MAGNESIUM
ANNUAL SURVEY COVERING THE YEAR 1974

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Contents

Magnesium, Annual Survey covering the year 1973 see J. Organometal. Chem., 95 (1975) 139-290.

1. INTRODUCTION

In his History Of The Grignard Reaction, Urbanski comes to the conclusion that, based on the work of Barbier, Valeur and others, the Grignard reaction should be renamed to Barbier-Grignard reaction [1]

Miginiac and Courtois published an extensive review on the Reactivity of allylic organometallic compounds of lithium, sodium, magnesium, zinc, cadmium and aluminium, dealing with the main recent results (since about 1960) [2].

Together with Laemmle and Neumann Ashby published a review on The Mechanisms of Grignard Reagent Addition to Ketones which contained some new information on work with Grignard reagents, prepared from single-crystal magnesium [3].

In his Recipes and Ingredients for Controlled C-C linkages with Organometallic Reagents Schlosser specially mentioned Cu-catalyzed alkylation with Grignard reagents [4].

Tagaki published a review on Grignard's reagent [5].

A lecture of Bickelhaupt on Free Radicals in Grignard reactions was reprinted in short [6].

In a journal for science education Medcalf published an instruction for small-scale preparations using a Grignard reagent [7].

The following dissertations, dealing with Grignard chemistry, have been published in the U.S.:

R.B. Allen, Free radical reactions of Grignard reagents and peroxy compounds. CIDNP (Chemically Induced Dynamic Nuclear Polarisation) study [8]; P.J. Wepplo, Use of allylic Grignard reagents in lactone synthesis, including iridolactone and nepetalactone [9]; D.L. Denton, Preparation and nuclear magnetic resonance studies of magnesium, zinc and cadmium derivatives of hexaborane (10) and nonahydrohexaboratokis (cyclopentadienyl)titanium(III) [10]; A.-B. Wu, 1,4-Conjugate addition of Grignard reagents to α,β-unsaturated ketones and structure of Grignard compounds, derived from hindered ketones [11]; R.P. Zerger, Bonding and stereochemical studies of Group IA and IIA organometallic compounds [12]; R.A. Lynd, Reactions of vinylaluminum compounds with Grignard coreagents [13]; S.S. Szucs, Reactions of Grignard and organolithium reagents at carbon-carbon multiple bonds [14]; H.S. Veale, Cyclizations of alkenyl Grignard reagents [15].

2. PREPARATION OF ORGANOMAGNESIUM COMPOUNDS

Introduction

As in the previous years Rieke and Bales reported improvements in the preparation of highly reactive magnesium [16]; the addition of potassium iodide to the reaction mixture containing metallic potassium (or sodium) and magnesium halide proved to be of great influence on the reactivity of Rieke's magnesium.

Another form of highly reactive magnesium was developed by Klabunde, Efner, Satek and Donley [17]; magnesium vapor (atoms) is cocondensed with solvents at -196^{o}; upon warming a Mg-solvent slurry is formed that allows reactions of unreactive aryl halides at relatively low temperatures.

W. Novis Smith Jr. extensively investigated the preparation of organomagnesium compounds in hydrocarbon solvents without organic bases [18]. In particular alkyl iodides gave high yields of organomagnesium compounds (round 85%).

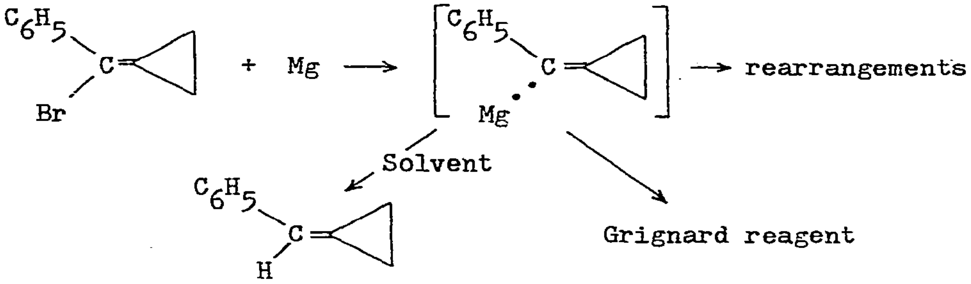
2A. Discussion of reactions leading to the formation of organomagnesium compounds

By means of competitive reactions of mixtures of organic halides with magnesium Whitesides, Rogers, Mitchell and Fujiwara determined relative reaction rates in diethyl ether [19]. Although correlation of the data obtained with $E_{1/2}$ for the alkyl halides is not particularly close it appeared better than that characterizing reductions with tri-n-butyltin hydride, which indicates that the rate-determining transition state in the formation of an alkyl Grignard reagent does not involve a heterolytic fission of the C-X bond, nor is it diffusion limited.

Martin, Méchin, Leroux, Paulmier and Meunier studied the rates of the metal-halogen exchange reaction of isopropylmagnesium chloride

with heterocyclic bromides such as 3-bromopyridine, 3- and 4-methyl-2-bromopyridines , 2-bromopyridine, 5-methyl-2-bromopyridine and 2-bromo-furan, -thiophene and selenophene [20].

Derocque and Sundermann discussed the radical nature of the reaction of cyclopropylidenephenylmethyl bromide with magnesium in different



solvents [21]. Remarkably high yields of hydrocarbons were isolated 10-15 minutes after the addition of the bromide (appr. 25%) which impossibly can be attributed to moisture that was inadvertently introduced as one of the referees of the paper pointed out.

For the reaction of trimethylchlorosilane with magnesium and phosphorous trichloride Schumann and Rösch applied triethylamine, dimethylsulfoxide,dimethylformamide and diglyme unsuccessfully as the solvents [22]. In THF as the solvent the authors claim to have observed the following equilibrium

$$(CH_3)_3SiCl \quad + \quad Mg \xrightleftharpoons{THF} (CH_3)_3Si\text{-}MgCl.nTHF$$

which however (in their opinion) is strongly shifted to the left; Addition of PCl_3 causes the formation of a precipitate of $MgCl_2$ and the formation of tri(trimethylsilyl)phosphine (62% yield)!

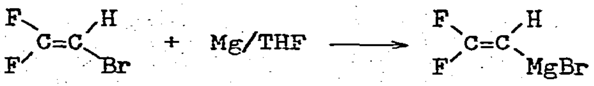
2B. Preparation of organomagnesium compounds

2Bi. Halide substituted organomagnesium compounds

C.F. Smith, Soloski and Tamborski obtained perfluoro-n-octylmagnesium bromide by the metal-halogen exchange reaction between perfluoro-n-octyl iodide and ethyl- or phenylmagnesium bromide:

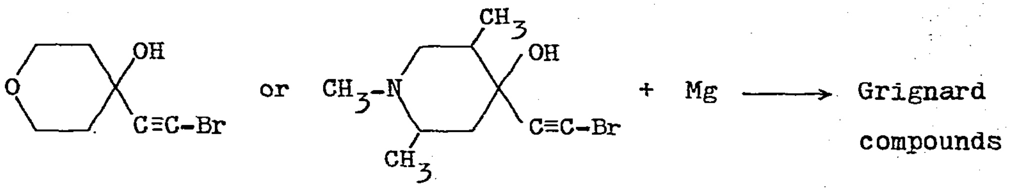
$$n\text{-}C_8F_{17}\text{-}I \quad + \quad C_2H_5\text{-}MgBr \xrightarrow{-40\ -70^\circ} C_2H_5\text{-}I \quad + \quad n\text{-}C_8F_{17}\text{-}MgBr$$

Yields as high as 100% in diethyl ether at -70° and 88% in THF at the same temperature were reported [23].
The same type of reaction was applied by Dua and Gilman for the preparation of n-decylmagnesium bromide (perfluoro) and of $CF_3\text{-}CF(CF_3)\text{-}O\text{-}(CF_2)_4\text{-}MgBr$ [24]. Both research groups investigated the thermal stability of the perfluorated Grignard compounds.
The following reaction was reported by Smirnov and Tomilov [25]:

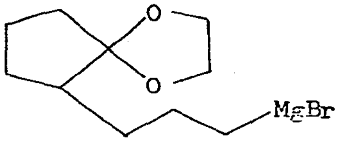


2Bii. Alkoxy-substituted organomagnesium compounds

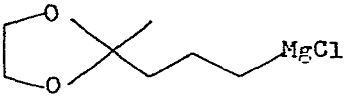
The following reactions of alkynyl halides with magnesium remain surprising although they don't seem to cause many difficulties [26]:



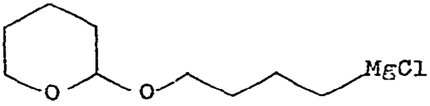
Furthermore the following acetalysed Grignard compounds were reported:



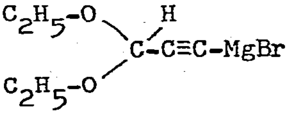
Ferard and Casals [27]



Abbas and Poller [28]



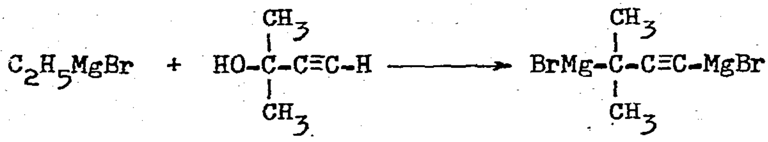
Posner, Whitten, Sterling and Brunelle [29]



Akhrem, Kamernitskii, Litrinovskaya and Reshetova [30]

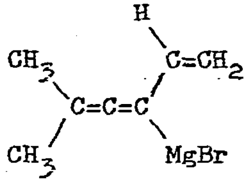
2Biii. Unsaturated organomagnesium compounds

Suprunova and Krichevskii prepared the following alkynylic Grigna reagent [31]:



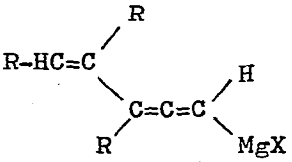
$$C_2H_5MgBr + HO-\underset{CH_3}{\overset{CH_3}{C}}-C\equiv C-H \longrightarrow BrMg-\underset{CH_3}{\overset{CH_3}{C}}-C\equiv C-MgBr$$

Vartanyan, Zhamagortsyan and Kucherov obtained $CH_2=\underset{CH_3}{C}-C\equiv C-MgBr$ [32



was prepared by Voskanyan, Pashayan and Badanyan [33].

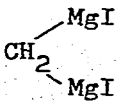
Gore, Dulcère and Roumestant prepared several substituted vinylallenylmagnesium derivatives [34] and [35]:



in which R either is a methyl group or two groups R belong to a ring-system.

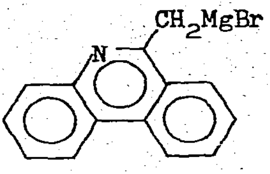
2Biv. Some other organomagnesium compounds

The bifunctional Grignard compound

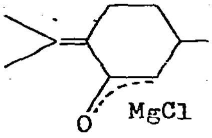


was utilised by Ohtake, Myano, Takeda and Hashimoto [36].

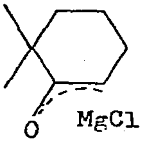
Heterocyclic aromatic Grignard compounds have been prepared by Martin and coworkers, as discussed in Chapter 2A [20]. Grishina, Zakhs and Martynova prepared the following hetero-aromatic organomagnesium compound and studied its reactivity towards ketones and aldehydes [37].



Among the enolate bromomagnesium compounds studied in 1974 the following two have to be mentioned:



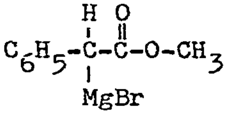
as studied by Ghozland, Maroni-Barnaud, and Maroni [38].



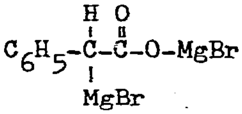
as studied by Näf and Decorzant [39].

Ester-functionalized Grignard compounds were studied by several groups:

Mladenova, Blagoev and Kurtev [40] and [41]:

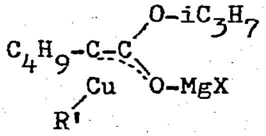


$C_6H_5-\underset{MgBr}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-O-CH_3$ and

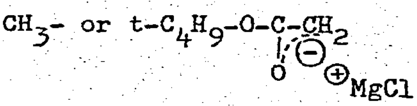


$C_6H_5-\underset{MgBr}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-O-MgBr$

Villiêras, Disnar and J.-F. Normant [42] and [43]:

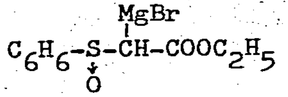


Maroni-Barnaud, Roux-Schmitt and Seyden-Penne [44]



CH_3- or $t-C_4H_9-O-\underset{O}{C}-\overset{\ominus}{C}H_2\ {}^{\oplus}MgCl$

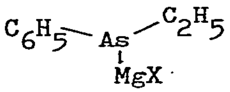
A new type of Grignard reagent, derived from ethyl α-phenylsulfinylacetate (by addition of one molar equivalent of ethylmagnesium bromide in diethyl ether) was reported by Kunieda, Nokami and Kinoshita [45].



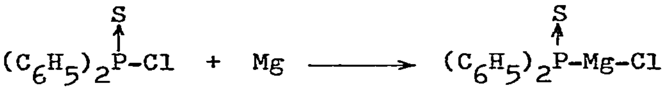
$C_6H_6-\underset{O}{\underset{\downarrow}{S}}-\overset{MgBr}{\overset{|}{C}}H-COOC_2H_5$

Continuing work of previous years Meyers, Temple, Haidukewych and Mihelich described the application of oxazoline substituted Grignard compounds as compounds containing masked carboxyl groups [46].

Gatilov, Ionov, Kokorina and Munkanov reported reactions of arsenic Grignard reagents [47]:



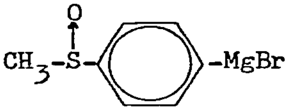
Emoto, Gomi, Masaaki, Okazaki and Inomoto prepared a phosphorus-functional Grignard reagent by the following reaction [48]:



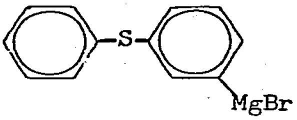
$$(C_6H_5)_2\overset{S}{\overset{\uparrow}{P}}-Cl \quad + \quad Mg \longrightarrow (C_6H_5)_2\overset{S}{\overset{\uparrow}{P}}-Mg-Cl$$

On treatment of the chloride with magnesium for longer periods $(C_6H_5)_2P-Mg-P-(C_6H_5)_2$ was obtained.

Jones and Shen used a sulfinyl-substituted Grignard reagent for synthetic purposes [49]:

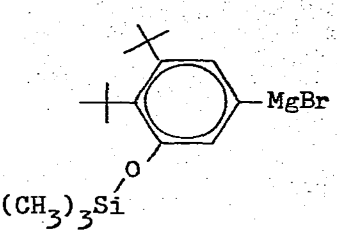


For the same reasons Bilow and Akawie utilized the Grignard derivative of diphenyl sulfide [50]:



Trialkylsilyl-substituted unsaturated compounds were prepared with the aid of the corresponding $R_3Si-CH=CH-MgBr$ vinylic Grignard compound as reported by Belyaev, Stadnichuk and Petrov [51].

