealing with organic peroxides [3]; Cardin, finally, in one chapter of an inorganic chemistry book reviewed the chemistry of magnesium compounds (with the emphasis on the inorganic chemistry) over the period 1969-1970 [4].

With some delay it is reported here that two more biographies of Victor Grignard, whose hundredth anniversary was commemorated in 1971, have appeared in that year: a short one by C.A. Russell [5] and another (short) one by J.C. Boudon [6].

In a special issue of its journal the Société Chimique de France published the plenary lectures given by Ashby, Blomberg, Noltes and H. Normant during its 1971 annual meeting, held in Lyon to celebrate the hundredth anniversary of the birth of Victor Grignard, each of the lectures reviewing a field of specialisation in organomagnesium chemistry [7], [8], [9] and [10].

Two more reviews appeared from Normant's desk: one on the preparation of organomagnesium compounds [11], the other one on Chemistry of Organomagnesium Compounds in France after Grignard [10']. Wakefield finally wrote a short review on Organomagnesium compounds in Organic Synthesis [12].

The following dissertations dealing with organomagnesium chemistry have appeared in the U.S. :
S.P. McPherson: Solutions of Grignard reagents and the determination of the stoichiometry of nonvolatile solutes in mixed solvent systems [13]. J.K. Thomson: Addition of unsaturated Grignard reagents to aldehydo and keto sugar derivatives [14]. S.-H.P. Yü: Synthesis and reaction mechanisms in organoaluminum and organomagnesium chemistry [15]. A.M. Cioffari: I) Radical cycloaddition reactions and rearrangements. II) Radical cyclization in the autoxidation of an alkenyl Grignard reagent [16]. W.J. Michaely: Organometallic induced cyclizations of ω-haloacetylenes [17]. W.C. Kossa: Intramolecular addition of Grignard reagents to carbon-carbon double bonds [18]. S.E. Rudolph: Kinetics and mechanisms of reductions of ketones by organomagnesium reagents [19]. J.E. Girard: Reactions of atomic magnesium [20]. J.T. Laemmle: Organometallic alkylation reactions [21]. B.R. Appleman: NMR-studies of dineopentylmagnesium exchange. Ab initio calculations of chemical shifts [22]. R.C. Wilkinson: Reactions of tetrachloroethylene carbonate with phenylmagnesium bromide and the preparation and reactions of dichlorovinylene carbonate [23]. P.R. Farina: Reactions of organometallics with nitrosamines and the nitrosylation of folic acid and related compounds [24]. S. Lowenkron: 2-Phenyl-2-butylmagnesium chloride. Structure, Stability and Stereochemistry [25]. H.W. Wolterman: Solvation of pseudo-Grignard reagents and the kinetics of pseudo-Grignard reactions [26].

2. PREPARATION OF ORGANOMAGNESIUM COMPOUNDS

Before the discussion of reactions leading to the formation of organomagnesium compounds, mention has to be made of the preparation of highly "Grignard-reactive" magnesium by Rieke and Hudnall [27]

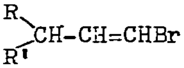
These authors report that finely divided magnesium is prepared by reduction of magnesium chloride or magnesium bromide in an inert ethereal solvent with the aid of an alkali metal. At -78^{o} bromobenzene reacts with this activated metal to form phenylmagnesium bromide in 60% yield in only 30 minutes. The authors even obtained the Grignard reagent from fluorobenzene (albeit in small yields, judging from the yield of benzoic acid, obtained on carbonation and hydrolysis : 5%) on refluxing this halide with the activated metal in diglyme for one hour. The question rises to what extent unreacted alkali metal must be held responsible for the activity of the magnesium metal, although the authors state that by starting with an excess of magnesium halide any problem with unreacted alkali metal can be avoided.

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

In a first report of their investigations on the mechanism of the reaction of an organic halide with magnesium, Bodewitz, Blomberg and Bickelhaupt [28] mention the observation by NMR of CIDNP in the Grignard reagents prepared (ethylmagnesium bromide and isobutylmagnesium bromide). According to the radical pair theory (Kaptein, Oosterhoff and Closs, 1969) nuclear polarization in the Grignard reagent indicates its formation via radical precursors. In a second report by the same authors (which will be discussed in the next years annual survey) the radical pair responsible for the nuclear polarization must consist of two $R^{\cdot}$ radicals : $\overline{R^{\cdot\cdot}R}$, formed by a mechanism in which the formation of the radical anion $R\text{-}X^{\cdot\ominus}$ is supposed to be the first step in the reaction of magnesium with an organic halide [29].
Méchin and Naulet have at last obtained compelling evidence for the steric stability of vinylic Grignard compounds [30]. The question rose

(Annual Survey '66) whether Grignard compounds, prepared from cis or trans vinylic halides, isomerized in solution or whether isomerization had already occurred in (one of the ?) processes leading to their formation. The French authors succeeded in a configurational assignment of ^1H-NMR signals of either the cis or the trans Grignard derivatives. Since their starting halides were 99% or 100% sterically pure the ^1H-NMR spectra of the Grignard solutions could give final evidence regarding the question of steric stability of such solutions.

Halides of the general formula:

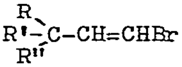


$\overset{R}{\underset{R'}{>}}CH\text{-}CH{=}CHBr$ (cis configuration)

R is CH_3, C_2H_5, n-C_3H_7 or i-C_3H_7; R' is H

with a steric purity of 99% gave 85-90% sterically pure Grignard compounds.

Halides with the general formula:



$R'\overset{R}{\underset{R''}{-}}C\text{-}CH{=}CHBr$ (trans configuration)

with steric purities between 99 and 100% gave Grignard compounds of inferior steric purity. With R = R' = H and R'' = i-C_3H_7 e.g. the Grignard compound had only 60% trans configuration!

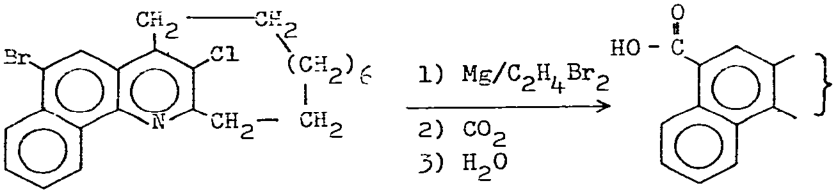
The authors conclude that radicals must play an important role in the formation reaction of Grignard compounds.

Each of the Grignard reagents was configurationnaly stable in solution

As a demonstration of complexity of the Grignard-formation reaction it is mentioned that Garst, C.D. Smith and Farrar assume the formation of biphenylmagnesium bromide in the reaction of bromobenzene with magnesium [31]:

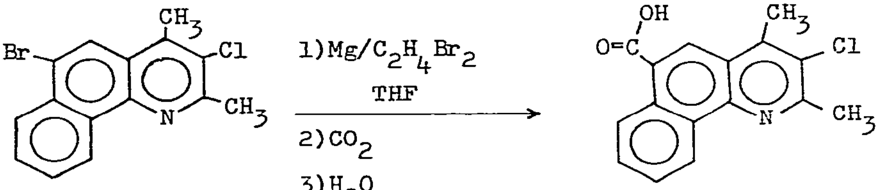
$C_6H_5\text{-}Br + Mg \longrightarrow C_6H_5\text{-}C_6H_4\text{-}MgBr$ among other products

While Grignard reagents are not generally considered to be useful intermediates for synthetic conversions in quinoline systems the results of Parham, Egberg and Salgar [32] establish that they are quite useful in the naphthopyridinophane series:



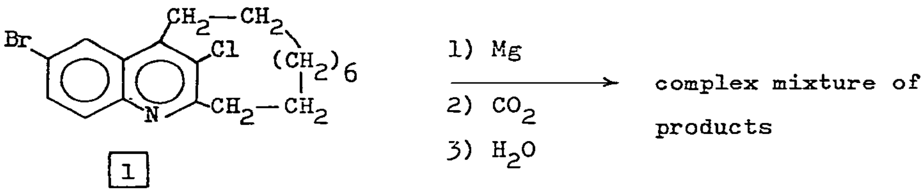
82 - 100 %

The results are less satisfactory with 2-alkylbenzo[h]quinolines:



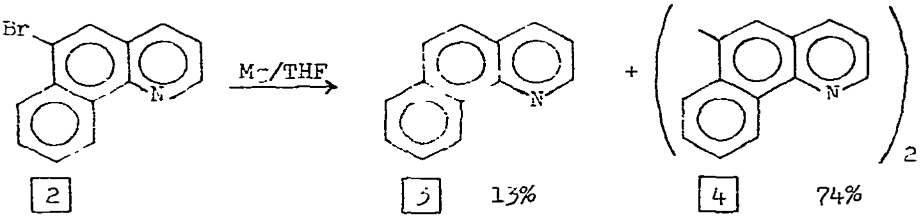
43%

Studies of the reaction of $\boxed{1}$ with magnesium, followed by carbonation indicate that a rather complex mixture of products is formed:



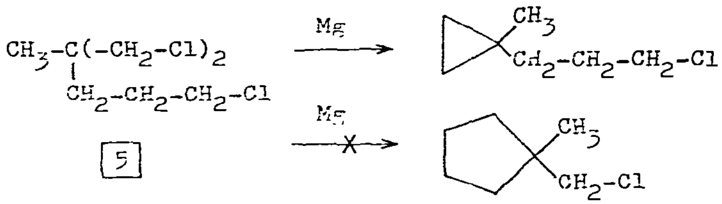
$\boxed{1}$

The quinoline $\boxed{2}$ when treated with magnesium and subsequently with carbon dioxide or benzaldehyde did not yield any carboxylic acid or carbinol. The products $\boxed{3}$ and $\boxed{4}$ were obtained in surprisingly high

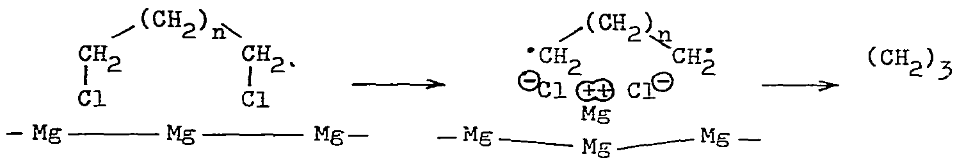


yields. Nucleophilic aromatic displacement of the bromide by Grignard reagent, leading to $\boxed{4}$ is not likely to occur since treatment of $\boxed{2}$ with phenylmagnesium bromide did not lead to the phenyl substituted benzo[h]quinoline; evidently (radical type?) side reactions occur during the reaction with magnesium leading to different sorts of products.

McCaffery and Shalaby propose a diradical mechanism for the Grignard coupling reaction of 2-methyl-2-(chloromethyl)-1,5-dichloropentane $\boxed{5}$ for which reaction the authors observed preferential formation of the strained cyclopropyl ring instead of formation of the nearly strainless cyclopentane ring [33]:



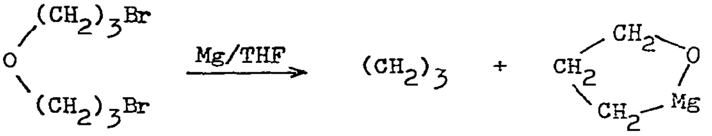
The proximity of the reactive centers is essential to the mechanism of the reaction: with n = 1 the dihalide absorbed on the magnesium



surface forms a complex with a single magnesium atom since the quasi-six-membered ring is energetically favorable. Desorption from the metal leaves the diradical which forms a cyclopropane ring.

In a footnote the authors report that preliminary investigations of this sort of reaction in which 2-methyl-2-(chloromethyl)-1,4-dichlorobutane was reacted with magnesium lead to an 80% probability for 1,3-coupling and a 20% probability for a 1,4-coupling.

It is known that γ-alkoxy-substituted Grignard compounds easily cyclize to form cyclopropane derivatives; indeed the reaction of 3,3'-dibromo-di-n-propyl ether with magnesium in THF leads to considerable amounts of cyclopropane when performed under drastic reaction conditions:



among other products

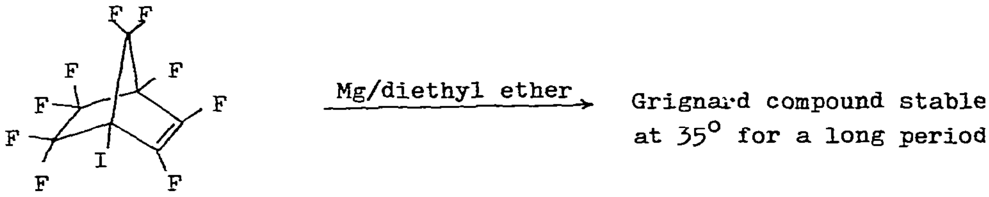
However, the desired bifunctional Grignard compound was obtained with not more than 4.5% impurities when the dihalide was added carefully to a well-stirred suspension of magnesium in THF (Blomberg, Schat, Grootveld, Vreugdenhil and Bickelhaupt [34].

Galy prepared alkoxycyclopropanes in good yields by the following reaction [35]:

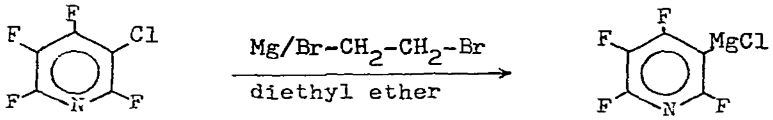
2B. Preparation of organomagnesium compounds

2Bi. Halide substituted organomagnesium compounds were reported by several groups.

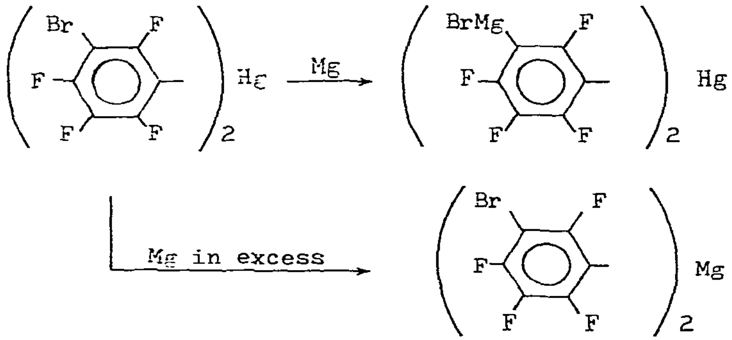
Campbell, Stephens, Tatlow and Westwood observed an unexpected stability of the Grignard reagent prepared from 1-iodo-nonafluorobicyclo-[2,2,1]hept-2-ene [36]:



Furin and Yakobson prepared the tetrafluoro-3-pyridinylmagnesium chloride by the entrainment method with diethyl ether as the solvent [37

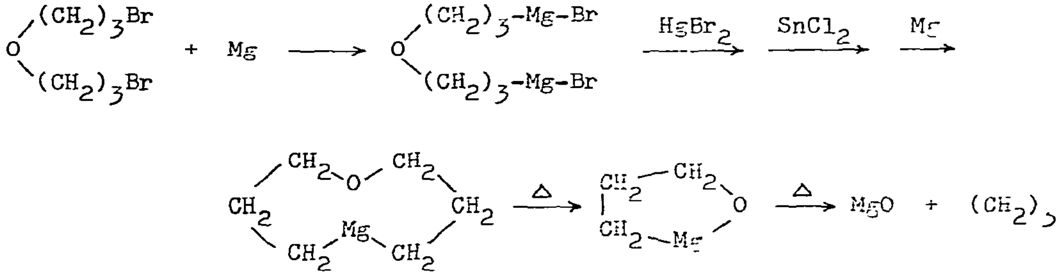


Fluorine substituted bis(monobromophenyl)mercurials may react with magnesium in a 2:1 ratio to form the corresponding Grignard compound (Delapa, Stern and Cohen [38]):

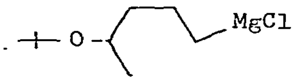


2Bii. Alkoxy substituted organomagnesium compounds

As already mentioned in Chapter 2A, 3,3'-dibromodi-n-propyl ether reacts with magnesium to form the expected Grignard reagent which was used for the preparation of several other remarkable alkoxy-substituted organomagnesium compounds [34]:



Among other alkoxy substituted Grignard compounds, reported this year, the following seem of interest:



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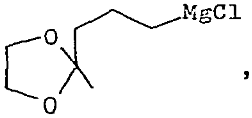

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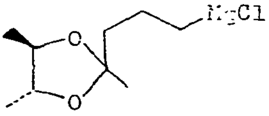

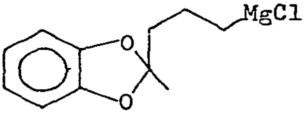

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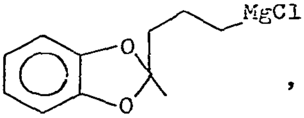

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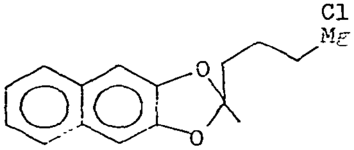
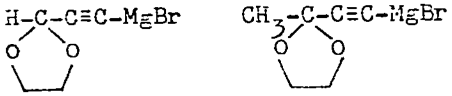
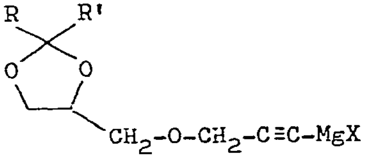


The catechol acetal moiety was found to suffer internal attack when the reaction with magnesium in THF was not carefully temperature-controled (beneath 40°). (Rosenberger, Andrews, DiMaria, Duggan and Saucy [39]).

Giusti [40] as well as Dubova, Shostakovskii, Atavin, Vasil'ev, Nedolya and Ignat'eva [41] prepared the following Iotsich reagents:

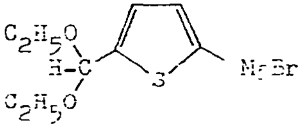


Ref. [40]

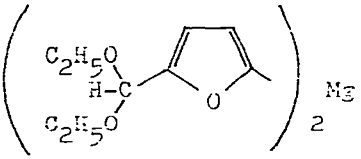


Ref. [41]

Kumishige, Sugii and Ichikawa [42] as well as Tertov, Nazarova, Gabarem and Shibaeva [43] prepared diethoxymethyl substituted organomagnesium compounds:

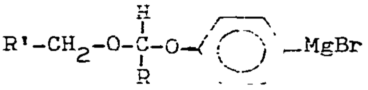


Ref. [42]



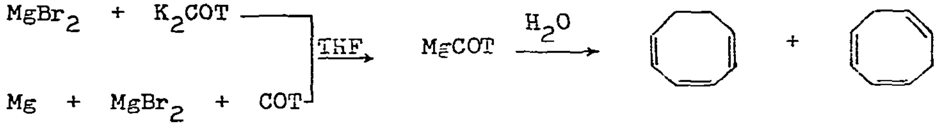
Ref. [43]

In a British Patent the following Grignard compound as well as its meta isomer were reported [44]:



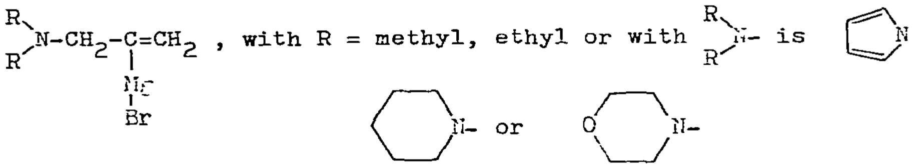
2Biii Organomagnesium compounds containing unsaturated C-C bonds

Lehmkuhl, Kintopf and Mehler prepared magnesiumcyclooctatetraene by either the reaction of potassium-COT with magnesium bromide or the reaction of magnesium with COT, catalyzed by magnesium bromide [45]:

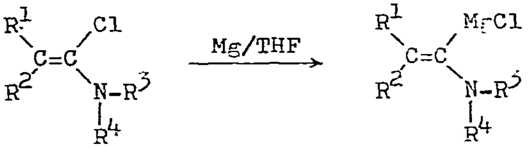


Vinylic, allenylic and acetylenic Grignard compounds have been prepared and used in a great number of references. The most important of these reactions will be discussed at the proper place in this survey. The following ones require special mention in this chapter:

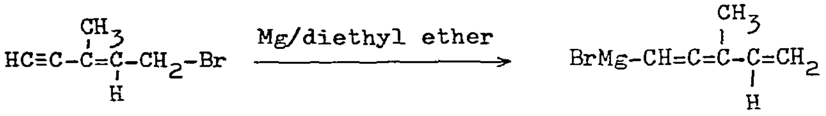
Bar, Marcinal and Marcinal-Lefebvre prepared the β-amino substituted vinylic Grignard compound of the following structure [46]:



Ghosez synthesized the α-dialkylamino-vinylic Grignard reagent of the following structure

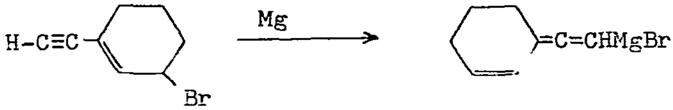


of which no other reactions are reported than the coupling reaction with a second molecule of the halide and the reaction with water [47]. As in the reactions of propargylic halides with magnesium, rearrangement of unsaturated bonds occurs in the reaction of the allylic-acetylenic bromide (or chloride) with magnesium as is indicated below (Dulcère, Roumestant and Gore [48]):

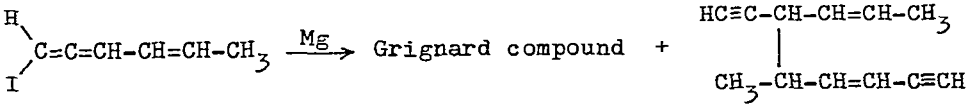


$$HC{\equiv}C-\underset{CH_3}{C}{=}\underset{H}{C}-CH_2-Br \xrightarrow{\text{Mg/diethyl ether}} BrMg-CH{=}C{=}\overset{CH_3}{C}-\underset{H}{C}{=}CH_2$$

Cyclic halides were among the halides investigated:



Hydrolysis of these Grignard compounds yielded allenylethylene derivatives but on reaction with acetone and acetaldehyde rearranged products were obtained.
The authors report that no definite information was obtained about the structure of the Grignard compound derived from iodo vinylallene:



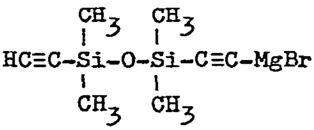
$$\begin{matrix}H\\I\end{matrix}\!\!>C=C=CH-CH=CH-CH_3 \xrightarrow{Mg} \text{Grignard compound} + \begin{array}{l} HC\equiv C-CH-CH=CH-CH_3 \\ \qquad\qquad | \\ CH_3-CH-CH=CH-C\equiv CH \end{array}$$

(considerable amounts)

The di- and tri-acetylenic Grignard compounds

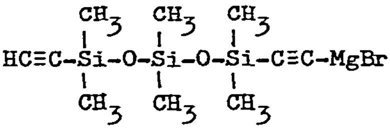
$C_6H_5-C\equiv C-C\equiv C-MgBr$ and $C_6H_5-C\equiv C-C\equiv C-C\equiv C-MgBr$

have been synthesized and used in reactions by Eastmond and Walton [49].
Komarov, Yarosh and Ivanova report the preparation and reactions of the following silyloxy-acetylenic Grignard compounds [50]:



$$HC\equiv C-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-C\equiv C-MgBr$$

and



$$HC\equiv C-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-C\equiv C-MgBr$$

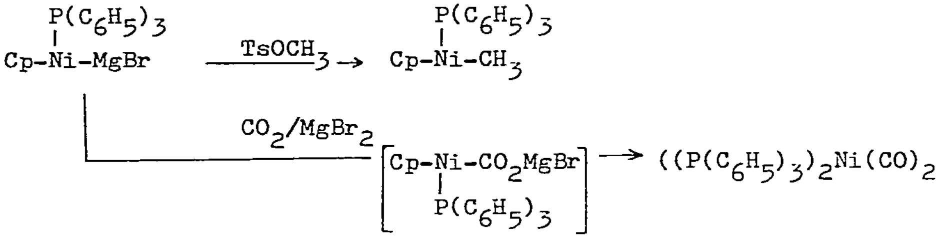
2Biv. Organomagnesium compounds containing other metals

Lahournère and Valade [51] and [52], as well as Williams [53] continued their researches in the field of "tin-" and "lead-Grignard compounds":

$(C_4H_9)_3Sn{-}MgCl$ and $(neo{-}C_5H_{11})_3Pb{-}MgCl$

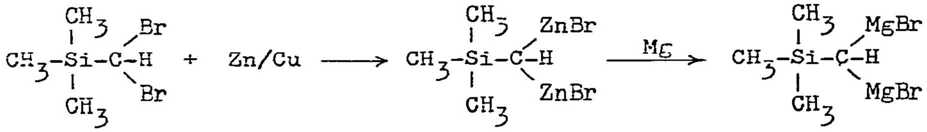
Ref. [51] and [52] Ref. [53]

One of the remarkable novel Grignard compounds reported this year is the "Nickel-Grignard compound" the existence of which had already been assumed in a previous report (Annual Survey, 1971, p.107) by Felkin and coworkers [54]:



Silicon substituted Grignard compounds do not seem very surprising anymore; Jarvie, Rowley and Bourne report (partially abnormal) reactions of methylsilylmethylmagnesium bromide ($CH_3SiH_2CH_2MgBr$) and of dimethylsilylmethylmagnesium bromide and chloride ($(CH_3)_2SiHCH_2MgX$) with phenyl substituted chlorosilanes [55], of dimethylsilylmethylmagnesium bromide with benzophenone [55A] and of the Grignard reagents prepared from (2-bromoethyl)triphenylsilane ($(C_6H_5)_3SiCH_2CH_2Br$) as well as from (2-bromopropyl)triphenylsilane ($(C_6H_5)_3SiCH_2CHBrCH_3$) of which the latter organomagnesium compound probably is not stable [56].

However the bifunctional α-silicon-substituted Grignard compound reported by Martel and Varache may be surprising, not only because of its structure but also because of the way in which it was prepared [57]:



Several complexes containing magnesium have been prepared; Seitz and Madel reported complexes with copper such as

$Cu_4Mg(C_6H_5)_6.(C_2H_5)_2O$, $Cu_4Mg(C_6H_4\text{-p-}CH_3)_6.(C_2H_5)_2O$ and

$Cu_4Mg(C_6H_4\text{-p-}CH_3)_6.xTHF$ (x probably 5) Ref.[58].

Ashby's complexes of di-isobutylmagnesium with alkali-metal hydrides were reported in the patent literature this year [59].
McVicker and Matyas report the synthesis of magnesium-transition meta complexes by the following reactions [60]:

$$M\text{-}M + Mg/Hg + base \longrightarrow base_x.Mg[M]_2$$

with M = $Fe(CO_2)C_5H_5$, $Mo(CO_2)C_5H_5L$ and other Co, Ni or Mn compounds, with L = CO and alkyl- or arylphosphines whereas THF, pyridine or tetramethylethylenediamine functioned as the bases.

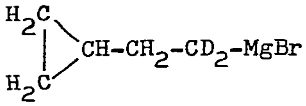
2Bv. Some other organomagnesium compounds

Khachaturov, Bresler and Poddubny prepared the deuterated methylmagnesium compound for the synthesis of the corresponding titanium(IV)-

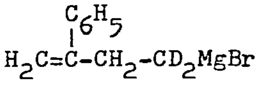
derivative [61]:

$$CD_3I + Mg \longrightarrow CD_3MgI \xrightarrow{+\ TiCl_4} (CD_3)_4Ti$$

Maercker and Theysohn synthesized the following α-deuterated Grignard compounds:



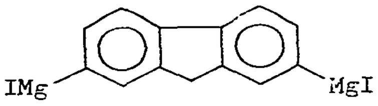
Ref. [62]



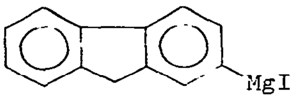
$H_2C{=}C(C_6H_5){-}CH_2{-}CD_2MgBr$

Ref. [63].

The fluorenyl Grignard compounds $\boxed{6}$ and $\boxed{7}$ were reported by Minabe and Suzuki [64]

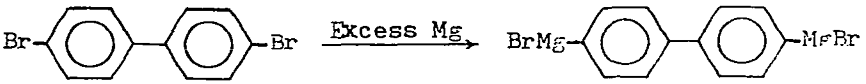


$\boxed{6}$



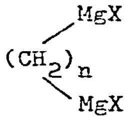
$\boxed{7}$

By using an extremely large excess of magnesium in the reaction of 4,4'-dibromobiphenyl with magnesium in THF Odabashyan, Romashin and Pashenko obtained the corresponding bifunctional Grignard compound in very high yields [65]:



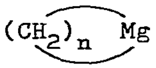
97% yield

The French groups of Soussan and Frêon and of Denise, Ducom and J.-F. Fauvarque have prepared the aliphatic bifunctional Grignard compounds $\boxed{8}$, and the latter group also synthesized the corresponding cyclic organomagnesium compounds $\boxed{9}$



n = 4,5 or 6 [66],[67] and [68] ;
and n = 10 [66]

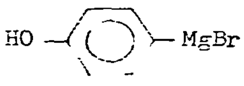
$\boxed{8}$



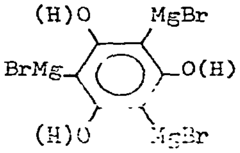
n = 4, 5 or 6 [68]

$\boxed{9}$

Two U.S. Patents claim the preparation of phenolic Grignard compounds, $\boxed{10}$ being monofunctional [69] and $\boxed{11}$ even being trifunctional !! [70

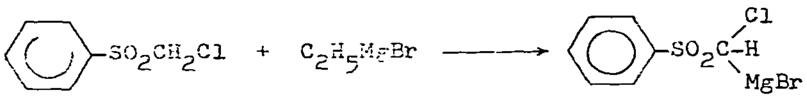


$\boxed{10}$



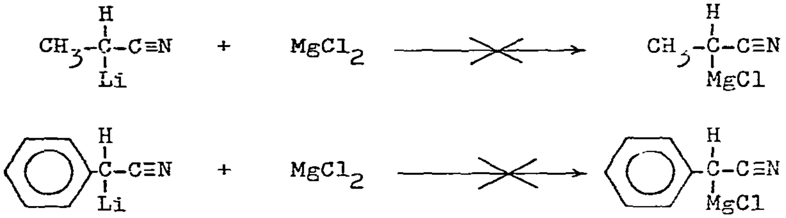
$\boxed{11}$

The chloro phenylsulfonylic disubstituted Grignard compound $\boxed{12}$ is reported to be stable; Stetter and Steinbeck obtained the expected products on reaction with carbon dioxide, aldehydes etc. [71]:

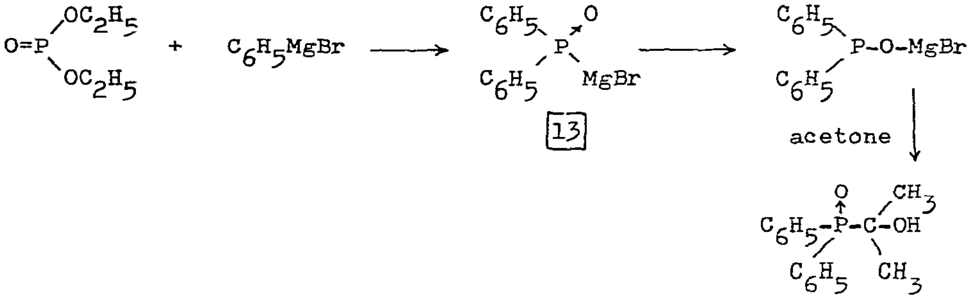


$\boxed{12}$

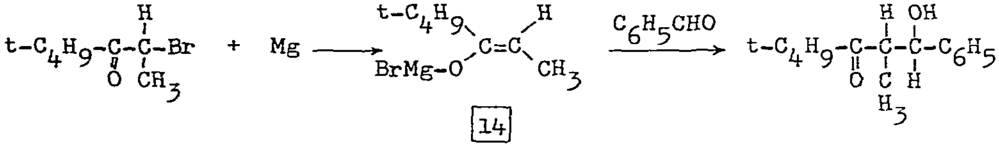
Das and Wilkie found no evidence for the formation of the Grignard reagent derived from acetonitrile or from phenylacetonitrile [72]; the infra-red spectra show absorption for C=N as well as for N-H but not for C≡N;



Cann, Warren and Williams reported the synthesis of diphenylphosphinyl derivatives by reactions of the "Grignard reagent of diphenylphosphine oxide" $\boxed{13}$ which in fact is the bromomagnesium ester [73]:

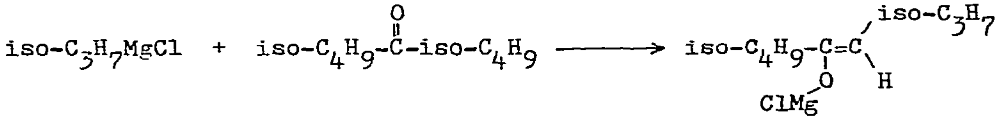


Dubois and Fellmann, repeating the preparation of the Grignard compound from 2-bromo-4,4-dimethyl-3-pentanone (Malmgren 1903) $\boxed{14}$, assigned an enolate structure to it [74]. On reaction with benzaldehyde the expected ketoalcohol is formed:

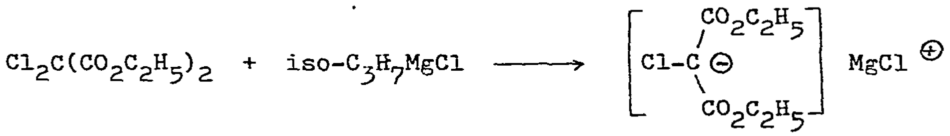


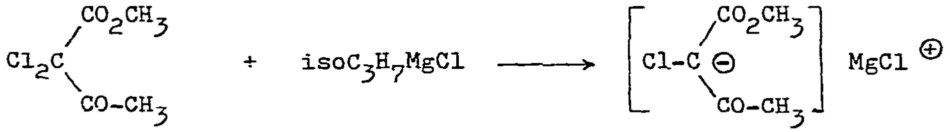
The same sort of Grignard reagent was investigated by Maroni-Barnaud and Koudsi [75] as well as by Maroni-Barnaud, Maroni and Gorrichon-

Guigon [76]; for example

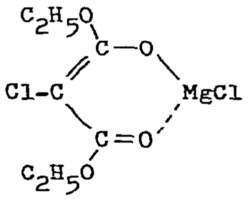


Villiêras prepared Grignard compounds derived from dichloromalonic esters as well as from dichloroacetoacetic ester in excellent yields [77]:

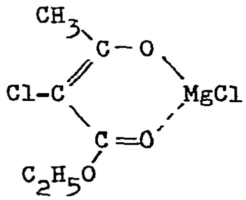




Although these Grignard compounds show no reactivity towards carbonyl compounds they do react with chloromethyl ethers and allyl bromide. The author proposes the following structures for the organomagnesium compounds



and



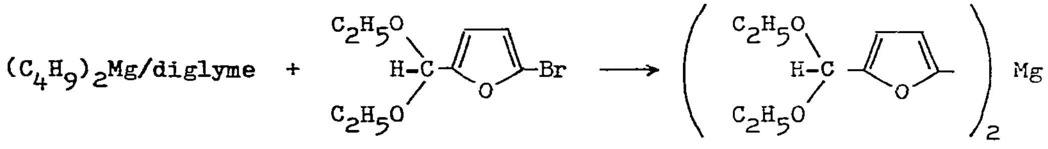
2C. New or uncommon reactions leading to the formation of organomagnesium compounds

There are not many reactions which lead to the formation of organomag sium compounds that may surprise modern chemists anymore; the exception in this year is the use of ground-state atomic magnesium (^1S) for this purpose by Skell and Girard [78]. High vacuum evaporation of heated magnesium produces this special type of magnesium which was co-deposited at -196° with alkyl halides to produce a black matrix. Warm-up of such a matrix produces unsolvated Grignard reagents, the yields of which were determined by hydrolysis: n-propyl iodide, 76%; isopropylbromide, 55%; tert-butyl bromide, 5%; chlorobenzene, 58%: vinyl bromide, 78%.