Razuvaev, Vasileiskaya, Oleinik, Muslin Klimov and Vavilina prepared and reacted a trimethylsilyloxy-substituted aromatic organomagnesium compound [52].



The following metal-containing organomagnesium compounds were reported in 1974:

Carrê and Corriu obtained evidence for the formation of a Germanium-Magnesium compound as an intermediate in a Ni(II) catalyzed reaction of benzylmagnesium chloride with a chiral Germane derivative [53].

Felkin, Knowles, Meunier, Mitschler, Ricard and Weiss reported the preparation of a cyclopentadienylironmagnesium derivative the structure of which will be discussed in Chapter 3B [54].

Block, Boschetto, Rasmussen, Demers and Whitesides synthesized and utilized the cyclopentadienylirondicarbonylmagnesium bromide [55]:

$$C_5H_5Fe(CO)_2MgBr$$

Benfield, Francis, Green, Ngoc Tuyet, Moser and Poland [56] as well as Green, Moser, Packer, Petit, Forder and Prout prepared complexes containing bis-cyclopentadienylmolybdenum or-tungsten entities bonded with magnesium [57].

A same type of complex, containing cyclopentadienylrhenium dicarbonyl bonded to magnesium was obtained by Nesmeyanov, Kolobova, Makarov and Anisimov [58].

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

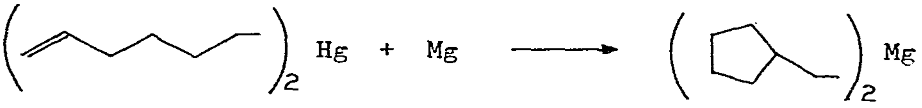
In a Hungarian patent Bor, Gabor, Kekessy, Kovats and Reif reported very high yields of vinylmagnesium chloride under the following reaction conditions [59]:

$$CH_2{=}CHCl\ (3\text{-}4\ atm)\ +\ Mg\ \xrightarrow[\text{toluene mixtures}\ 60\text{-}70^{\circ}]{\text{THF-benzene or}}\ CH_2{=}CHMgCl\ 98\%$$

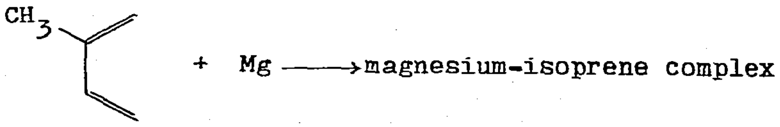
Ashby and Nackashi prepared alkyl- or arylmagnesium fluorides by the reaction of the diorganomagnesium compounds with fluorinating agents, such as BF_3.etherate, SiF_4 etc [60]; e.g.

$$CH_3MgCH_3\ +\ SiF_4\ \longrightarrow\ CH_3MgF\ +\ Si(CH_3)_4\quad (100\%)$$

During the metal exchange reaction between di-5-hexenylmercury and magnesium St. Denis, Oliver, Dolzine and Smart observed almost quantitative formation of the di-cyclopentylmethylmagnesium derivative although the presence of the hexenyl derivative of magnesium was indicated by the high field triplet in the NMR spectrum [61]:

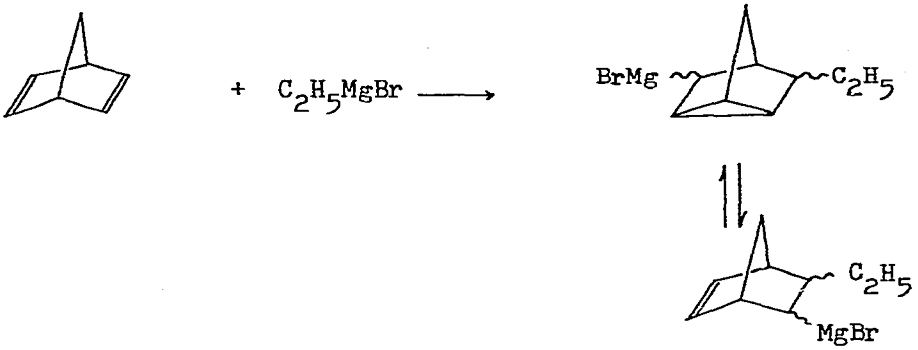


A magnesium-isoprene complex was reported in a Japanese patent by Inoue, Kanbe, Takada, Miyazaki and Yokokawa [62]; reaction of the

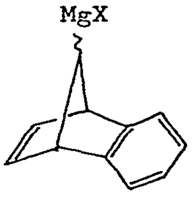


complex with zinc chloride at -80° in THF yielded the correspondin zinc complex.

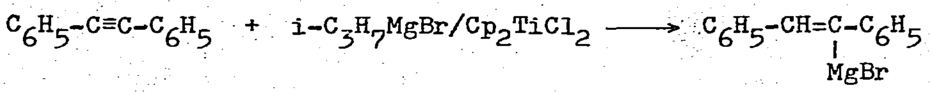
In an US patent Shepard claims the reaction of ethylmagnesium bromide and of allylmagnesium bromide with polycyclic unsaturated hydrocarbons [63]; a typical and remarkable example is given hereby:



Ford and Buske investigated the stereochemistry of different routes to 7-benzonorbornadienyl Grignard reagents either via cycloaddition of benzyne to cyclopentadienylmagnesium bromide, via reaction of syn- or anti-7-chlorobenzonorbornadiene with magnesium in THF or, finally, via reaction of these two halides with sodium naphthalenide in THF which contains an excess of anhydrous $MgCl_2$ [64]. anti-7-Chlorobenzonorbornadiene forms a Grignard reagent at saturated carbon with Mg more stereoselectively than any other alkyl halide known. According to the authors two disturbing features of their results are the formation of substantial amounts of undeuterated products (after deuterolysis of the reaction mixtures) and the low yields obtained with the syn-7-chloronorbornadiene.

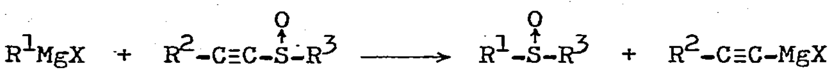


Vinyl Grignard reagents could be obtained, according to Colomer and Corriu, by the reaction of diphenylacetylene with isopropylmagnesium bromide in the presence of dicyclopentadienyltitanium(IV) dichloride [65]:



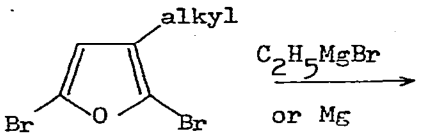
$$C_6H_5{-}C{\equiv}C{-}C_6H_5 \;+\; i{-}C_3H_7MgBr/Cp_2TiCl_2 \longrightarrow C_6H_5{-}CH{=}\underset{MgBr}{C}{-}C_6H_5 \;,$$

Vermeer, Meyer and Eylander reported the following reaction, leading to the formation of an acetylenic Grignard reagent [66]:



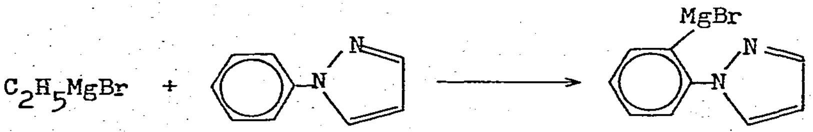
$$R^1MgX \;+\; R^2{-}C{\equiv}C{-}\overset{O}{\overset{\uparrow}{S}}{-}R^3 \longrightarrow R^1{-}\overset{O}{\overset{\uparrow}{S}}{-}R^3 \;+\; R^2{-}C{\equiv}C{-}MgX$$

The reaction of 2,5-dibromo-3-alkylthiophene with ethylmagnesium bromide demonstrates an isomer distribution in the halogen-metal exchange which is similar to that obtained with ethyllithium, as studied by Gronowitz, Cederlund and Hörnefeldt [67]; the direct reaction with magnesium is susceptible to steric hindrance, in particular with a tert-butyl group in the 3-position.

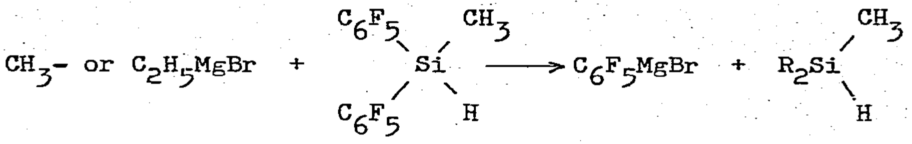


Gilman and Dua [24](see also Chapter 2Bi) and Gilman, Howells and Dua reported the formation of perfluoroaliphatic and -aromatic Grignard reagents by metal-halogen exchange, either at low temperatures or by inverse addition [68].

The following metallation reaction was published by Marxer and Siegrist [69]:



Gilman, Sethi and Howells reported the formation of perfluorophenylmagnesium bromide in the following reaction [70]:

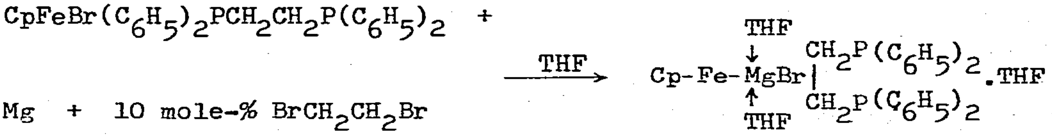


Maksimova, Koshutin and Danyushin, in a Russian patent, claim the formation of alkylmagnesium halides in diethyl ether by the reaction of alkyl halides with magnesium in the presence of SiH_4 as an initiator of the reaction [71].

In a German patent Vit claims the preparation of ethylmagnesium chloride complexes with magnesium alkoxides, useful for reactions with ketones and esters [72]:

$$Mg + ROH \text{ and } R'OH + C_2H_5Cl \xrightarrow[\text{of } NaAlH_2(OCH_2\text{-}CH_2\text{-}OCH_3)_2]{\text{in toluene in the presence}} nC_2H_5MgCl.Mg(OR)OR')$$

Felkin and coworkers reported the following reaction for the preparation of "iron"-Grignard reagent [54]:

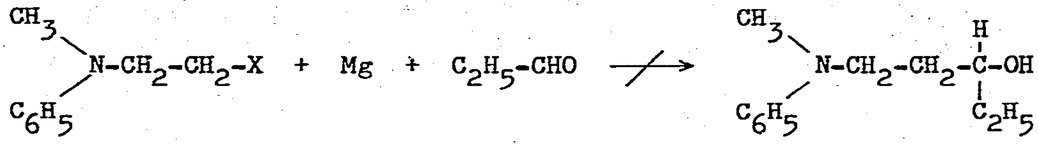


$$\begin{array}{l} CpFeBr(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2 \; + \\ Mg \; + \; 10 \text{ mole-\% } BrCH_2CH_2Br \end{array} \xrightarrow{THF} Cp\text{-}Fe\text{-}\overset{THF \atop \downarrow}{\underset{\uparrow \atop THF}{MgBr}}\Big| \begin{matrix} CH_2P(C_6H_5)_2 \\ CH_2P(C_6H_5)_2 \end{matrix} .THF$$

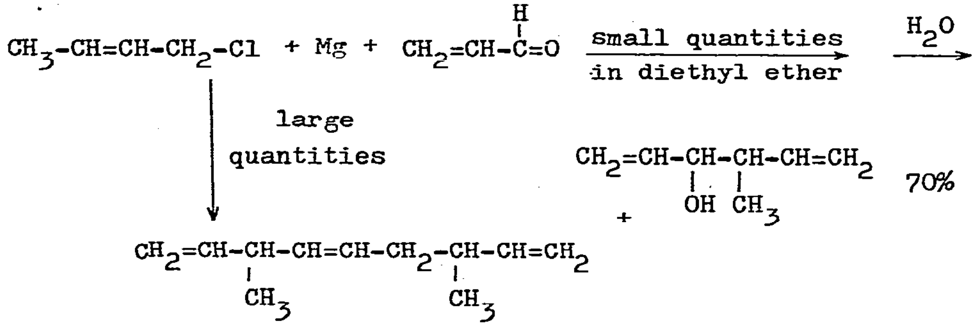
One THF molecule was easily displaced e.g. by recrystallisation from benzene.

2D.Reactions with "in situ" Grignard compounds

Sato, Ogawa, Kojima, Takeuchi and Shirai reported the unsuccessful one step synthesis of γ-amino alcohols, derived from propanal [73]:

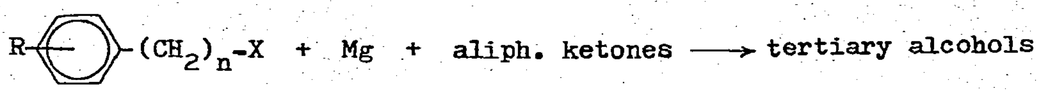


With crotyl chloride and acroleine Richet and Pecque observed the following interesting anomaly [74]: working with small quantities (0.10 - 0.25 moles) the expected product was obtained by the "in situ" method:



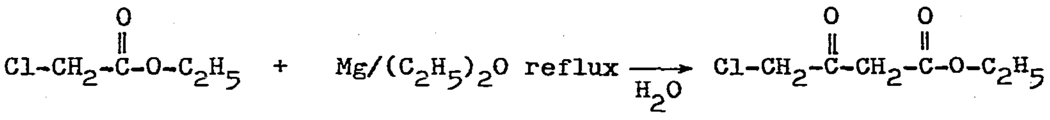
Working with larger quantities (2 - 4 moles) causes the decrease of the amount of the expected product and the formation of an unsaturated hydrocarbon in amounts up to 25% of the yield of the unsaturated alcohol.

In a Japanese patent Kato and Hirayama report the successful application of "in situ" reactions with aliphatic ketones when the Grignard reactions were first started in an ether followed by the addition of the ketones in benzene and refluxing at higher temperatures. With acetone e.g. 90% yield of the tertiary alcohol was observed [75]:



n = 0-3

Campaigne and Rogers obtained surprisingly high yields of keto-esters in the following reaction [76]:

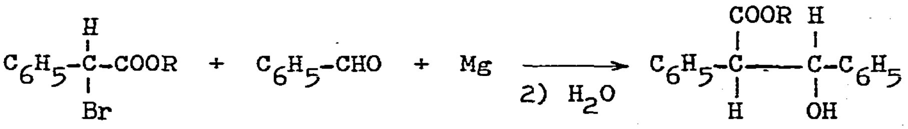


$$Cl-CH_2-\overset{O}{\overset{\|}{C}}-O-C_2H_5 \quad + \quad Mg/(C_2H_5)_2O \text{ reflux} \xrightarrow[H_2O]{} Cl-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-O-C_2H_5$$

Trialkylgallium compounds were prepared by reaction of alkyl iodides with a magnesium-gallium alloy at 160° (Zakharkin, Yushkov, Gravilenko, Ivanov, Fatyushina and Sychev) [77]:

$$R-I \quad + \quad Ga/Mg \text{ (mixture or alloy)} \xrightarrow{160^{o}} R_3Ga$$

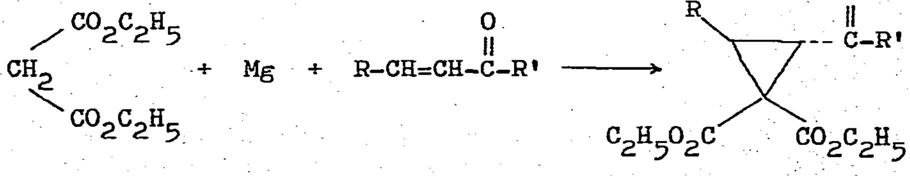
Mladenova, Blagoev and Kurtev probably applied the one step synthetic method for the synthesis of β-hydroxy-esters [40]:



$$C_6H_5-\underset{Br}{\overset{H}{C}}-COOR \quad + \quad C_6H_5-CHO \quad + \quad Mg \xrightarrow[2)\ H_2O]{} C_6H_5-\underset{H}{\overset{COOR}{C}}-\underset{OH}{\overset{H}{C}}-C_6H_5$$

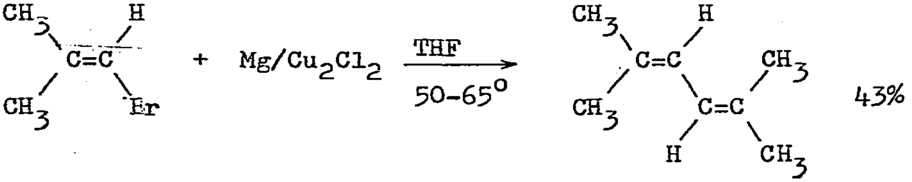
mixture of diastereomers

Gaudemar and Gaudemar-Bardone published the following interesting reaction [78]:



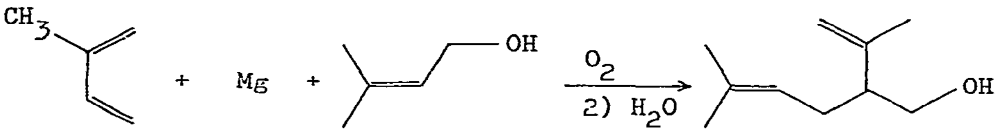
The same type of reaction was also performed with an unsaturated diester.

Esafov, Kachakov and Maiskii obtained vinylic coupling products in reasonable yields in the following Cu(I)-catalysed reaction [79]:



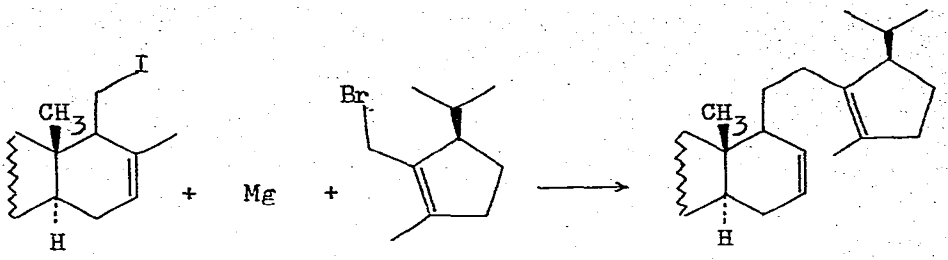
Ramsden, in a German Patent claims the preparation of organomagnesium halides by the one-step reaction of conjugated dienes with magnesium in the presence of allyl- or alkyl halides [80]. Reaction temperatures vary between 5 and 200°; ethereal solvents of different types, such as THF or dioxan (!?) as well as the diethyl ether of diethyleneglycol can be used.

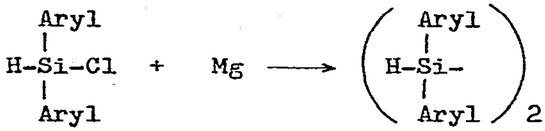
In another (US) patent, Ramsden claims the preparation of lavendulol in the reaction of isoprene with magnesium and prenylchloride, followed by air-oxidation[81]:



Although it is not at all sure that in the following Würtz-type coupling reactions Grignard compounds are really formed as intermediates they will be mentioned in this chapter for systematic reasons:

Van Tamelen, Grieder and Lees reported the following coupling reaction [82]:

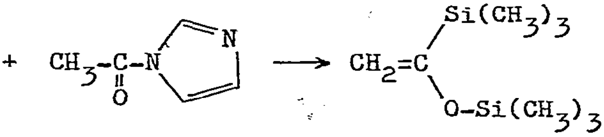




$$\underset{\text{Aryl}}{\overset{\text{Aryl}}{\text{H-Si-Cl}}} + \text{Mg} \longrightarrow \left(\underset{\text{Aryl}}{\overset{\text{Aryl}}{\text{H-Si-}}}\right)_2$$

Gerval, Frainnet, Lain and Moulines [83].

The research group in Bordeaux reported several results, obtained with the $(CH_3)_3SiCl/Mg/HMPA$ couple:

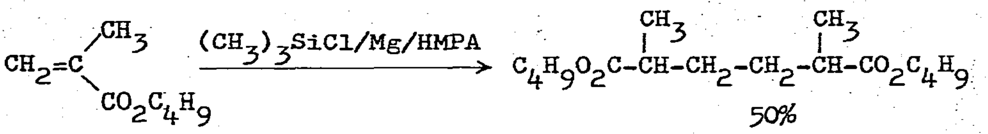


; Bourgeois, Dunoguès, Duffaut and Lapoujade [84]

+ chlorinated organic compounds such as $t\text{-}C_4H_9\text{-}\underset{\displaystyle Cl}{C}=N\text{-}C_6H_5$ to give (on hydrolysis) $t\text{-}C_4H_9\text{-}\underset{\displaystyle O}{\overset{}{\underset{\|}{C}}}\text{-}Si(CH_3)_3$;

Bourgeois [85] and Dunoguès, Jousseaume and Calas [86]. In this latter publication the authors discuss the mechanism of formation of products and retain their conclusion that no Si-Mg compounds are possibly formed as intermediates (see also Chapter 2A, Schumann and Rösch's work [22]).

The reaction of the silylating couple with unsaturated esters was studied by Picard, Dunoguès and Calas [87]. Besides C-silylation in the β-position reactions take place that lead to the formation of 1,4-diesters by a reduction together with coupling:



$$CH_2{=}C(CH_3)CO_2C_4H_9 \xrightarrow{(CH_3)_3SiCl/Mg/HMPA} C_4H_9O_2C\text{-}CH(CH_3)\text{-}CH_2\text{-}CH_2\text{-}CH(CH_3)\text{-}CO_2C_4H_9$$

50%

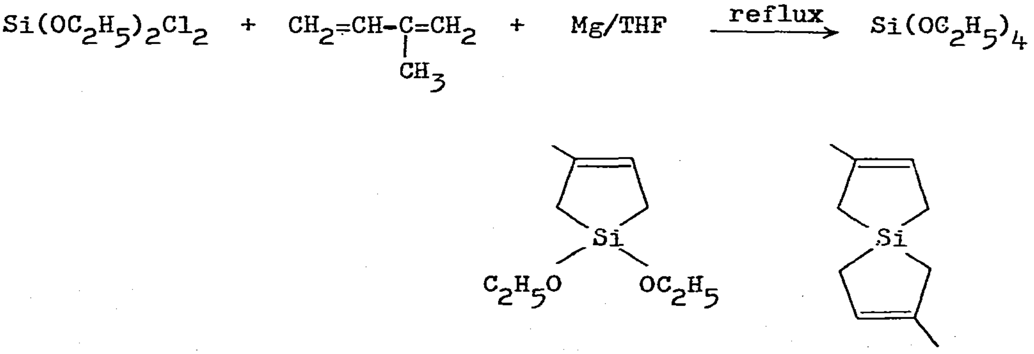
Dunoguès, Pillot, Duffaut and Calas finally studied the reaction of the couple with vinylsilanes in the presence of iron(III) and titanium(IV) salts [88]:

$$(CH_3)_3Si\text{-}CH{=}CH_2 \xrightarrow[\text{couple + Fe salts}]{\text{silylating}} (CH_3)_3Si\text{-}CH{=}CH\text{-}Si(CH_3)_3$$

and other products

In a series of three papers Bazant and Cerny investigated the reaction of para-dihalobenzenes with magnesium in the presence of several diphenylsilanes [89], [90] and [91]; depending on the type of magnesium used [89] as well as on the solvent and the starting dihalobenzenes mono- as well as disubstituted diphenylsilyl-benzenes could be obtained.

The reaction of isoprene with magnesium in the presence of dichlorodiethoxysilane in THF yields the following products:



$$Si(OC_2H_5)_2Cl_2 + CH_2{=}CH\text{-}C(CH_3){=}CH_2 + Mg/THF \xrightarrow{\text{reflux}} Si(OC_2H_5)_4$$

The spirosilane could be isolated in 80% yield when 0.185 mole of isoprene was reacted with 0.074 mole of the dichlorosilane in the presence of 0.185 gat Mg (Terunuma, Hata and Araki [92]. The same type of spirosilane was obtained by Salomon in the reaction of active magnesium with butadiene in the presence of $SiCl_4$ [93].

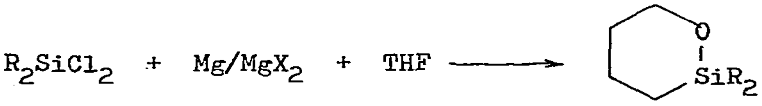
Two reports have appeared on the ring-opening reaction of tetrahydrofuran under influence of halides:

According to Louis the tetrahydrofuran ring is opened by MgI_2, formed on reaction of Mg with methyl iodide; in the presence of trimethylchlorosilane the following products are obtained [94]:

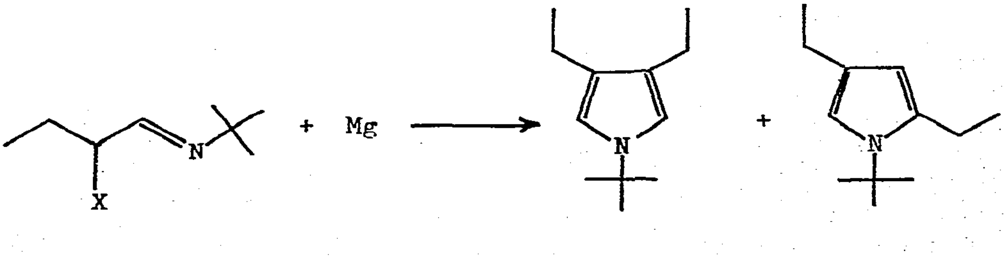
$(CH_3)_3Si{-}O{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}Si(CH_3)_3$ and

$(CH_3)_3Si{-}O{-}(CH_2)_4{-}(CH_2)_4{-}O{-}Si(CH_3)_3$

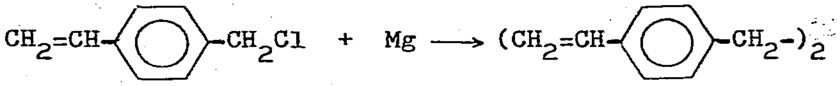
By the same type of reaction C.L. Smith and Gooden observed the formation of a cyclic siloxane [95]; the reaction of magnesium diphenyl-, dimethyl- or methyldichlorosilane in THF, catalysed by magnesium halides yields ring opening products of THF:



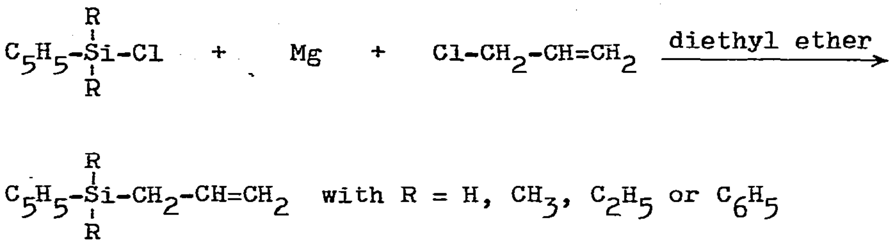
Duhamel, Duhamel and Valnot observed the following azole-formation reaction [96]:



Benzylic and allylic halides were used in coupling reactions with the aid of magnesium:



as reported by Tanimoto, Miyake and Okano [97];



$$C_5H_5\text{-}\overset{R}{\underset{R}{Si}}\text{-}Cl \quad + \quad Mg \quad + \quad Cl\text{-}CH_2\text{-}CH{=}CH_2 \xrightarrow{\text{diethyl ether}}$$

$$C_5H_5\text{-}\overset{R}{\underset{R}{Si}}\text{-}CH_2\text{-}CH{=}CH_2 \quad \text{with } R = H,\ CH_3,\ C_2H_5 \text{ or } C_6H_5$$

(Maksimova, Koshutin and Smirnov [98]).

Markov, Chorbadzhiev and Tarpanov synthesized dibenzyl sulfide in the following one-step reaction [99]:

$$C_6H_5CH_2Cl \quad + \quad Mg \quad + \quad S \xrightarrow{NH_3.\text{liq}} C_6H_5CH_2\text{-}S\text{-}CH_2C_6H_5$$

2E. Miscellaneous

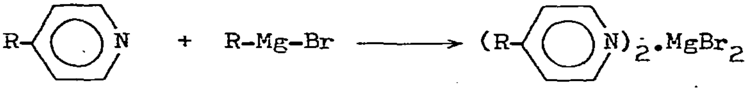
Westera, Blomberg and Bickelhaupt, investigating reactions of ethyl magnesium bromide with 2-ethyl-1,3-dioxolane, prepared the Grignard compound in benzene in the presence of one molar equivalent of either tetrahydrofuran, diethyl ether or diisopropyl ether [100]:

$$C_2H_5Br \quad + \quad \text{Mg/one equivalent of a basic solvent} \xrightarrow{\text{benzene}}$$

$$C_2H_5MgBr.\text{solvent}$$

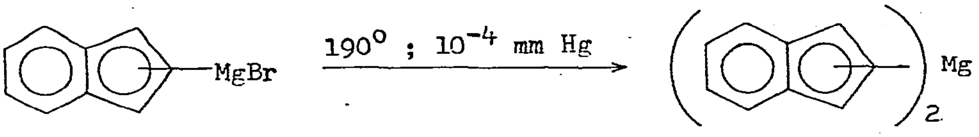
With diisopropyl ether a precipitate is formed which contains considerable amounts of organomagnesium compounds resulting in a ratio of C_2H_5MgBr:ether = 1 : 1.32. With THF (which was perdeuterated) considerable precipitation of $MgBr_2$ occured resulting in the formation of a solution containing diethylmagnesium and ethylmagnesium bromide in a ratio 1.0 : 1.3

Mixing equimolecular amounts of a 4-substituted pyridine with either ethyl-, allyl- or phenylmagnesium bromide resulted in the formation of a white amorphous precipitate of the formula $MgBr_2$.2-pyridine (substituted in the 4-position) as reported by Thiessen, Desseyn and Alderweireldt [101]:



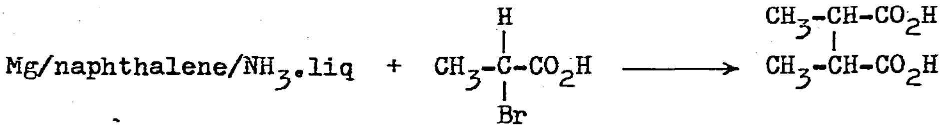
It is noteworthy that 4-C_6H_5-CO-pyridine did not lead to the formation of adducts of the same type.