These solvent-free Grignard reagents do not behave like "normal" ones. With acetone e.g. only enoliztion is observed by n-propylmagnesium bromide.

The production of dialkylmagnesium compounds by reaction of organomagnesium halides with alkyllithium compounds (Eastham and Kamienski, Annual Survey 1967, p. 200) appeared in the patent literature this year [79].

The following transmetallation reaction requires special mention [43]:



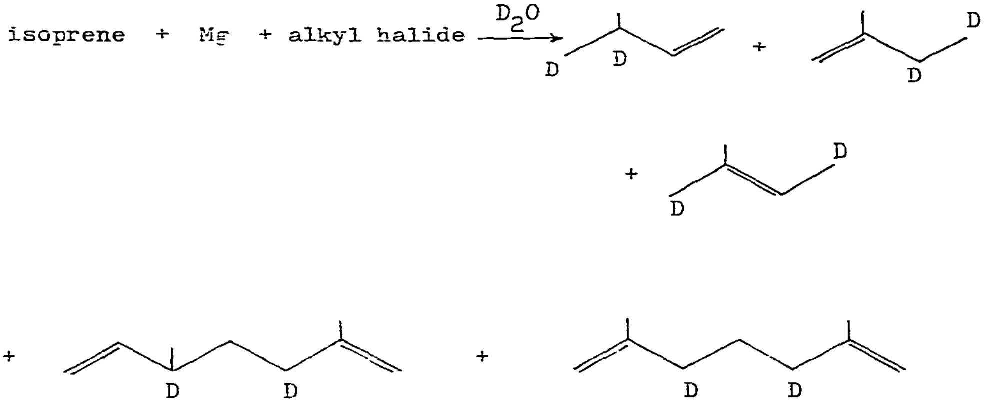
The formation of a bifunctional α-silicon substituted Grignard compound by reaction of magnesium with the corresponding bromozinc derivative has been mentioned in Chapter 2Biv [57].

In Chapter 2Biii an example has been given of the production of unsaturated organomagnesium compounds by reaction of cyclooctatetraene with magnesium in the presence of some catalysts. The patent literature this year reports several more reactions of this type:

Ramsden reacted magnesium with diolefins in THF with bromoethane or 1,2-dibromoethane as the "activators" [80].

Sakaguchi, Akutagawa and Komasu [81] and [82], as well as Moriya, Akutagawa and Komatsu [83] obtained bifunctional organomagnesium compounds on reaction of isoprene with magnesium in the presence of catalysts such as Pd/C or $PdCl_2$/benzonitrile [81], bis(triphenylphosphine) nickel(II) chloride and butylmagnesium bromide [82] and iron (III) or copper(II) chloride [83].

In an extension of this type of reaction, Nakano, Natsukawa, Yasuda and Tani [84] compared the products obtained with two different catalysts, alkyl halide (1%-mol of Mg) and bis(triphenylphosphine)nickel (II) bromide.



With the nickel catalyst the reaction yields D-free products whereas monodeuterated products are obtained on deuterolysis. The authors suggest that nickel hydride, produced by reduction of the nickel catalyst by the organomagnesium compound, transfers hydrogen which originates from the isoprene and not from the solvent: no deuterium was present in the hydrolysis products when the reaction was performed in THF-d_8. Although not leading to the formation of an organomagnesium compound, the report in the patent literature of the preparation of magnesium hydride by the following reaction

$$\text{Mg(turnings)} + \text{butadiene} \xrightarrow[H_2,\ 80\ \text{atm.}]{\text{THF}\ 90^{\circ}\ 6\ \text{hr}} MgH_2$$

requires to be mentioned in the context of the previous reports [85]. Finally the synthesis of magnesium-transition metal complexes as mentioned in Chapter 2Biv is also rather uncommon [60]:

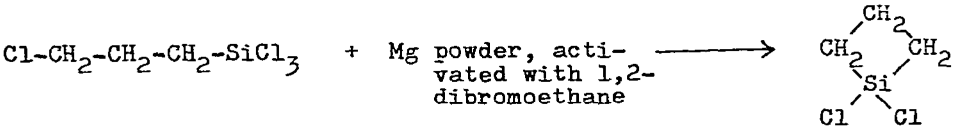
$$\text{M-M} + \text{Mg/Hg} + \text{base} \longrightarrow \text{base}_x\text{.Mg[M]}_2$$

with M= e.g. $Fe(CO)_2C_5H_5$ and base e.g. is pyridine.

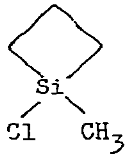
2D. Reactions with intermediate or "in situ" Grignard compounds

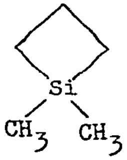
A surprisingly large number of publications appeared this year on the synthesis of organic compounds with the aid of intermediate or "in situ" Grignard compounds. However, the question rises whether in all cases of so-called Wurtz-type coupling reactions, which will be mentioned first in this chapter, intermediate Grignard compounds indeed have been formed.

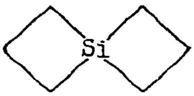
The formation of silacyclobutanes was reported by Damrauer, Davis, Burke Karn and Goodman [86]:



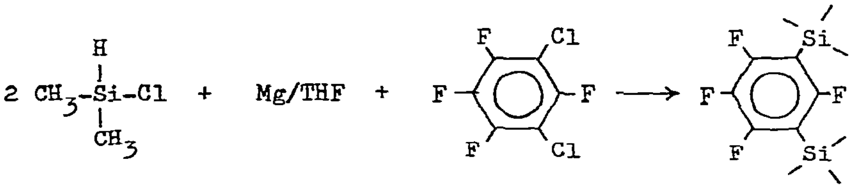
Also prepared by the same procedure were:



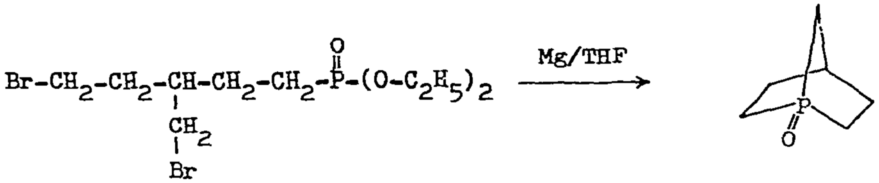




The same sort of coupling reaction was reported in a German Patent [87]:



It was already mentioned in Chapter 2Bv that tne bifunctional Grignard compound derived from para dibromobenzene was obtained in good yields by using an excess of magnesium. The authors report that the highest yields of coupling products with trimethylchlorosilane were obtained by the "in situ" Grignard procedure where the dibromide is allowed to react with magnesium in the presence of the silane [65]. From the report by Wetzel and Kenyon it is not clear whether in the reaction



an intermediate bifunctional Grignard compound has been formed, or whether cyclization occurs directly during the reaction of the dibromide with magnesium [88].

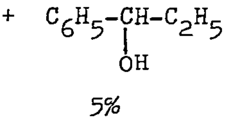
Miyano, Miyazaki, Takeda and Hashimoto discovered that the amount of mercury in the magnesium amalgam used in the reaction with diiodomethane and benzaldehyde (Cainelli and coworkers, Annual Survey 1970 p.342) is of rather great influence on the yield of styrene [89]

$$CH_2I_2 \quad + \quad \text{Mg/ one gat-\% Hg} \quad + \quad C_6H_5CHO \longrightarrow C_6H_5\text{-}CH{=}CH_2$$

Yields with p-methylbenzaldehyde, 75%; p-chlorobenzaldehyde, 67 %; n-heptaldehyde, 48%; 3-pentanone, 68%; cyclohexanone 38%.

In another publication, the Japanese authors state that the same reaction in the absence of mercury gives a mixture of products [90]:

$$CH_2I_2 \quad + \quad Mg \quad + \quad C_6H_5CHO \longrightarrow \underset{29\%}{C_6H_5\text{-}CH{=}CH_2} \quad + \quad \underset{22\%}{C_6H_5\text{-}CH_2OH} \quad +$$

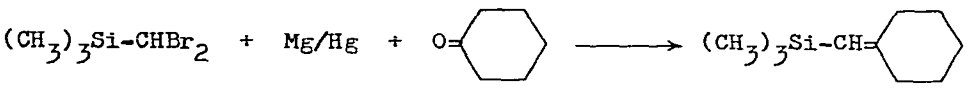


$$+ \quad \underset{5\%}{C_6H_5\text{-}\underset{\displaystyle OH}{\underset{|}{C}H}\text{-}C_2H_5}$$

\+ tarry residues
after distillatio

The formation of alcohols and of tarry materials appears to limit the yield of carbonylmethylenated products.

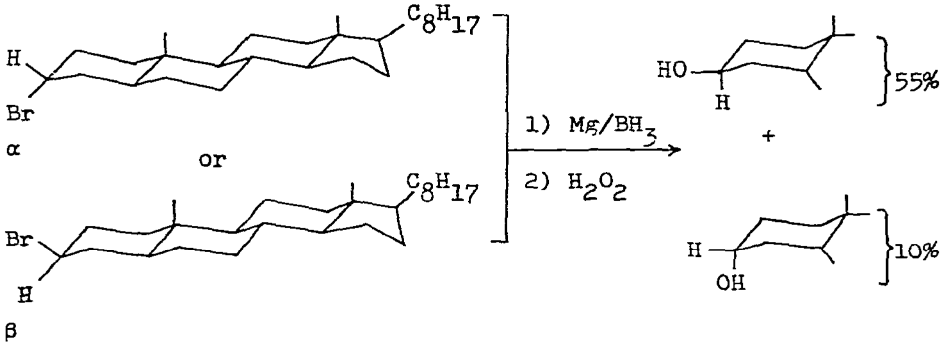
An analogous bifunctional Grignard intermediate was used by Martel and Varache in the following synthesis [57]:



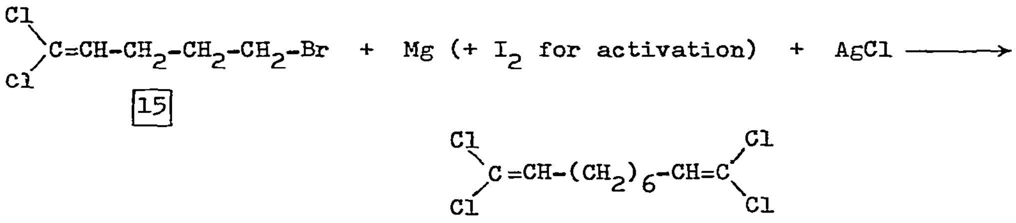
Breuer and Broster found a convenient new route to organoboranes by reacting alkyl or aryl halides with magnesium in the presence of diborane [91] and [92]:

$$R\text{-}X + Mg + B_2H_6 \xrightarrow[\text{reflux}]{\text{THF}} R_3B$$

Even for 1-bromoadamantane the method works satisfactorily: 48% 1-hydroxyadamantane was obtained on subsequent oxidation.
Breuer also investigated the stereochemical course of the reaction by using steroidal halides [93]: the boranes obtained were converted to the alcohols by treatment with alkaline hydrogen peroxide.

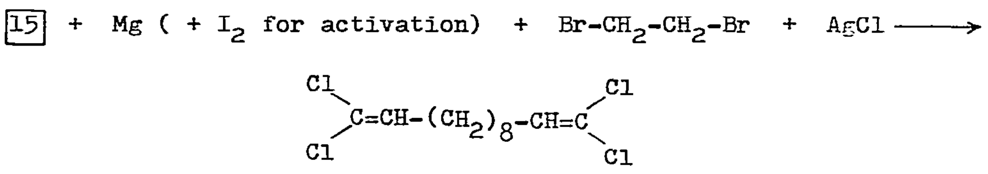


From both the 3α- and the 3β-bromo-5α-cholestanes the β-hydroxy derivative was obtained in excess.
Kruglova and Freidlina used freshly prepared silver chloride for an "in situ" Grignard coupling reaction [94]:


15

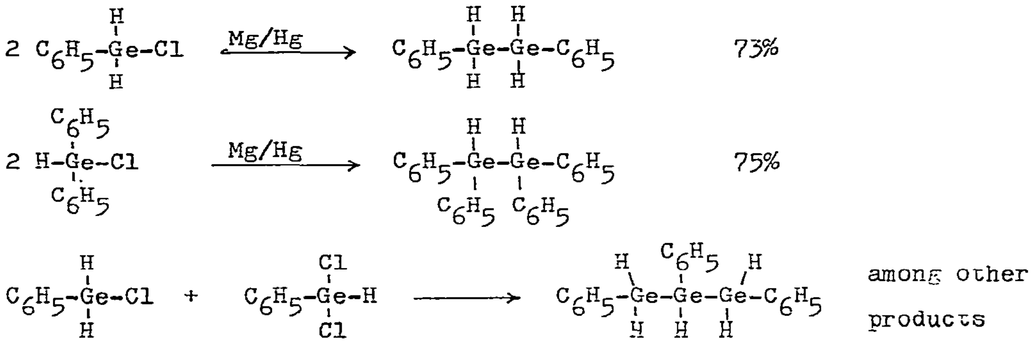
$$Cl_2C{=}CH{-}CH_2{-}CH_2{-}CH_2{-}Br + Mg\ (+\ I_2 \text{ for activation}) + AgCl \longrightarrow Cl_2C{=}CH{-}(CH_2)_6{-}CH{=}CCl_2$$

Very surprising is their report of the following reaction:



$$\boxed{15} + Mg\ (+\ I_2 \text{ for activation}) + Br-CH_2-CH_2-Br + AgCl \longrightarrow Cl_2C=CH-(CH_2)_8-CH=CCl_2$$

Rivière and Satgé obtained di- and tri-germanes in excellent yields when chlorogermanes were subjected to Wurtz-type coupling reactions [95]:

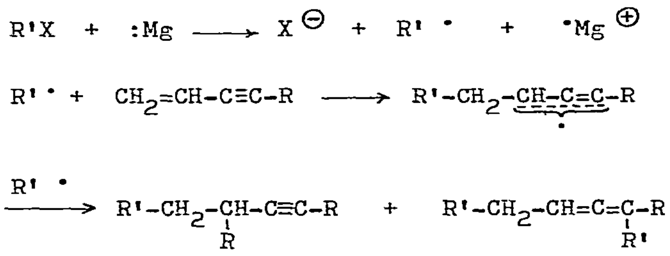


$$2\ C_6H_5-GeH_2-Cl \xrightarrow{Mg/Hg} C_6H_5-GeH_2-GeH_2-C_6H_5$$ 73%

$$2\ H-Ge(C_6H_5)_2-Cl \xrightarrow{Mg/Hg} C_6H_5-GeH(C_6H_5)-GeH(C_6H_5)-C_6H_5$$ 75%

$$C_6H_5-GeH_2-Cl + C_6H_5-GeHCl_2 \longrightarrow C_6H_5-GeH_2-GeH(C_6H_5)-GeH_2-C_6H_5$$ among other products

As Pis'mennaya, Cherkasov, Petrov and Bal'yan observed, vinylacetylenes do not react react with Grignard reagents, contrary to vinylacetylenyl thioethers (Radchenko, Cherkasov, Pis'mennaya and Bal'yan, Annual Survey 1970, p. 374); However, vinylacetylenes do react with "in situ" Grignard compounds [96]. In THF the Grignard adds to the enynes in the 1,2- as well as in the 1,4-position. In diethyl ether or in dibutyl ether, hexane or triethylamine two alkyl radicals of the halides used add to the multiple bonds, possibly according to a diradical scheme:



$$R'X + :Mg \longrightarrow X^{\ominus} + R'^{\bullet} + {}^{\bullet}Mg^{\oplus}$$

$$R'^{\bullet} + CH_2{=}CH{-}C{\equiv}C{-}R \longrightarrow R'{-}CH_2{-}\underbrace{CH{=}C{=}C}_{\bullet}{-}R$$

$$\xrightarrow{R'^{\bullet}} R'{-}CH_2{-}\underset{R}{\underset{|}{C}}H{-}C{\equiv}C{-}R + R'{-}CH_2{-}CH{=}C{=}\underset{R'}{\underset{|}{C}}{-}R$$

In a later report Radchenko and Cherkasov report the same sort of addition reaction of "in situ" ethylmagnesium bromide with seleno and telluro ethers of vinylacetylene [97]:

$$CH_2{=}CH{-}C{\equiv}C{-}Se{-}CH_3 + C_2H_5Br + Mg \longrightarrow C_3H_7{-}CH{=}C{=}C{-}Se{-}CH_3$$

A more unexpected coupling reaction

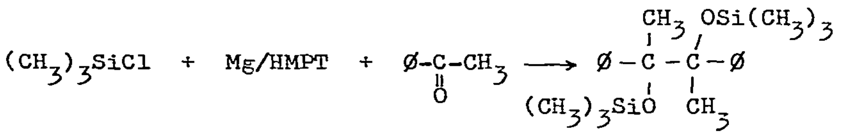
$$N{\equiv}C{-}CH{=}CH_2 + Mg + CoCl_2 \longrightarrow \text{product} \xrightarrow{H_2O} N{\equiv}C{-}(CH_2)_4{-}C{\equiv}N$$

was mentioned in a Japanese patent [98].

Obe, Sato and Matsuda investigated the Barbier-Grignard method for th synthesis of 4-undecanol: the reaction of n-butyl halides with magnesium in the presence of heptanal [99]. Only when using the bromide did the authors obtain a slightly better yield of the undecanol by the Barbier-Grignard method, as compared with the results obtained by the common two-step Grignard synthesis: 50.7% as compared with 46.1%. When iodobutane was used in a two-fold excess over heptanal, 43% undecanol was obtained. In a 1:1 reaction mixture only 1.2% of this product was formed!

Ten publications have appeared this year dealing with the reaction of "in situ" trimethylsilylmagnesium chloride, formed in the reaction of trimethylchlorosilane with magnesium in HMPT in the presence of a substrate.

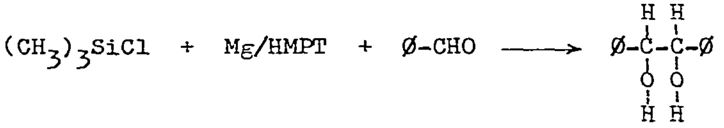
Chan and Vinokur exclude a ketyl radical intermediate in the following duplication reaction of acetophenone [100]:



$$(CH_3)_3SiCl + Mg/HMPT + \varnothing\text{-}\underset{\overset{\|}{O}}{C}\text{-}CH_3 \longrightarrow \varnothing-\underset{(CH_3)_3SiO}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{OSi(CH_3)_3}{C}}-\varnothing$$

Ø = phenyl

With benzaldehyde the authors observed the following reaction:



$$(CH_3)_3SiCl + Mg/HMPT + \varnothing\text{-}CHO \longrightarrow \varnothing\text{-}\underset{\underset{H}{O}}{\overset{H}{C}}\text{-}\underset{\underset{H}{O}}{\overset{H}{C}}\text{-}\varnothing$$

d,l : meso = 3 : 1

over 90% yield

Nine other publications of reactions including the trimethylchlorosilane/Mg/HMPT reagent came from the laboratory of Calas. It is to be hoped for that a review paper will soon appear!

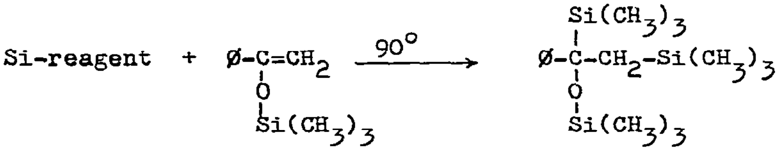
The nine publications will only very shortly be summarized here.

Reference [101]:

$$\text{Si-reagent} + Br\text{-}CH_2\text{-}C{\equiv}CH \xrightarrow{50-60^{\circ}} (CH_3)_3Si\text{-}CH_2\text{-}C{\equiv}CH \text{ and } (CH_3)_3Si\text{-}CH{=}C{=}CH_2$$

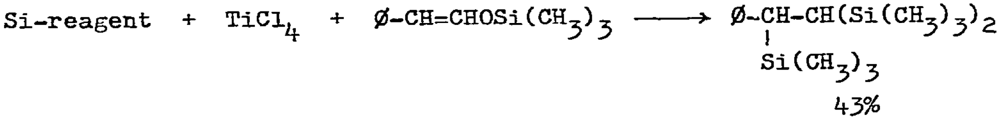
both products in a 3:1 ratio with a total yield of 71%

Reference [102]:



$$\text{Si-reagent} + \varnothing\text{-}\underset{\underset{Si(CH_3)_3}{O}}{C}{=}CH_2 \xrightarrow{90^{\circ}} \varnothing\text{-}\underset{\underset{Si(CH_3)_3}{O}}{\overset{Si(CH_3)_3}{C}}\text{-}CH_2\text{-}Si(CH_3)_3$$

45%

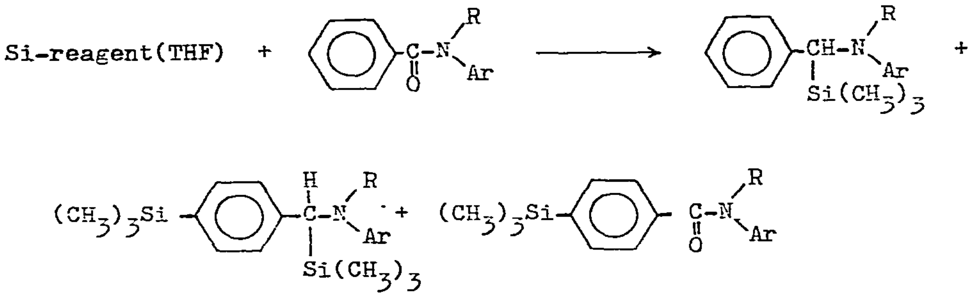


$$\text{Si-reagent} + TiCl_4 + \text{Ø-CH=CHOSi}(CH_3)_3 \longrightarrow \underset{\substack{|\\ Si(CH_3)_3}}{\text{Ø-CH}}\text{-CH(Si}(CH_3)_3)_2$$

43%

Reference [103]:

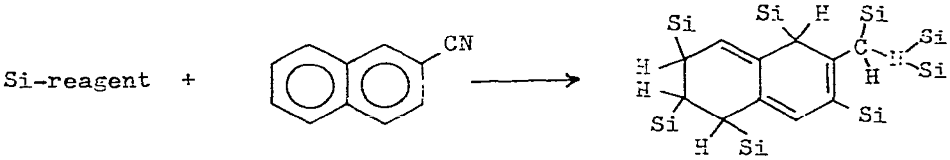
THF used instead of HMPT in the Si-reagent



Radical intermediates are supposed to be formed, which may take up an electron from magnesium to form an anion, stabilized by the aromatic ring.

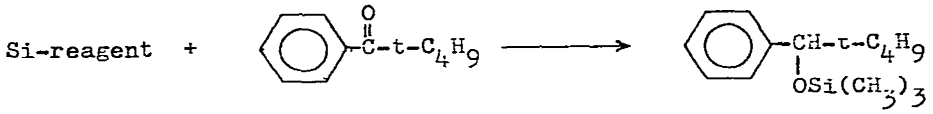
Reference [104]:

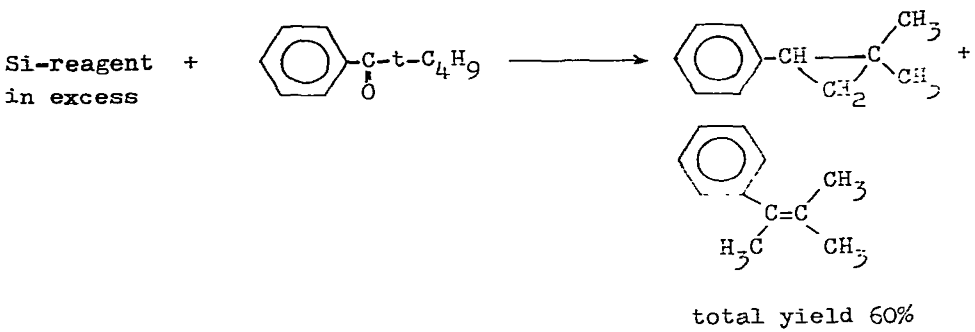
Si-reagent may react with aromatic nitriles to give several products of which the following one is an example of a repeated addition reaction:



Si = $(CH_3)_3Si-$

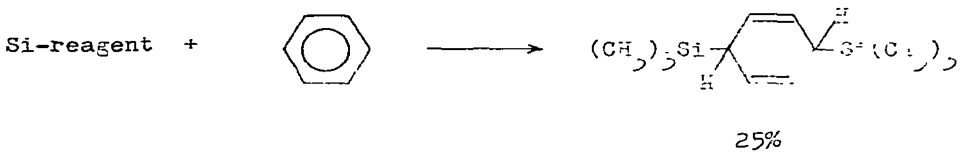
Reference [105]:





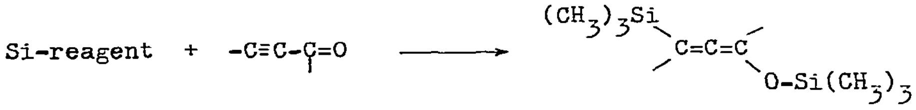
The authors prefer to assume a mechanism with carbenoid intermediates in this reaction.

Reference [106]:

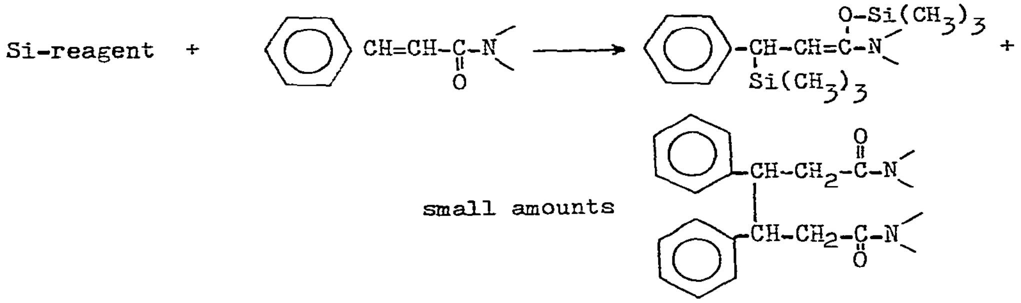


When lithium is used instead of magnesium in the Si-reagent the yield of the same product increases to 60%.

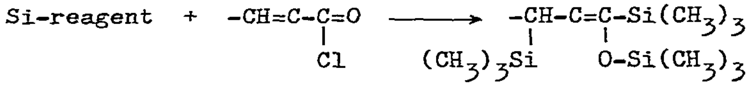
Reference [107]:



Reference [107A]:



Reference [107B]:



$$\text{Si-reagent} + \text{-CH=}\underset{\text{Cl}}{\text{C}}\text{-C=O} \longrightarrow \text{-}\underset{(\text{CH}_3)_3\text{Si}}{\text{CH}}\text{-C=}\underset{\text{O-Si(CH}_3)_3}{\text{C}}\text{-Si(CH}_3)_3$$

A very peculiar "in situ" Grignard was reported by Martel and Varache [108]:

$$(CH_3)_3SiCl + CH_2ClC{\equiv}N + i\text{-}C_3H_7MgCl \xrightarrow[THF]{-50^\circ} [\ ClMgCHC{\equiv}N\ ]$$

$$\longrightarrow C_3H_8 + MgCl_2 + (CH_3)_3SiCHC{\equiv}N$$

When the reaction was performed in two steps, product analysis suggested the existence of the bifunctional Grignard reagent

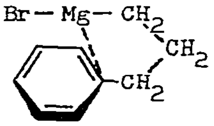
$$(ClMg)_2CClC{\equiv}N$$

as an intermediate!

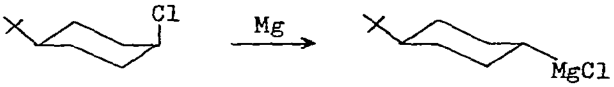
3. PHYSICAL PROPERTIES, STRUCTURE AND MOLECULAR ASSOCIATION OF ORGANOMAGNESIUM COMPOUNDS

3A. NMR studies of organomagnesium compounds

Magnuson and Roberts observed the appearence of two overlapping quartets from the methylene proton resonances in the NMR-spectrum of 0.33M ethylmagnesium bromide in THF in the presence of 0.18 M N,N,N',N'-tetramethylethylenediamine when the temperature of the solution was lowered to -50° [109]. These different signals have to be attributed to methylene groups in two different species, i.e. C_2H_5MgBr and $(C_2H_5)_2Mg$ "which supports the existence of the Schlenk equilibrium". Together with Leibfritz and Wagner, Roberts published the results of ^{13}C-NMR investigations of Grignard compounds in diethyl ether [110]. These indicate that at higher concentrations , benzylmagnesium chloride exists almost completely as a mixture of dibenzylmagnesium and magnesium chloride. ^{13}C-NMR spectra also were measured of 2-phenylethylmagnesium bromide and 3-phenylpropylmagnesium bromide. In the latter compound, the ^{13}C-chemical shift of the aromatic C_1 indicates that interaction occurs between the magnesium atom of the Grignard compound and the carbon atom as is shown in the following structure:



From the ^{13}C-NMR spectra of solutions of methylmagnesium iodide and of ethyl-, n-propyl-, n-butyl-, n-pentyl- and isopropylmagnesium bromide as well as of cyclohexyl- and 4-tert-butylcyclohexylmagnesium chloride it must also be concluded that R_2Mg is the main compound in diethyl ether solution. Furthermore, the results indicate that 4-tert-butylcyclohexylmagnesium chloride is mainly in the trans-form in solution

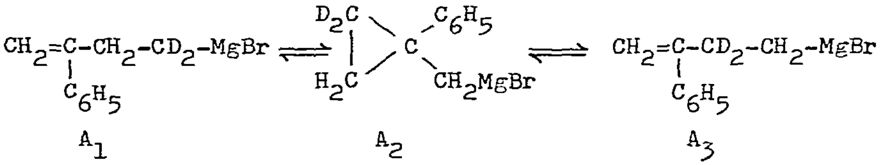


The extraordinary chemical shifts in allylmagnesium bromide justify the existence of an ion-pair

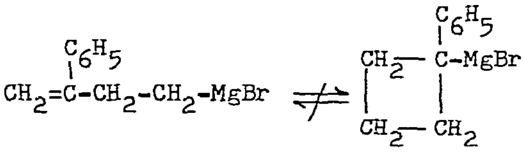
allyl ⊖...⊕MgBr

which seems in contradiction with earlier results, obtained by J.D. Roberts and Zieger (1969).
The authors also studied the ^{13}C-NMR spectra of cyclopentadienylmagnesium bromide.
Ladd and Parker examined the NMR-spectra of a variety of meta- and para-substituted phenylmagnesium bromides in diethyl ether. The large chemical shifts differences between the ring protons permitted a detailed analysis of the spectra and thus of the influence of the substituent on both the chemical shift and the spin-spin coupling constants [111].
^{1}H-NMR spectra of cyclopentadienylmagnesium halides differ from those of dicyclopentadienylmagnesium in THF at room temperature (Ford and Grutzner [112]). On cooling, the spectra of the Grignard compound show a second peak which is the only one at -75°. The authors conclude that at roomtemperature in THF the R-Mg-X form predominates. The change in the spectra with temperature allowed the authors to calculate Schlenk equilibrium constants for both the bromide and the chloride. The constants vary with temperature (for the bromide from 13.6 at -90° to 233 at -65°).