Atwood and Smith reported the isolation of bis(indenyl)magnesium by thermal decomposition at 190° of indenylmagnesium bromide under vacuum (ca. 10^{-4} mm Hg)[102]; the white crystalline substance was separated from an accompanying yellow oil and could be purified by



sublimation.

Savel'eva investigated the reactivity of the product, obtained by hydrogenation of ethylmagnesium bromide in THF or benzene [103]. Magnesium naphthalenide was prepared in liquid ammonia by Markov, Dimitrova and Ivanov [104]; it reacted with 2-bromo-propanoic and -butanoic acid under formation of the duplication products:



$$Mg/naphthalene/NH_3.liq + CH_3-\overset{H}{\underset{Br}{C}}-CO_2H \longrightarrow \begin{matrix} CH_3-CH-CO_2H \\ | \\ CH_3-CH-CO_2H \end{matrix}$$

3. PHYSICAL PROPERTIES OF ORGANOMAGNESIUM COMPOUNDS

3A. NMR spectra

The NMR spectra of various Grignard reagents, derived from bromopyridine, -furan, -thiophene and -selenophene, as mentioned in Chapter 2Biv (Martin and coworkers [20]) were measured and related to the electronic structure. Furthermore these authors evaluated the activation functions for the rate-determining step of the formation and for the Schlenk equilibrium.

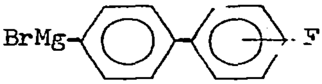
Oliver and coworkers determined the NMR spectra of bis(cyclopentylmethyl)magnesium as well as of bis(5-hexenyl)magnesium [61] (see Chapter 2C).

Fraenkel, Appleman and Ray investigated the ligand magnesium exchange kinetics of the system l-sparteine, dineopentylmagnesium and THF-dimethoxymethane [105].

Together with Yu, Fraenkel studied the kinetics and thermodynamics of carbon-magnesium bond exchange in the system diphenylmagnesium-dineopentylmagnesium [106].

Ashby and Parris studied the structure of a monoetherate of cyclopentadienylmethylmagnesium dissolved in benzene , diethyl ether or THF among others by means of NMR techniques [107].

Westera, Blomberg and Bickelhaupt studied the kinetics of the reaction of ethylmagnesium bromide with 2-ethyl-1,3-dioxolane in benzene with the aid of NMR spectroscopy [100] (see also Chapter 2E). The ^{19}F NMR spectrum was measured of the following biphenylmagnesium bromide derivatives, as prepared by Koridze, Gubin and Ogorodnikova [108]:



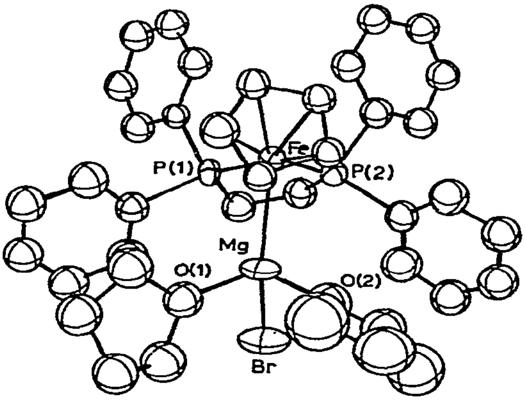
(meta or para position)

3B. Other techniques

X-ray analysis of organomagnesium compounds was reported by several groups:

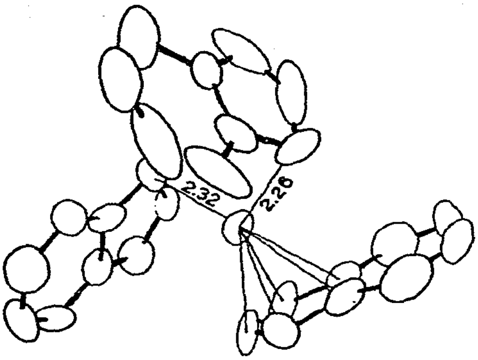
Paradies determined cell-constants, densities and space-groups of magnesium derivatives of 2-pyridyl (R) such as RMgBr.2THF, RMgI.THF, RMgBr.2$(C_2H_5)_2O$, R_2Mg.RI and even of a compound which was mentioned RMgBr in the table (solvent-free Grignard compounds have not been demonstrated before) [109].

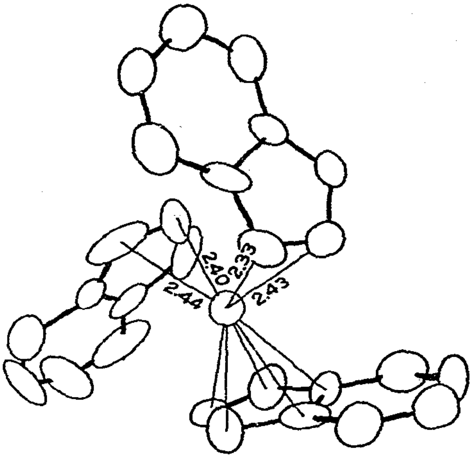
The following crystal structures have been reported:



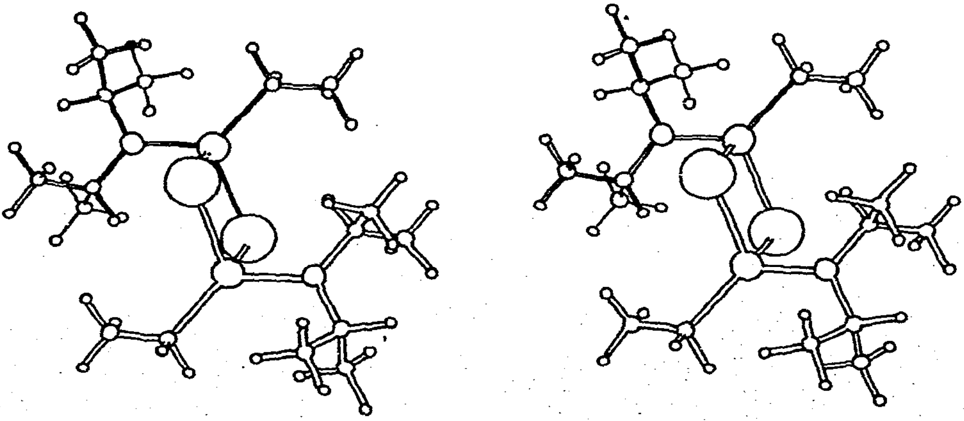
Cyclopentadienyl-1,2-bis(diphenylphosphino)ethaneironmagnesium bromide tris(tetrahydrofuran), which was already mentioned in Chapter 2Biv [54] (Weiss and coworkers).

Bis(indenyl)magnesium (see also Chapter 2E [102]; Atwood and Smith) in the solid state exhibits magnesium atoms in two different environments and indenyl groups of a fundamentally different nature:





Spek, Voorbergen, Schat, Blomberg and Bickelhaupt reported the following structure of dimeric ethylmagnesium bromide/diisopropyl ether complex [110] (a stereoscopic pair of the dimer is shown in the figure):



The molecular structure of dicyclopentadienylmagnesium was determined by gas-phase electron diffraction by Haaland, Lusztyk, Novak, Brunvoll and Starowieyski [111]; no significant deviation from planarity is found for the C_5H_5 rings and no indication is found for an asymmetric position of magnesium between the two rings as was found earlier for dicyclopentadienylberyllium.

Ashby and Parris studied the structure of cyclopentadienylmethylmagnesium monoetherate with the aid of infrared spectroscopy [107]; in the solid state the magnesium atoms are associated via methyl bridge bonds, the cyclopentadienyl ring has approximately D_{5h} symmetry. There is partial cleavage of the methylbridge bonds when the etherate is dissolved in diethyl ether, cleavage of these bonds is complete in THF.

With the aid of infrared and Raman spectroscopy Sourisseau, Guillermet and Pasquier studied (among others) magnesium derivatives of allylic compounds; vibrations of metal-allyl valences were 325 cm^{-1} for C_3H_5MgCl, 311 cm^{-1} for C_3H_5MgBr and 317 for $(C_3H_5)_2Mg$ [112]. The force constants for these compounds were smaller than 1.0 mdynes/Å which indicates that the bonds of magnesium with cyclopentadienyl groups are much stronger than with the allyl group.

In another publication the same authors reported the mean frequencies $\nu\overline{CH}$ of the same allylmagnesium compounds [113].

Kress and Novak reported infrared and Raman spectral studies of solid $MgBr_2.2(C_2H_5)_2O$ at temperatures between 90 and 300 K in the 4000 to 30 cm^{-1} range and at various pressures up to 10 kbar [114].

Vapor pressures as well as heats of vaporisation of magnesium bromide were measured by Topor and Moldoveanu [115]. In the vapor phase magnesium bromide exists in monomeric and dimeric form.

The basicity of Grignard compounds in THF solutions was measured by

Chevrot, Folest, Troupel and Périchon by determining zero current potentials of hydrogen electrodes in such solutions [116]. The authors proved the dissociation of RMgX to $RMg^{\oplus}$ and $X^{\ominus}$.
Acid-base constants of the system RH/RMgX were determined by Chevrot, Folest, Troupel, Cachelou and Périchon [117].
Electrolysis of alkylmagnesium bromides was reported by T. Holm using platinum electrodes [118]. Two different mechanisms for the discharge process were detected: one for allyl-, benzyl- and t-butylmagnesium bromide and one for methylmagnesium bromide. Ethyl-, butyl- and isopropylmagnesium bromide behave like methylmagnesium bromide at low current densities but change over toward t-butylmagnesium bromide at high current densities. Values of the anodic polarisation at high current densities were correlated by the author to the reactivity of the Grignard reagent toward benzophenone.
Tuulmets deduced an equation for the quantitative description of the influence of the solvent upon the reaction kinetics of organomagnesium compounds [119]. Apart from a suggested formulation of the "effective" basicity of the solvent the author introduced the notion "index of effective acidity" of the Grignard compound; such indexes were given in a Table for phenylmagnesium bromide, methylmagnesium bromide, ethylmagnesium bromide and for diphenyl- , diethyl- and di-n-propylmagnesium.
Horiba, Hara, Inoue and Kubo determined the magnetic susceptibility of magnesium 2,2'-dipyridylide in THF at 1,6 and 20 K [120].

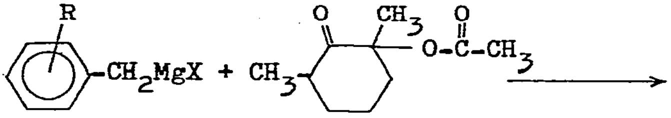
3C. Structure and reactions

In two publications Tomoi and Kakiuchi determined the activity of RMgBr/HMPA mixtures in styrene polymerisation [121] and [122]. The activity decreases in the series

benzyl > allyl > aryl ~ sec-alkyl > n-alkyl

and the phenomenon was explained by the ease of formation of a carbanion from RMgBr and its activity.

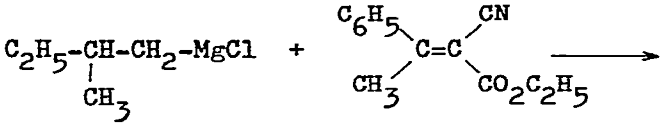
G. Miller noted that in the following reaction



1,2 as well as 1,4-addition products

attack at the carbonyl oxygen increased with increasing electron-donating powers of the substituent R, independent of any steric effects [123].

In the reaction



reduction, addition and enolisation products

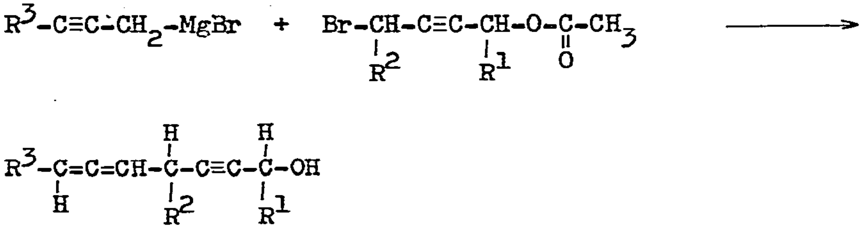
as studied by Cabaret, Welvart and Carrie, Grignard reagents prepared either from a racemic or from a chiral halide have the same reactivity, which suggests that the species R_2Mg does not participate significantly in the reaction [124].

According to Sonnet, Bierl and Beroza in the reaction of allylic Grignard reagents with allylic halides in THF/HMPA products are formed in which the double bond from the Grignard reagent is predominantly cis [125]:

$$\underset{\text{(Z) and (E)}}{n\text{-}C_4H_9\text{-}CH{=}CH\text{-}CH_2MgCl} + \underset{\text{(Z)}}{Cl\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_6\text{-}O\text{-}THP} \longrightarrow$$

$$\text{(Z,Z)}\ n\text{-}C_4H_9\text{-}CH{=}CH\text{-}CH_2\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_6\text{-}O\text{-}THP$$

The following propargylic allenylic rearrangement was observed by Perriot and Gaudemar [126]:

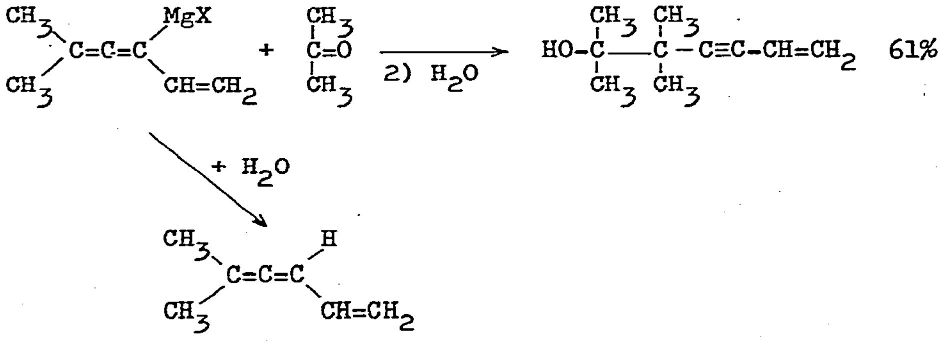


$$R^3\text{-}C{\equiv}C\text{-}CH_2\text{-}MgBr + Br\text{-}\underset{R^2}{CH}\text{-}C{\equiv}C\text{-}\underset{R^1}{CH}\text{-}O\text{-}\underset{O}{\overset{}{C}}\text{-}CH_3 \longrightarrow$$

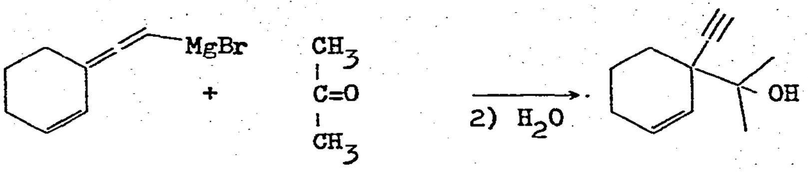
$$R^3\text{-}\underset{H}{C}{=}C{=}CH\text{-}\overset{H}{\underset{R^2}{C}}\text{-}C{\equiv}C\text{-}\overset{H}{\underset{R^1}{C}}\text{-}OH$$

The same type of rearrangements were given in the next two publications:

Voskanyan and coworkers [33]:



Roumestant, Dulcère and Gore [35]:



The coupling reaction of a Grignard compound with an aromatic or vinylic halide, catalysed by Ni(II) salts, as investigated by Kumada, Tamao, Sumitani and Kiso, is accompanied by rearrangement from secondary to primary when secondary alkyl Grignard reagents are applied [127].

3D. Theoretical calculations

Charkin published the results of MO LCAO spin-lattice relaxation calculations of MgX_2 (X = F, Cl and CH_3) [128].

4. MECHANISMS OF REACTIONS OF ORGANOMAGNESIUM COMPOUNDS

4A. Reactions with carbonyl compounds

4Ai. Addition and reduction reactions

Tuulmets and his group continued studies on solvent effects in the reactions of organomagnesium compounds; with Viirlaid he studied the effect of anisole on the reaction of n-propylmagnesium bromide with 2,2-dimethyl-3-butanone [129]. Anisole seems to solvate the Grignard reagent weakly. Comparison of the present results with those obtained earlier by Tuulmets and coworkers demonstrates that the effect of the medium on the rate of the reaction is determined by polarity, basicity and steric effects of the solvent.

Tuulmets, together with Viirlaid and Kurrikoff studied the kinetics of the reaction of diphenylmagnesium with benzophenone in dibutyl ether, diethyl ether, anisole, tetrahydrofuran and their mixtures with n-heptane [130]. The sensitivity of the reaction rate to changes in the polarity of the medium could be demonstrated; the magnitude of this sensitivity is apparently determined by the effective basicity of the solvent.

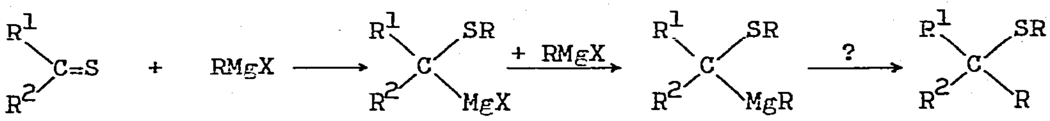
As already discussed in Chapter 3B, in a third publication, Tuulmets, in a further refinement of his interpretation of solvent effects, introduced the notion "index of effective acidity of the Grignard reagent" [119].

In a further study of the influence of impurities in magnesium on the mechanism of reactions of organomagnesium compounds with ketones Ashby and Wiesemann concluded that it is clear that CH_3MgBr reacts with benzophenone predominantly, if not entirely, by a polar mechanism, whereas the reaction of t-C_4H_9MgCl under the same conditions is proceeding by a Single Electron Transfer pathway.[131]. Furthermore the authors conclude that it is also clear that a reaction that would normally proceed by a polar mechanism can proceed by a SET pathway, if the magnesium used to prepare the Grignard reagent contains parts per million of transition metal impurities.

The amounts of benzopinacol formed in the reaction of methylmagnesium bromide with benzophenone in diethyl ether with increasing amounts of $FeCl_3$ is as follows:

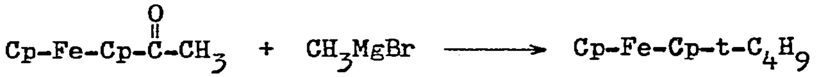
1.0 % benzopinacol for 4 ppm $FeCl_3$
2.6 % benzopinacol for 40 ppm $FeCl_3$
18.7 % benzopinacol for 400 ppm $FeCl_3$
46.0 % benzopinacol for 4.000 ppm $FeCl_3$
70.5 % benzopinacol for 40.000 ppm $FeCl_3$

For the double addition of RMgX to thioketones Dagonneau proposed a two-step-mechanism [132]:



As indicated, it is not clear by what mechanism the second step proceeds. According to the author the solvent may play a role there. The same sort of two-step mechanism was proposed by Dagonneau for the reaction of vinylic Grignard reagents with several different thioketones [133].

Abram and Watts discussed the reaction of methylmagnesium bromide with acetylferrocene which leads to the formation of t-butylferrocene [134]:

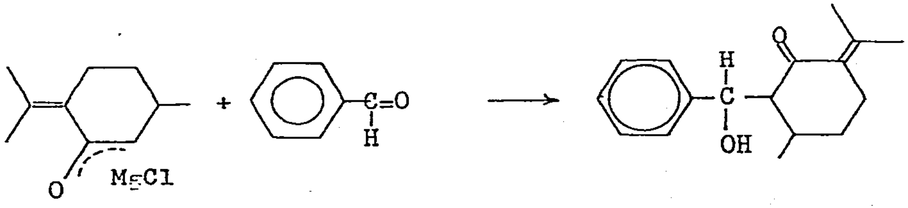


$$Cp\text{-}Fe\text{-}Cp\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 + CH_3MgBr \longrightarrow Cp\text{-}Fe\text{-}Cp\text{-}t\text{-}C_4H_9$$

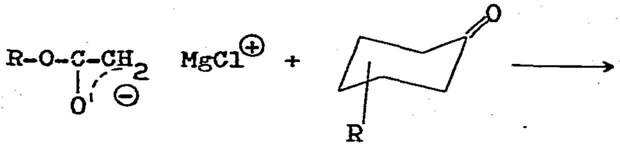
A stabilised carbonium ion is supposed as an intermediate in this uncommon reaction.

4Aii Steric course of reactions with carbonyl compounds

Mme Maroni and coworkers studied the stereochemistry of the reaction of bromomagnesium enolates with carbonyl compounds: with benzaldehyde a mixture of diastereomers is obtained [38]

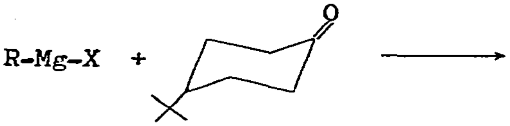


With substituted cyclohexanones axial and equatorial attack was studied [44]:



axial and equatorial attack

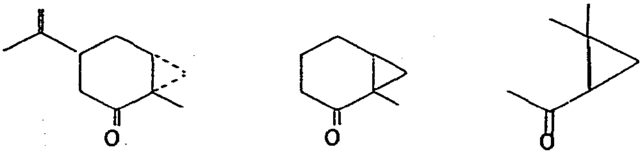
The stereochemistry of the addition of methyl- and propyl Grignard reagents to tert-butylcyclohexanone in the presence of lithium perchlorate or of tetrabutylammonium chloride was studied by Chastrette and Amoroux [135]:

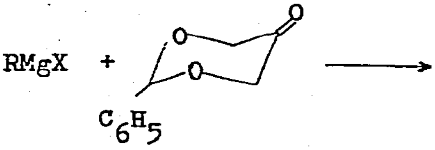


axial and equatorial attack

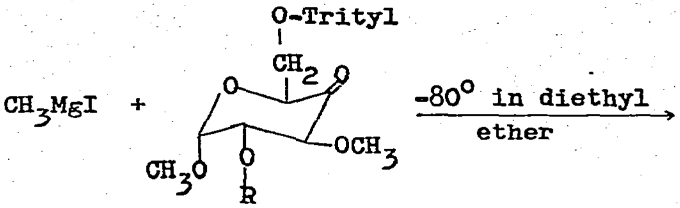
Other researches of this same type were those with the following cyclic ketones:

Rocquet and Sevin [136]: acetylenic Grignard reagents with



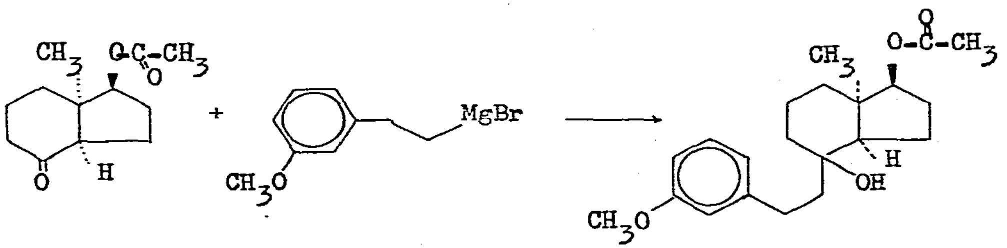


; Jochims, Kobayashi and Skrzelewski [137]

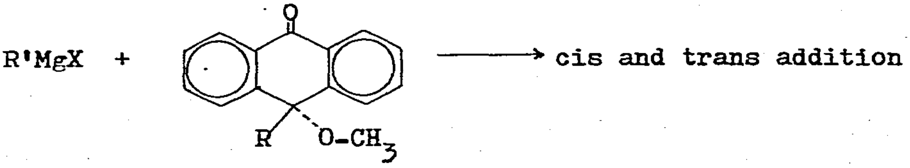


exclusively axial attack [138]; under the same reaction conditions methylmagnesium iodide reacted with 4-tert-butylcyclohexanone to form both axial and equatorial attack products (Miljkovic, Gligorijevic, Satoh and Miljkovic).

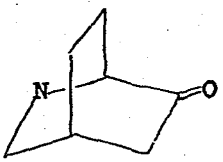
Andryushina and Grinenko observed stereospecific addition to the carbonyl group in the following reaction [139]:

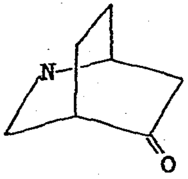


Montebruno, Fournier, Battioni and Chodkiewicz [140]:

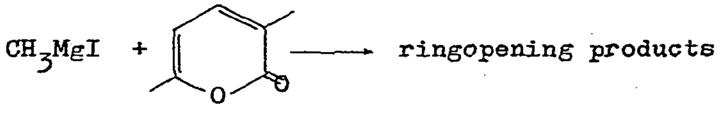


According to Borne, Clark and Wade the reaction of phenylmagnesium bromide with either of the following cyclic ketones proceeds stereoselectively to give only one of the possible two phenylcarbinols [141]:



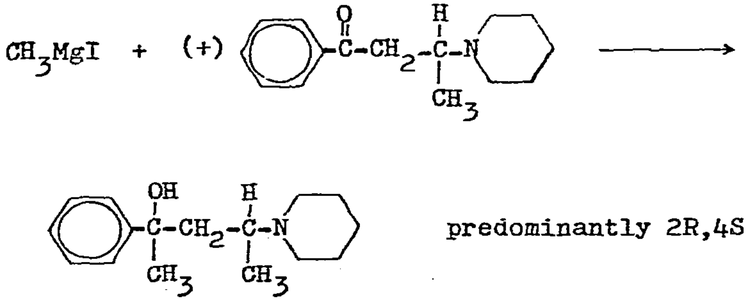


For the interpretation of the regioselectivity observed in the reaction


CH_3MgI + → ringopening products

Trolliet, Royer, Longeray and Dreux developed a model which is based on an enlarged electronic delocalisation in the transition state [142].

The following stereospecific reaction


CH_3MgI + (+) →

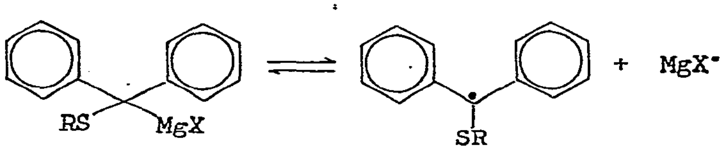
predominantly 2R,4S

was reported by Tramontini, Angiolini, Fouquey and Jacques [143].

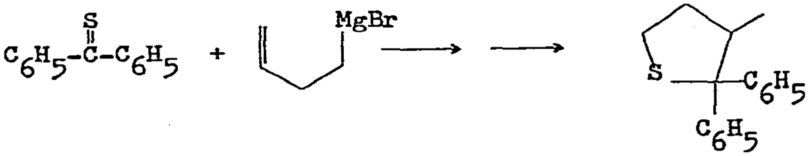
4B. Radical reactions of organomagnesium compounds

As has already been mentioned in Chapter 4Ai Ashby and Wiesemann observed the formation of radical products in the reaction of methylmagnesium bromide with benzophenone when small amounts of iron-

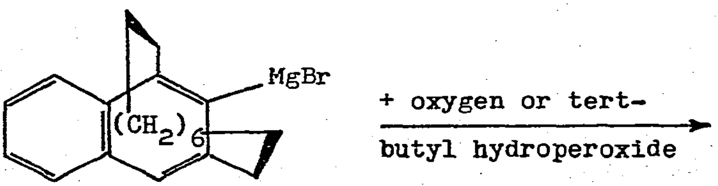
(III) salts were present in the reaction mixture. For tert-butylmagnesium chloride however the reaction with benzophenone proceeds by a SET pathway, even when pure magnesium was used for the preparation of the Grignard compound [131]. Besides benzopinacol also the 1,6-addition reaction product was isolated by the authors. Radical intermediates have been observed by Dagonneau and Vialle in the reaction of several aliphatic Grignard reagents with thiobenzophenone [144]. The authors suggest the following equilibrium to exist in solution



which might, among others be responsible for the formation of a thiacyclopentane derivative in the reaction of thiobenzophenone with 3-butenylmagnesium bromide:



Parham and Montgomery discussed the radical nature of the reaction of the meta-cyclophane organomagnesium reagent indicated below with oxygen or tert-butyl hydroperoxide [145]:



The reaction of tert-butyl peroxide with Grignard reagents was also studied by Kochi, Nugent and Bertini [146]. The relative rates of reactions were as follows:

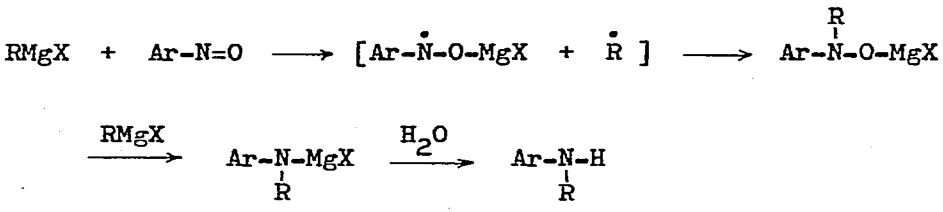
Phenyl : 0; methyl : 1.0; ethyl : 52; isopropyl : 590; tert-butyl : 1800.

This sequence is expected for the process :

$$R^{\ominus} \longrightarrow R^{\bullet} + e^{\ominus}$$

since it reflects both decreasing stability of the radical and increasing stability of the carbanion. The authors accounted for all the tert-butyl and ethyl fragments among the products; the product distribution could be quantitatively related to known values for the relative rates of the combination and disproportionation reactions of tert-butoxy and ethyl radicals which are postulated to arise via a single mechanistic pathway.