In Chapter 2A it has already been reported that Mêchin and Naulet, with the aid of NMR techniques, came to the conclusion that substituted vinylic Grignard compounds were configurationally stable [30].
Maercker and coworkers investigated rearrangements of allylcarbinyl and of cyclopropylethyl Grignard reagents with the aid of NMR-spectroscopy.
The equilibrium:



is reached within eight hours at 100° in diethyl ether, whereas in THF this requires a much longer period of heating (Maercker and Weber [63]). No evidence was found for the equilibrium:

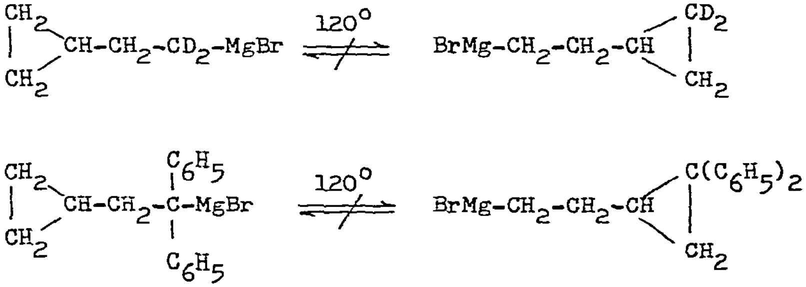


In a second paper Maercker and Weber studied the kinetics of the above mentioned homoallylic rearrangement ($A_1 \rightleftharpoons A_2 \rightleftharpoons A_3$) with the aid of NMR-spectroscopy [113]. Neither chemical nor spectroscopical evidence was found for the existence of the cyclopropyl intermediate. The rate of equilibration depended on several factors: a) the temperature, b) the basicity of the solvent (faster in diethyl ether than in THF) c) the electropositivity of the metal (rate of rearrangement of dialkylmagnesium compound faster that of the Grignard compound), d) the concentration (rate increases linear with the concentration), e) the presence of salt in the solution (magnesium bromide enhances the rate of rearrangement).

Furthermore, the authors found that an unusually high secondary isotope effect was found to promote the formation of A_3.

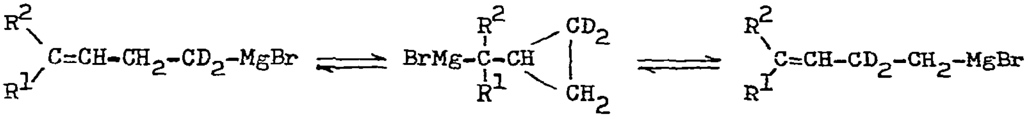
The mechanism for this rearrangement of the organomagnesium compound probably is a bimolecular one in which ate-complexes of the compounds are involved.

In a third paper with Theysohn, Maercker reports that no rearrangement whatsoever was observed of the following Grignard compounds [62]:

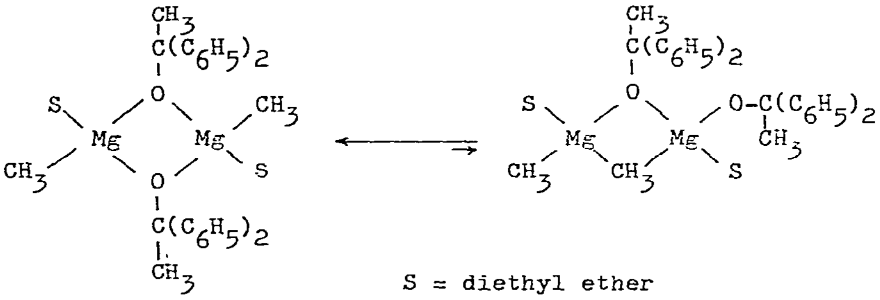


In several weeks the Grignard reagent reacted with the solvent and the concentration diminished gradually.

Together with Streit Maercker studied the rearrangement of 3-butenyl Grignard reagents [114]:



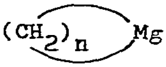
No CIDNP signals could be observed and since also the four different Grignard reagents under investigation rearranged with very different rates, the authors concluded that a radical mechanism for the rearrangement is eliminated. From the kinetic results the authors conclude that the cyclopropyl derivative has to be a bona fide intermediate. NMR-spectroscopical data suggest that the following equilibrium is shifted completely to the left (Ashby and Nackashi [115]):



The same authors also investigated the structure of the complex formed by the abovementioned alkoxide with dimethylmagnesium: CH_3Mg-O-$C(C_6H_5)_2CH_3.Mg(CH_3)_2$. This complex too may have one structure with and one structure without a methyl-group in the bridge position. As it might be of (future ?) interest for organomagnesium chemistry, it is reported now that a rather late abstract was registered of a report by Magnusson and Bothner-By on the ^{25}Mg NMR-spectroscopy of complexes in biochemistry [116].

3B. Other techniques

Denise, Ducom and Fauvarque studied the degree of association of magnesiacycloalkanes:



n = 4, 5 or 6

by cryoscopic methods [67]. Both in dioxane and in HMPT the cyclic magnesium compounds appear to be monomeric: i-values between 1.11 and 1.5, Conductometric measurements by the same authors showed that the bifunctional Grignard compounds

$$BrMg\text{-}(CH_2)_n\text{-}MgBr \qquad n = 4,\ 5 \text{ or } 6$$

are excellent conductors in HMPT. For n = 4 the conductivity in this solvent is equal to the conductivity of magnesium bromide. For n = 5 er 6 it was even slightly better! Since the conductivity of magnesiacyclopentane is very small in HMPT these results indicate that the bifunctional Grignard compound exists in the equilibrium

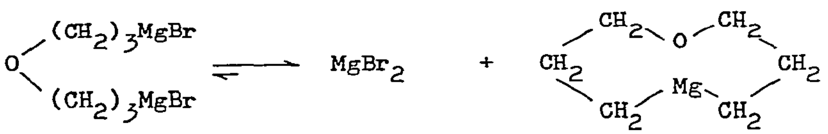
$$(CH_2)_nMg_2Br_2 \rightleftharpoons (CH_2)_nMg_2Br^{\oplus} + Br^{\ominus}$$

which is completely shifted to the right.

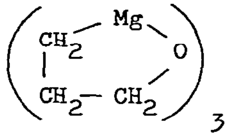
In the weakly basic solvent diisopropyl ether ethylmagnesium bromide is essentially dimeric at concentrations up to 0.040M at 27.7^{o} (Voorbergen, Blomberg and Bickelhaupt [117]). Diethylmagnesium is present in a dimer-tetramer equilibrium with K_1 = 24.9 l/mol. Addition of magnesium bromide to a solution of diethylmagnesium in the same solven causes the formation of ethylmagnesium bromide which associates with excess diethylmagnesium to form a complex with the formula:

$$C_2H_5MgBr.(C_2H_5)_2Mg$$

(The degrees of association were measured in an apparatus in which the rate of quasi-isothermal distillation of the solvent is measured) By the same technique the degree of association was measured of the bifunctional Grignard compound derived from 3,3'-dibromodipropyl ether [34]. The equilibrium

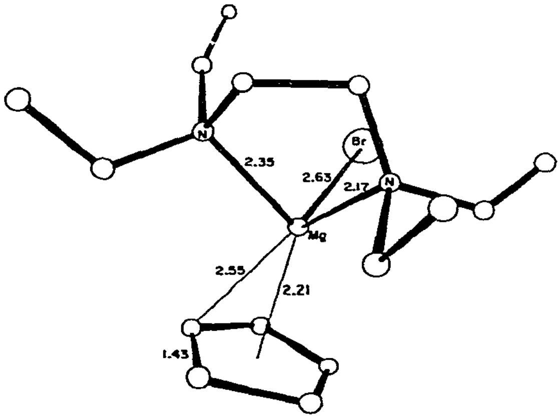


is completely shifted to the right. At the same laboratory it was found that the thermal decomposition product of the cyclic oxamagnesia compound is trimeric:



Evans, Green, Jewitt, Orchard and Pygall measured He(I) photoelectron spectra of bis(π-cyclopentadienyl)magnesium as well as of bis(π-methylcyclopentadienyl)magnesium [118]. Their results among others lend support to the traditional picture of Mg(π-cyclopentadienyl) as an "ionic" compound.

C. Johnson, Toney and Stucky obtained the following "average configuration" of $C_5H_5MgBr.(C_2H_5)_2N(CH_2)_2N(C_2H_5)_2$ by means of X-ray analysis [119]:

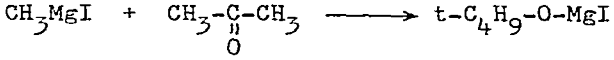


The Mg-Br distance is the same as that for the six-coordinate magnesium in $MgBr_2(C_4H_8O)_4$. The C-C distance of 1.43 Å is consistent with a π-$C_5H_5^{\ominus}$ group being coordinated to the magnesium.

It might be of interest for organomagnesium chemists to know that Guillermet and Novak interpreted the IR-spectra of $MgBr_2((C_2H_5)_2O)_2$ in terms of a single ether conformer [120]. The spectral changes upon complexation are supposed to be due principally to the weakening of the bonds.

Turova and Turevskaya reported that the following two reactions yielded the same tert-butylalkoxide [121]:

$$CH_3MgI + t\text{-}C_4H_9\text{-}OH \longrightarrow t\text{-}C_4H_9\text{-}O\text{-}MgI$$



$$CH_3MgI + CH_3\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_3 \longrightarrow t\text{-}C_4H_9\text{-}O\text{-}MgI$$

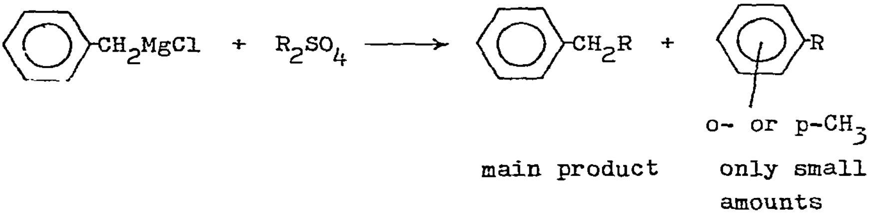
IR-spectra as well as diffraction patterns showed that magnesium had a tetrahedral coordination, as found for the bromide analog, and the molecule was dimeric.

Allavena and Besnainou made some conformational studies of the MgF_2 molecule with the aid of à priori as well as of semi-empirical calculations [122].

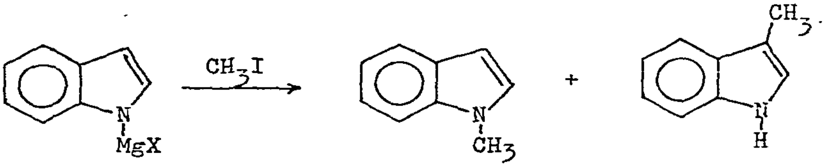
By the same sort of theoretical conformational analysis, Lebarre and Leibovici concluded that the X-M-X angles in magnesium fluoride and in magnesium chloride are 140° and 136°, respectively [123].

3C. Structure and reactions

Benkeser reports the results of reactions of benzylmagnesium chloride with dialkylsulfates which yield mainly the unrearranged products and only small amounts of ortho and para substituted benzene derivatives [124]

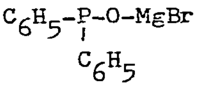


Reinicke, Sebastian, Johnson and Pyun investigated another type of Grignard reagent, well-known for its rearrangement during reactions with typical substrates: i.e., the indolylmagnesium halides [125]:



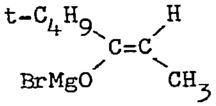
In THF as the solvent the bromide yields exclusively the C-methylated product; in HMPT, however, the N-methylated product was the only one that could be isolated. Apparently in weaker basic solvents the indole Grignard reagent holds the magnesium atom so tightly that N-alkylation is not obtained. In HMPT, "a solvent with a remarkable ability to dissociate organometallic compounds", N-methylation is obtained exclusively. In a mixture of HMPT and THF containing 2.8 equivalent HMPT for each -MgX, the chloro, bromo and iodo Grignard compounds yield 11%, 37% and 79% C-methylation, which might be explained by the increased electronegativity of the latter halogen, imparting more ionic character to the N-MgX bond, thereby leading to more extensive dissociation by the solvent.

The rather unorthodox Grignard compounds as mentioned in Chapter 2Bv such as

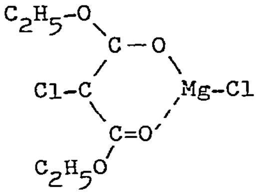


$$C_6H_5-\underset{\displaystyle C_6H_5}{\underset{|}{P}}-O-MgBr$$

Ref. [73]



Ref.[74]

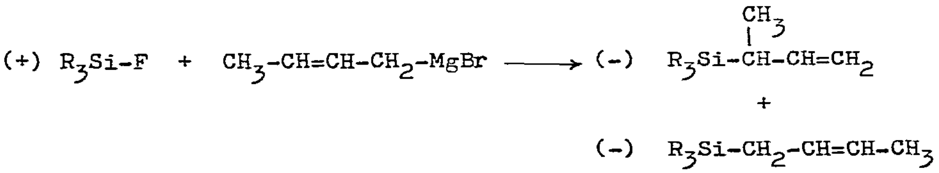


Ref. [77]

all yield rearranged products (i.e. P- or C- bonded ones) on reaction with ketones and chloromethyl ethers, respectively.

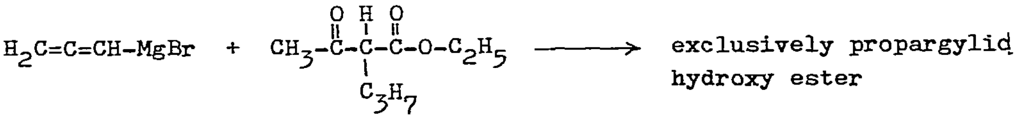
Also rearrangements of crotylic and propargylic Grignard compounds have been reported again this year:

among others : by Corriu and Massé [126].



$$(+)\ R_3Si-F + CH_3-CH{=}CH-CH_2-MgBr \longrightarrow (-)\ R_3Si-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH{=}CH_2 + (-)\ R_3Si-CH_2-CH{=}CH-CH_3$$

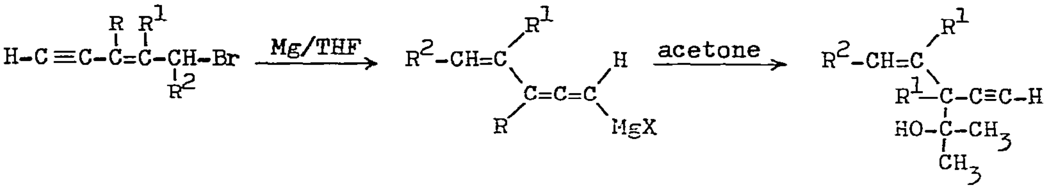
and by Couffignal [127]:



$$H_2C{=}C{=}CH-MgBr + CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle C_3H_7}{\underset{|}{C}}}}-\overset{\displaystyle O}{\overset{\|}{C}}-O-C_2H_5 \longrightarrow$$

exclusively propargylic hydroxy ester

The remarkable sequence of rearrangements, observed by Dulcère, Roumes tant and Gore [48] is schematically represented as follows



4. MECHANISMS OF REACTIONS OF ORGANOMAGNESIUM COMPOUNDS

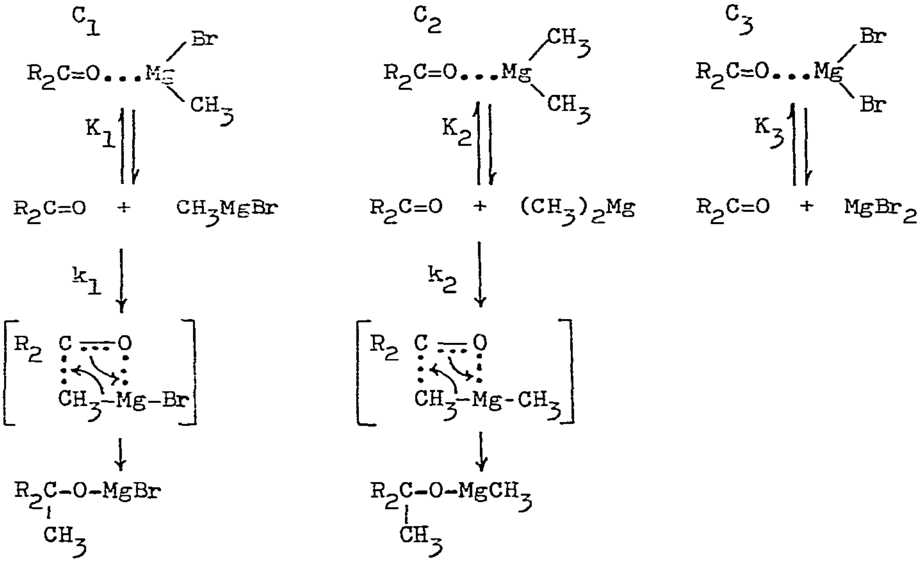
4A. Reactions with carbonyl compounds

4Ai. Addition and reduction reactions

Ashby, Laemmle and Neumann have given a detailed description of the mechanism of the reaction of methylmagnesium bromide with 2-methylbenzophenone [128].

This reaction was chosen because it yields "normal" C-O double bond addition products only without any other products, resulting from various side-reactions, known in Grignard chemistry. 100% Diphenylmethyl carbinol was obtained on hydrolysis of the reaction mixture. Use was made of an extremely pure sample of magnesium for the preparation of the Grignard compound: 99.9995% purity. The progress of the reaction was followed by observing the disappearance of a strong absorption which has appeared in the 400-600 nm region, immediately after mixing excess ketone (approximately 0.50 M) with methylmagnesium bromide (approximately 0.0126 M). Although the change in absorbance over the entirety of the reaction did not adhere to any simple integral order behavior, meaningful rate constants were obtained by treating the initial disappearance of the complex in a pseudo-first order fashion.

The reaction proceeds by two paths: one first order in CH_3MgBr, the other first-order in $(CH_3)_2Mg$; the relative concentrations of the two organomagnesium compounds and the reaction rates of each with ketone are such that the reaction proceeds almost equally through both paths

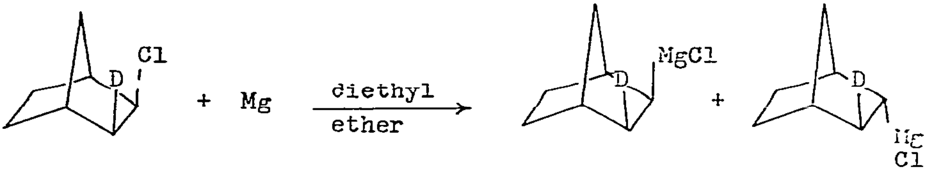


The reaction becomes rather complex because of interaction of the product of CH_3MgBr addition to ketone, R-O-MgBr, with the species CH_3MgBr, $(CH_3)_2Mg$ and $MgBr_2$ and respective ketone complexes. Independent experiments were performed to investigate these effects. The whole complex of reaction possibilities is given in a scheme containing seven reactions.

Although at 545 nm an absorbance for the ketyl was observed, the absolute amount of this species formed apparently was very small since only 100% addition product could be isolated. In certain reactions th ketyl absorbance persisted, long after the addition reaction was complete.

With the aid of stopped-flow techniques Koppel and Tuulmets studied the kinetics of the reaction of dipropylmagnesium with methyl-tert-bu tyl ketone [129] in different solvents. It was shown that the rate of the reaction is dependent on the polarity of the reaction media. The correlation with the general equation for solvent effects, as developed by Koppel and Palm (1972) was poor and only the introduction of a cross-term, which takes into account the non-additivity of the solvent effects leads to a good correlation.

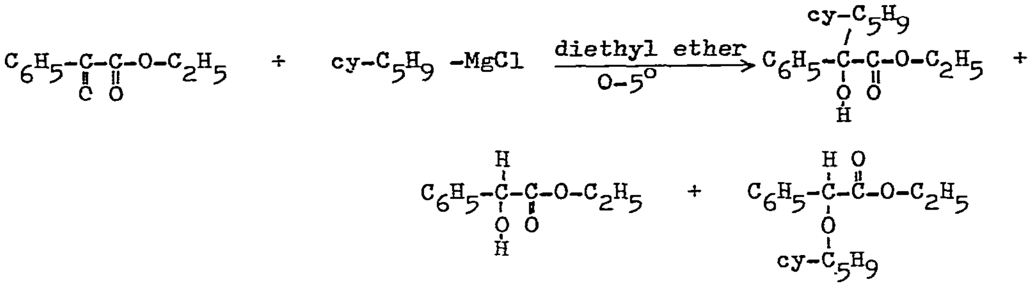
According to Morrison and Lambert an equilibrated Grignard reagent from 2-exo-chloro-3-exodeuterionorbornane



reduces benzophenone (added in 0.5 molar equivalent) in a formal sense via a cis-exo eliminative transfer of H and MgCl [130]. No cis-endo transfer was observed; when the exo and endo Grignard reagents compete for a limited amount of benzophenone there is exclusively eliminative transfer of "DMgCl" from the exo direction.

Continuing their investigations on the reductive power of cyclomagnesiaalkanes $(CH_2)_2Mg$ with n = 4, 5 or 6, Denise, Fauvarque and Ducom studied the stereochemical requirements of the reduction of ketones (Annual Survey 1970, p.357) [67].

Again so-called "abnormal" addition to the C=O bond is observed with a Grignard reagent: Bobysheva, Volkova, Kuznetsov and Stepanova, upon reaction of cyclopentylmagnesium chloride in diethyl ether at 0-5^{o} with benzoylformic acid ester [131]:

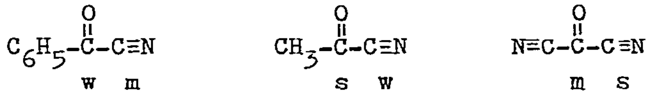


$$C_6H_5-\underset{C}{\underset{\|}{C}}-\underset{O}{\underset{\|}{C}}-O-C_2H_5 \quad + \quad cy-C_5H_9-MgCl \xrightarrow[0-5^{o}]{\text{diethyl ether}} C_6H_5-\overset{cy-C_5H_9}{\underset{\underset{H}{O}}{C}}-\underset{O}{\underset{\|}{C}}-O-C_2H_5 \quad +$$

$$C_6H_5-\overset{H}{\underset{\underset{H}{O}}{C}}-\underset{O}{\underset{\|}{C}}-O-C_2H_5 \quad + \quad C_6H_5-\overset{H}{\underset{\underset{cy-C_5H_9}{O}}{C}}-\overset{O}{\overset{\|}{C}}-O-C_2H_5$$

obtained small amounts of the inverse addition reaction product in which reaction C-C formation has taken place. No further details are given by the authors.

As the result of calculations the electronic character of the following three acyl cyanides has been summarized by Borch, Levitan and Van-Catledge as indicated [132]:

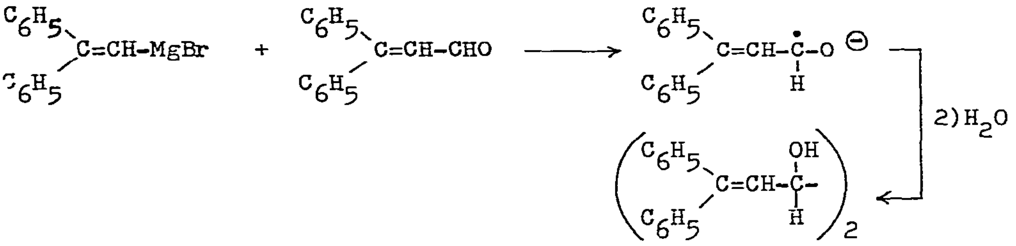


$$\underset{w\quad m}{C_6H_5-\overset{O}{\overset{\|}{C}}-C{\equiv}N} \qquad \underset{s\quad w}{CH_3-\overset{O}{\overset{\|}{C}}-C{\equiv}N} \qquad \underset{m\quad s}{N{\equiv}C-\overset{O}{\overset{\|}{C}}-C{\equiv}N}$$

s = strong
m = medium
w = weak

On reaction with Grignard compounds benzoyl and carbonyl cyanides with their relatively stabilized carbonyl groups, undergo reactions leading to addition. Acetyl and isobutyryl cyanides however react predominantly by reduction. "A possible explanation for the correlation between carbonyl group polarization and reduction lies in the fact that the complexing of an organomagnesium reagent will be much stronger in the case of a highly polarized carbonyl group and thus the Mg-C bond will be substantially weakened. This in turn would assist the hydride transfer from the β-carbon due to the increase in electron density on the carbon bonded to magnesium". Addition of alkylmagnesium reagents occurs exclusively at carbonyl in both aroyl and acyl cyanide systems. The authors forward an explanation for the predominant attack on the cyanide group in carbonyl cyanide by phenylmagnesium bromide.

The formation of the glycol $\boxed{16}$ during the reaction of diphenylacroleine with the Grignard reagent derived from bromodiphenylethylene, is attributed by Cheminat, Guillaumet and Rambaud to a reduction of the aldehyde by the Grignard compound [133]:

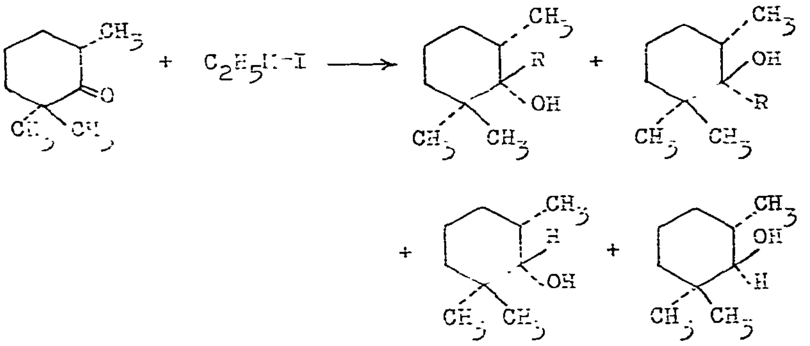


16

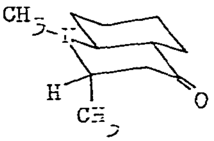
4Aii Steric course of reactions with carbonyl compounds

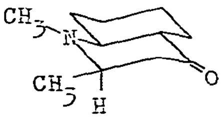
The reaction of dimethylmagnesium in THF, triethylamine or benzene as well as the reaction of methylmagnesium fluoride, bromide or iodide in THF, with 4-tert-butylcyclohexanone lead predominantly (68-75%) to the formation of the axial tertiary alcohol (Ashby, Yu and Roling [134]).

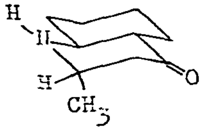
2,2,6-Trimethylcyclohexanone reacts with ethylmagnesium iodide in diethyl ether to form both the addition and reduction products; the ratio of the epimers is indicated in the following scheme (Matsumoto, Sakata, Tachibana and Fukui [135]):



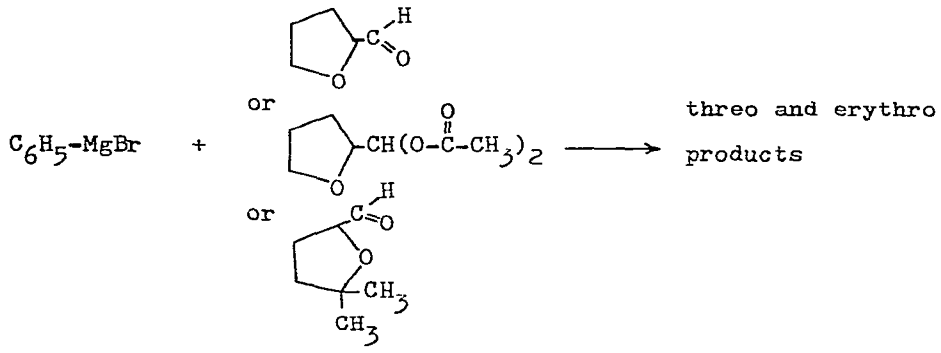
A remarkable stereoselectivity was observed by Akhrem, Ukhova and coworkers in the reaction of saturated as well as of unsaturated Grignard compounds with 1- and 1,2-substituted decahydro-4-quinolones





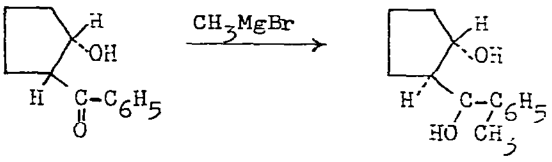


The only product in several of the reactions investigated was the one with the R-group in the equatorial position (depending on the position of the substituents on carbon atom 2)[136] and [137].
In order to clarify the cause of the anomalous stereoselectivity of reactions of Grignard reagents with N-substituted 2,3-O-isopropylidene-D-glyceraldimine, Yoshimura, Ohgo, Ajisaka and Konda examined the reactions of Grignard reagents with the following tetrahydrofurfural derivatives [138]:



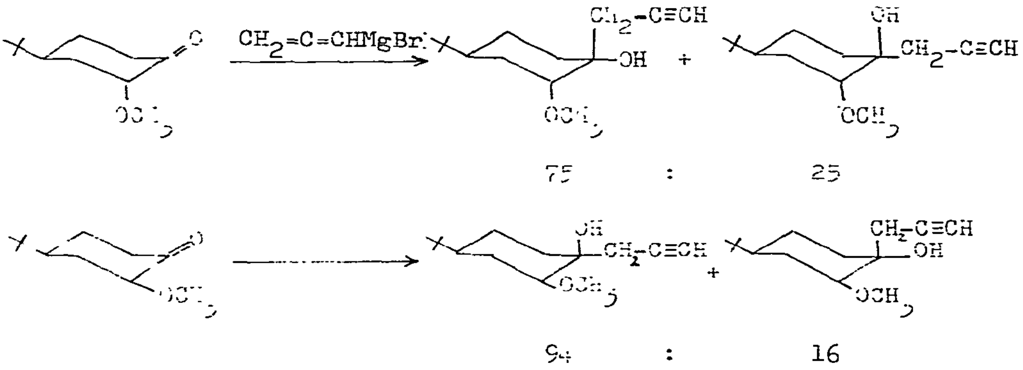
The presumption that the anomality in the stereochemistry, previously observed, might be caused by coordination of magnesium with the C_3-oxygenin the glyceraldimine derivative is supported by the present results.

Ghera and Shoua reported more detailed results of their investigations of the reaction of Grignard compounds with β-hydroxy ketones, having one oxygen-containing function situated on a five- or six-membered ring and another one on a side chain (Annual Survey 1971, p. 45) [139]. The reactions proceed with high stereospecificity except when chelation is sterically inhibited as was found in the reaction with trans-acyl-cyclopentanols:

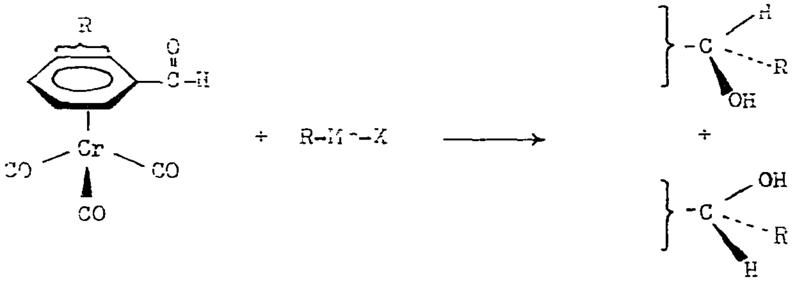


stereoselectivity only 60%

Guillerm-Dron, Capmau and Chodkiewicz investigated the stereoselectivity of reactions of allenylmagnesium halides with cis- and trans-4-tert-butyl-2-methoxycyclohexanone [140] as compared with the stereoselectivity of reactions of the corresponding aluminum compounds. Some of their results are indicated below:



Chiral carbonyl derivatives of ortho or meta disubstituted benchrotrenes allowed Meyer and Dabard to investigate asymmetric inductions in reactions of these compounds with Grignard reagents [141]:

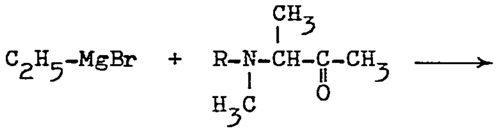


The results indicate that when R is in the meta position to the aldehyde function no steric or electronic effects of R are encountered and that conformational factors of the $Cr(CO)_3$ group must play an important role in the stereoselectivity found.