For the formation of N-alkylanilines in the reaction of 2,4,6-tri-tert-butylnitrosobenzene with isopropyl- or tert-butylmagnesium halides Okazaki, Inagaki and Inamoto proposed the following mechanism [147]:

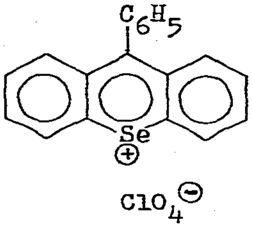


$$RMgX + Ar{-}N{=}O \longrightarrow [Ar{-}\dot{N}{-}O{-}MgX + \dot{R}\,] \longrightarrow Ar{-}\overset{R}{N}{-}O{-}MgX$$

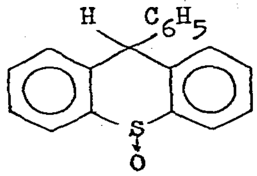
$$\xrightarrow{RMgX} Ar{-}\underset{R}{N}{-}MgX \xrightarrow{H_2O} Ar{-}\underset{R}{N}{-}H$$

The yield of the aniline was 6% with isopropyl- and 43% with tert-butylmagnesium halides.

Hori, Kataoka, Shimizu, Hsu, Asahi and Mizuta [148] and Hori, Kataoka and Shimizu [149] proposed radical mechanisms for the reactions of aromatic Grignard reagents with the following heterocyclic compounds:



ref [148] and

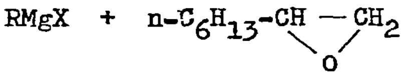


ref [149]

4C. Miscellaneous reactions

For the reaction of ethylmagnesium bromide with 2-ethyl-1,3-dioxolane in different ethereal solvents Westera, Blomberg and Bickelhaupt proposed the formation of several complexes which reacted with first-order kinetics [100]. The rate constants observed were related to basicities of the ethers. The results confirmed that the reaction proceeds via a transition state with oxocarbonium ion character.

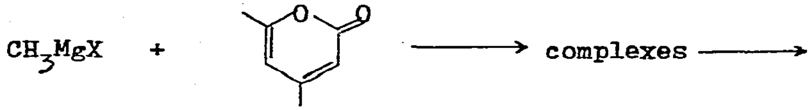
Kinetics and mechanism of the reaction of Grignard reagents with hexyloxirane in diethyl ether or THF were studied by Sano, Kodama, Matsuda and Matsuda [150];



$$RMgX + n\text{-}C_6H_{13}\text{-}\underset{\diagdown \ O \ \diagup}{CH - CH_2}$$

The order of the reaction depends, among many other things, of the degree of association of RMgX in the solvents studied.

For the reaction of substituted 2-pyrones with methylmagnesium compounds Lhoste, Moreau and Dreux propose the formation of complexes between the organomagnesium reagent and the pyrone before reaction



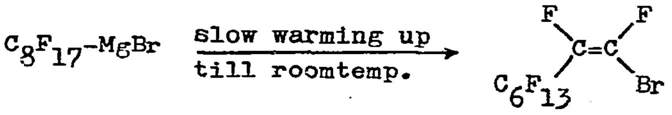
occurs [151].

Richey and Veale determined the rates of cyclisation of 5-hexenylmagnesium derivatives [152]:

At 100° the rate of cyclisation is 1×10^{-6} sec^{-1} for the RMgBr species and 44.8×10^{-6} sec^{-1} for the R_2Mg compound. Since the Schlenk equilibrium between the two compounds in THF

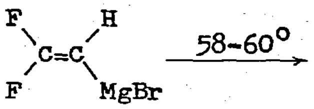
$$R_2Mg + MgBr_2 \rightleftharpoons 2\ RMgBr$$

has a value of 30-40 the authors concluded that the rate determining step of the addition of the Grignard function to the alkene function proceeds without involvement of an external molecule. Howells and Gilman reported the following pyrolysis reaction of perfluorooctylmagnesium bromide [153]:



47% yield
96% pure

Another elimination reaction of a fluoro Grignard compound was reported by Smirnov and Tomilov [25]:



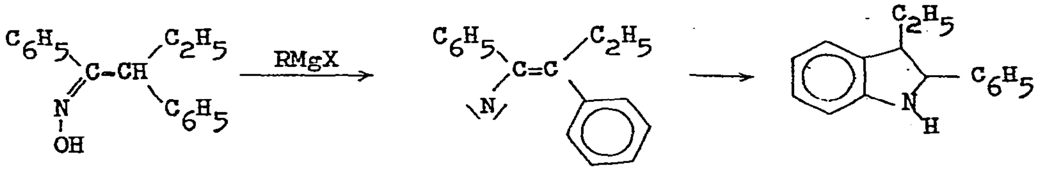
F-C≡C-H (more than 41.6%) together with some $CH_2=CF_2$ and HC≡CH

In the reaction of phenylmagnesium bromide with some peroxides having oxygen- and nitrogen-atoms adjacent to the peroxide function these hetero atoms seem to play an important role in offering a possibility to the the cationic species to form coordination complexes (Okubo, Saito and Tomiyoshi [154]).

According to Bolton and Kearns the reaction of aryl Grignard reagents with benzoyl peroxides or tert-butyl peroxybenzoate exhibits a bright red chemiluminescence [155]. The emitting species was identified as $(C_6H_5)_3C^{\bullet}$.

The same authors studied the chemiluminescence of the reaction of aryl Grignard reagents with oxygen [156]. The main emitting species in the chemiluminescent reactions of phenylmagnesium bromide and p-chlorophenylmagnesium bromide were identified as an isomeric mixture of brominated biphenyls, identical with that formed through photolysis of the Grignard precursor.

For the formation of 1-3% indole derivatives in the reaction of methyl- or ethylmagnesium halide with phenyl-substituted oximes



Bartnik and Laurent propose the intermediate existence of a vinyl nitrene [157].

The enhancement of the reaction rate of organomagnesium compounds by the addition of lithium or quaternary ammonium halides or perchlorates was studied kinetically for the systems benzonitrile/propylmagnesium bromide and benzonitrile/dipropylmagnesium (Chastrette, Amouroux and Subit [158]).

$$C_3H_7\text{-Mg-} \quad + \quad C_6H_5CN \quad \xrightarrow[\text{tetrabutylammonium halides}]{\text{+ Li halides or}}$$

Except for LiBr all the salts investigated gave rate enhancements; the results were related to the formation of complexes between the organomagnesium reagents and the salts.

A. Holm, T. Holm and Huge-Jensen investigated the reaction of Grignard reagents with alkyl cyanates. Alkylmagnesium halides and phenylmagnesium bromide react with alkyl cyanates to form a white complex that has the following composition [159]:

$$R'OCN \quad + \quad RMgX \xrightarrow{(C_2H_5)_2O} R'OMgX.RCN.1/2(C_2H_5)_2O$$

Yields of the alcohol and the nitrile are high in several cases. Kinetic measurements of these reactions were published in two other papers [160] and [161]. Towards aryl cyanates arylmagnesium bromides are found to be more reactive than dibutylmagnesium, which again is more reactive than butylmagnesium bromide. The reaction is best described as involving a concerted four-center mechanism, first order both in cyanate and organomagnesium species.

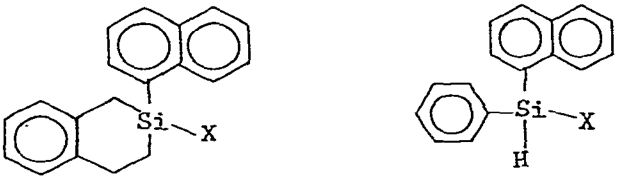
Tüzün and Erdik, continuing their earlier work reported the kinetic measurements of the reaction:

$$RMgX \quad + \quad (C_2H_5)_2N\text{-}H \xrightarrow[25^{\circ}]{\text{diethyl ether}}$$

The authors propose a S_Ei mechanism for the reaction [162].
Two more reactions of this type have been investigated:
Emptoz and Huet compared the reactivity of 1-hexyne towards diethylmagnesium, ethylmagnesium bromide, diethyl-zinc and diethylcadmium [163].
Pällin and Lääne investigated the rate of reaction of acetylene with phenylmagnesium bromide in diethyl ether at 0° in the presence of catalytic amounts of amines [164]:

$$C_6H_5MgBr + H\text{-}C{\equiv}C\text{-}H \longrightarrow BrMg\text{-}C{\equiv}C\text{-}MgBr + C_6H_6$$

Siginificant catalytic activity was found for diethyl- and triethylamine. The latter enhanced the rate of reaction 2180 times !
Other amines investigated were ethylamine and ammonia.
Corriu and Henner published the kinetic studies of the coupling reactions of Grignard reagents with organosilane derivatives such as



X = F or $O\text{-}CH_3$

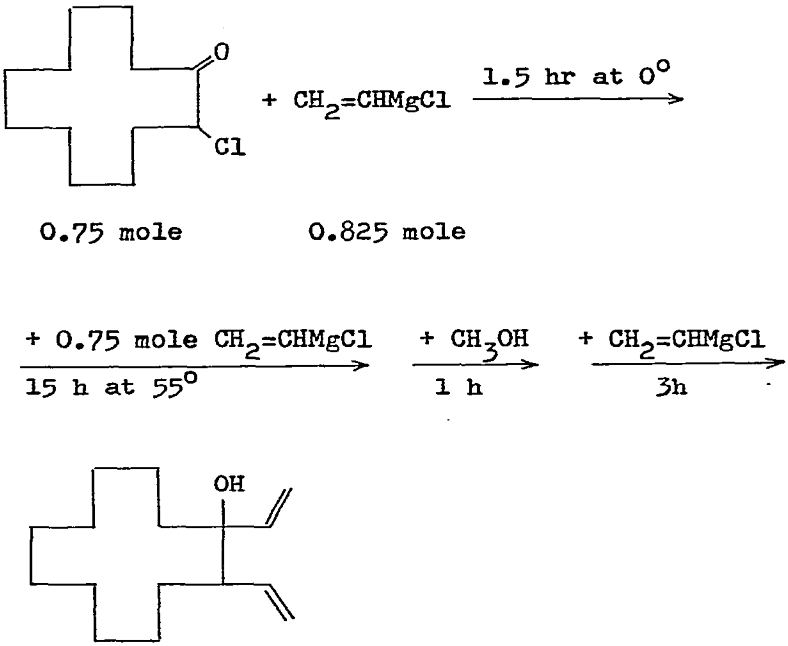
The rate of reaction increases in the order diethyl ether < THF < dimethoxyethane [165].
By means of competition reactions Dubois, together with MacPhee and Boussu studied the relative rates of reactions of Grignard compounds with acid chlorides, catalysed by copper (I) chloride [166]. The results are consistent with a cyclic transition state in which the

chloride is displaced from acid chloride without addition to the carbonyl group, by either a mixed cuprate(I) intermediate or a loose RCu...MgX_2 complex.

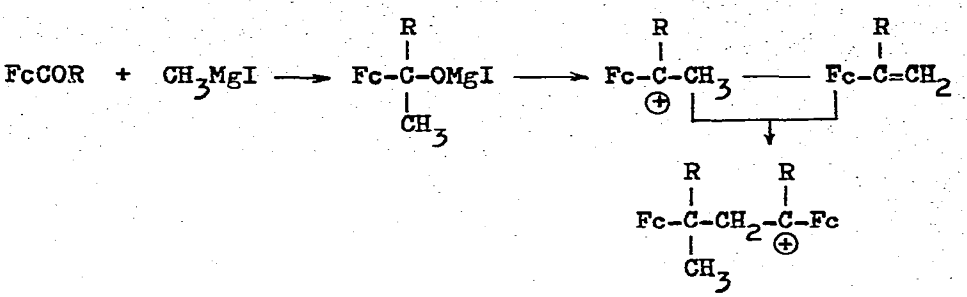
5. REACTIONS OF ORGANOMAGNESIUM COMPOUNDS

Introduction

In two Japanese patents Miyake, Kondo, Nishido and Onagawa report the preparation of vinyl cyclododecanols by a rather uncommon sequence of reaction [167] and [168]:

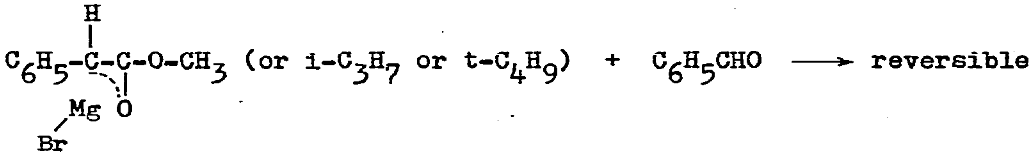


Another abnormal reaction of acylferrocenes was reported by Bozak, Riley, Fawns and Javaheripur [169]: with methylmagnesium iodide or with phenylmagnesium iodide in a diethyl ether benzene solvent mixture the authors isolated products resulting from the following type of reaction:



$$\mathrm{FcCOR + CH_3MgI \longrightarrow Fc\text{-}C(R)(CH_3)\text{-}OMgI \longrightarrow Fc\text{-}\overset{\oplus}{C}(R)\text{-}CH_3 \text{ --- } Fc\text{-}C(R){=}CH_2 \longrightarrow Fc\text{-}C(R)(CH_3)\text{-}CH_2\text{-}\overset{\oplus}{C}(R)\text{-}Fc}$$

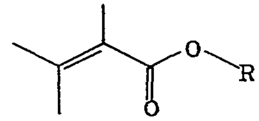
Mladenova, Blagoev and Kurtev observed reversibility in the following reaction [40]:



$$\mathrm{C_6H_5\text{-}C(H)(MgBr)\text{-}C(=O)\text{-}O\text{-}CH_3 \; (or\ i\text{-}C_3H_7\ or\ t\text{-}C_4H_9) + C_6H_5CHO \longrightarrow reversible}$$

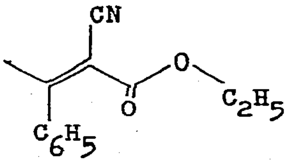
Cabaret and Welvart studied the reaction of the following unsaturated esters with chiral organomagnesium compounds [170] and [171];

for

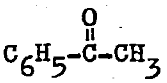


$\xrightarrow{\text{+ chiral RMgX}}$ Prelogs rule for predicting the stereoselectivity is no longer valid for the reduction reactions. The difference is rationalized by the degree of complexation of metallic ions in the transition state.

The reduction of



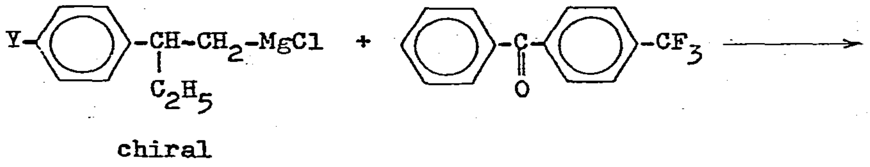
and



$\mathrm{C_6H_5\text{-}C(=O)\text{-}CH_3}$

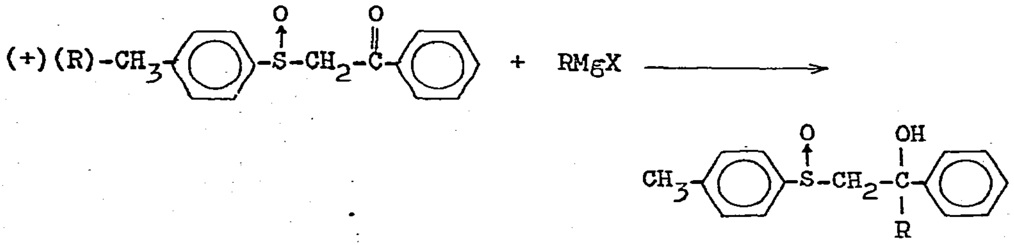
by chiral organomagnesium compounds gives opposite stereoselectivity. These results were rationalised by the cyclic mechanism of Whitmore (1938) for the ketone reduction and by a non-cyclic mechanism with polar orientation of the reagents in the reduction of the ethylenic compound [171].

Remarkably high asymmetric reductions were observed by Guetté, Capillon, Perlat and Guetté in the following reaction [172]:

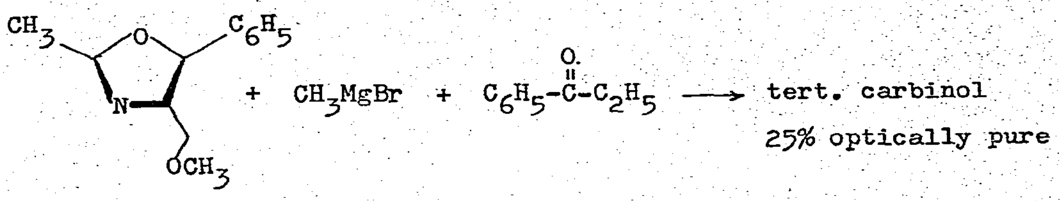


With Y = H an optical purity of 26.5 % of the benzhydrol was obtained; with Y = OCH_3 even 32%. The authors suppose that a rather stable charge-transfer complex between two aromatic nuclei must be held responsible for this effect.

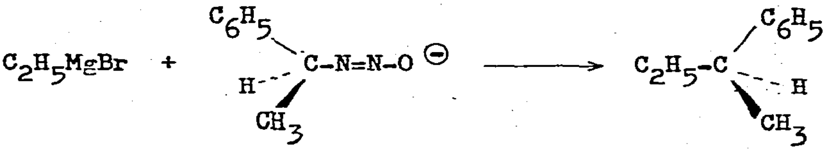
A 7 : 3 mixture of R,S and R,R diastereoisomers was obtained by Kunieda, Nokami and Kinoshita in the following reaction of a Grignard compound with a chiral substrate [173]:



Complexation of a Grignard reagent with chiral oxazolines followed by addition of ketones leads to asymmetric synthesis of tertiary carbinols with optical purities as high as 25%; Meyers and Ford [174]:



According to Moss and Banger the reaction of Grignard compounds with chiral diazotates leads to inversion at carbon atom in a degree depending from the temperature of the reaction mixture [175]:

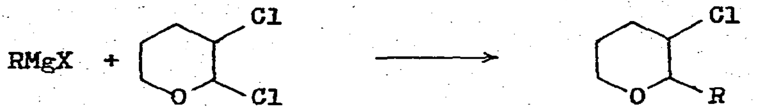


8-24% inversion

The reaction of 2-butylmagnesium chloride with aromatic or vinylic halides in the presence a chiral Ni(II) catalyst, existing of a complex of $NiCl_2$ and (-)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-diphenylphosphinobutane, leads to the formation of coupling products with enantiomeric excesses of about 15% (Kiso, Tamao, Miyake, Yamamoto and Kumada [176])

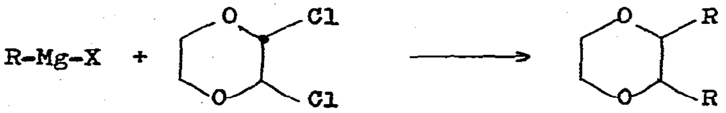
$$2\text{-}C_4H_9MgCl \;+\; C_6H_5\text{-}X \xrightarrow{Ni[(-)\text{-}diop]Cl_2} 2\text{-}C_4H_9\text{-}C_6H_5$$

Arbuzov, Klimovitskii, Yuldasheva, Remizov and Lygin investigated the stereochemistry of the following reactions [177]:



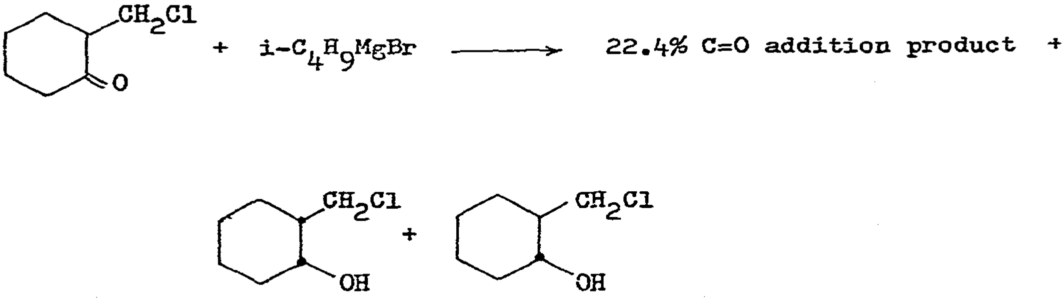
cis-trans isomer mixture

as the diequatorial cis isomer



R = p-Cl-benzyl-

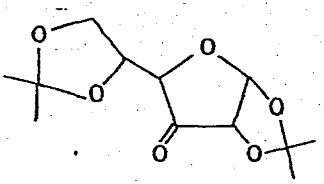
The following asymmetric reduction reaction was reported by Portyuagin and Chernyk [178]:



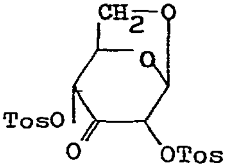
65% 9.8%

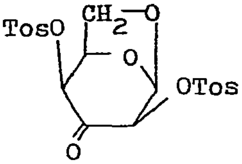
According to Arventiev and Wexler combined steric hindrance of the 4-methyl and the 3-phenyl groups in the following substituted coumaronones is responsible for a decreased evolution of methane in the reaction with methylmagnesium iodide as compared with the coumaronone without substituent in the 4-position [179]:

Addition to carbonyl functions in carbohydrates were reported by Funabashi, Sato and Yoshimura [184]:

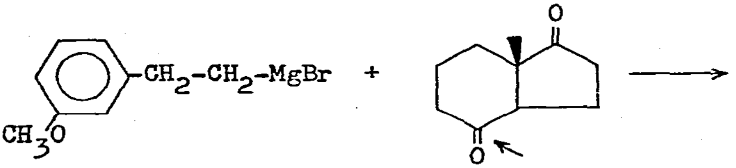


Buchanan, Dunn and Edgar who observed C=O addition in the reaction of H-C≡C-MgBr with 2,3-O-isopropylidene-D-ribose or with 2,3:5,6-di-O-isopropylidene-D-mannofuranose [185]. Cerny, Kollmann, Pacak and Budesinsky reported reactions of methylmagnesium iodide with 1,6-anhydro-2,3-di-O-p-toluenesulfonyl-β-D-ribo-hexopyranos-3-ulose and the corresponding D-lyxo-derivative [186]:



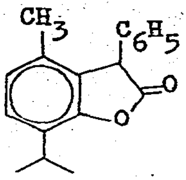


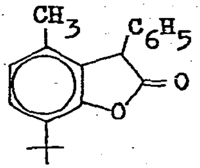
Bannerjee and Venkataramu reported the following reaction [187]:

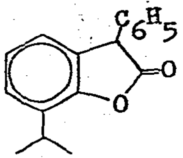


attack at the least hindered carbonyl function

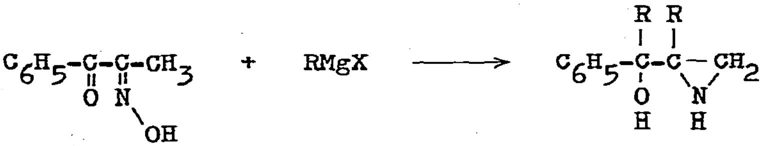
Reactions with dihydroanthraquinone derivatives have already been mentioned in Chapter 4Aii [140]:





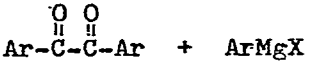


Bartnik and Laurent determined the ratio of stereoisomers, obtained in the following reaction [180].

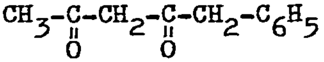


5A. Reactions with aldehydes and ketones

Normal addition to the C=O double bond was reported for the following carbonyl compounds:

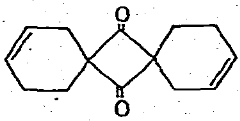


$\mathrm{Ar{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}Ar}$ + ArMgX ; with twofold excess of RMgX both C=O groups react; Baddar, Fahmy and Aly [181].

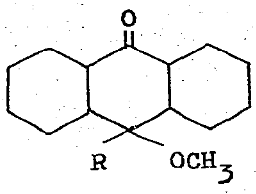


$\mathrm{CH_3{-}\underset{\underset{O}{\|}}{C}{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}CH_2{-}C_6H_5}$; Castelli and Canonne [182].

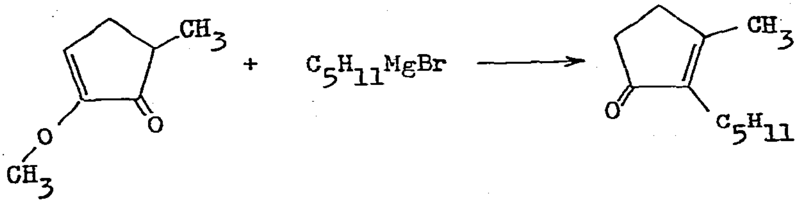
With the following spirobifunctional carbonyl compound reaction takes place under ringopening:



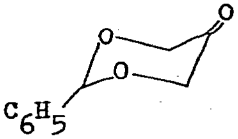
; Ismailov, Musaev and Bairamov [183]



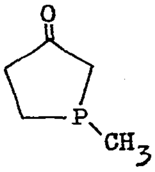
Barco, Benetti and Pollini reported [188]:



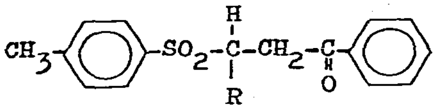
The stereochemical investigation with the following 1,3-dioxa-5-one was already reported in Chapter 4Aii [137]



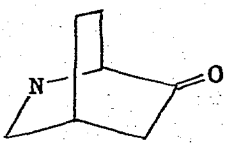
Reaction of methylmagnesium iodide with the following phospha-cyclopentanone yields mostly the cis-isomer, as reported by Quin and Stocks [189]:



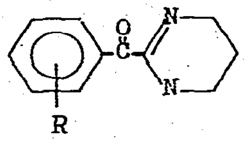
Messinger reported the reaction with the sulfonyl ketone [190]:



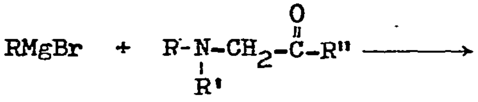
Nitrogen-containing ketones were also used in reactions with organomagnesium compounds:
in Chapter 4Aii the reaction with:
was already mentioned [141].



In a German Patent phenyl 1,3-diazine ketones were reported in reactions with Grignard reagents [191]

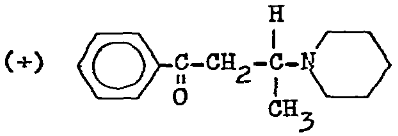


Gaset and Lattes studied 1,2-asymmetric inductions in α-aminoketones [192]:



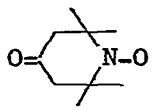
$$\mathrm{RMgBr} + \mathrm{R\text{-}\underset{R'}{N}\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}R''} \longrightarrow$$

A similar type of asymmetric induction with an amino ketone

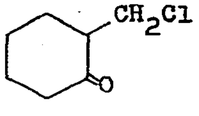


has already been reported in Chapter 4Aii [143].

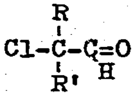
Schlude reported the reaction of a nitroxide containing ketone [193]:



Several reactions of organomagnesium compounds with chloroketones were published:

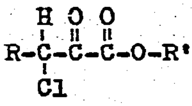


was used for stereochemical studies as already mentioned in the Introduction of Chapter 5 [178].

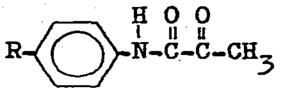


$$\mathrm{Cl\text{-}\overset{R}{\underset{R'}{C}}\text{-}\underset{H}{C}{=}O}$$

reacts under formation of products arising either from H-migration or from migration of the group introduced by the Grignard reagent (Riehl, Smolikiewicz and Thil [194]).

According to Juy, Combret and Coutrot  $R-C(H)(Cl)-C(=O)-C(=O)-O-R'$ reacts very stereoselectively with Grignard compounds in THF or in HMPA [195].

Arylmagnesium halides react with keto acidamides like

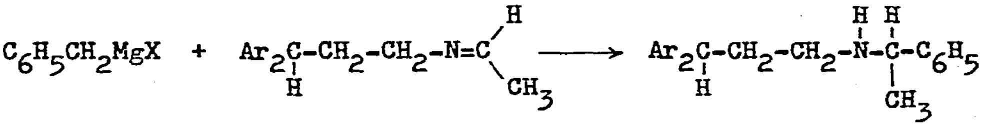


under formation of products, resulting from addition to the ketonic carbonyl function (Petyunin, Mashevskaya and Konshin [196]).

Mention has to be made of another publication by Dagonneau and Vialle dealing with reactions of organomagnesium compounds with thioketones[197]: the authors studied the reactions of such ketones with allylic Grignard reagents (for other publications see Chapter 4Ai [132] and [133] and Chapter 4B [144]).

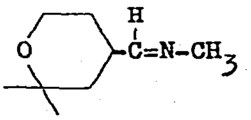
Several reactions have been reported with derivatives of aldehydes and ketones:

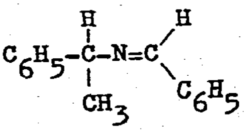
Shimuchi, Matsumoto and Nakajima reported addition to the C=N double bond [198]:



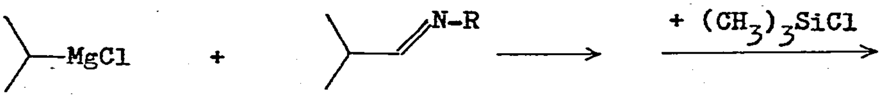
$$C_6H_5CH_2MgX + Ar_2CH-CH_2-CH_2-N=C(H)(CH_3) \longrightarrow Ar_2CH-CH_2-CH_2-NH-CH(CH_3)-C_6H_5$$

The same type of addition was mentioned by Noravyan, Sarkisyyan and Vartanyan with the following aldimine [199]

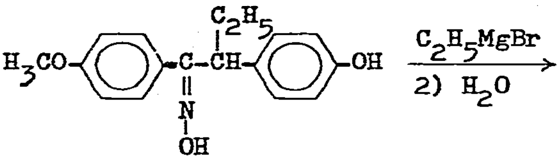


as well as by Bracheva, Vsemirnova and Potapov with  $C_6H_5-CH(CH_3)-N=CH-C_6H_5$ [200].