The reaction of ethylmagnesium bromide with α-aminoketones which results in the formation of α-aminoalcohols, occurs with high stereoselectivity:

a) in case of a strongly basic amine (R = CH_3) when benzene or cyclohexane is used as the solvent,

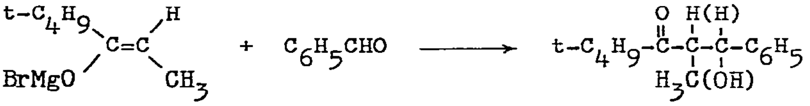
b) in case of an amine of low basicity (R = C_6H_5) when the Grignard reagent is added to a mixture of the aminoketone and magnesium bromide in benzene solution (Gaset and Lattes [142]):



$$C_2H_5\text{-}MgBr + R\text{-}N(CH_3)\text{-}CH(CH_3)\text{-}C(=O)\text{-}CH_3 \longrightarrow$$

threo and erythro products of addition and reduction reactions

The reaction of the Grignard compound derived from 2-bromo-4,4-dimethyl-3-pentanone (which has the enolate structure; Chapter 2Bv), with benzaldehyde leads to the formation of the erythro product under kinetically controled conditions. Since the reaction is reversible the threo product becomes the predominant one on prolonged heating of the reaction mixture (Dubois and Fellmann [74]):



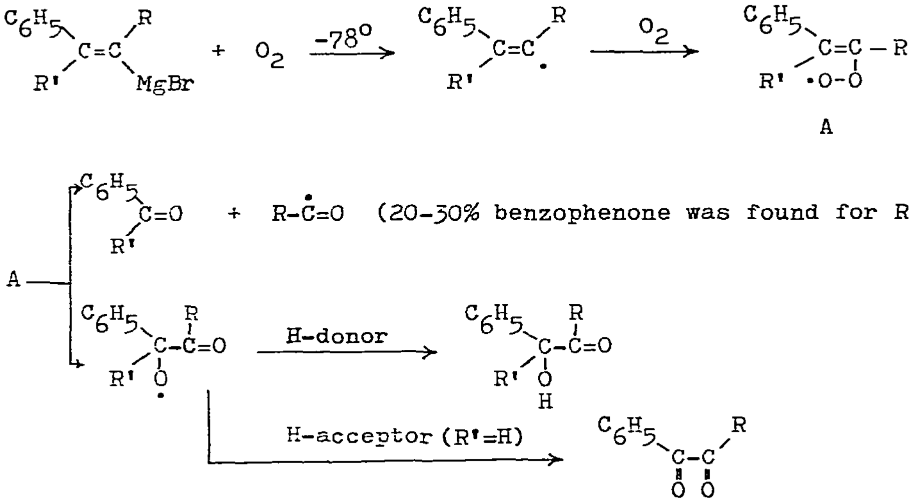
$$t\text{-}C_4H_9\text{-}C(=O)\text{-}CH(CH_3)\text{-}CH(OH)\text{-}C_6H_5$$

kinetic control: 95% erythro

thermodynamic control: 95% threo

4B. Radical reactions of organomagnesium compounds

Alkyl and aryl Grignard reagents are known to undergo reactions with oxygen via radical mechanisms. Since acetylenic Grignard reagents are almost inactive towards oxygen it remained uncertain whether vinylic Grignard reagents react with oxygen or not. Wada and Tokumaru reported that these reagents do indeed react with oxygen; the authors propose a radical mechanism as follows [143]:



(20-30% benzophenone was found for R = C_6H_5).

R' = C_6H_5 or H   R = H, CH_3 or C_6H_5

By bubbling oxygen through a solution of phenylmagnesium bromide and bromobenzene in diethyl ether, Garst, C.D. Smith and Farrar [31] obtained ortho, meta and para bromobiphenyl among other reaction products. The isomer distribution was equal to the one obtained when bromobenzene reacted with phenyl radicals from other well-recognized sources which implicates phenyl radicals as true intermediates in the oxygenation. However, "the detailed reaction pathways remain uncertain" the authors conclude their paper.

As in the case of reactions of Grignard reagents with alkyl halides (Ward, Lawler and Marzilli, Annual Survey 1970 p.344), CIDNP phenomena were observed in the reaction of diethylmagnesium with ethyl and isopropyl iodide (Kasukhin, Ponomarchuk and Buteiko [144]), indicating that radicals play a role in the observed exchange of alkyl groups of the iodides. As expected the reaction is accelerated by the addition of 5% cobalt(II) chloride.

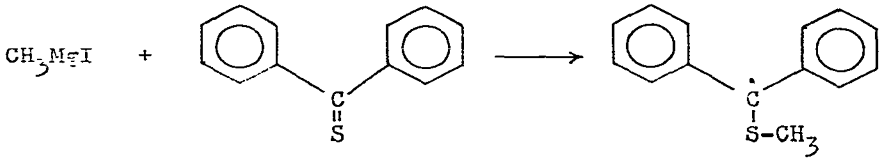
Trityl bromide, added to a large excess of phenylmagnesium bromide in diethyl ether, reacts with formation of 5% triphenylmethane, 2-3% biphenyl, 1.5% 1-phenylethanol and 1% ethylbenzene (Mapes, Gregory and Berlin [145]). The overall conversion of trityl bromide was less than 10%. The authors propose a radical mechanism to account for the formation of the different products:

$$(C_6H_5)_3C\text{-}Br \longrightarrow \underset{\text{ion pair}}{(C_6H_5)_3\overset{\oplus}{C}\ \overset{\ominus}{Br}} \xrightarrow{C_6H_5MgBr} (C_6H_5)_3C^{\bullet} + C_6H_5^{\bullet} + MgBr_2$$

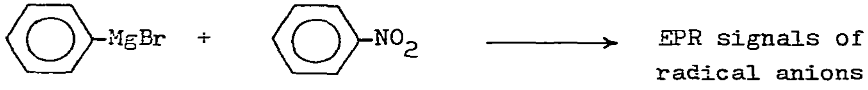
The same sort of mechanism was proposed for the reaction of Grignard compounds with benzyl, benzhydryl and trityl chloride by Singh, Tayal and Nigam [146]. The following table is illustrative for their results

R'-X'	+ RMgX	R-R' %	R'-R' %	R-R %	R-H %
$C_6H_5CH_2Cl$	C_6H_5MgBr	56	6	4	12
$(C_6H_5)_2CHCl$	C_6H_5MgBr	60	6	6	10
$(C_6H_5)_3CCl$	C_6H_5MgBr	46	5	4	10
$(C_6H_5)_3CCl$	$C_6H_5CH_2MgCl$	55	5	15	-

The (partially) abnormal reactions of silylmethylmagnesium halides as mentioned in Chapter 2Biv ([55], [55A] and [56]) may proceed via radical reactions as supposed by the authors.
The reaction of 0.6 M methylmagnesium iodide with 0.04 M thiobenzophenone in diethyl ether or THF yields the sulfur-substituted products and the reaction mixture exhibits a well resolved EPR spectrum, corresponding to 4.10^{-5} M methylthiodiphenylmethyl radicals:

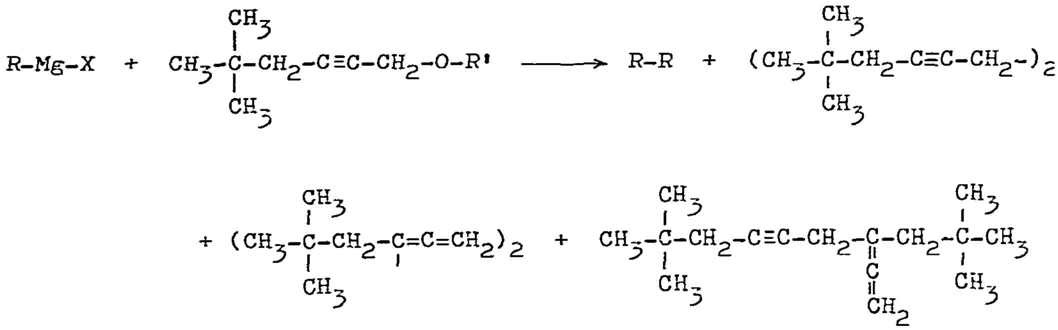


In THF ethyl- and methylmagnesium bromide yield 95% resp. 75% of the sulfur alkylated products (Dagonneau, Hemidy, Cornet and Vialle [147]) Degtyarev, Ponomarchuk and Kasukhin observed intermediate radical anions by EPR measurements during the reaction of substituted nitrobenzene with phenylmagnesium bromide in THF [148]:



R = 2-Cl, 4-Cl, 3-Br, H, 3-NO_2, 4-C_6H_5 and 4-(4-Br-C_6H_4-)

The reaction of simple alkylmagnesium bromides with alkyl ethers of dimethylhexynol does not yield alkylation products but gives dimers, R-R as well as dimers of the dimethylhexynyl radical (Mkryan, Gasparyan, Ppazyan and Voskanyan [149]):



$$\text{R-Mg-X} + \text{CH}_3\text{-}\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\text{-CH}_2\text{-C}\equiv\text{C-CH}_2\text{-O-R}' \longrightarrow \text{R-R} + (\text{CH}_3\text{-}\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\text{-CH}_2\text{-C}\equiv\text{C-CH}_2\text{-})_2$$

$$+ (\text{CH}_3\text{-}\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\text{-CH}_2\text{-}\underset{|}{\text{C}}\text{=C=CH}_2)_2 + \text{CH}_3\text{-}\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\text{-CH}_2\text{-C}\equiv\text{C-CH}_2\text{-}\underset{\substack{\| \\ \text{C} \\ \| \\ \text{CH}_2}}{\text{C}}\text{-CH}_2\text{-}\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\text{-CH}_3$$

There is little doubt that radicals play a role in reactions of this type. The same may be true for the following reactions, reported by Uchida, Nakazawa, Kondo, Iwata and Matsuda [150]:

$$\text{C}_6\text{H}_5\text{-C}\equiv\text{C-MgBr} + \text{SOCl}_2 \longrightarrow (\text{C}_6\text{H}_5\text{-C}\equiv\text{C-})_2$$

$$\text{C}_6\text{H}_5\text{-CH=CH-MgBr} + \text{SOCl}_2 \longrightarrow (\text{C}_6\text{H}_5\text{-CH=CH-})_2$$

The formation of glycol $\boxed{16}$, reported in Chapter 4Aii by the reaction of 2,2-diphenylvinylmagnesium bromide with diphenylacroleine has to be attributed to a single electron transfer reaction from the Grignard reagent to the unsaturated aldehyde [133].

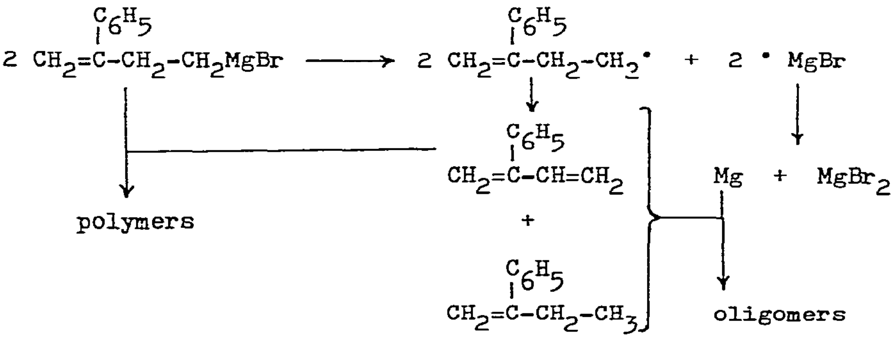
4C. Miscellaneous reactions

To start with what might be considered as the simplest reaction a Grignard compound may undergo, i.e. pyrolysis, two publications appeared this year dealing with this reaction:

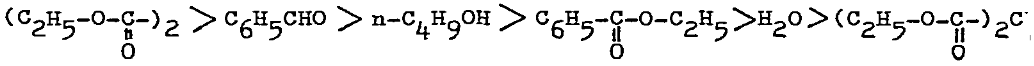
Hill, studying pyrolysis of the Grignard reagent from 4-bromo-1-chloro-1-butene, in which studies he included experiments with deuterium labeled compounds, concludes that a mechanism, involving cyclization to the cyclopropylcarbenoid $\boxed{17}$ is in best accordance with the data [151]:

$\boxed{17}$

For the formation of metallic magnesium during the pyrolysis of 3-phenylallylcarbinylmagnesium bromide Maercker and Weber [152] suppose a mechanism as follows:



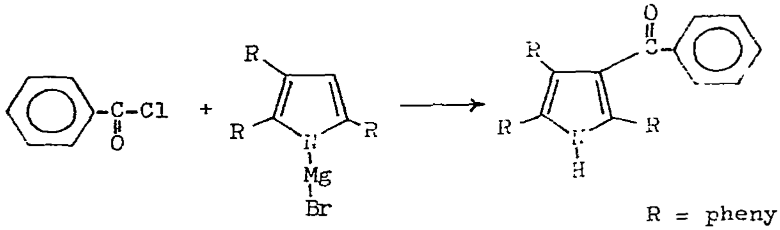
Karavanov measured the heats of reaction of ethyl-, phenyl-, and nonylmagnesium compounds with several substrates and found the following order of heat evolution [153]:



$$(C_2H_5-O-\underset{\underset{O}{\|}}{C}-)_2 > C_6H_5CHO > n-C_4H_9OH > C_6H_5-\underset{\underset{O}{\|}}{C}-O-C_2H_5 > H_2O > (C_2H_5-O-\underset{\underset{O}{\|}}{C}-)_2C$$

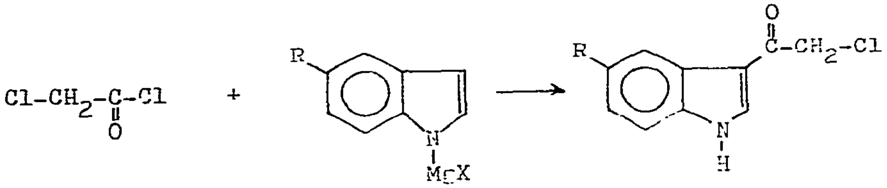
The following rearrangements of pyrrole- and indolemagnesium halides were reported:

Giambrone [154]:



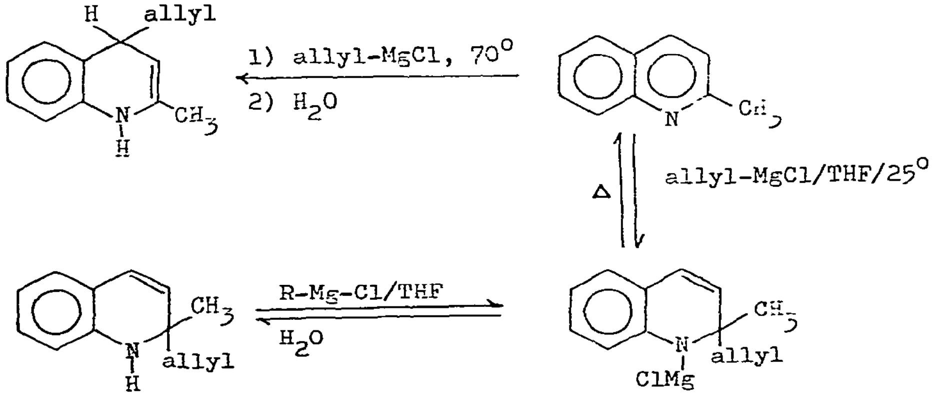
R = phenyl

Plasvic, Kveder and Iskric [155]:



R = H or C_6H_5-CH_2-O-

Eisch and Comfort uncovered a genuine organometallic rearrangemen unprecedented in the quinoline system, described in the following scheme [156]:

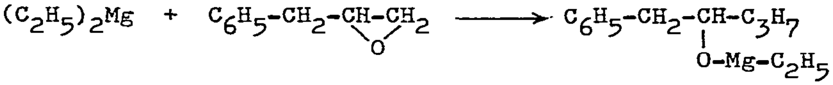


This interplay of 1,2- and 1,4-addition to the quinoline nucleus represents a case of competitive kinetic and thermodynamic control of reactions.

The stereochemical outcome of the cyclization reaction of 2,7-octadienyl-1-magnesium bromide (which leads almost exclusively to cis-1-methyl-2-vinylcyclopentane on hydrolysis) strongly suggests a mechanism involving a six-membered cyclic transition state (Felkin, Umpleby, Hagaman and Wenkert [157]):

Thus addition of allylic Grignard reagents to a non-activated double bond occurs via a cyclic mechanism in the case of simple, non-functional olefins.

Boireau, Abenhaim and Namy investigated the kinetics and mechanism of the following reaction [158]:

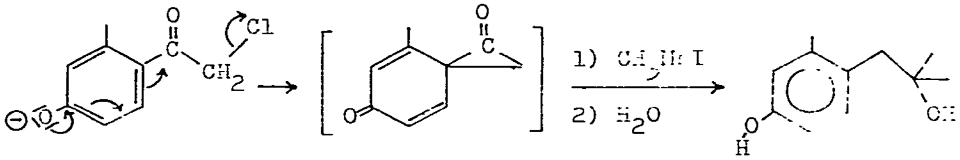


$$(C_2H_5)_2Mg + C_6H_5\text{-}CH_2\text{-}\underset{\diagdown O \diagup}{CH\text{-}CH_2} \longrightarrow C_6H_5\text{-}CH_2\text{-}\underset{\text{O-Mg-}C_2H_5}{\underset{|}{CH}}\text{-}C_3H_7$$

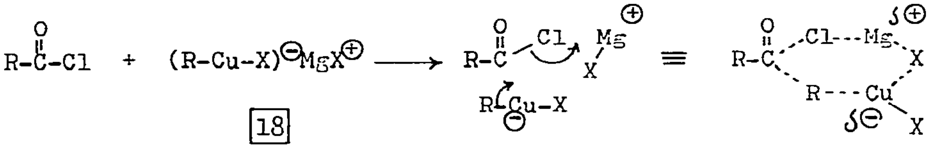
The oxirane ring is almost exclusively opened at the least sterically hindered site. The reaction proceeds much faster in diethyl ether than in THF and no reaction takes place at all in HMPT. Complex formation therefore has to occur before reaction takes place. The product formed, as indicated above, reacts extremely slowly with oxiranes.

In another publication the same authors demonstrate that the reaction of diallylmagnesium with the same oxirane derivative is also stereospecific [159]; determination of the Hammett ρ constants for the reaction leads to the conclusion that no important charge is built up in the transition state, contrary to the transition state of the same organomagnesium compound with stilbene oxides with the aromatic nucleus in the α-position of the oxirane ring.

For the reaction of 4-hydroxy-2-methylchloroacetophenone with alkylmagnesium halides Bohlmann and Kapteyn propose a cyclopropanone-derivative as the intermediate instead (or besides ?) the carbene-intermediate previously (Annual Survey 1968, p. 251) proposed by Bohlmann and Zdero [160]:

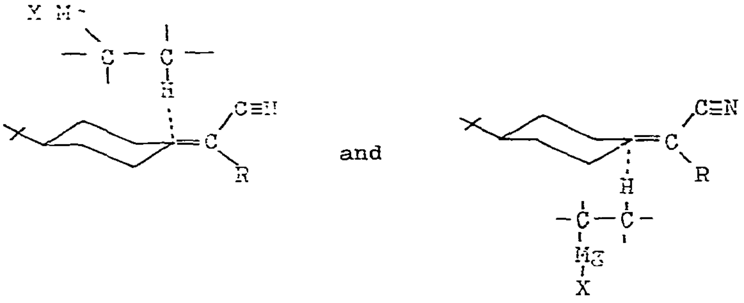


For the reaction of acid chloride with alkylmagnesium halides in the presence of excess copper(I) chloride MacPhee and Dubois propose a mechanism in which the halogen of the acid chloride is displaced by the organocopper intermediate for which they propose structure $\boxed{18}$ [161]:



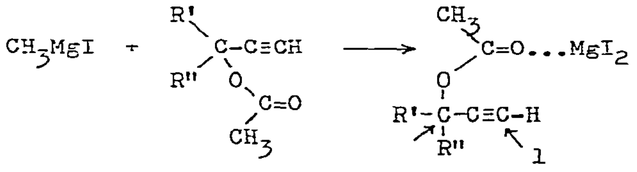
By means of competition reactions of two acid chlorides with neopentylmagnesium chloride the authors obtained an order of reactivity of the acid chlorides with substituents R; the change in relative reactivities with changing alkyl substituent is successfully correlated by means of the Taft σ^* alone.

From the relative amounts of cis and trans products, obtained on reduction of 4-t-butylcyclohexylidenemalonitrile or of 4-t-butylcyclohexylidenecyanoacetate by means of t-butyl-, iso-propyl- or cyclohexylmagnesium chloride (which reduction reactions all gave the same rat of cis and trans products), Cabaret, Pertuisot and Welvart conclude that the same mechanism must be forwarded for each reaction: a non-cyclic mechanism with polar orientation of the reactants in the transition state [162]:



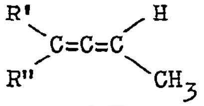
R = -C≡N or $-CO_2C_2H_5$

According to Roumestant and Gore, the reaction of methylmagnesium iodide with acetates of homologues of propargylic alcohols proceeds via complexation of the acetate with magnesium iodide [163]:



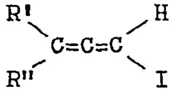
Complexation makes the acetate a better leaving group for what the authors describe as a S_N1' reaction on the propargylic system.
In case the amount of magnesium iodide is too large the nucleophilicity of the organomagnesium compound is reduced too much and so, on

hydrolysis, the acetate is recovered unchanged. Attack by the Grignard compound on the different sites of the molecule (indicated with $\longrightarrow$) yields several different products. Attack on position 1, e.g., yields compounds $\boxed{19}$ and $\boxed{20}$.



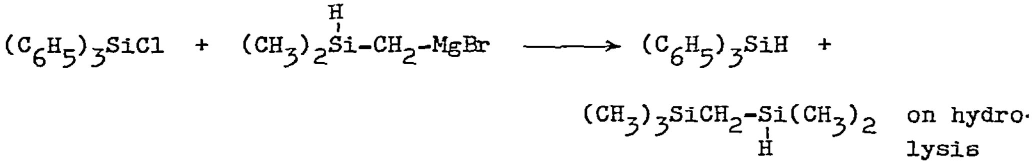
$\boxed{19}$

and



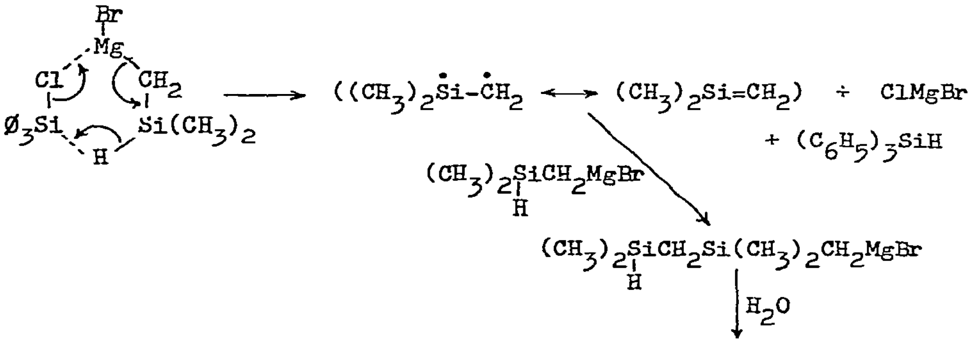
$\boxed{20}$

For the reduction of triphenylchlorosilane by dimethylsilylmethylmagnesium bromide:



$$(C_6H_5)_3SiCl + (CH_3)_2\overset{H}{Si}\text{-}CH_2\text{-}MgBr \longrightarrow (C_6H_5)_3SiH + (CH_3)_3SiCH_2\text{-}\underset{H}{Si}(CH_3)_2 \text{ on hydrolysis}$$

Jarvie and Rowley found a reasonable explanation in the following mechanism [55]:



although the possibility remains that the reaction proceeds via a direct exchange process.

The reaction of organomagnesium compounds with optically active α-naphthylphenyl-R-silanes leads either to inversion or to retention of configuration at the Si-atom (Corriu and Royo, [126] and [164]). The stereochemical course of the reaction not only depends on the leaving group, the type of Grignard reagent and the reaction medium but also it is related with the polarity and the polarizability of the leaving group and with the electron donating ability of the entering nucleophile.

5. REACTIONS OF ORGANOMAGNESIUM COMPOUNDS

Introduction

In the following chapters hundreds of reactions of organomagnesium compounds with different substrates will only be summarized and (sometimes) briefly discussed. The most important kinetic and mechanistic aspects of these reactions have been discussed in some more detail in Chapter 4.

It might be of interest to report in this survey of organomagnesium chemistry that the one-step alternative to the Grignard reaction, as reported by Pearce, Richards and Scilly [165] (see also Annual Survey 1970, p.373), and in which the authors use lithium metal, really leads to excellent results for several types of reactions. In fact their method is the lithium version of the Barbier-synthesis which, in general, is not a very attractive alternative in organomagnesium chemistry (see Chapter 2D, reference [99]).

Ishii, Tsuda and Tokoro used the Zerewitinoff method for the determination of active hydrogen in microanalysis; methane is determined by GLC-techniques; with 0.1 mg samples a standard deviation of 2.5% can be obtained [166].

Six reports on asymmetric synthesis with the aid of organomagnesium compounds may be mentioned:

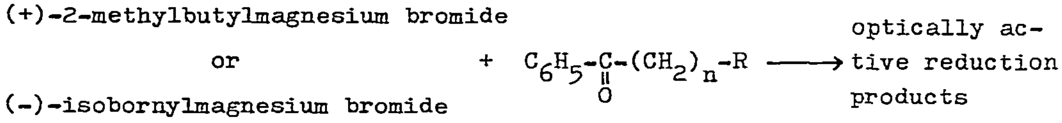
The well-known asymmetric synthesis of atrolactic acid (McKenzie 1909 and 1931; Prelog 1953) was performed by El'yanov, Murina, Klabunovskii, Petrov and Parfenova at extremely high pressures (till 5000 kg/cm^2). The decrease in optical activity of the product is the result of limited conformational mobility in the development of the transition state of the reaction [167]. The results confirm the authors' hypothesis that the accelerating effect of pressure in sterical reactions is due to a decrease in the free volume.

Kretchmer obtained optically active products in the reaction of Grignard compounds in the presence of (-)sparteine with α,β-unsaturated ketones [168].

Kawana and Emoto report the first example of asymmetric synthesis of atrolactic acid (optical yield 65% !) by the reaction of methylmagnesium iodide with the phenylglyoxylic ester of 1,2-O-cyclohexylidene-α-D-xylofuranose, bound to a styrene-2% divinylbenzene copolymer [169].

Mosher and coworkers found 7.5% asymmetric synthesis in the reaction of methylmagnesium iodide with (S)-(-)-n-butyl-t-butylcarbinylbenzoylformate with diethyl ether as the solvent; the stereoselectivity of the same reaction was essentially zero in THF [170].

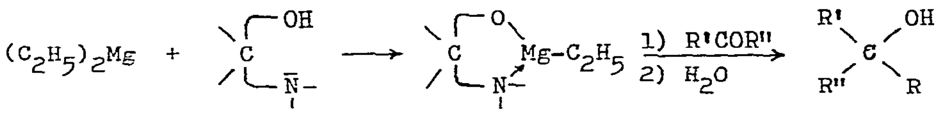
High optical yields were obtained by Tomina, Klabunovskii, Petrov, Lubuzh and Cherkasova in the following reduction reactions [171]:



$$\begin{matrix}\text{(+)-2-methylbutylmagnesium bromide}\\ \text{or}\\ \text{(-)-isobornylmagnesium bromide}\end{matrix} + C_6H_5\text{-}\underset{\underset{O}{\parallel}}{C}\text{-}(CH_2)_n\text{-}R \longrightarrow \begin{matrix}\text{optically ac-}\\ \text{tive reduction}\\ \text{products}\end{matrix}$$

n = 1 or 2
R = dimethylamino, diethylamino, N-piperidinyl or N-morpholinyl

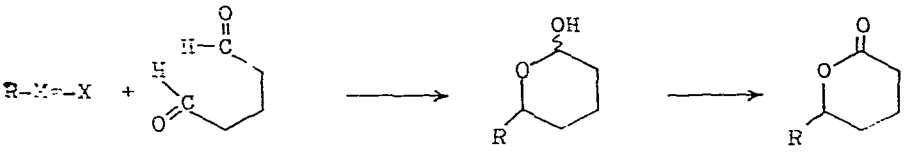
Battioni and Chodkiewicz obtained optically active tertiary alcohols by the reaction of ketones with ethylmagnesium alkoxides, prepared by reaction of diethylmagnesium with optically active aminoalcohols such as N-methylephedrine [172]:



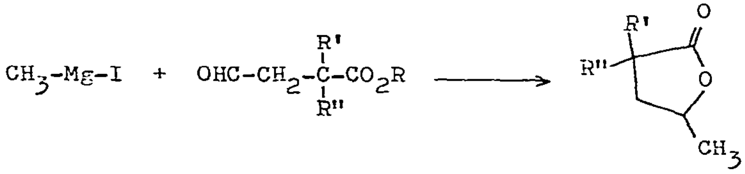
5A. Reactions with aldehydes and ketones

Andreeva, Koton, Madorskaya, Turbina and Pokrovskii report reactions of free aldehyde functions in polymethacroleine with Grignard reagents [173].

The synthesis in satisfactory yields by reaction of glutaraldehyde with Grignard reagents followed by oxidation was reported by Rosenberger, Andrews, SiMaria, Duggan and Saucy [39]:

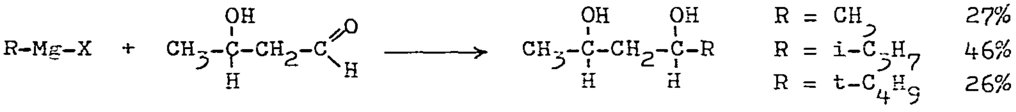


In a reaction of the same type Des Abbayes, Salmon-Legagneur and Neveu obtained γ-lactones from aldehyde esters [174]:



The stereochemical investigations of the reactions of Grignard compounds with aldehyde derivatives from benchrotrenes has already been discussed in Chapter 4Aii [141].

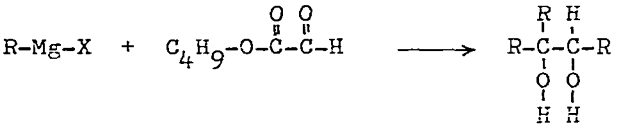
Cazaux and Maroni obtained β-diols in "acceptable" yields by reaction of methyl-, iso-propyl- and tert-butylmagnesium halides with acetaldol [175]:



$$\text{R-Mg-X} + \text{CH}_3\text{-}\overset{\text{OH}}{\underset{\text{H}}{\text{C}}}\text{-CH}_2\text{-C}{\overset{\text{O}}{\underset{\text{H}}{\lessgtr}}} \longrightarrow \text{CH}_3\text{-}\overset{\text{OH}}{\underset{\text{H}}{\text{C}}}\text{-CH}_2\text{-}\overset{\text{OH}}{\underset{\text{H}}{\text{C}}}\text{-R}$$

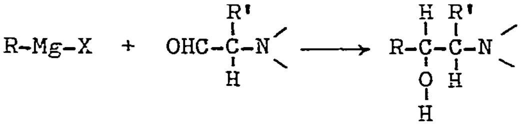
R = CH_3 27%
R = i-C_3H_7 46%
R = t-C_4H_9 26%

Butyl glyoxylate reacts with benzyl- or cyclohexylmagnesium halides to form 1,2-diols (Akimova and Orlikova [176]):



$$\text{R-Mg-X} + \text{C}_4\text{H}_9\text{-O-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-H} \longrightarrow \text{R-}\overset{\text{R}}{\underset{\text{OH}}{\text{C}}}\text{-}\overset{\text{H}}{\underset{\text{OH}}{\text{C}}}\text{-R}$$

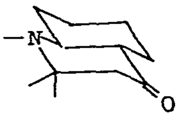
The synthesis of α-aminoalcohols by reaction of the corresponding aldehydes with Grignard compounds was reported by Duhamel, Duhamel and Gralak [177]:



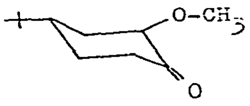
$$\text{R-Mg-X} + \text{OHC-}\overset{\text{R}'}{\underset{\text{H}}{\text{C}}}\text{-N}\langle \longrightarrow \text{R-}\overset{\text{H}}{\underset{\text{OH}}{\text{C}}}\text{-}\overset{\text{R}'}{\underset{\text{H}}{\text{C}}}\text{-N}\langle$$

(eryhtro and threo forms)

The stereochemistry of the reactions of Grignard compounds with the following cyclic ketones has been discussed in Chapter 4Aii:

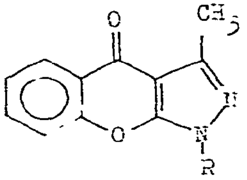


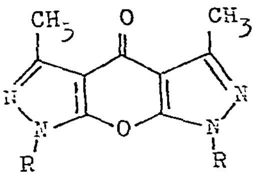
Ref. [137]

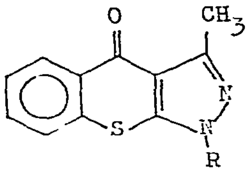


Ref. [140]

Reactions of organomagnesium compounds with the following xanthone analogues proceed as expected under the formation of alcohols (Sarenko, Kvitko and coworkers [178] and [179]):

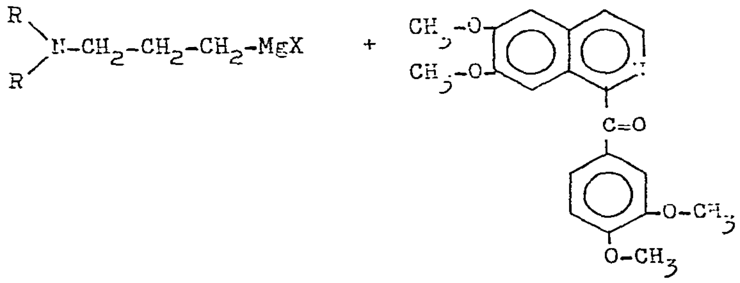




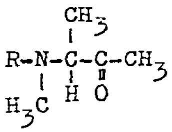


The following nitrogen-containing ketones were subjected to reactions with Grignard compounds:

Papaveraldine (Debaert, Lespagnol, Devergnies and Boniface [180]:

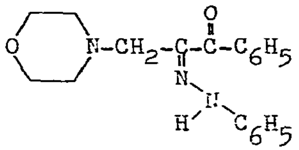


Gaset and Lattes investigated the stereochemistry of the reactions of the following ketones with ethylmagnesium bromide [142]

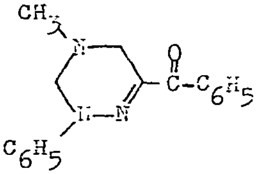


$$\underset{H_3C}{\underset{|}{R-N}}-\overset{CH_3}{\overset{|}{\underset{H}{\underset{|}{C}}}}-\underset{O}{\underset{\|}{C}}-CH_3$$

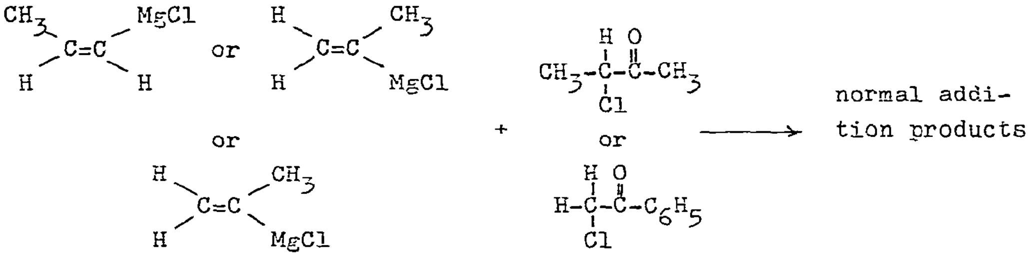
The following phenyl ketones react with phenylmagnesium bromide to form the tertiary alcohols in high yields (67-84%) (Hahn and Zielinski [181]):



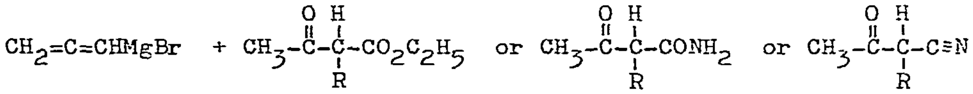
and



The reaction of ethylenic Grignard compounds with α-chloroketones affords the normal addition products in good yields (Sauleau, Bouget and Huet [182]):



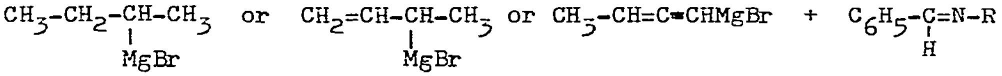
Couffignal investigated the reaction of allenylmagnesium bromide with β-ketoesters, amides and nitriles [183]



$$CH_2{=}C{=}CHMgBr \;+\; CH_3-\overset{O}{\overset{\|}{C}}-\underset{R}{\overset{H}{C}}-CO_2C_2H_5 \;\text{ or }\; CH_3-\overset{O}{\overset{\|}{C}}-\underset{R}{\overset{H}{C}}-CONH_2 \;\text{ or }\; CH_3-\overset{O}{\overset{\|}{C}}-\underset{R}{\overset{H}{C}}-C{\equiv}N$$

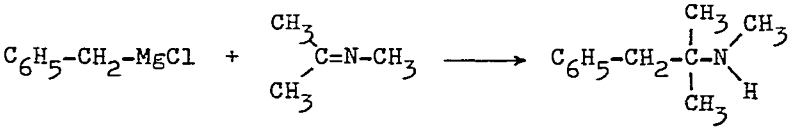
R = H or isopropyl

Moreau and Gaudemar studied the stereochemistry of reactions of Grignard compounds derived from 2-bromobutane, 3-bromo-1-butene [184] and from 3-bromo-1-butyne [185] with N-substituted benzaldimines:



$$CH_3-CH_2-\underset{\underset{\mathrm{MgBr}}{|}}{CH}-CH_3 \text{ or } CH_2=CH-\underset{\underset{\mathrm{MgBr}}{|}}{CH}-CH_3 \text{ or } CH_3-CH=C=CHMgBr + C_6H_5-\underset{\underset{\mathrm{H}}{|}}{C}=N-R$$

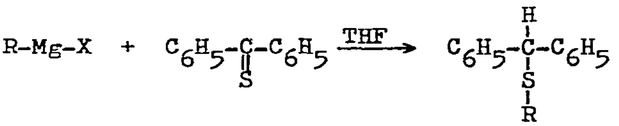
In a Brittish Patent the following addition reaction is reported [186]:



No aziridine could be isolated by Alvernhe and Laurent from the reaction of Grignard compounds with acetonoxime [187]; instead the authors obtained the corresponding amines

A surprisingly large number of publications appeared this year dealing with the reaction of Grignard compounds with thioketones:

Dagonneau and Vialle obtained S-substituted products in the reaction of ten Grignard compounds with thiobenzene [188]:

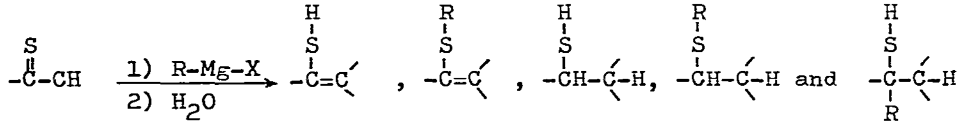


$$R-Mg-X + C_6H_5-\underset{\underset{\mathrm{S}}{\|}}{C}-C_6H_5 \xrightarrow{THF} C_6H_5-\overset{\overset{\mathrm{H}}{|}}{\underset{\underset{\underset{\underset{\mathrm{R}}{|}}{\mathrm{S}}}{|}}{C}}-C_6H_5$$

yields up to 95%

As already reported in Chapter 4B, Dagonneau, Hemidy, Cornet and Vialle found ESR evidence for the occurence of radical anions during such reactions [147].

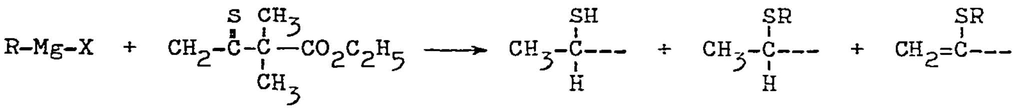
The reaction of Grignard compounds with aliphatic thioketones leads to a complex mixture of products; Paquer and Vialle examined the reactions of methyl-tert-butyl thioketone and of diisopropyl thioketone with methyl-, ethyl-, isopropyl-, t-butyl- and vinylmagnesium halides [149]:



$$\overset{S}{\overset{\|}{-C}}-CH \xrightarrow[2)\ H_2O]{1)\ R-Mg-X} \overset{\overset{H}{|}}{\overset{S}{|}}{-C}=C\lt\ ,\ \overset{\overset{R}{|}}{\overset{S}{|}}{-C}=C\lt\ ,\ \overset{\overset{H}{|}}{\overset{S}{|}}{-CH}-\overset{/}{\underset{\backslash}{C}}-H,\ \overset{\overset{R}{|}}{\overset{S}{|}}{-CH}-\overset{/}{\underset{\backslash}{C}}-H \text{ and } \underset{\underset{R}{|}}{\overset{\overset{H}{|}}{\overset{S}{|}}{-C}}-\overset{/}{\underset{\backslash}{C}}-H$$

Methyl- and vinylmagnesium halides give C-addition, the other three Grignard compounds give mainly reduction reactions.

Paquer and Pou obtained three different products from the reaction of aliphatic Grignard compounds with β-thioketoesters [190]:



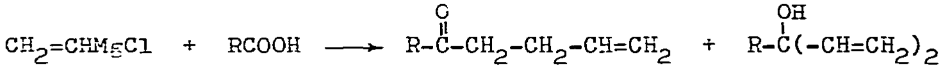
$$R-Mg-X + CH_2-\overset{S}{\overset{\|}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CO_2C_2H_5 \longrightarrow CH_3-\underset{\underset{H}{|}}{\overset{\overset{SH}{|}}{C}}--- + CH_3-\underset{\underset{H}{|}}{\overset{\overset{SR}{|}}{C}}--- + CH_2=\overset{\overset{SR}{|}}{C}---$$

with in general the S-addition product being the major one in the mixture of products.

When α-methyl groups were replaced by hydrogen different products were obtained, mainly resulting from reaction with the ester function.

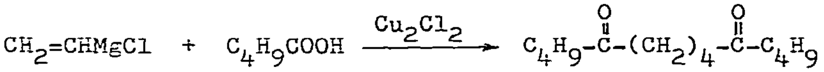
5B. Reactions with acids, esters, lactones, lactams, imines, etc.

Watanabe, Suga, Fujita and Takahashi investigated the reactions of vinylmagnesium chloride with various acids [191] and [191A]: With aliphatic acids the following mixture of products was obtained:



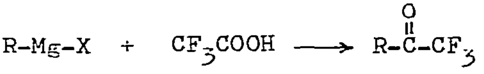
$$CH_2{=}CHMgCl \;+\; RCOOH \longrightarrow R{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}CH_2{-}CH{=}CH_2 \;+\; R{-}\overset{OH}{\overset{|}{C}}(-CH{=}CH_2)_2$$

With benzoic acid only the ketone is formed. The reaction of vinylmagnesium chloride with pentanoic acid in the presence of copper(I) chloride leads in a rather unexpected fashion to the 1,6-diketone [191B]:



$$CH_2{=}CHMgCl \;+\; C_4H_9COOH \xrightarrow{Cu_2Cl_2} C_4H_9{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_4{-}\overset{O}{\overset{\|}{C}}{-}C_4H_9$$

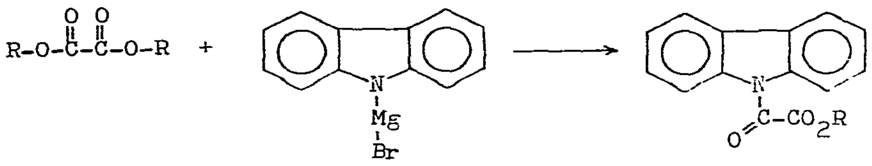
When the ester was used instead of the acid the only product formed is the monoketone as mentioned above. Trifluoroacetic acid reacts with aryl- and hexylmagnesium halides to form trifluoromethyl ketones (Lapkin, Dormidontov and Dormidontova [192]:



$$R{-}Mg{-}X \;+\; CF_3COOH \longrightarrow R{-}\overset{O}{\overset{\|}{C}}{-}CF_3$$

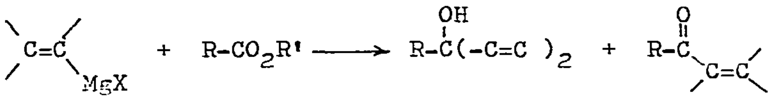
R	Yield
phenyl	42%
p-anisyl	36%
n-hexyl	70%

The reaction of carbazoyl-9-magnesium bromide with oxalic esters leads to the formation of ketoesters (Lapkin and Dormidontov [192A]:

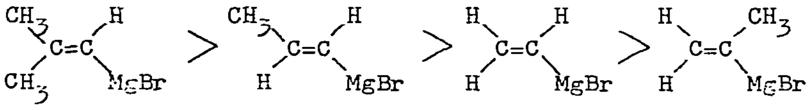


R = ethyl, propyl, isopropyl, butyl and isobutyl

Boccara and Maitte studied the reactions of vinylic Grignard compounds with esters [193]. With ethyl formate and ethyl benzoate as well as with isopropyl acetate the vinylic carbinols were the main products:

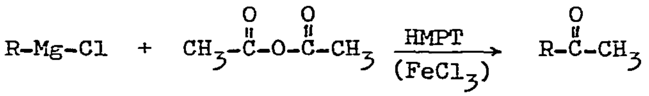


With ethyl acetate, ethyl phenylacetate, ethyl propionate and ethyl isovalerate however mainly ketone formation occured.
Methyl substitution in vinylmagnesium halides favors carbinol formation in the reactions with esters; the following order for this reaction was found:



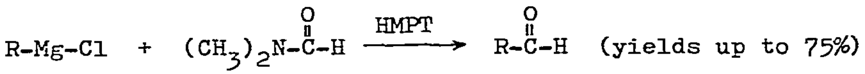
The reaction of alkylmagnesium halides with esters in HMPT (followed by acetylation of the product obtained with acetic anhydride) indicates that in this solvent the esters are hardly enolized (Huet, Emptoz and Jubier [194]). Furthermore the authors found that enolates with the smallest number of substituents are formed preferentially.

Alkylmagnesium halides react with acetic acid anhydride in HMPT to form ketones (Fauvarque, Ducom and Mme. Fauvarque [195]):



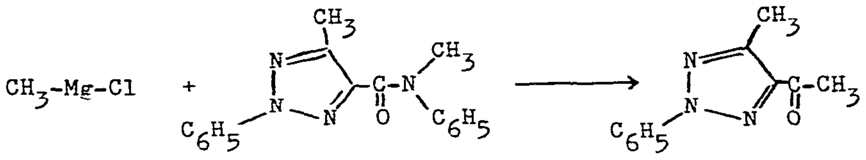
$$\mathrm{R\text{-}Mg\text{-}Cl} \;+\; \mathrm{CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3} \xrightarrow[\mathrm{(FeCl_3)}]{\mathrm{HMPT}} \mathrm{R\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3}$$

The yield of ketones is improved considerably by the addition of iron(III) chloride to the reaction mixture.
The same authors obtained aldehydes in excellent yields by reaction of Grignard compounds with dimethylformamide in HMPT:

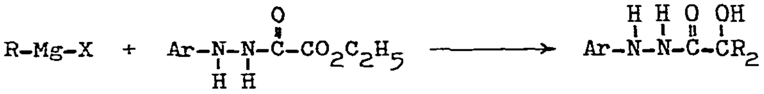


$$\mathrm{R\text{-}Mg\text{-}Cl} \;+\; \mathrm{(CH_3)_2N\text{-}\overset{O}{\overset{\|}{C}}\text{-}H} \xrightarrow{\mathrm{HMPT}} \mathrm{R\text{-}\overset{O}{\overset{\|}{C}}\text{-}H} \quad \text{(yields up to 75\%)}$$

Klingsberg reported the following ketone synthesis [196]:



Bis-(p-biphenylyl)phenylglycolic acid arylhydrazides were obtained by the following reaction of Grignard compounds (Berdinskii and Tenenboim [197]):

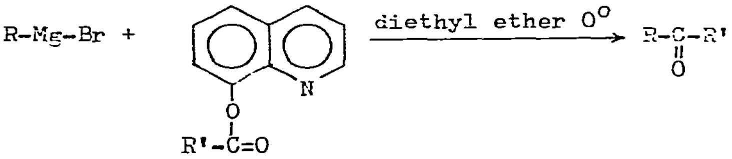


$$\mathrm{R\text{-}Mg\text{-}X} \;+\; \mathrm{Ar\text{-}\underset{H}{\underset{|}{N}}\text{-}\underset{H}{\underset{|}{N}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}CO_2C_2H_5} \longrightarrow \mathrm{Ar\text{-}\overset{H}{\overset{|}{N}}\text{-}\overset{H}{\overset{|}{N}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{OH}{\overset{|}{C}}R_2}$$

R = p-biphenylyl

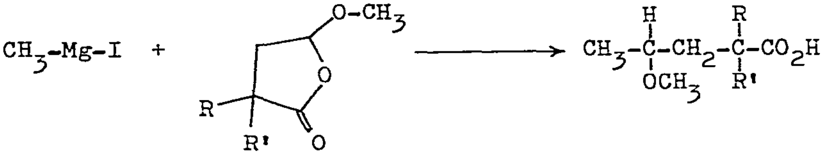
The same type of product was obtained by Berdinskii and Pilipenko by using thienylmagnesium bromide [197A].

Sakan and Mori reported the formation of ketones by reaction of Grignard reagents with the acetate or benzoate of 9-hydroxyquinoline [198

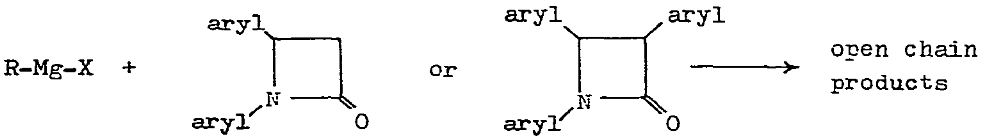


R = phenyl, hexyl, benzyl or ethyl
R' = methyl or phenyl

Methylmagnesium iodide reacts with methoxy-γ-lactones exclusively by ring-scission at the C_4-O bond [174]:

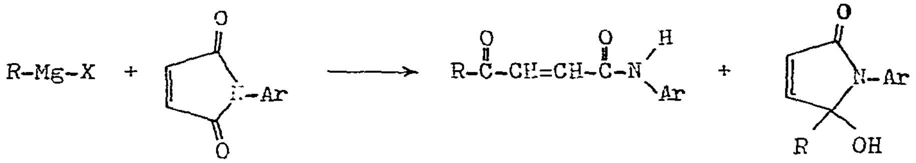


Panajotova, Pentscheva and Spassov report further details of the products obtained on reaction of Grignard compounds with di- and triaryl substituted β-lactams (azetidin-2-ones) [199] and [200]:



Ref. [199]   Ref. [200]

Awad and Ismael reported ring-opening as well as carbonyl addition products from the reaction of phenyl or methyl Grignard compounds with N-substituted imines [201]:

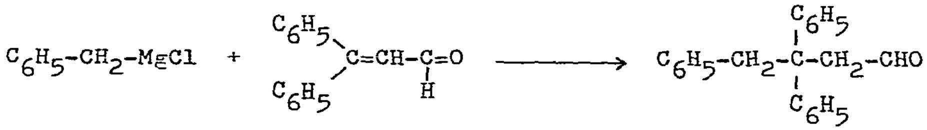


5C. Reactions with unsaturated aldehydes, ketones, esters, etc.

Nii, Furukawa and Iwakiri report the reaction of C_4-, C_6- and C_8-organomagnesium halides with acroleine [202]; addition to the carbonyl group leads to the formation of secondary alcohols with high molecular weights.

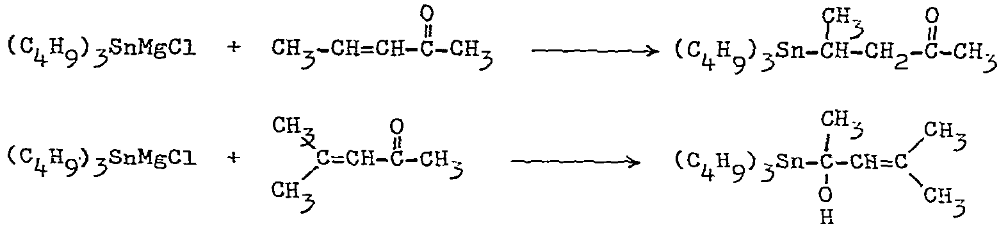
In a Russian patent the reaction is described of Grignard compounds with α-alkoxyacroleine [203].

As already reported in Chapter 4Ai, 2,2-diphenylvinylmagnesium bromide reacts with β,β-diphenylacroleine to form a diol, probably via a single electron transfer mechanism [133]; in another publication the same authors report that β,β-diphenylacroleine reacts "normally" with its carbonyl function when methyl-, ethyl-, phenyl- or allylmagnesium halides are added [204]; with benzylmagnesium chloride however the 1,4-addition product was mainly formed:

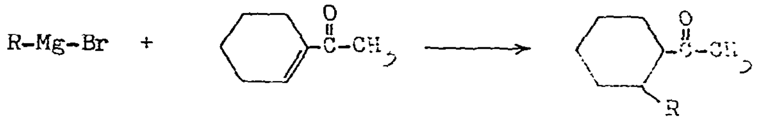


$$C_6H_5-CH_2-MgCl + (C_6H_5)_2C=CH-\underset{H}{C}=O \longrightarrow C_6H_5-CH_2-\underset{C_6H_5}{\overset{C_6H_5}{C}}-CH_2-CHO$$

The reaction of tributyltinmagnesium chloride with unsaturated ketones leads to both 1,2- and 1,4-addition [51]; steric hindrance may prevent 1,4-addition as is illustrated in the following reactions:

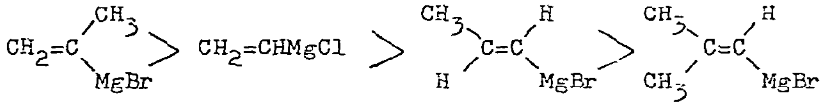


Pishnamazzade and Guseinov obtained exclusively 1,4-addition products in the reaction of Grignard compounds with cyclohexenyl methyl ketone [205]:



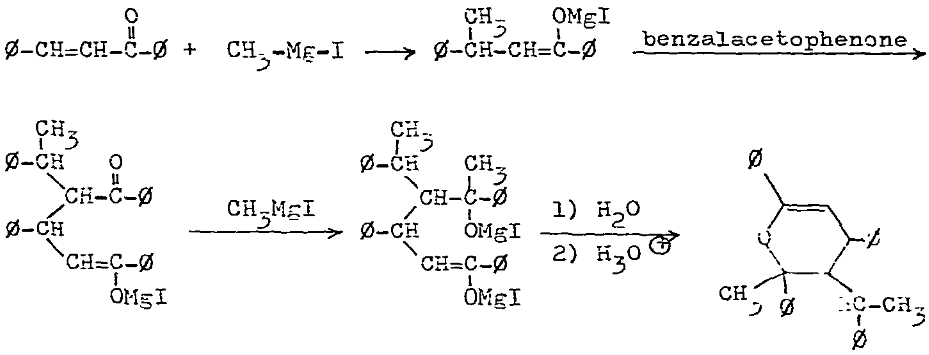
R = ethyl, isopropyl, butyl, isobutyl and allyl

The reactions of ethylenic Grignard compounds with α-unsaturated carbonyl compounds have been extensively investigated by Boccaro and Maitte [193]. The authors found the following order of reactivity in conjugate addition reactions with unsaturated ketones:



With unsaturated aldehydes the main product (in several instances 100% of the total yield) is the alcohol, resulting from "normal" carbonyl addition. In case of alkyl substitution steric hindrance is an important factor determining the course of the reaction. With phenyl substitution electronic effects play an important role.

Kretchmer elucidated the structure of a high molecular weight product formed in the reaction of benzalacetophenone with methylmagnesium iodide [206]; the author proposed the following reaction scheme for the formation of the dihydropyran:

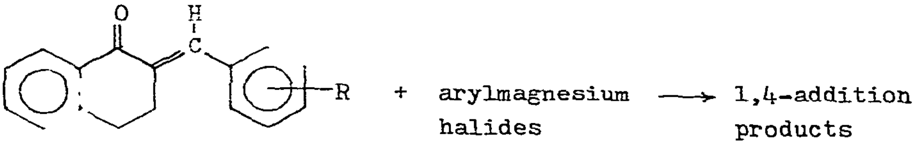


∅ = phenyl

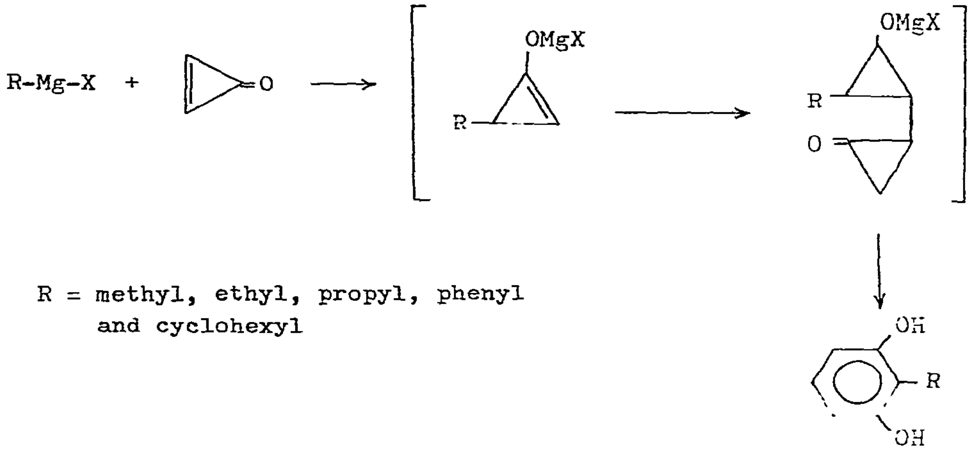
20%

Sammour and Elkasaby reported the results of reactions of arylmagnesium halides with several substituted benzalacetophenones [207]; the only products obtained were 1,4-addition products.

Also in the reactions of arylmagnesium halides with 2-benzylidene-3,4-dihydro-1-(2H)naphthalenone 1,4-addition is observed (Awad, Moustafa and Raouf [208]):

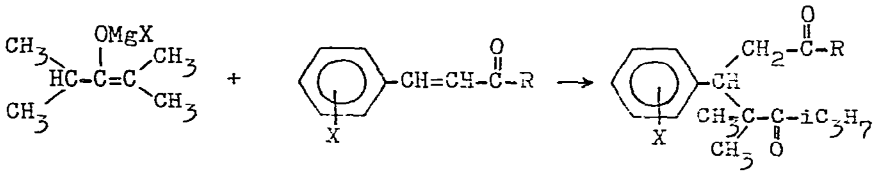


Independent of the order of mixing of the reactants, Grignard compound react with 2 molecules of cyclopropene to form dihydroxybenzene derivatives as reported by Oda, Breslow and Pecoraro [209]. The product of conjugate addition in the first reaction step reacts with a second molecule of cyclopropenone in what "amounts to an ene reaction":



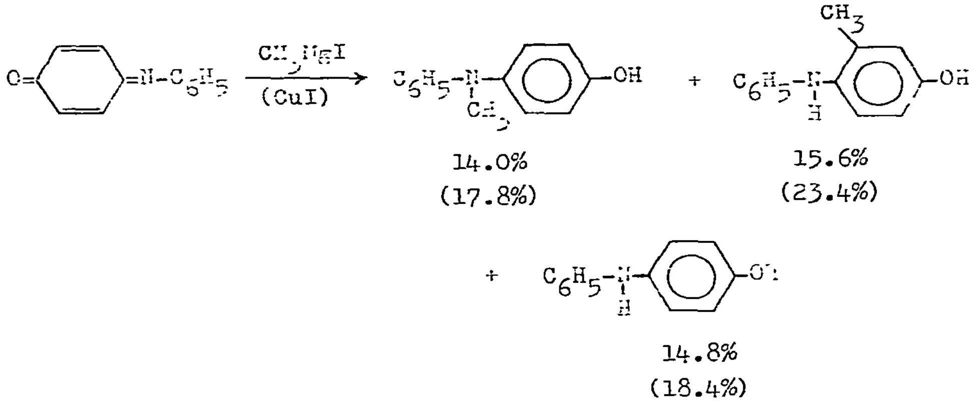
R = methyl, ethyl, propyl, phenyl
and cyclohexyl

The reactions of unsaturated ketones with enolate derivatives of ketones as prepared by a French group (see Chapter 2Bv) afforded δ-diketones in excellent yields as the result of 1,4-addition [76]:

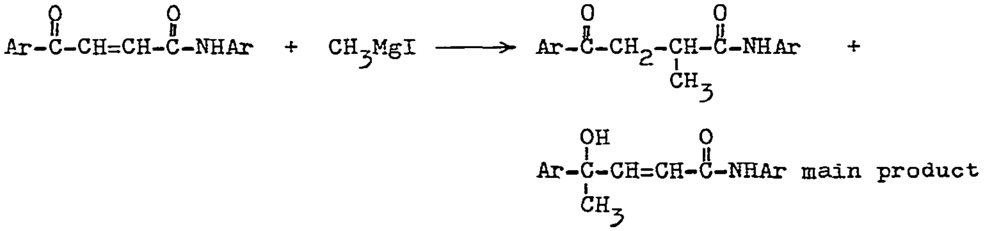


R = methyl or phenyl

The authors have also studied the stereochemistry of the reaction. The reaction of methylmagnesium iodide with N-phenyl-p-quinoneimine leads to products resulting from 1,4- and 1,6-addition reactions as well as from reduction reactions (via semiquinones) (Tlustakova and Honzl [210]):



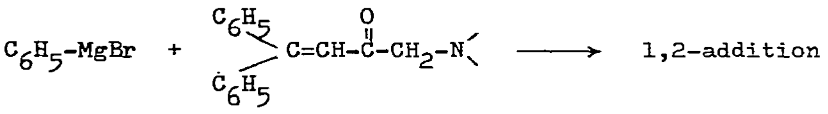
As indicated in the reaction scheme, addition of copper(I) iodide slightly changes the yields of the various reaction products. Unsaturated keto-amides, investigated by Awad, Ismael and Nour-El-Deen give 1,2- as well as 1,4-addition reaction products with Grignard compounds [211]:



$$\mathrm{Ar{-}\overset{O}{\overset{\|}{C}}{-}CH{=}CH{-}\overset{O}{\overset{\|}{C}}{-}NHAr} + \mathrm{CH_3MgI} \longrightarrow \mathrm{Ar{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}\underset{\underset{CH_3}{|}}{CH}{-}\overset{O}{\overset{\|}{C}}{-}NHAr} +$$

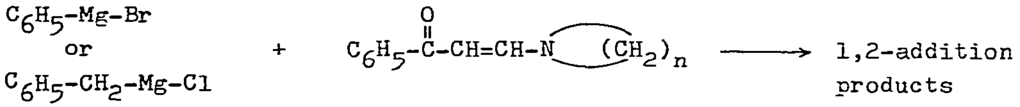
$$\mathrm{Ar{-}\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}{-}CH{=}CH{-}\overset{O}{\overset{\|}{C}}{-}NHAr}\ \text{main product}$$

Different products were obtained with phenylmagnesium bromide. Gautier, Miocque, Combret-Farnaux and Girardou found exclusively 1,2-addition reaction products of phenylmagnesium bromide with amino-substituted unsaturated ketones [212]:

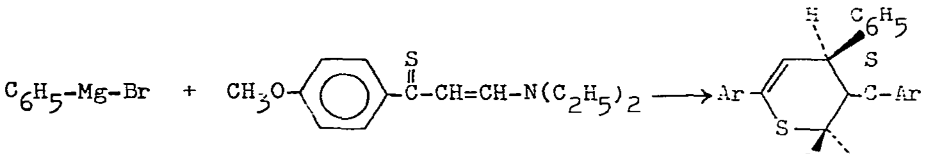


-N< is morpholino, piperidino or pyrrolidino

Also in the following reactions Hahn, Bartnik, Drabowicz and Zielinski observed exclusively 1,2-addition [213]:

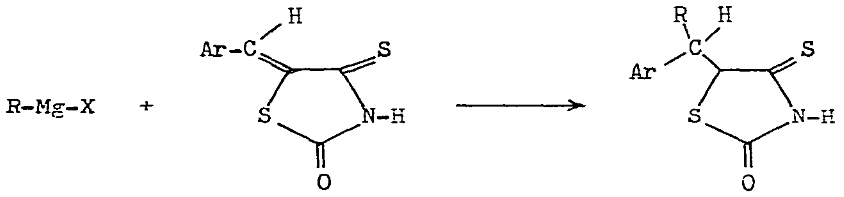


Phenylmagnesium bromide reacts with the thioketoenamine $\boxed{22}$ via a complicated mechanism to form the thiopyran derivatives (epimers are formed) (Pradere, Bouet and Quiniou [214]):

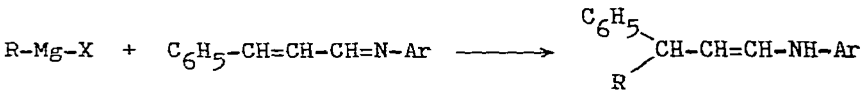


$\boxed{22}$

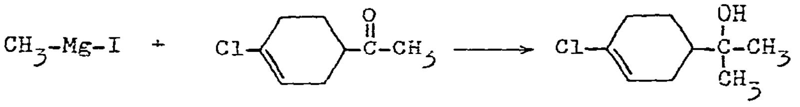
Kassab, Elnagdy, Messcha and Ead report 1,4-addition in the following reaction [215]:



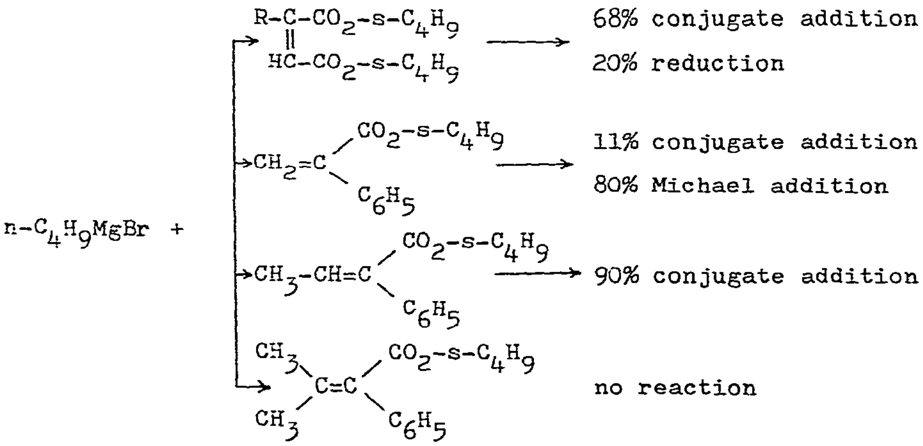
β-Phenylacroleine-N-arylaldimines also react with Grignard compounds to form 1,4-addition products (Sammour, Selim and Nour ElDeen [214]):



Tsizin and Drabkina reported the following reaction [217]:

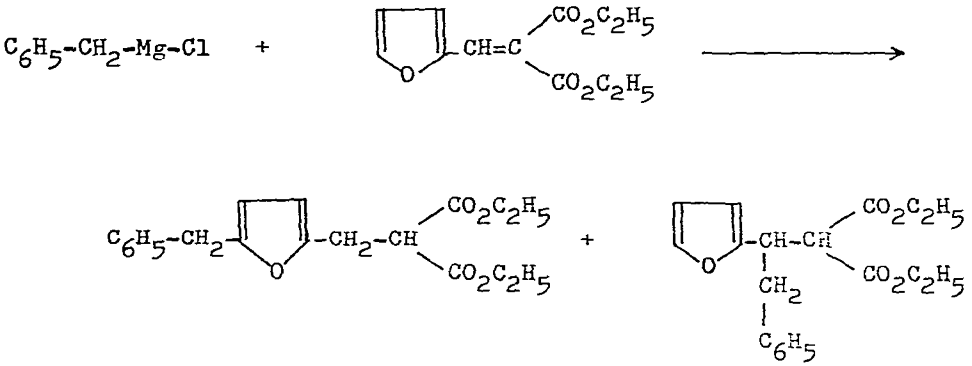


Hansen, Rosendahl Jensen and (the late) Munch-Petersen investigated the reaction of butylmagnesium bromide with, maleic acid, acrylic acid and crotonic acid derivatives [218]:



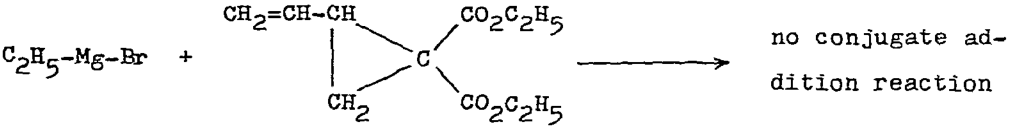
The addition of copper(I) chloride had some effect on the ratios of the products formed.

Whereas in general Grignard reagents react with diethyl furfurylidenemalonate to yield 1,4-addition products (although isopropyl- and isobutylmagnesium halides also yield small amounts of reduction products) benzylmagnesium chloride gives both 1,4- and 1,8-addition products in a 65 : 35 ratio (Holmberg, Karlsson, Ulfstedt and Olli [219]):



The authors exclude a cyclic mechanism for the formation of the 1,8-addition product but make the remark that the formation of relatively large quantities of dibenzyl supports a radical mechanism for this reaction.

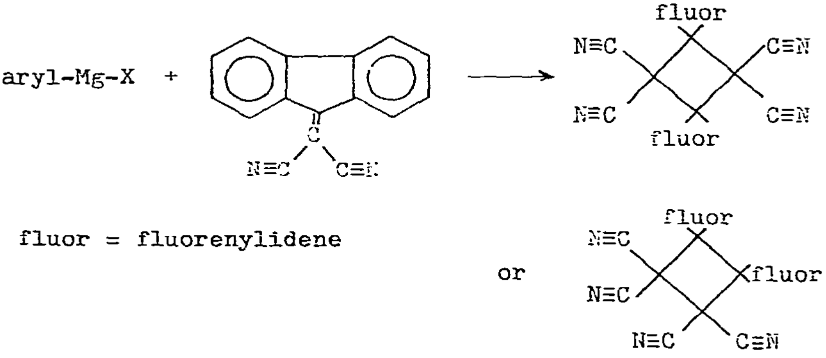
Daviaud and Miginiac found no products resulting from conjugate addition reactions of ethylmagnesium bromide with diethyl 2-vinylcyclopropyl-1,1-dicarboxylic acid [220]:



In Chapter 4C mention has been made of the stereochemical investigations by a French group of the reduction reactions of Grignard compounds with 4-t-butylcyclohexylidenemalonitrile or with ethyl 4-t-butylcyclohexylidenecyanoacetate [162].

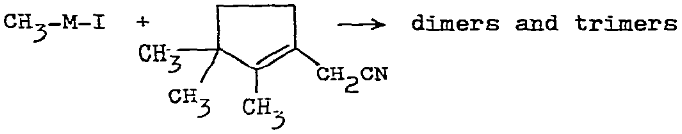
Also in Chapter 4C mention has been made of the investigations by Roumestant and Gore of the reaction of methylmagnesium iodide with acetates of propargylic alcohols, leading to allenyl iodides or bromides (depending on the magnesium halide added to the reaction mixture) among other products [163] and [221].

Latif, Mishriky and Hammad reported the following unusual reaction [222]:

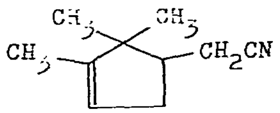


fluor = fluorenylidene

Dimeric and trimeric products were isolated by Pirisino and Sparatore from the reaction of methylmagnesium iodide with β-campholenonitrile [223]:



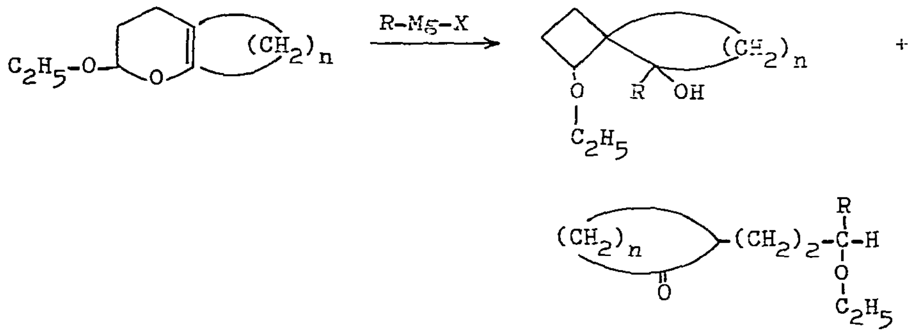
Normal products of nitrile reactions were obtained with the isomeric α-campholenonitrile:



The peculiarities of the reaction of simple alkylmagnesium halides with alkyl dimethylhexynyl ethers, which lead to dimers of the radical from the Grignard compound as well as of the dimethylhexynyl radical have been discussed in Chapter 4B [149].

In Chapter 2D attention has been paid to the reaction of "in situ" or "nascent" ethylmagnesium bromide with vinylacetylenic seleno and telluro ethers [97].

Vu Moc Thuy, Maitte and Petit reported the reaction of methyl- or b tylmagnesium halides with 2-ethoxy-dihydropyran derivatives which lead to either ring opening or ring contraction reactions [224]:



R = methyl or butyl

Gore and Dulcère report the reaction of methylmagnesium iodide with 5-chloro-3-pentene-1-yn [225]

$$CH_3\text{-}M\text{-}I \quad + \quad Cl\text{-}CH_2\text{-}CH{=}CH\text{-}C{\equiv}CH \longrightarrow CH_3\text{-}CH{=}CH\text{-}CH{=}C{=}CH_2$$

5D. Reactions with double bonds

In two U.S. patents reactions are reported of diallylmagnesium as well as of dipentylmagnesium with olefins [226] and [227]: the reactions are performed at temperatures as high as 150° and at pressures up till 200 atm.

Lehmkuhl and Reinehr report that alkylmagnesium halides with tertiary or secondary alkyl groups show enhanced reactivity towards olefins [228]; furthermore these authors report that organomagnesium compounds with allylic double bonds, among which they mention octadienediylmagnesium

$$\text{-Mg-CH}_2\text{-CH=CH-CH}_2\text{-CH}_2\text{-CH=CH-CH}_2\text{-Mg-}$$

react with allene or 1,3-dienes (butadiene or isoprene) to yield cyclohexane derivatives.

The addition of "in situ" Grignard reagents to conjugated enynes as reported by a Russian group has been discussed in Chapter 2D [96].

In Chapter 4C the intramolecular addition to a double bond in 2,7-octadienyl-1-magnesium bromide has been mentioned in relation to the stereochemistry of the cyclization [157].

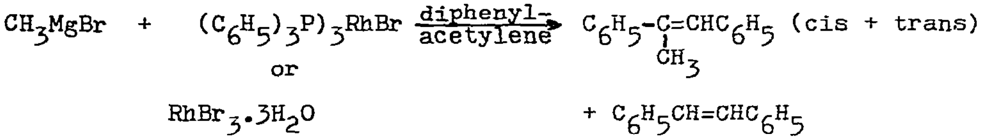
St. Denis, Dolzine and Oliver studied the intramolecular cyclization reactions of several hexen-5-yl metal derivatives among which also the magnesium compound [229]. This magnesium derivative is prepared from the mercury compound by heating at 110° during 24 hours without solvent; during this process cyclization occurs.

Mauzé, Courtois and Miginiac reported the following reaction [230]:

$$\text{CH}_2\text{=CH-CH}_2\text{-Mg-Br} \;+\; \text{HC}\equiv\text{C-CH=CH-CH}_2\text{-OH} \longrightarrow$$

$$\underset{34\%}{\text{HC}\equiv\text{C-CH}_2\text{-CH(CH}_2\text{-CH=CH}_2\text{)-CH}_2\text{OH}} \;+\; \underset{16\%}{\text{CH}_2\text{=C=CH-CH(CH}_2\text{-CH=CH}_2\text{)-CH}_2\text{OH}}$$

Together with Balog Michman studied the reaction of methylmagnesium bromide with rhodium salts and diphenylacetylene [231];



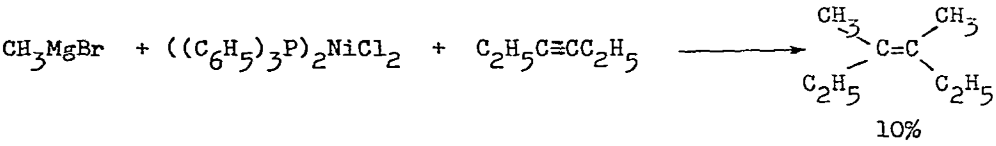
$$CH_3MgBr + ((C_6H_5)_3P)_3RhBr \text{ or } RhBr_3 \cdot 3H_2O \xrightarrow[\text{acetylene}]{\text{diphenyl-}} C_6H_5\text{-}C(CH_3)\text{=}CHC_6H_5 \text{ (cis + trans)} + C_6H_5CH\text{=}CHC_6H_5$$

α-Methylstilbene is the main component among the addition products, but the formation of stilbene shows that hydrogen transfer occurs as well.

In the presence of palladium compounds of the type L_2PdCl_2 (where L is either benzonitrile or norbornadiene) methylmagnesium bromide reacts with diphenylacetylene to give α,α'-dimethylstilbene as the main product (65%); stilbene and α-methylstilbene form as side products (25%)(Garty and Michman [232]):

$$CH_3MgBr + L_2PdCl_2 \xrightarrow[\text{acetylene}]{\text{diphenyl-}} C_6H_5C(CH_3)\text{=}C(CH_3)C_6H_5 \text{ (cis + trans)}$$
$$+ C_6H_5C(CH_3)\text{=}CHC_6H_5 + C_6H_5CH\text{=}CHC_6H_5$$

Duboudin and Jousseaume used bis(triphenylphosphine)nickel(II) chloride as the catalyst in the same sort of reactions where also addition to 3-hexyne was observed [233]:



$$CH_3MgBr + ((C_6H_5)_3P)_2NiCl_2 + C_2H_5C{\equiv}CC_2H_5 \longrightarrow (CH_3)(C_2H_5)C\text{=}C(CH_3)(C_2H_5)$$

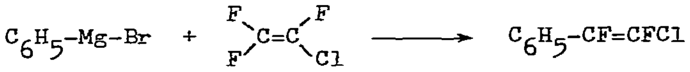
Farady and Marko continued their earlier work on the nickel(II) chloride catalyzed addition of an α-olefin to Grignard reagents [234];

repeated exchange reactions produce double bond shifts in the α-olefin and positional isomerisation in the Grignard compound.
Disproportionation of olefins is observed by Takagi, Hamaguchi, Fukuzumi and Aoyama [235] in the reaction with tungsten (VI) chloride and butylmagnesium iodide (in a 1 : 2 ratio) in a benzene solution: 2-heptene is converted into butane and 5-decene (olefin : W = 100 : 1) Addition of ether or THF to the benzene solution effectively destroys the catalytic activity.

In the light of the previous report it may seem surprising to read that Raven and Wharton obtained 31% conversion in the disproportionation of cis-2-pentene in an ether/benzene solution of WCl_6/n-propylmagnesium bromide [235A].

5E. Reactions with organic halides

In Chapter 4B the following reactions of organomagnesium compounds with organic halides have already been discussed:
the reaction of diethylmagnesium with ethyl and isopropyl iodide, where nuclear polarization was observed [144];
the reaction of phenylmagnesium bromide with tritylbromide [145];
the reaction of phenyl and benzyl Grignard compounds with benzyl, benzhydryl and tritylchloride [146];
In each of these reactions radical intermediates were proposed by the authors.
Sauvêtre and J.-F. Normant reported the reaction of phenylmagnesium bromide with trifluorochloroethylene [236]:

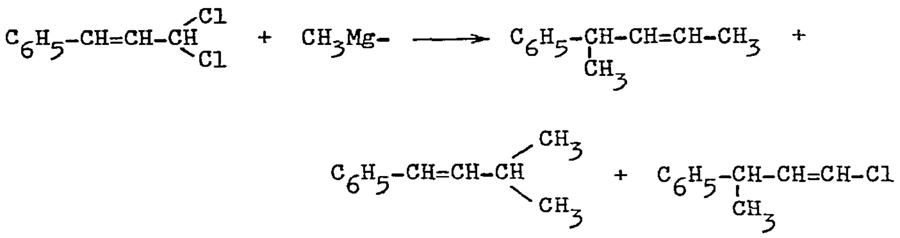


$$C_6H_5\text{-Mg-Br} + F_2C{=}CFCl \longrightarrow C_6H_5\text{-CF=CFCl}$$

cis and trans
82% yield

No reaction is observed with alkylmagnesium halides though.

Brodzki, Wakselman and Wartski investigated the reaction of methylmagnesium compounds with 1-phenyl-3,3-dichloro-1-propene [237];



$$C_6H_5\text{-CH=CH-}CH\begin{matrix}\diagup Cl\\ \diagdown Cl\end{matrix} + CH_3Mg\text{-} \longrightarrow C_6H_5\text{-}\underset{CH_3}{\underset{|}{CH}}\text{-CH=CH-}CH_3 +$$

$$C_6H_5\text{-CH=CH-}CH\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix} + C_6H_5\text{-}\underset{CH_3}{\underset{|}{CH}}\text{-CH=CH-Cl}$$

the product composition depended on the solvent and on the presence of magnesium halides.

Kruglova and Freidlina obtained high yields of coupling products as the result of reactions of benzyl- or allylmagnesium halides with ω,ω'-dichloro-1-bromoalkenes and -alkanes [94]; e.g.:

$$CH_2\text{=CH-}CH_2\text{-Mg-Br} + \text{Br-}CH_2CH_2\text{-}CHCl_2 \xrightarrow[2h]{60^o} \underset{80\%}{CH_2\text{=CH-}(CH_2)_3\text{-}CHCl_2}$$

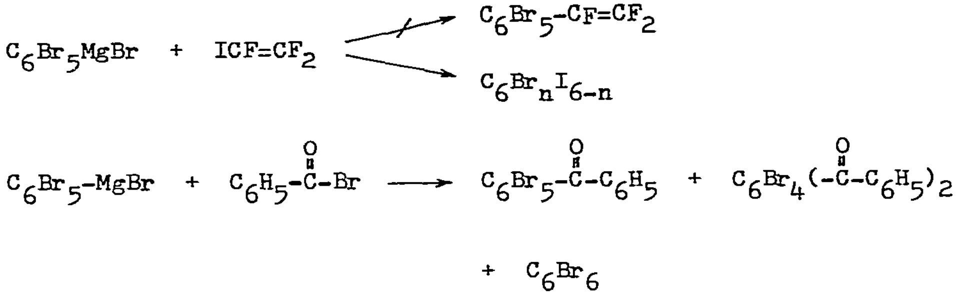
The reaction of methylmagnesium iodide with 5-chloro-3-pentene-1-yn was mentioned earlier [225].

Kulibekov and Gorban' report that as the result of the drastic reaction conditions the following rearrangement occured [238]

$$HC{\equiv}C\text{-Mg-Br} + BrCH_2\text{-CH(-}OC_4H_9)_2 \xrightarrow[\text{one night}]{90^o/\text{THF}} HC{\equiv}C\text{-}CH_2\text{-CH(-}OC_4H_9)_2$$

$$+\ CH_3\text{-}C{\equiv}C\text{-CH(-}OC_4H_9)_2 + HC{\equiv}C\text{-CH=CH-}OC_4H_9$$

Smith, Moore and Tamborski report the reaction of pentabromophenylmagnesium bromide with benzoyl chloride as well as with iodotrifluoroethylene [239].



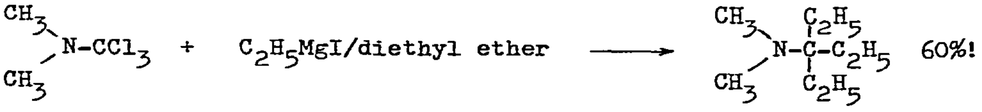
$$C_6Br_5MgBr + ICF{=}CF_2 \begin{array}{l} \not\longrightarrow C_6Br_5{-}CF{=}CF_2 \\ \longrightarrow C_6Br_nI_{6-n} \end{array}$$

$$C_6Br_5{-}MgBr + C_6H_5{-}\overset{O}{\overset{\|}{C}}{-}Br \longrightarrow C_6Br_5{-}\overset{O}{\overset{\|}{C}}{-}C_6H_5 + C_6Br_4(-\overset{O}{\overset{\|}{C}}-C_6H_5)_2 + C_6Br_6$$

Both reactions seem an example of a multiple intermolecular metal-halogen exchange reaction.

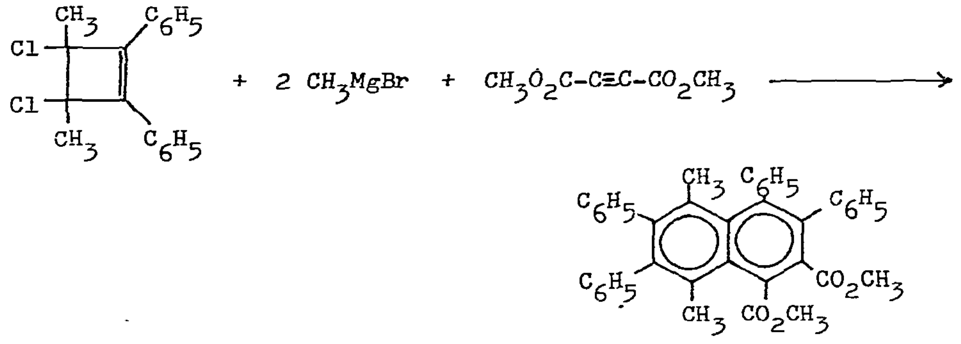
The mechanistic aspects of the reaction of 4-hydroxy-2-methylchloroacetophenone with alkylmagnesium halides have been discussed in Chapter 4C [160].

The following method to prepare sterically hindered tertiairy amines as published by Kukhar and Pasternak needs special mention [240]:

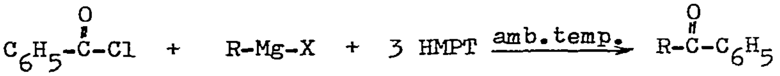


$$\begin{array}{l} CH_3 \\ \quad \rangle N{-}CCl_3 \\ CH_3 \end{array} + C_2H_5MgI/\text{diethyl ether} \longrightarrow \begin{array}{l} CH_3 \quad C_2H_5 \\ \quad \rangle N{-}\underset{|}{\overset{|}{C}}{-}C_2H_5 \\ CH_3 \quad C_2H_5 \end{array} \quad 60\%!$$

Müller and Huth report the formation of a naphthalene derivative in the reaction of methylmagnesium bromide with the following dichlorocyclobutene compound [241]:



The reaction of Grignard compounds, solvated by HMPT, with benzoyl chloride affords phenyl ketones in excellent yields [195]:



$$C_6H_5-\overset{O}{\overset{\|}{C}}-Cl \;+\; R-Mg-X \;+\; 3\ HMPT \xrightarrow{\text{amb.temp.}} R-\overset{O}{\overset{\|}{C}}-C_6H_5$$

R = C_2H_5, 95%; C_4H_9, 95%; i-C_3H_7, 70%; sec-C_4H_9,60%; tert-C_4H_9, 30%; etc.

The mechanistic aspects of the copper(I) chloride catalyzed reactions of alkylmagnesium halides with acid chlorides have been mentioned in Chapter 4C [161].

The cross coupling reaction:

$$Ar-Mg-X \;+\; R-X' \longrightarrow Ar-R$$

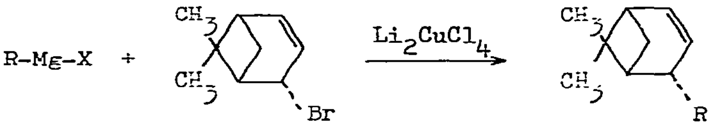
leads to excellent yields when alkyl iodides are used and when as the catalyst the bidentate amine-copper system, copper(I)-N,N,N',N'-tetramethylethylenediamine, is present in the reaction mixture (Onuma and Hashimoto [242].

Tamura and Kochi published an extensive paper on the copper-catalyzed coupling of Grignard reagents and alkyl halides in THF solution [243].

The following process is suggested by the authors:

$$R\text{-}Mg\text{-}Br + Cu^{I}Br \longrightarrow R\text{-}Cu^{I} + MgBr_2$$
$$R\text{-}Cu^{I} + R'\text{-}Br \longrightarrow R\text{-}R' + Cu^{I}Br, \text{ etc.}$$

Alkyl radicals are not viable intermediates in the coupling process. Only disproportionation products are produced from secondary and tertiary halides due to the unfavorable displacement process. Joulain, Moreau and Pfau report Li_2CuCl_4 catalyzed coupling reactions of several organomagnesium halides with trans-bromo-apopinene [244]



Cobalt(II) and nickel(II) chlorides were used as catalysts by Collet and Jacques in the reaction of arylmagnesium halides with tri- and tetrachloroethylene [245]. The formation of biaryls and Ar-H as by-products accompanies the reaction:

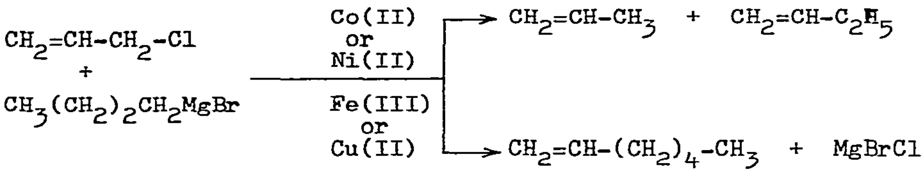
$$Ar\text{-}Mg\text{-}Br + \begin{matrix} ClCH{=}CCl_2 \\ \text{or} \\ Cl_2C{=}CCl_2 \end{matrix} \xrightarrow[\text{catalyst}]{Co^{II} \text{ or } Ni^{II}} Ar\text{-}C{\equiv}C\text{-}Ar + Ar\text{-}Ar + Ar\text{-}H$$

For Ar = phenyl Ar-Ar = 85%; for Ar = mesityl the yield of the acetylene is appr. 50% as is the yield on the Ar-Ar product.

Corriu and Masse found nickel(II) acetylacetonate ($Ni(acac)_2$) to be the most effective catalyst in the reaction of arylmagnesium bromides with trans-bromostyrene or with trans-dichloroethylene [246]; with p-dibromobenzene para-terphenyls were obtained in excellent yields:

$$p\text{-}Br\text{-}C_6H_4\text{-}Br \quad + \quad 2\ Ar\text{-}Mg\text{-}Br \xrightarrow{Ni(acac)_2} p\text{-}Ar\text{-}C_6H_4\text{-}Ar$$

For Ar = phenyl or 3-methylphenyl the yields were better than 80%. Whereas iron(III) and copper(II) salts added to a reaction mixture with allyl chloride and butylmagnesium bromide lead to the formation of the expected coupling product, cobalt(II) and nickel(II) salts cause the formation of propene and 1-butene (Ohbe and Matsuda [247]).

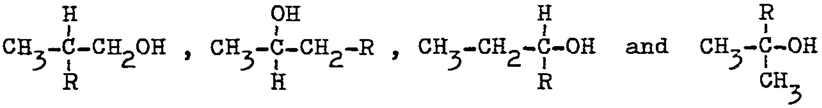


$$CH_2{=}CH\text{-}CH_2\text{-}Cl + CH_3(CH_2)_2CH_2MgBr \xrightarrow{Co(II)\text{ or }Ni(II)} CH_2{=}CH\text{-}CH_3 + CH_2{=}CH\text{-}C_2H_5$$

$$CH_2{=}CH\text{-}CH_2\text{-}Cl + CH_3(CH_2)_2CH_2MgBr \xrightarrow{Fe(III)\text{ or }Cu(II)} CH_2{=}CH\text{-}(CH_2)_4\text{-}CH_3 + MgBrCl$$

5F. Reactions with oxiranes and thiiranes

Sano, S. Matsuda and H. Matsuda investigated the reaction mechanisms of the ring opening reaction of methyloxirane with ethylmagnesium bro- and iodide, isopropylmagnesium bromide and iodide and phenylmagnesium bromide in different solvents [248]. Besides four different alcohols:

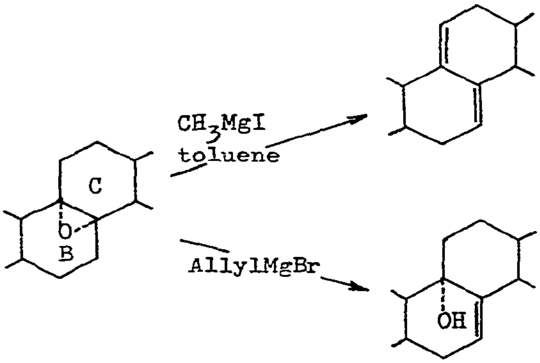


$$CH_3\text{-}\underset{R}{\overset{H}{C}}\text{-}CH_2OH \;,\; CH_3\text{-}\underset{H}{\overset{OH}{C}}\text{-}CH_2\text{-}R \;,\; CH_3\text{-}CH_2\text{-}\underset{R}{\overset{H}{C}}\text{-}OH \;\text{ and }\; CH_3\text{-}\underset{CH_3}{\overset{R}{C}}\text{-}OH$$

also halohydrines are formed especially with increasing ratio R-Mg-X : oxirane.

Contrary to the corresponding aluminum derivatives, diisobutylmagne-

sium does not give reduction products in its reaction with phenyloxirane (Namy and Abenhaim [249].
Boireau, Namy and Abenhaim conclude from the results obtained with reactions of diethylmagnesium with benzyloxirane that the first step in the reaction is a rapid equilibrium with formation of a complex between the magnesium compound and the oxirane [158]. In the following step, which is slow, product formation occurs, leading to only one product, i.e. 1-phenyl-2-pentanol. In strongly basic solvents, such as HMPT, no reaction occurs at all.
The same authors studied the mechanism of the reaction of diallylmagnesium with substituted oxiranes [159].
Although Pettit and W.R. Jones did not obtain products involving alkylation of the lanostane skeleton, their efforts to modify the B/C ring juncture of lanosterol led to the following remarkable reactic products [250]:



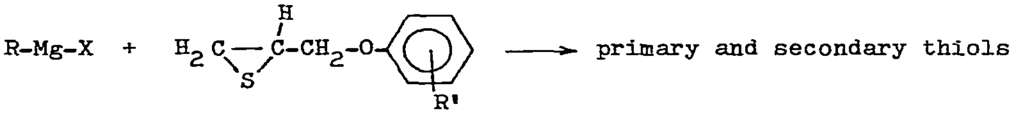
dihydroagnosterol

3β,9αdihydro-5α-lanost-7-ene

Vitali and Gardi observed acetylene-allene rearrangement in the reaction of steroid 4α,5α-oxides with propargylic Grignard reagents [251] These rearrangements seem to be determined by the presence of an oxyg nated function at C_3 which enables complexation with the magnesium atom of the reagent.

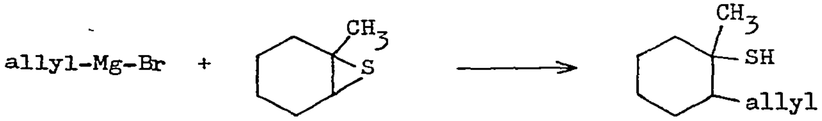
Lahournère and Valade studied the reactivity of tributyltinmagnesium chloride with oxiranes and oxetanes [52].

The following reaction:

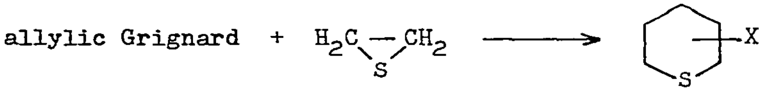


leads exclusively to secondary thiols when R>C_3 (Takeda [252]). With a nitrosubstituent in the aromatic ring only the primary thiol is formed.

Dronov and Krivonogov reported the following reaction [253]:



Kondo and Negishi, in a Japanese patent report the formation of thianes in the reaction of allylic Grignard compounds with thiirane [254]:



X = 3-CH_3, 70%
X = 4-CH_3, 70%
X = 4-C_6H_5, 80%

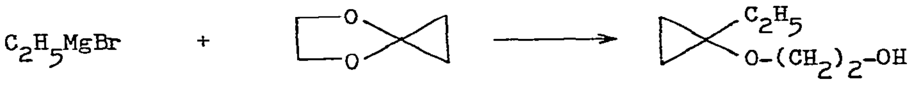
5G. Reactions with ethers, acetals, etc.

Maercker and Weber observed in their pyrolysis experiments with 3-phenylallylcarbinylmagnesium bromide that, surprisingly, diethyl ether at temperatures above 100° is attacked by the Grignard reagent about 20 times faster than is tetrahydrofuran [152]. The dialkylmagnesium compound reacts more rapidly with both solvents.

As already mentioned in the previous chapter, Lahournère and Valade studied the reaction of tributyltinmagnesium chloride with substituted oxetanes [52].

Several reports of ringopening reactions of Grignard compounds with 1,3-dioxolanes have appeared this year:

Giusti [255]:

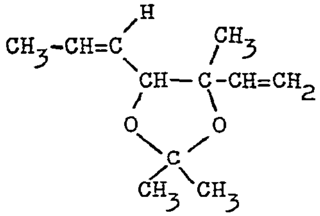


For the reaction of 2,2-dipiperidino- or -dimorpholino-1,3-benzdioxolane Cabiddu, Marongiu and Sotgiu propose a mechanism involving an intermediate enamine [256]; e.g.:

R = piperidino or morpholino

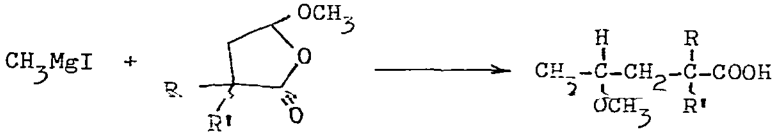
In another paper Cabiddu, Gelli and Maccioni report the cleavage of carbon-oxygen bonds in alkoxybenzenes and in 1,3-benzodioxolane by magnesium bromide [257].

Mousset investigated the reaction of methyl, ethyl and phenyl Grignard compounds with unsaturated substituted 1,3-dioxolanes such as [258]:



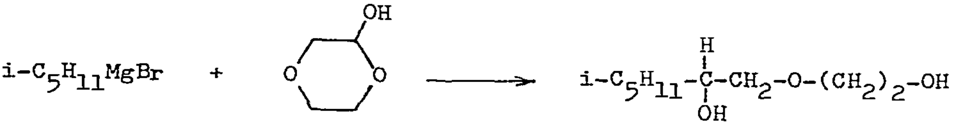
Atavin, Dubova and Sukhomazova used oxa substituted dioxolanes [259]:

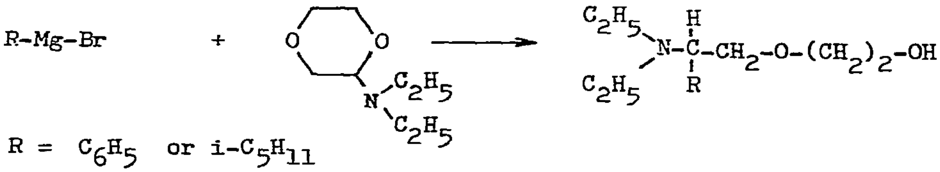
Des Abbayes, Salmon-Legagneur and Neveu observed C_4-O bond scission in the following reaction [174]:



The ring opening or ring contraction reactions of Grignard compounds with 2-ethoxydihydropyran derivatives have been mentioned in Chapter 5C [224].

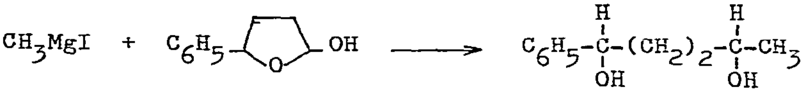
Kuznetsov, Krasavtsev and Myrsina reported the following reactions of substituted 1,4-dioxanes [260]:



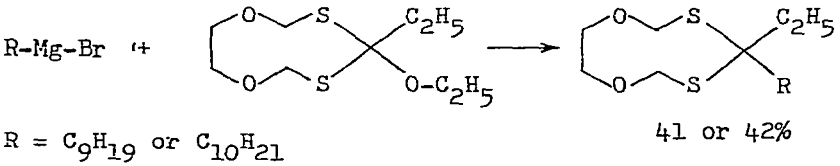


R = C_6H_5 or i-C_5H_{11}

A similar ringopening reaction was reported by Dana and Girault [261]



Abdullaev, Ali-Zade and Dadasheva published the reaction of high molecular Grignard compounds with ethoxy substituted dithiadioxacyclononane [262]:



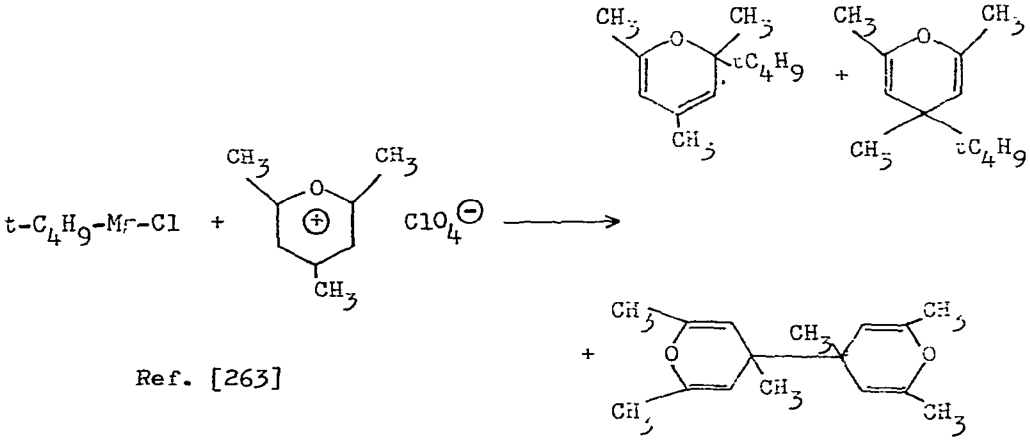
R = C_9H_{19} or $C_{10}H_{21}$

41 or 42%

5H. Reactions with heterocyclic compounds

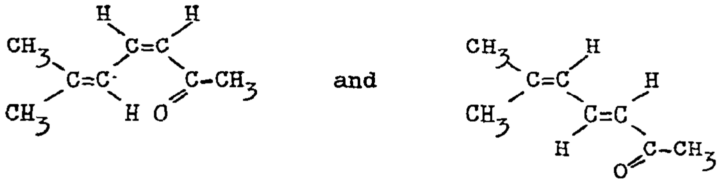
A considerable number of publications on reactions of organomagnesium compounds with heterocycles has appeared this year. They will be summarized in this chapter in the order: O containing compounds, O and S- containing compounds, S- and N-heterocycles with some underdivision in the ring-size of these compounds.

In a series of five papers Dreux, together with Saffieddine, Royer, and in one case with Chalvet and Decoret studied the reactions of organomagnesium compounds with (mainly 2, 4 and 6) substituted pyrylium perchlorates [263], [264], [265], [266] and [267]. As an example, the reaction of tert-butylmagnesium chloride is shown which not only gives the 2H- and 4H-pyran derivatives (which are the normal reaction products) but which also yields a dimerisation product as the result of a reduction of the pyrylium salt:



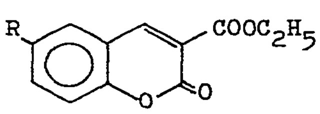
Ref. [263]

Methylmagnesium iodide reacts with 2,6- dimethylpyrylium perchlorate to give ring opening products (besides the normal 2H- and 4H-pyrans) [264]:

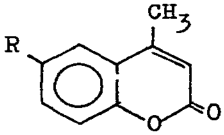


Ref. [265]

According to Sammour, Selim and Elkady the coumarin derivatives $\boxed{23}$ and $\boxed{24}$ react with arylmagnesium halides to yield the 2,2-diaryl chromane homologues [268];

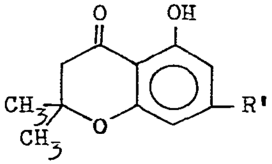


23



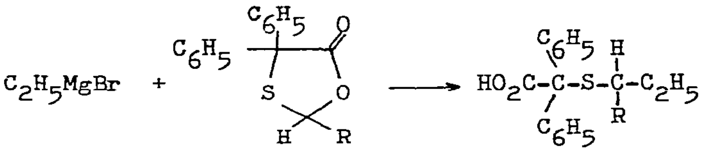
24

A German Patent contains the report of a normal carbonyl-addition reaction of Grignard compounds with the substituted chromanone 25 [269]



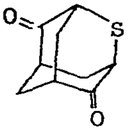
25

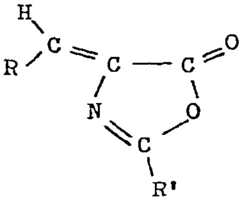
The only product isolated by Frandsen and Pedersen in the reaction of ethylmagnesium bromide with 2,4,4-triaryl substituted 1,3-oxathiolan-5-ones was the acid resulting from attack on carbon-2 subsequently leading to cleavage of the C-O bond [270]:



appr. 50%

Reaction of 2-thiaadamantane-4,8-dione leads both to mono and di-addition products (Janku and Landa [271]).

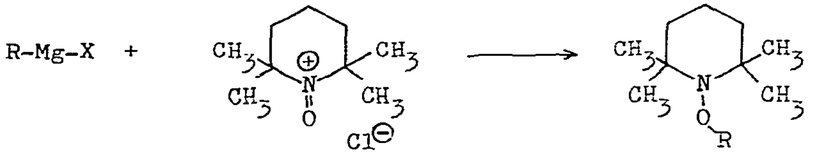




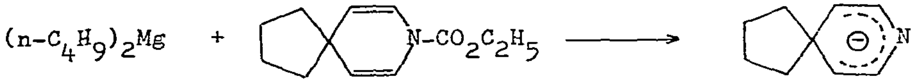
$\boxed{26}$

Harhash and Kashab studied the reactions of alkylmagnesium halides with the 5(4H)-oxazolone $\boxed{26}$ depicted above [272].

Golubev and Kobylyanskii prepared alkoxy- and phenoxypiperidine by the reaction of the corresponding Grignard compound with the oxopiperidinium chloride [273]:

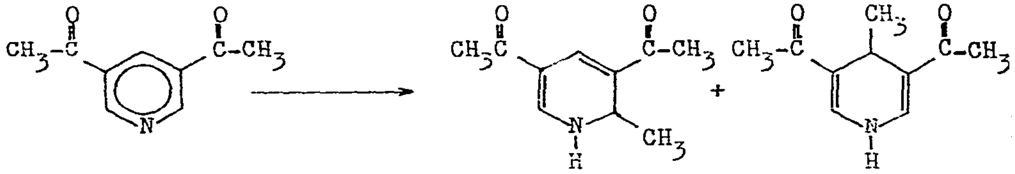


Fraenkel, Ho, Liang and Yu obtained a deep red solution of a dihydropyridinium anion by the following reaction [274]:

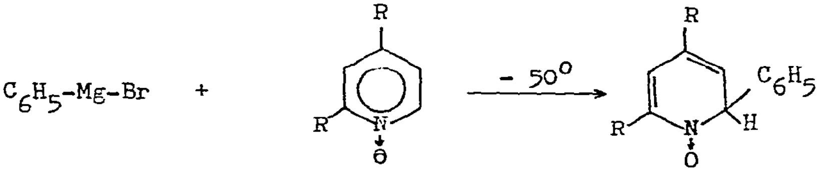


The solution remained unchanged even after heating at 85° during a period of eighteen days.

3,5-Diacetylpyridine reacts with methylmagnesium iodide to give ring-substitution products besides normal carbonyl addition products (Palecek, Vavruska and Kuthan [275]):

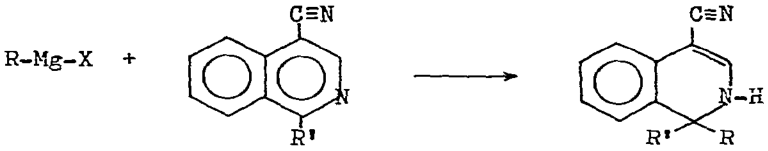


The reaction of phenylmagnesium bromide with pyridine-N-oxides, when carried out at low temperatures (-50°) leads to 2-phenyl-1,2-dihydropyridine-N-oxides according to Schiess and Ringele [276];

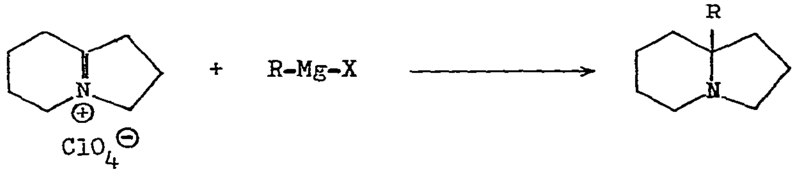


The reaction of allylmagnesium chloride with 2-methylquinoline which shows an unprecedented rearrangement in the quinoline series has been discussed in Chapter 4C [156].

Natsume and Wada observed the following addition reaction [277]:

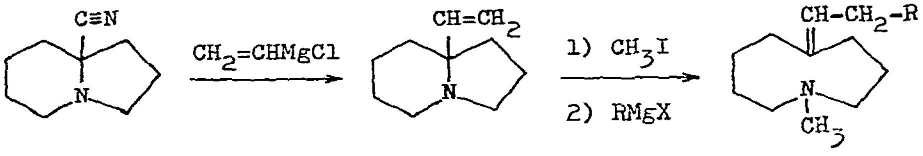


Reinecke, Kray and Francis obtained 9-allyl- or 9-benzylindolizidine from the reaction of the corresponding Grignard compounds with $\Delta^{4(9)}$-dehydroindolizidinium perchlorate [279]:



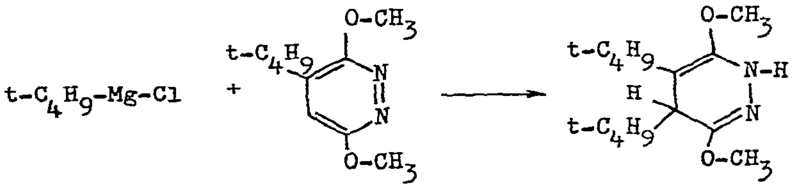
R = allyl or benzyl

Together with Francis, Reinecke published the following route to the 5-substituted N-methyl-1-azacyclononane via the methiodide of 9-vinyl indolizidine [278]:

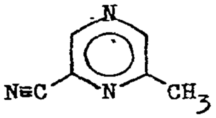


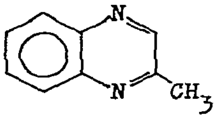
R = C_2H_5 or C_6H_5

In the series of the diaza-compounds the following reports were made:
By Crossland [280]:

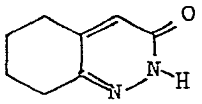


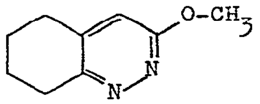
Schwaiger and Ward report addition of the Grignard reagent to the 3,4 C-N bond in reactions with pyrazine and quinoxaline derivatives [281]:





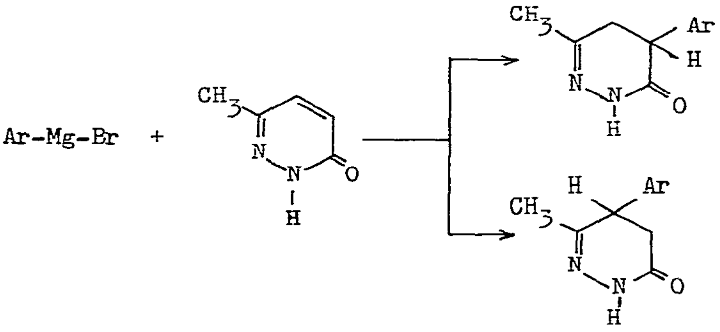
The reaction of organomagnesium halides with 5,6,7,8-tetrahydro-3-cinnolones and of 5,6,7,8-tetrahydro-3-methoxycinnalones





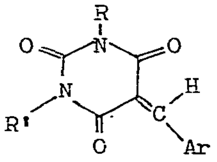
as studied by Daunis, Guerret-Rigal and Jacquier, proceeds preferentially via addition to the unsaturated -C=C-C=N system and not via addition to the carbonyl function [282].

1,4-Addition to both the -C=C-C=N- and the -C=C-C=O system was observed by Baddar, Nosseir, Doss and Messiha in the reaction of phenyl- and p-methoxyphenylmagnesium bromides with 6-methylpyridazin-3(2H)-one [283]:

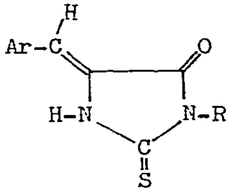


The following reports deal with the reactivity of exocyclic double bonds in heterocyclic compounds:

Shalaby and Abd El-Gawad [284]: and Shalaby and Daboun [285]:

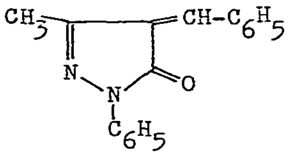


5-arylidene-barbituric acid derivatives



5-arylidene-2-thiohydantoin derivatives

In the same sort of investigations Abdel-Megeid, Elkaschef, Mokhtar and Yassin added Grignard compounds to 4-benzylidene-3- methyl-5-oxo-pyrazoline derivatives [286]:



Harhash together with Elnagdy and Hafez [287] as well as with Kassab and Abdallah [288] investigated reactions of phenylmagnesium bromide with arylazo substituted 2-imidazolinones and 3-pyrazolones. Mansour and Ibrahim finally investigated reactions of thioalkyl substituted 1,2,4-triazines and 1,2,4-triazin-ones [289].

51. Reactions with boron, silicon, phosphorus, sulfur and arsenic compounds

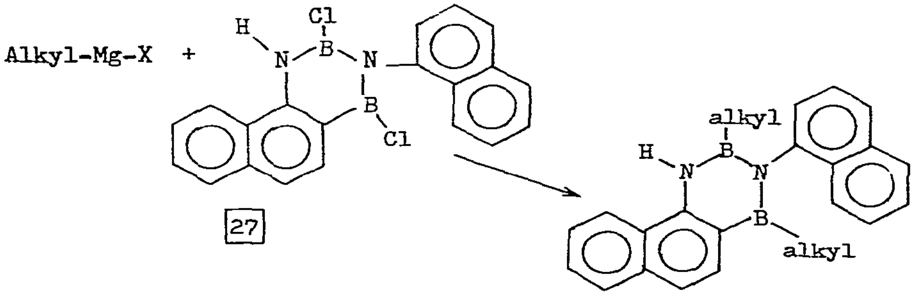
Boron compounds

In Chapter 2D mention has been made of the one step synthesis of alkylboron compounds by reaction of the alkyl or aryl halide with magnesium in the presence of diborane [91], [92] and [93].
^{10}B-labelled alkyl and aryl compounds were prepared by Pirtskhalava and Abashmadze [290]: e.g.

$$i\text{-}C_3H_7MgBr + {}^{10}BF_3.(CH_3)_2O \longrightarrow {}^{10}B(i\text{-}C_3H_7)_3$$

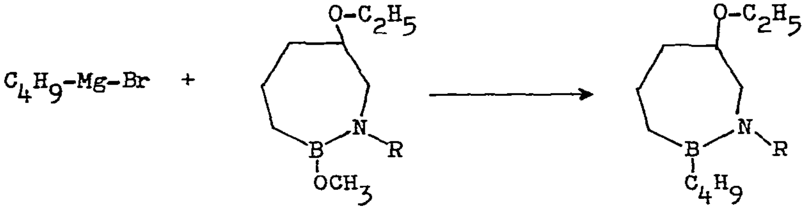
$$^{10}B(i\text{-}C_3H_7)_3 + C_6H_5MgBr \longrightarrow C_6H_5\text{-}{}^{10}B(i\text{-}C_3H_7)_2$$

The reactive chlorine atoms in the diboradiaza-compound $\boxed{27}$ underwent facile displacement reactions with methyl, ethyl and n-propyl Grignard compounds (Cueilleron and France [291]):

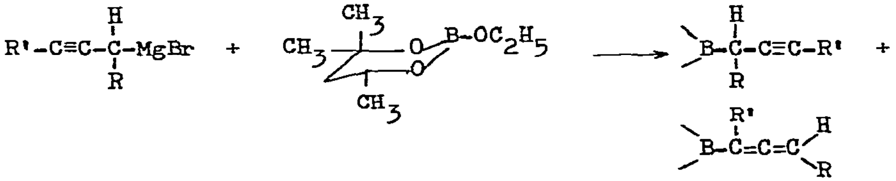


27

Vasil'ev, Vartanyan and Mikhailov reported the following reaction [292]:



The same type of displacement reaction on boron was observed by Soulie and Cadiot [293] although the authors obtained two different products because of rearrangement in the acetylenic Grignard compound:



Silicon compounds

In Chapter 4C the stereochemical investigations with optically active silicon compounds have been mentioned [126] and [164].

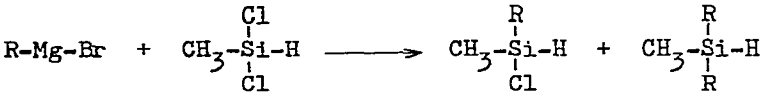
Romashkin, Odabashyan and Pushakov obtained mono- and di-substituted phenylsilanes in the reaction [294]:

$$\text{Br-Mg-}C_6H_4\text{-Mg-Br (p)} + R_2SiHCl \longrightarrow \text{mono- and disubstituted products.}$$

Addition of zinc chloride improved the yield on disubstituted product considerably.

The best method however to obtain the disubstituted derivatives was the "in situ" Grignard technique where p-Br-C_6H_4-Br reacted with magnesium in the presence of the chlorosilanes [65]. See also Chapter 2D.

From the same group the following reaction has to be mentioned [295]:



$$\text{R-Mg-Br} + CH_3\text{-}\underset{Cl}{\overset{Cl}{Si}}\text{-H} \longrightarrow CH_3\text{-}\underset{Cl}{\overset{R}{Si}}\text{-H} + CH_3\text{-}\underset{R}{\overset{R}{Si}}\text{-H}$$

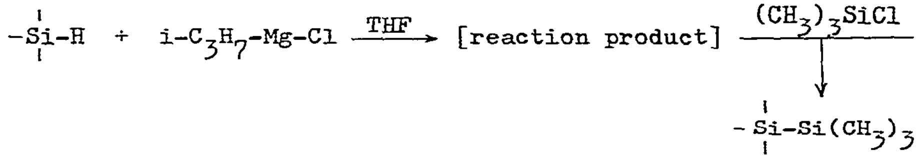
R = m-CF_3-phenyl

The "in situ" reactions of trimethylchlorosilane with magnesium and acetophenone or benzaldehyde in HMPT have been referred to in Chapter 2D [100].

In the same Chapter the same sort of reaction of dimethylchlorosilane with 1,3-dichlorotetrafluorobenzene in THF has been mentioned [87].

In Chapter 2D a short summary is given of the nine publications which have appeared this year from the laboratory of Calas and Dunoguès who reported the "in situ" reactions of trimethylchlorosilane/Mg/HMPT with all sorts of substrates such as benzene, 2-cyanonaphthalene, phenyl-tert-butyl ketone, etc. [101] - [107B].

Hosomi and Sakurai obtained products containing Si-Si bonds by addition of a secondary or tertiary alkylmagnesium halide to an appropriate hydrosilane with subsequent addition of trimethylchlorosilane to the reaction mixture [296].

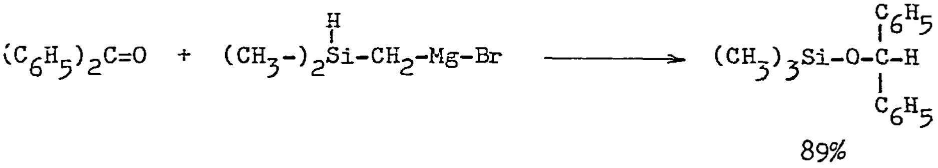


$$-\overset{|}{\underset{|}{Si}}-H \;+\; i\text{-}C_3H_7\text{-}Mg\text{-}Cl \xrightarrow{THF} [\text{reaction product}] \xrightarrow{(CH_3)_3SiCl} -\overset{|}{\underset{|}{Si}}-Si(CH_3)_3$$

The reaction does not take place in diethyl ether; furthermore the intermediacy of a "silyl Grignard" could not be proved: addition of D_2O did not lead to the formation of a product containing a Si-D bond.

In Chapter 4C the anomalous reaction of dimethylsilylmethylmagnesium bromide with triphenylchlorosilane has been mentioned and discussed [55].

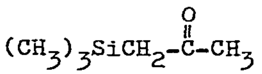
The same authors report that dimethylsilylmethylmagnesium bromide reacts as expected with acetone but that with benzophenone unusual reaction products were isolated [55A]:



$$(C_6H_5)_2C{=}O \;+\; (CH_3\text{-})_2\overset{H}{\overset{|}{Si}}\text{-}CH_2\text{-}Mg\text{-}Br \longrightarrow (CH_3)_3Si\text{-}O\text{-}\overset{C_6H_5}{\overset{|}{\underset{\underset{C_6H_5}{|}}{C}}}\text{-}H \quad 89\%$$

Several mechanistic possibilities are discussed by the authors.

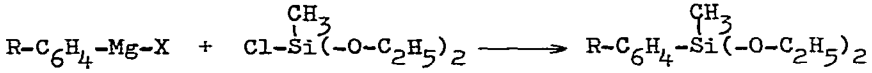
Grignard compounds react normally with



$$(CH_3)_3SiCH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3$$

as reported by Hudrlik and Peterson [297].

Kuroda and Ishikawa obtained the expected coupling reaction products in the following reaction [298]:



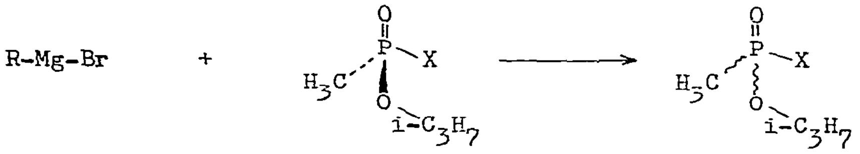
$$R\text{-}C_6H_4\text{-}Mg\text{-}X \;+\; Cl\text{-}\overset{CH_3}{\overset{|}{Si}}(\text{-}O\text{-}C_2H_5)_2 \longrightarrow R\text{-}C_6H_4\text{-}\overset{CH_3}{\overset{|}{Si}}(\text{-}O\text{-}C_2H_5)_2$$

Phosphorus compounds

The direct cyclization of 5-bromo-3-bromomethylpentylphosphonate on reaction with metallic magnesium to form a phospha-bicyclo[2,2,1]-heptane derivative has been referred to in chapter 2C.

The synthesis of diphenylphosphinyl derivatives with the aid of the "Grignard reagent of diphenylphosphineoxide" has been mentioned in Chapter 2B v [73].

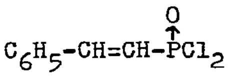
The Grignard displacement reaction of X in



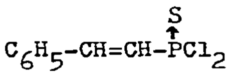
proceeds with retention when X = S-CH_3 but proceeds with inversion when X = F or Cl (Van den Berg, Platenburg and Benschop [299]).

A Russian patent reports the preparation of tertiary phosphine oxides by treating phosphorus pentachloride with R-Mg- compounds in an inert solvent, followed by treatment with aqueous ammonium chloride [300].

Timokhin, Grechkin, Kalabina, Dorokhova, Ratovskii and Sukharukova determined the mechanism of the reaction of Grignard reagents with the dichlorides of unsaturated phosphonic or phosphonicthioacids [301]:



$C_6H_5\text{-}CH{=}CH\text{-}\overset{\overset{O}{\uparrow}}{P}Cl_2$



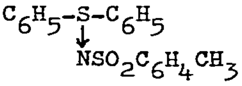
$C_6H_5\text{-}CH{=}CH\text{-}\overset{\overset{S}{\uparrow}}{P}Cl_2$

Sulfur compounds

In Chapter 5A the course of the reactions of Grignard compounds with thio-ketones has been discussed [188] and [189].

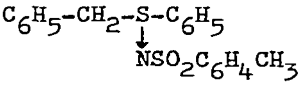
Also in Chapter 5A the reaction of Grignard compounds with β-thioketo-esters has been mentioned [190].

Oae, Yoshimura and Furukawa investigated the reaction of phenylmagnesium bromide with



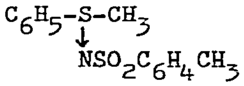
$C_6H_5\text{-}\underset{\underset{NSO_2C_6H_4CH_3}{\downarrow}}{S}\text{-}C_6H_5$

diphenyl N-p-tosyl-sulfilimine



$C_6H_5\text{-}CH_2\text{-}\underset{\underset{NSO_2C_6H_4CH_3}{\downarrow}}{S}\text{-}C_6H_5$

benzyl phenyl N-p-tosyl sulfilimine



$C_6H_5\text{-}\underset{\underset{NSO_2C_6H_4CH_3}{\downarrow}}{S}\text{-}CH_3$

methyl phenyl N-p-tosylsulfilimine

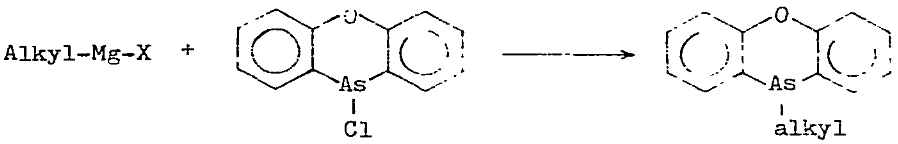
and proposed mechanisms to explain the formation of the different products [302].

The reaction of benzylmagnesium chloride with dialkylsulfates has been referred to in Chapter 3C [124].

Arsenic compounds

Mixed trialkylarsines were obtained by the reaction of Grignard compounds with arsenic(III)thioacid esters (Chadaeva, Kamai and Mamakov [303].

Gigauri, Chachava, Chernokalskii and Ugulava obtained alkyldiphenylarsines from the reaction of alkylmagnesium halides with bis(diphenylarsine)oxide or with diphenylarsine chloride [304].
Gavrilov, Khlebnikov, Gavrilova and Chernokals'kii obtained 10-alkyl substituted phenoxarsines by reaction of the corresponding alkylmagnesium halide with the chloro-derivative [305]:



Kralichkina, Yambushev and Gatilov synthesized mixed alkylarsines by the reaction of Grignard reagents with $AsCl_3$ [306].

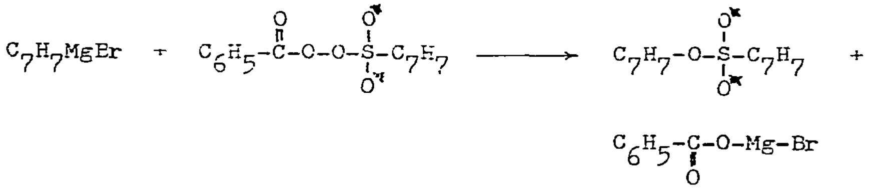
5J. Reactions with oxygen, ozone, peroxides, sulfur and tellurium

The reactions of vinylic Grignard compounds with oxygen, as studied by a group of Japanese workers [143] and those of phenylmagnesium bromide with oxygen in the presence of bromobenzene, which were studied by a group in the U.S. [31] have been discussed in Chapter 4B. Sherrodd and Waters [307] as well as Waters, Pike and Rivera [308] have investigated the ozonolysis of Grignard compounds. This method seems to offer little synthetic utility; in the reaction with phenylmagnesium bromide the study has produced evidence that supports the idea that for the same rate of addition of ozone, the more concentrated Grignard reagent would yield more phenol.

The reactions of phenylmagnesium bromide with tert-butyl peroxy phosphates follow the pathway of the carbon peresters and not that of the phosphate esters to give high yields of tert-butyl phenyl ether and moderate to high yields of the corresponding dialkylphosphoric acid (Sosnovsky, Zaret and Konieczny [309]):

$$(RO-)_2P(O)OO-t-C_4H_9 \quad + \quad C_6H_5-Mg-Br \longrightarrow C_6H_5-O-t-C_4H_9 \quad + \quad (RO-)_2P(O)OH$$

In the reaction of benzoyl p-toluenesulfonyl($-^{18}O$) peroxide with p-tolylmagnesium bromide, it was found that the sulfonyl oxygens of the peroxide were completely retained in the two sulfonyl oxygens of the p-tolyl p-toluenesulfonate formed (Hisada, Kobayashi and Minato [310]):



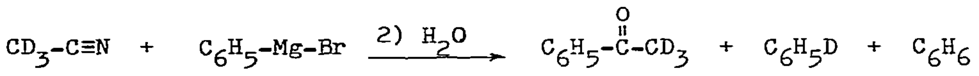
$$C_7H_7MgBr \; + \; C_6H_5-\overset{\overset{O}{\|}}{C}-O-O-\underset{\underset{O^*}{|}}{\overset{\overset{O^*}{|}}{S}}-C_7H_7 \longrightarrow C_7H_7-O-\underset{\underset{O^*}{|}}{\overset{\overset{O^*}{|}}{S}}-C_7H_7 \; + \; C_6H_5-\underset{\underset{O}{\|}}{C}-O-Mg-Br$$

Pentabromophenylmagnesium bromide reacts in a normal fashion with sulfur to form the thiophenol derivative [239].

In THF as the solvent phenylmagnesium bromide reacts with elemental tellurium (in which reaction the presence of a limited amount of oxygen is essential) to form diphenyl ditelluride in a 50 - 85% yield according to Haller and Irgolic [311]. 2-Methyl-, 4-methyl-, 2-chloro-, 4-bromo-, 4- and 3-fluorophenylmagnesium bromide as well as 4-biphenylylmagnesium bromide gave the same sort of products albeit in less satisfactory yields. Grignard reagents with 2-fluorenyl, 1-naphthyl, 2,5-diphenyl, 2,4,6-triphenyl and pentafluorophenyl substituents as well as Grignard reagents derived from butyl chloride and from octyl and pentyl bromide did not react with tellurium. The authors make the remark that the observed initiation of the reaction by benzoyl peroxide points towards participation of radicals in these reactions.

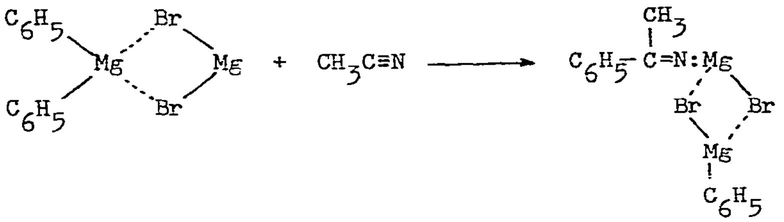
5K. Reactions with nitriles

In Chapter 4Ai a discussion is given of the different reactivities of aroyl and acyl cyanides as well as of carbonyl cyanide [132]. In Chapter 2D the intermediate formation of $ClMgCHC{\equiv}N$ and of $(ClMg-)_2CClC{\equiv}N$ formed by the reaction of isopropylmagnesium chloride with chloroacetonitrile has been mentioned [108].
Jones, Pearson and Gordon studied in more detail the reaction of acetonitrile with phenylmagnesium bromide [312]. The reaction is known to give poor yields of acetophenone whereas on the other hand considerable amounts of benzene are formed. Working with trideuteroacetonitrile:



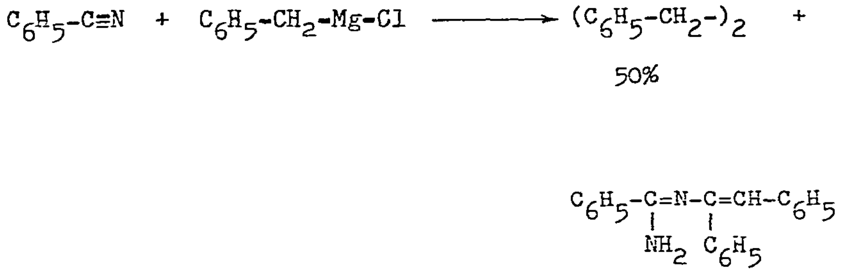
$$CD_3\text{-}C{\equiv}N \quad + \quad C_6H_5\text{-}Mg\text{-}Br \xrightarrow{2)\ H_2O} C_6H_5\text{-}\overset{\overset{O}{\|}}{C}\text{-}CD_3 \quad + \quad C_6H_5D \quad + \quad C_6H_6$$

and hydrolysing the reaction mixture with H_2O revealed that only 47 % of the benzene was monodeuterated. When unlabelled acetonitrile was used and deuterolysis was effectuated with DCl in D_2O, 52% deuterated benzene was obtained. The authors suppose that the formation of a complex like



is the key step in the reaction.

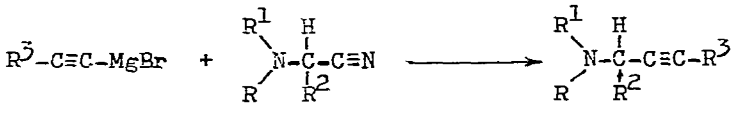
Another unusual reaction of a nitrile with a Grignard reagent was reported by Marxer [313]. Benzonitrile reacts with benzylmagnesium chloride in the following manner



$$C_6H_5\text{-}C{\equiv}N + C_6H_5\text{-}CH_2\text{-}Mg\text{-}Cl \longrightarrow \underset{50\%}{(C_6H_5\text{-}CH_2\text{-})_2} + C_6H_5\text{-}\underset{NH_2}{C}{=}N\text{-}\underset{C_6H_5}{C}{=}CH\text{-}C_6H_5$$

This new method to synthesize these hitherto unknown vinylamidines (the aryl group may be substituted) will be further investigated by the author.

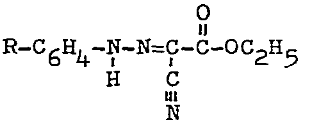
Thies, Schoenenberger and El-Zanaty report the following displacement reaction of Grignard compounds wih α-aminonitriles [314]:



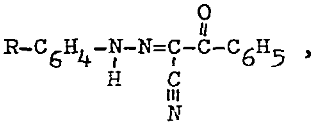
$$R^3\text{-}C{\equiv}C\text{-}MgBr + \begin{matrix}R^1\\ R\end{matrix}\!\!>\!N\text{-}\underset{R^2}{\overset{H}{C}}\text{-}C{\equiv}N \longrightarrow \begin{matrix}R^1\\ R\end{matrix}\!\!>\!N\text{-}\underset{R^2}{\overset{H}{C}}\text{-}C{\equiv}C\text{-}R^3$$

R^2 = alkoxy or hydroxy substituted aryl group

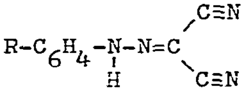
Elnagdi, Kassab, Sobhy, Hamza and Wahby report reactions of Grignard compounds with nitriles of the following types [315]:



$$R{-}C_6H_4{-}\underset{\displaystyle H}{N}{-}N{=}\underset{\displaystyle C\equiv N}{C}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OC_2H_5$$

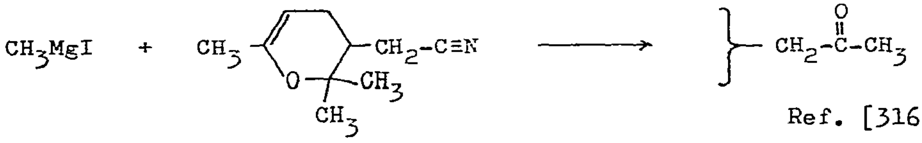


$$R{-}C_6H_4{-}\underset{\displaystyle H}{N}{-}N{=}\underset{\displaystyle C\equiv N}{C}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}C_6H_5$$

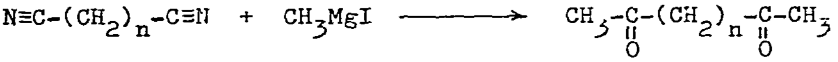


$$R{-}C_6H_4{-}\underset{\displaystyle H}{N}{-}N{=}C(C\equiv N)_2$$

Normal addition to one or both nitrile functions in the following compounds has been reported by Bondavalli, Schenone and Longobardi [316] and by Ono and Terasawa in a Japanese Patent [317]:



Ref. [316]



$$N\equiv C{-}(CH_2)_n{-}C\equiv N \;+\; CH_3MgI \longrightarrow CH_3{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}(CH_2)_n{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}CH_3$$

Ref [317]

n = 8 and 14

The formation of a cyclobutane derivative in the reaction of arylmagnesium halides with α-(9-fluorenylidene)malonitrile has been mentioned in Chapter 5C [222].

5L. Reactions with or in the presence of metal salts

Because of the large number of publications in this field a subdivision will be made into a) reactions with metal salts in order to prepare organometallic derivatives of these metals, and b) reactions in which metal salts are used as catalysts in order to change the "normal course" of the reaction of the organomagnesium compound.

5La. Preparation of organometallic compounds

Lahuerta Pena and Uson obtained tetrabenzyltitanium by the reaction of benzylmagnesium chloride with titanium(IV) chloride·2pyridine adduct [318]. The authors observed a remarkable stability of trimethylamine or 2,2'-dipyridyl adducts of tetrabenzyltitanium. Furthermore the same authors prepared $(C_6F_5)_4Ti$ which is intrinsically more stabl than the corresponding unfluorinated titanium compound.

Hofstee, Van Oven and De Liefde Meyer obtained 1-methylallyl(cyclooct tetraene)titanium by reaction of the corresponding titanium chloride with 1-methylallylmagnesium bromide [319].

Cycloheptadiene derivatives of Ti, V, Cr, Fe and Co were obtained by the reaction of the corresponding halides with 1,3-cycloheptadiene an isopropylmagnesium chloride (Müller and Mertschenk [320]). No such compounds could be isolated when Mn, Nb, Mo, Mo, Ta and W salts were used in the reaction.

Tsuda and Kochi conclude from their experiments with chromium(IV)tetr tert-butoxide that organochromium(IV) species of the following type

$$Cr(O\text{-}t\text{-}C_4H_9)_4 \;+\; nRMgX \longrightarrow R_nCr(O\text{-}t\text{-}C_4H_9)_{4-n} \;+\; n\ t\text{-}C_4H_9OMgX$$

are too unstable to be isolated [321]. With mesityl-, phenyl-, ethyl- and methylmagnesium halides triorganochromium compounds were formed. For example

$$4\ C_6H_5MgBr \;+\; Cr(O\text{-}t\text{-}C_4H_9)_4 \longrightarrow (C_6H_5)_3Cr \;+\; C_6H_5\text{-}C_6H_5 \;+\; 4\ t\text{-}C_4H_9\text{-}O\text{-}MgBr$$

In a U.S. Patent a reaction to prepare fluorinated phenylcopper compounds is reported [322]:

$$F_nC_6H_{5-n}MgBr + Cu_2Br_2 \longrightarrow F_nC_6F_{5-n}Cu$$

The reaction of cyclohexene with diiodomethane and "in situ" diethylzinc, prepared from ethylmagnesium bromide and zinc halide, does not lead to the formation of bicyclo[4.1.0]heptane (norcarane) but to n-propyl iodide (23%) and n-butyl iodide (21%) (Kawabata, Noda and Yamashita [323]).

As already reported in Chapter 2Biv [53], the reaction of neopentylmagnesium chloride with lead(II) chloride yields $(neo\text{-}C_5H_{11})_3PbMgCl$; the following reactions of this"lead-Grignard compound" were also reported:

$$(neo\text{-}C_5H_{11})_3PbMgCl + neo\text{-}C_5H_{11}Cl \longrightarrow (neo\text{-}C_5H_{11})_6Pb_2 \quad (65\%)$$

$$(neo\text{-}C_5H_{11})_3PbMgCl + neo\text{-}C_5H_{11}Br \longrightarrow (neo\text{-}C_5H_{11})_6Pb_2 \quad (64\%)$$
$$+ (neo\text{-}C_5H_{11})_4Pb \quad (11\%)$$

Williams and Thomas, in a U.S. Patent, report the formation of tetramethyl- or tetraethyllead in the reaction of the corresponding chloride with a magnesium-lead-sodium alloy in THF or diethyl ether [324]:

$$CH_3Cl + Mg/Pb/Na \xrightarrow{THF} (CH_3)_4Pb \quad 61\%.$$

The preparation of di- and trigermanes from chlorogermanes has been mentioned in Chapter 2D [95].

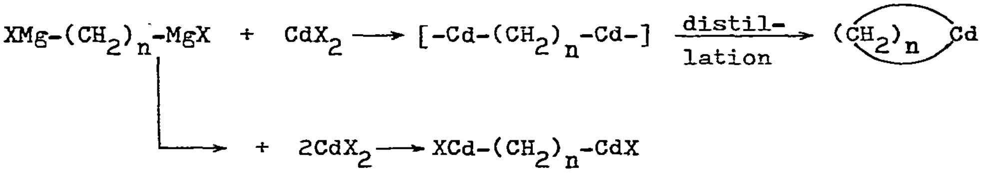
Acetylenylmagnesium halides react with triethylbromogermane as indicated below [49]:

$$C_6H_5-(C\equiv C)_n-MgBr \quad + \quad ((C_2H_5)_3GeBr \longrightarrow C_6H_5-(C\equiv C)_n-Ge(C_2H_5)_3$$

$$n = 2 \text{ or } 3$$

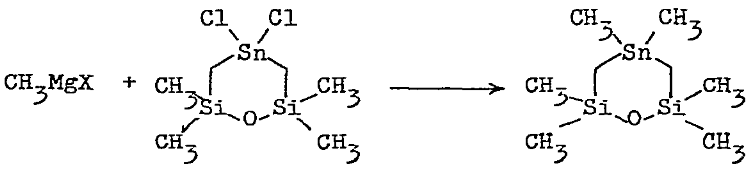
When potential ligands such as triphenylphosphine, 1,2-bis(diphenylphosphino)ethane, triphenyl phosphite and several others were added to the mixture of $(C_6H_5CN)_2PdCl_2$ and CH_3MgBr at -70 or -60° the corresponding dimethylpalladium compound $L_2Pd(CH_3)_2$ could be isolated [232].

The reaction of bifunctional Grignard compounds with cadmium chloride has been studied by a French group [66] and [67]. The following reaction scheme may be illustrative:



The different reactivities of the two cadmium compounds leads the authors to the conclusion that two different species are present in solution.

Mironov, Stepina and Shiryaev prepared the following heterocyclic tin derivative with the aid of methylmagnesium halide [325]:



Two reports have appeared dealing with the preparation of organogold derivatives:

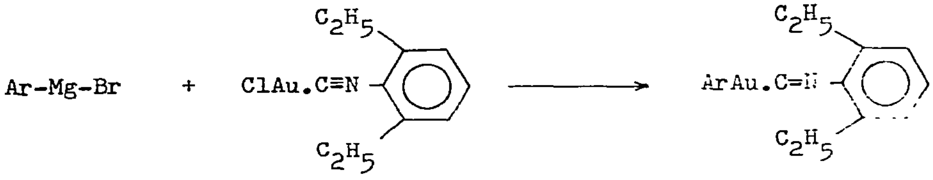
Nesmeyanov, Perevalova, Krivykh, Kosina, Grandberg and Smyslova [326]:

$$\text{R-Mg-X} + \text{Cl-Au.P}(C_6H_5)_3 \xrightarrow[\text{THF}]{\text{toluene or}} \text{R-Au.P}(C_6H_5)_3$$

R = benzyl : yield 85 % in toluene and 40% in THF

R = vinyl : yield 90% in THF

In a U.S. Patent the preparation of arylgold complexes with 2,6-diethylphenyl isocyanide is reported [327]:



A German Patent claims the preparation of ethylmercury bromide in 75% yield by the reaction of ethylmagnesium bromide with mercury(II) chloride in THF at temperatures between 20 and 70° [328].

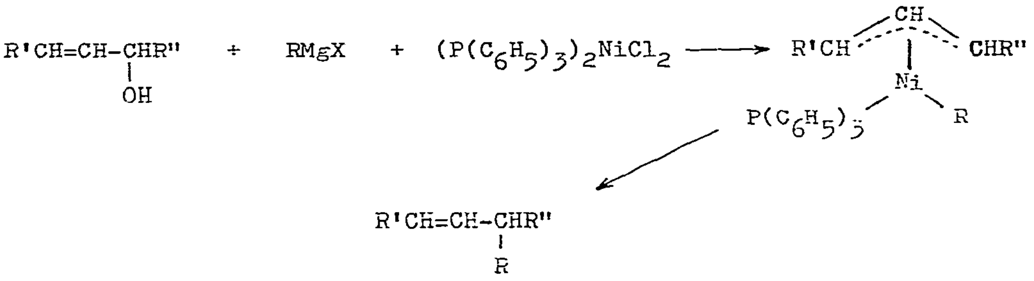
Contrary to the "popular myths", alkylation of dialkylthallium halides is not limited to alkyllithium reagents, according to Heyman [329]; Grignard reagents in either of the common ether solvents, diethyl ether or tetrahydrofuran, have sufficient carbanion character to alkylate a dialkylthallium halide.

b. Metal salts as catalysts

It has been mentioned in Chapter 5E that cobalt(II) or nickel(II) chloride can be used as catalysts in the reaction of arylmagnesium halides with tri- or tetrachloroethylene to yield diarylacetylenes [245].

In Chapter 5D the use of rhodium and nickel catalysts has been mentioned for the addition reaction of methylmagnesium halides to acetylene derivatives [231] and [233].

Felkin and Swierczewski report the use of a stereochemical criterion which indicates that the reaction of allylic alcohols with excess Grignard reagent in the presence of catalytic amounts of bis(triphenylphosphine)nickel dichloride occurs exclusively via π-allylnickel intermediates [330]:



The nickel(II) catalyzed addition of Grignard reagents to an α-olefin [234] as well as the tungsten(VI) catalyzed disproportionation of olefins [235] and [235A] have been mentioned in Chapter 5D.

According to Mme. H. Rivière and Ping-Wah Tang, copper(I) enolates are the active intermediates in the conjugate addition reaction of phenylmagnesium bromide to 1-mesityl-3-methyl-2-butenenone catalyzed by copper(I) iodide [331].

The reactions of n-butylmagnesium bromide with sec-butyl esters of maleic, acrylic and crotonic acid, catalyzed by copper(I) chloride have been referred to in Chapter 5C [218].

In Chapter 5B.mention has been made of the formation of 1,6-diketones in the reaction of vinylmagnesium chloride with fatty acids in the presence of copper(I) chloride [191C].

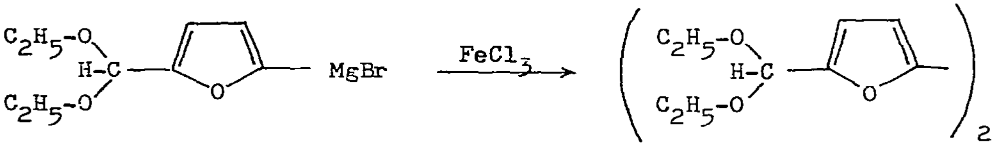
Farády and Markó detected small amounts of ethane and ethylene in the gas phase above a reaction mixture consisting of methylmagnesium iodide, nickel(II) chloride and olefins [332]. The results of their investigations make it seem probable that some nickel carbene complex is responsible for the formation of ethylene in this system:

$$CH_3ML_n \rightleftharpoons CH_2MHL_n \xrightarrow{CH_2MHL_n} CH_2{=}CH_2 + 2MHL_n$$

or

$$\begin{tikzcd}
(CH_3)_2ML_n \arrow[r] \arrow[d, shift left] & CH_3{-}CH_3 + M(O) + nL \\
(CH_2)_2MH_2L_n \arrow[r] \arrow[u, shift left] & CH_2{=}CH_2 + MH_2L_n
\end{tikzcd}$$

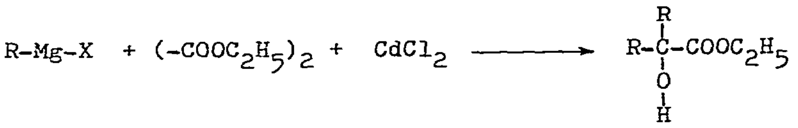
Reaction of the Grignard reagent prepared from 5-bromo-2-diethoxymethylfuran with iron(III) chloride yields the bis-5,5'-difuran derivative [43]:



The reaction of Grignard compounds complexed with HMPT with acetic acid anhydride gives far better yields of ketones when catalyzed by iron(III) chloride [195].

The determination of the relative reactivities of acid chlorides (wit $t\text{-}C_4H_9\text{-}COCl$ as the reference) towards $t\text{-}C_4H_9MgCl$, catalyzed by coppe (I) chloride has been mentioned in Chapter 4C [161].

A USSR patent reports the preparation of tertiary α-hydroxy esters by the reaction of Grignard compounds with three equivalents of oxalic acid ester and one equivalent cadmium chloride [333]:



$$R\text{-}Mg\text{-}X + (\text{-}COOC_2H_5)_2 + CdCl_2 \longrightarrow R\text{-}\overset{\displaystyle R}{\underset{\displaystyle \underset{\displaystyle H}{O}}{C}}\text{-}COOC_2H_5$$

Most of the reactions of Grignard reagents with organic halides, catalyzed by metal salts, have already been reported in Chapter 5E and therefore will be mentioned only briefly here:

Trans stilbenes are obtained by the reaction of ethylenic Grignard compounds with aryl halides in the presence of a nickel(II) acetoacetonate [246]. Reaction of arylmagnesium halides with p-dibromobenzene yields terphenyls.

Tamao, Sumitani and Kumada obtained cross-coupling reaction products in excellent yields in the reaction of aryl or alkyl Grignard compounds with aryl or vinyl chlorides in the presence of nickel(II) phosphine complexes [334]. For example

$$C_6H_5MgBr + Cl_2C{=}CH_2 \xrightarrow{Ni(II)} (C_6H_5)_2C{=}CH_2 \quad (82\%)$$

$$n\text{-}C_4H_9MgBr + C_6H_5Cl \xrightarrow{Ni(II)} n\text{-}C_4H_9\text{-}C_6H_5 \quad (76\%)$$

Using secondary alkyl Grignard reagents, however, Tamao, Kiso, Sumitani and Kumada observed alkyl group isomerization in the cross-coupling reaction with nickel-biphosphine complexes as the catalysts [335]:

$$\text{iso-}C_3H_7MgCl + C_6H_5Cl \xrightarrow{\text{catalyst}} C_6H_5\text{-iso-}C_3H_7 + C_6H_5\text{-n-}C_3H_7 + C_6H_6$$

With 1,2-bis(dimethylphosphino)ethane as the ligands e.g., 84% of the products obtained (total conversion 84%) was the n-propyl derivative and only 9% isopropylbenzene was obtained.

The different reaction products obtained by addition of pentylmagnesium bromide to allyl chloride with cobalt(II) and nickel(II) salts on the one hand and with iron(III) and copper(II) salts on the other has been mentioned in chapter 5E [247].

In the same chapter the following coupling reactions have been reported:

The copper(I) catalyzed coupling of Grignard reagents with alkyl halides [234]

The coupling reaction of arylmagnesium halides with alkyl iodides with copper(I)-N,N,N',N'-tetramethylethylenediamine as the catalyst [242].

The Li_2CuCl_4 catalyzed reaction of RMgX with trans-bromo-apopinene [244].

In Chapter 5I the zinc chloride catalyzed reaction of R_xSiHCl_{3-x} with para-dibromomagnesiobenzene has been mentioned [294].

Tamura and Kochi extensively investigated the character of the silver complex obtained in the reaction of Grignard compounds with silver(I) nitrate or with siver(I) perchlorate in the presence of lithium nitrate or nitrogen dioxide in THF [336]. The soluble silver complex was not formed in the reaction of silver nitrate with phenyl-, allyl- or benzylmagnesium bromide or in the reaction of ethylmagnesium bro-

mide with silver perchlorate in the presence of methyl nitrate.
The authors detected the existence of two complexes of zero valent silver: complex A reacts with allyl or benzyl bromide to yield the dimerization products. Furthermore it does not react with ethyl bromide and on addition of water no ethane is evolved, indicating that no ethyl-silver bond is present.
On reaction with ethylmagnesium bromide complex B is formed, which does react with ethyl bromide to yield ethylene, ethane and butane.

5M. Organomagnesium compounds in polymerization reactions

From the numerous reports, mostly in the patent literature dealing with the application of organomagnesium compounds as polymerization catalysts the following examples will be given briefly:
Yamamoto, Katsunuma, Doya and Tsuchya used the following catalyst mixtures for the polymerization of oxiranes:
diethylmagnesium, di-n-butylmagnesium or diphenylmagnesium together with a phosphonium or an ammonium compound [337];
an organomagnesium compound mixed with an orthovanadate $VO(OR)_3$ or with a molybdate $MoO_2(OR)_2$ [338];
a symmetrical organomagnesium compound, R_2Mg, mixed with an isocyanate isothiocyanate, cyanide or a cyanate [339];
diethylmagnesium mixed with potassium or calcium cyanide [340].
For the polymerization of ethylene Haward, Roper and Nummelin used a mixture of n-butylmagnesium chloride/titanium(IV) chloride with tri-alkylaluminum in which the alkyl-group contained eight to eighteen carbon atoms [341].
On heating magnesium with iodine, titanium(IV) chloride and n-butyl

chloride in hexane during five hours a brownish black precipitate is obtained which is used as a polymerization catalyst for ethylene after mixing with triethylaluminum (Durand and Mangin [342]).

Phenyl- or methylmagnesium bromide, complexed with diethyl ether is used as a polymerization catalyst for ethylene after mixing with titanium(IV) chloride and tri-isobutylaluminum (Grant [343]).

According to the report by Kulichuk and Kortenko powdered n-butylmagnesium bromide is a more powerful catalyst for the anionic polimerization of ε-caprolactam than is metallic sodium [344].

Katsunuma and Tsuchiya report the use of a coordination complex, prepared by treating an organomagnesium compound with an aliphatic lactone or an azo compound, as a polymerization catalyst for oxiranes. For example a liquid catalyst was obtained by heating diethylmagnesium/dioxane and β-propiolactone in a sealed tube during 20 hours at 60° [345].

Kagawa and Hashimoto used a mixture of phosphine derivatives, cobaltous chloride and a Grignard reagent for the codimerization of butadiene and ethylene [346].

For the polymerization of alkyl vinyl ether Lamb applied derivatives of alkylmagnesium halides, obtained on reaction with oxygen, sulfur dioxide, carbon dioxide, isobutyraldehyde, nitrogen dioxide and carbon disulfide [347].

5N. Miscellaneous

Besides the one mentioned in chapter 4Aii [141] another report dealing with the stereochemistry of the reaction of Grignard compounds with chiral benchrotenic ketones comes from Besançon, Card, Dusausoy and Tirouflet [348].

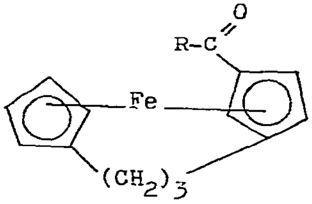
Darensbourg investigated the reaction of benzylmagnesium chloride with cyclopentadienyliron tricarbonyl and its derivatives [349]:

$$C_6H_5\text{-Mg-Cl} + [(C_5H_5)Fe(CO)_2Y]^{\oplus}[B(C_6H_5)_4]^{\ominus} \longrightarrow$$

$$Y = CO,\ CS \text{ or } P(C_6H_5)_3$$

Although with the compound with $Y = CS$ reaction very evidently occurs it has been impossible to the author to isolate any products of this reaction. However when $Y = CO$ or $P(C_6H_5)_3$ the only products obtained were those in which addition of the benzylmagnesium chloride to the cyclopentiadienyl ring had taken place.

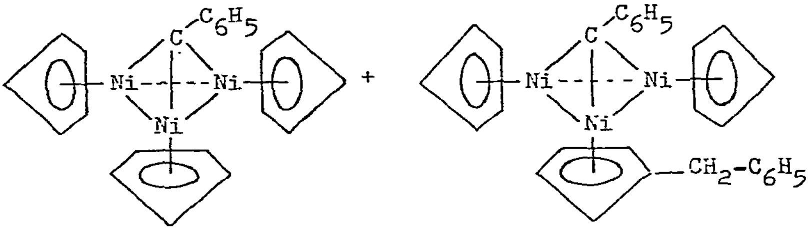
Moise, Monin and Tirouflet studied the stereochemistry of the reaction of phenylmagnesium bromide with the ferrocene derivative $\boxed{28}$ [350]:



$\boxed{28}$

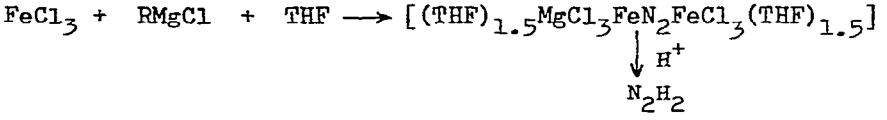
Like in the reaction of cyclopentadienyliron derivatives (see above Ref. [349]) nickelocene also undergoes ring-substitution reaction with benzylmagnesium chloride as is represented in the following reaction, reported by Voyevodskaya, Pribytkova and Ustynyuk [351]:

$$\text{nickelocene} + C_6H_5\text{-}CH_2\text{-MgCl} \xrightarrow{\text{room temp.}}$$



The same results were obtained with p-methylbenzylmagnesium chloride. Dormond, Leblanc, LeMoigne and Tirouflet had some success in their N_2-fixation experiments in which the reaction of benzoyl chloride with a reaction mixture obtained by bubbling nitrogen through a solution of ethylmagnesium bromide and dicyclopentadienyltitanium(IV) chloride yielded 16% benzonitrile (isolated as benzylamine after reduction with $LiAlH_4$) [352]. With benzoic acid anhydride comparable results were obtained. Reduction of the titanium compound with a mixture of Mg/MI_2 led to less success in the nitrogen-fixation. Nitrogen-fixation was also achieved by Borodko, Ivleva, Kachapina, Salienko, Shilová and Shilov when these authors bubbled nitrogen through a reaction mixture from methylmagnesium iodide and chlorobis-(π-cyclopentadienyl)titanium [353]. The authors isolated a new intermediate complex $Cp_2TiN{=}NTiCp_2$.

In similar experiments by Jezowska-Trzebiatowska, Sobota, Kozlowski and Jezierski, in which iron(III) chloride is used together with THF the intermediate formation of a Grignard compound is assumed by the authors. In general the nitrogen fixation process may than be expressed as [354] and [355]:

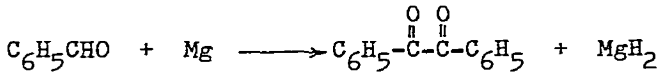


$$FeCl_3 + RMgCl + THF \longrightarrow [(THF)_{1.5}MgCl_3\underset{\displaystyle N_2H_2}{\underset{\downarrow H^+}{FeN_2}}FeCl_3(THF)_{1.5}]$$

Ashby and Schwartz investigated the reaction of Grignard compounds with $LiAlH_4$ [356]. In general a compound with the stoichiometry $HMgAlH_3R$ is formed; such compounds are stable for R = ethyl or n-butyl and these compounds disproportionate to MgH_2 and $Mg(AlH_3R)_2$ for R = methyl, phenyl or sec-butyl.

Ashby and Watkins synthesized complex metal hydrides, including those of magnesium by $LiAlH_4$-reduction of the "ate"-complex, formed on mixing alkyllithium compounds and alkylmagnesium derivatives [357].

Givelet, in a French Patent claims the formation of dibenzoyl by the following reaction [358]:



$$C_6H_5CHO + Mg \longrightarrow C_6H_5-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-C_6H_5 + MgH_2$$

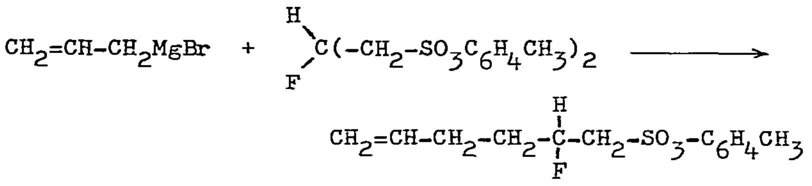
The reaction of Grignard compounds with aromatic nitro derivatives has been reported in Chapter 4B [148].

The application of the reaction product, obtained on addition of nitrogen dioxide to a solution of R-Mg-X, as a polymerization catalyst has been mentioned in Chapter 5M [347].

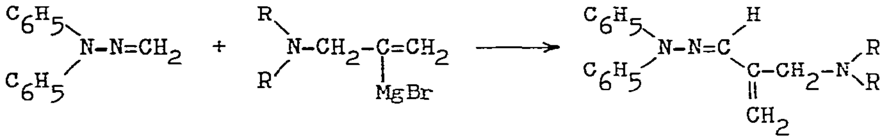
The concept of a simple electrophilic substitution at the carbon-magnesium bond of phenylmagnesium bromide by the nitrosyl cation is complicated by further reaction of the initial complex with excess Grignard reagent, as was found by Marsh and Waters [359].

Although no nitrosobenzene could be detected in the reaction mixture after the inverse reaction was done the authors found a new compound with the general formula $(C_6H_5)_2N_2O$ the identification of which may give valuable clues to the exact mechanism in force. The formation of dimerization products on reaction of the Grignard compound, prepared from phenylacetylene, with $SOCl_2$ has been referred to in Chapter 4B [150].

Tolman and Veres report the following reaction of allylmagnesium bromide with a bifunctional p-toluenesulfonate [360]:



Bar, Marcinal and Marcinal-Lefebvre report the following reaction in which a diphenylhydrazone is involved [46]:



Turova and Turevskaya, studying the synthetic routes to alkoxymagnesium halides, ROMgX, found that in order to effect complete decomposition of methylmagnesium iodide on reaction with aliphatic alcohols a 1.5-fold excess of methanol and a 1.2-fold excess of ethanol was necessary [361]. For n-propyl or tert-butyl alcohol gas evolution ceases at the stoichiometric ratio of the components. Stabilisation of Grignard reagents towards reaction with active hydrogen may be explained by assuming that soluble complexes of the type RMgI.nR'OMgI are formed. The authors indicate another route to these alkoxymagnesium halides: thermolysis of cements (solidified equimolar mixtures of $(RO)_2Mg$ and MgX_2).

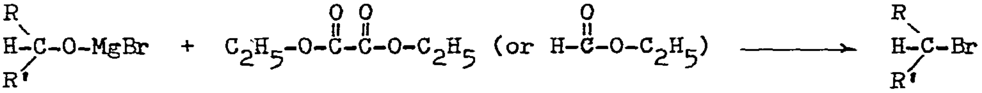
Combret, Moraud and Leroux obtained selective O-alkylation of α-acetylenic alcohols by using HMPT as the solvent [362]:

$$C_2H_5MgBr + H\text{-}C{\equiv}C\text{-}CH_2OH \xrightarrow{C_4H_9Br} H\text{-}C{\equiv}C\text{-}CH_2\text{-}O\text{-}C_4H_9 \quad (80 - 90\%)$$

$$2\ C_2H_5MgBr + H\text{-}C{\equiv}C\text{-}CH_2OH \xrightarrow{C_4H_9Br} H\text{-}C{\equiv}C\text{-}CH_2\text{-}O\text{-}C_4H_9 \quad (60 - 70\%)$$

$$+ \ C_4H_9\text{-}C{\equiv}C\text{-}CH_2\text{-}OH \quad (15 - 20\%)$$

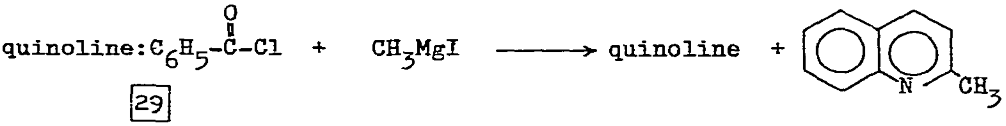
Rybakova and Indeikina observed the following reaction of bromomagnesium alkoxydes [363]:



$$RR'CH\text{-}O\text{-}MgBr + C_2H_5\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}C_2H_5 \ (\text{or } H\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}C_2H_5) \longrightarrow RR'CH\text{-}Br$$

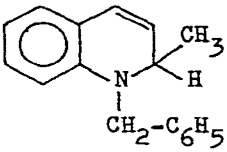
R and R' = substituted aryl groups. No such reaction was observed with R' = CCl_3 or CBr_3.

Addition of the quaternary addition product of benzoyl chloride and quinoline. 29 to a solution of methylmagnesium iodide results in the following reaction (Sheinkman and Prilepskaya [364]):



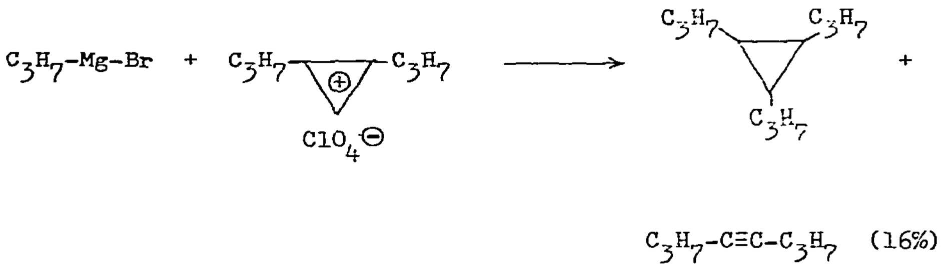
29

In the inverse addition reaction 30 is formed:

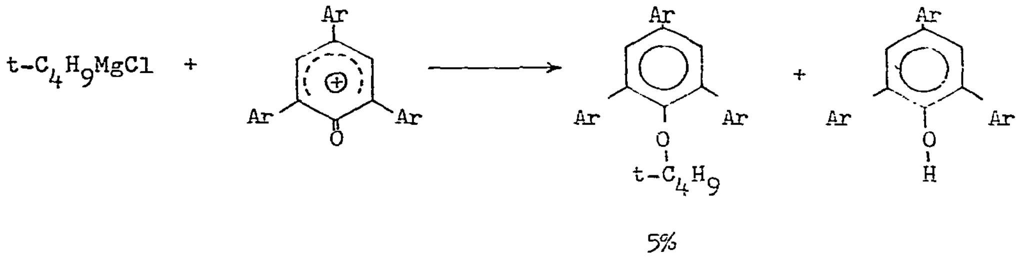


30

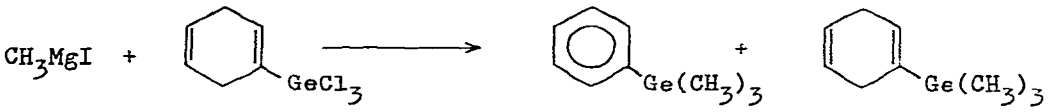
Geusler and Langone reported the following peculiar reaction of a cyclopropenylium salt [365]:



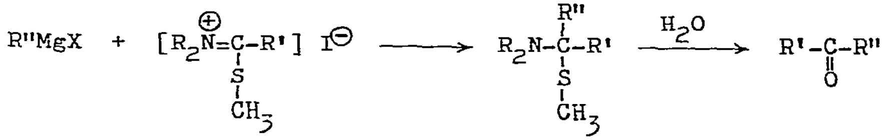
The fate of the missing carbon atom remains to be discovered. Dimroth and Laufenberg succeeded for the first time to obtain carbanion addition to the "carbonyl-group" in 2,3,6-triaryloxocyclohexadienylium tetrafluoroborate [366]:



Mazerolles, Laporterie and Dubac observed a most uncommon aromatization reaction when methylmagnesium iodide was utilized to methylate cyclohexadienyltrichlorogermane [367]:



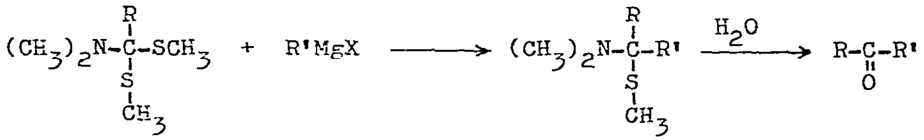
In attempts to find convenient routes for the preparation of carbonyl compounds Yamaguchi, Shimizu and Suzuki investigated reactions of Grignard compounds with S-alkylthioamidium salts [368]:



$$R''MgX + [R_2\overset{\oplus}{N}=\underset{\underset{CH_3}{|}}{\underset{S}{\underset{|}{C}}}-R'] I^{\ominus} \longrightarrow R_2N-\overset{R''}{\overset{|}{\underset{\underset{CH_3}{|}}{\underset{S}{\underset{|}{C}}}}}-R' \xrightarrow{H_2O} R'-\underset{O}{\underset{\|}{C}}-R''$$

With R' = H aldehydes are obtained in yields as high as 80%. Also the yields of ketones could be over 90%.

Furthermore the authors found the following route to ketones:



$$(CH_3)_2N-\overset{R}{\overset{|}{\underset{\underset{CH_3}{|}}{\underset{S}{\underset{|}{C}}}}}-SCH_3 + R'MgX \longrightarrow (CH_3)_2N-\overset{R}{\overset{|}{\underset{\underset{CH_3}{|}}{\underset{S}{\underset{|}{C}}}}}-R' \xrightarrow{H_2O} R-\underset{O}{\underset{\|}{C}}-R'$$

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