Belavin, Fedoseeva, Baukov and Lütsenko obtained unexpected products on trimethylsilylation of the reaction mixture, obtained by the following reaction [201]:



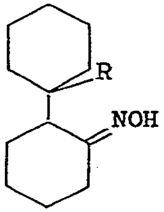
Reaction of ethylmagnesium bromide with the ketoxime

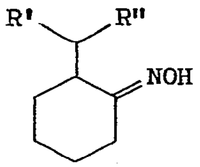


no formation of aziridine

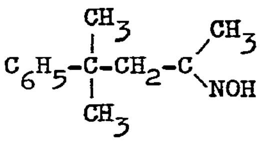
did not lead to the formation of an aziridine(Campbell, 1944) as Hamacher observed but instead a nitrile and a styrene derivative were isolated [202].

Investigations of aziridine formation in such reactions were reported by Imai Kawazoe and Taguchi [203] with oximes of the following type:



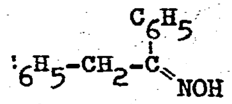


and



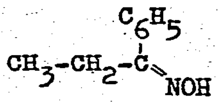
$C_6H_5-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-C\begin{smallmatrix}CH_3\\ NOH\end{smallmatrix}$

Several other publications on the aziridine formation by reaction of Grignard compounds with oximes came from Laurent and coworkers (see also Chapter 5 Introduction [190]). Together with Diab and Misson Laurent investigated



$${}_6H_5-CH_2-\overset{C_6H_5}{C}{=}NOH$$

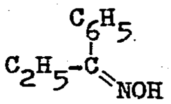
,



$$CH_3-CH_2-\overset{C_6H_5}{C}{=}NOH$$

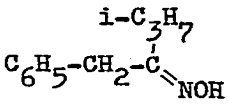
which gave reduction reaction products with isobutylmagnesium bromide [204]

and



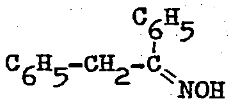
$$C_2H_5-\overset{C_6H_5}{C}{=}NOH$$

,



$$C_6H_5-CH_2-\overset{i-C_3H_7}{C}{=}NOH$$

and

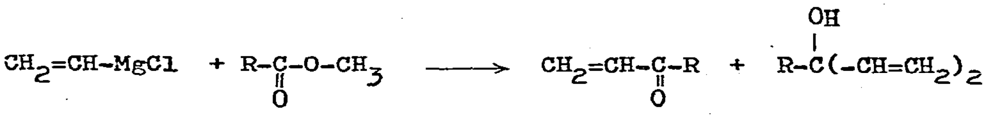


$$C_6H_5-CH_2-\overset{C_6H_5}{C}{=}NOH$$

which also gave reduction reaction products with isobutylmagnesium bromide but different products with isopropylmagnesium bromide [205]. In Chapter 4C mention has already been made of nitrene intermediates formed during reactions of this type [157].

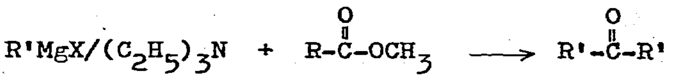
5B. Reactions with esters, lactones, anhydrides, amides, etc.

Watanabe, Suga, Fujita, Takahashi and Koiso continued their researches in the field of reactions of vinylic Grignard reagents with acids and esters; with esters vinylmagnesium chloride yields ketones and divinyl carbinols [206]:



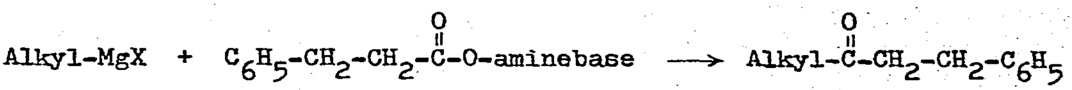
$$CH_2{=}CH-MgCl + R-\underset{O}{\underset{\|}{C}}-O-CH_3 \longrightarrow CH_2{=}CH-\underset{O}{\underset{\|}{C}}-R + R-\overset{OH}{\overset{|}{C}}(-CH{=}CH_2)_2$$

Ketone formation in reactions with esters has been mentioned in several papers:



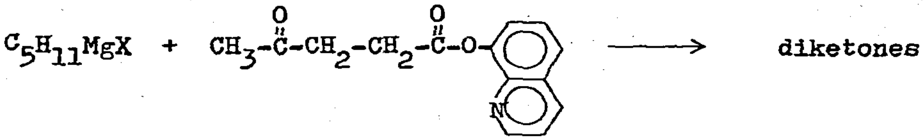
$$R'MgX/(C_2H_5)_3N + R-\overset{O}{\overset{\|}{C}}-OCH_3 \longrightarrow R'-\overset{O}{\overset{\|}{C}}-R'$$

; Kitsukawa [207]

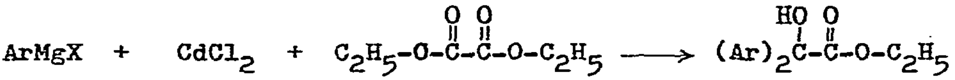


$$Alkyl-MgX + C_6H_5-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-O\text{-aminebase} \longrightarrow Alkyl-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-C_6H_5$$

As the amine base 2-pyridyl, 2-benzoxazole or N-methyl-2-imidazole can be utilized; yields are as high as 100% (Mukaiyama, Araki and Takei [208]; and Araki, Sakata, Takei and Mukaiyama [209]).
Mori and Sakan reported excellent yields of diketones in the following reaction [210]:

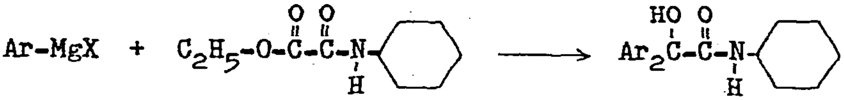


Karavanov and Krasnodar obtained products from the reaction of Grignard reagents, modified with cadmium chloride and diethyl oxalate [211]:

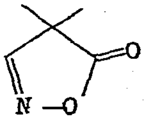


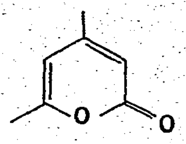
$$ArMgX + CdCl_2 + C_2H_5\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}C_2H_5 \longrightarrow (Ar)_2\overset{HO}{\overset{|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}C_2H_5$$

The same type of products was obtained with oxalic amides (Petyunin, Bezuglyi and Petyunin [212]):



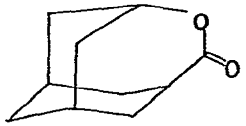
Reactions of keto esters were studied by Castelli and Canonne [182] who made a detailed investigation of the experimental conditions required to obtain the desired products.
The following 4,4-disubstituted 5-oxazolone reacted with Grignard reagents to give normal C=O addition reaction products [213]: (Jacquier, Petrus, Verducci and Vidal).



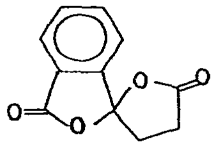


Reaction of Grignard reagents with 2-pyrones: as investigated by Dreux and coworkers have been mentioned in Chapter 4Aii [142] because of the stereochemistry and in Chapter 4C [151] because of the complex formation, preliminary to reaction. In order to check if only 4-substituted 2-pyrones lead to 2-H pyrans Trolliet, Longeray and Dreux studied reactions of 4-unsubstituted 2-pyrones [214]. 5,6-disubstituted 2-pyrones give only linear products, 3,5,6-trisubstituted 2-pyrones may give 2H-pyrans.

Other lactones studied were



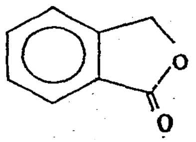
Hamon and Taylor [215]



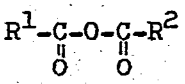
Gourmelon, Graff and Le Tutour [216]

which both, among others gave ketones on reaction with organomagnesium compounds.

Reaction of two molar equivalents of a Grignard compound with the following lactone leads to a step-wise double addition (J.G. Smith and Wikman [217]):



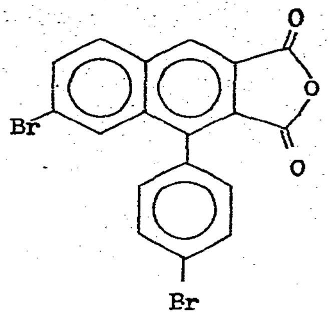
The following anhydrides were reacted with Grignard reagents:



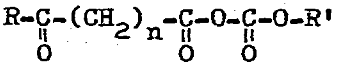
$R^1-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-R^2$

R^1 = 1-phenylethyl or 3-ketobutyl

R^2 = tert-butyl, 2,4-dichlorophenyl, 4-methoxyphenyl and 4-ethoxyphenyl (Araki and Mukaiyama) [218].



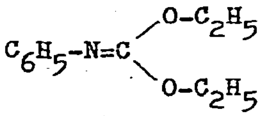
Baddar, Sherif and Shenouda [219].



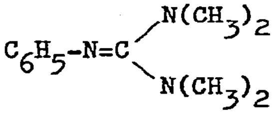
$R-\underset{O}{\underset{\|}{C}}-(CH_2)_n-\underset{O}{\underset{\|}{C}}-O-\underset{O}{\underset{\|}{C}}-O-R'$

Araki, Sakata, Takei and Mukaiyama [220].

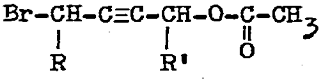
Miginiac and Pornet used iminocarbonates and guanidines [221]:



and

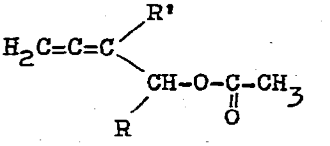


Gaudemar reported reactions of unsaturated esters:



$Br-\underset{R}{\underset{|}{C}H}-C\equiv C-\underset{R'}{\underset{|}{C}H}-O-\underset{O}{\underset{\|}{C}}-CH_3$

Perriot and Gaudemar [126] [222].

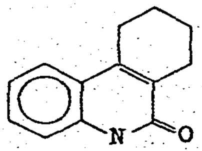


Perriot and Gaudemar [222].

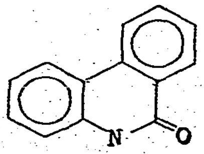
Three distinct modes of reaction of Grignard reagents with carbamates were observed by Patai [223].

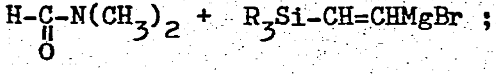
Reactions with amides were reported by

Kraatz and Korte [224]:

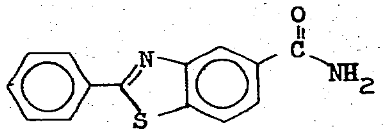


and

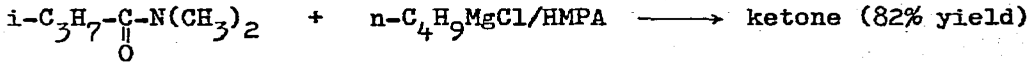




$H\text{-}\underset{\substack{\| \\ O}}{C}\text{-}N(CH_3)_2 + R_3Si\text{-}CH{=}CHMgBr$; Belyaev, Stadnichuk and Petrov [51]

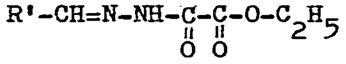


Miyamatsu, Ueno and Shimizu [225].



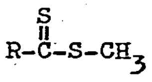
$i\text{-}C_3H_7\text{-}\underset{\substack{\| \\ O}}{C}\text{-}N(CH_3)_2 \quad + \quad n\text{-}C_4H_9MgCl/HMPA \longrightarrow$ ketone (82% yield)

as reported by Cuvigny, Hullot, Larchevêque and H. Normant [226]. Villiéras, Disnar and J.-F. Normant studied reactions of Grignard reagents with α,α-dichloro esters and copper salts [43]. Berdinskii, Kazakova, Petyunin and Petyunin applied the following esters in reaction with Grignard reagents [227]:



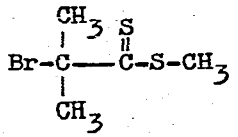
$R'\text{-}CH{=}N\text{-}NH\text{-}\underset{\substack{\| \\ O}}{C}\text{-}\underset{\substack{\| \\ O}}{C}\text{-}O\text{-}C_2H_5$

Leger and Saquet investigated reactions with thioesters and observed S-alkylation [228].



$R\text{-}\overset{\substack{S \\ \|}}{C}\text{-}S\text{-}CH_3$

Wesdorp, Meyer, Vermeer, Bos, Brandsma and Arens observed remarkable solvent effects in reactions of the following thioester with Grignard reagents in THF and diethyl ether [229]:

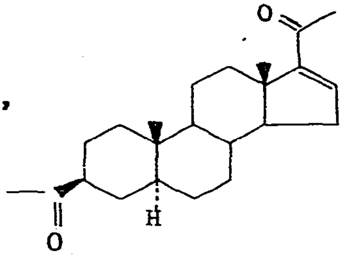


$Br\text{-}\underset{\substack{| \\ CH_3}}{\overset{\substack{CH_3 \\ |}}{C}}\text{—}\overset{\substack{S \\ \|}}{C}\text{-}S\text{-}CH_3$

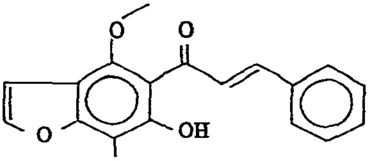
5C. Reactions with unsaturated carbonyl compounds, esters, amines, halides, nitriles, etc.

Conjugate addition to unsaturated ketones was observed by the following groups:

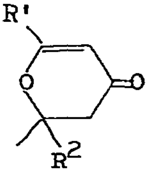
Menshova, Sorokina, Grinenko, Suvorov, Gurevich, Kemertilidze, and Pkheidze [230]:



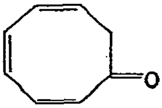
Nosseir, Aziz, Doss and Risk [231]:



Duperrier, Moreau, Gêlin and Dreux [232]:

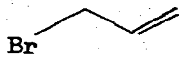


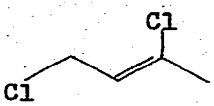
Ogawa, Tagaki and Matsuda [233]:

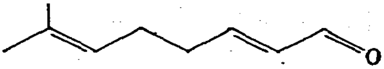


Gocmen and Soussan [234]:

Näf and Decorzant investigated conjugate addition of magnesium bromide enolates (see Chapter 2Biv) with different unsaturated compounds such as the following ones [39]:



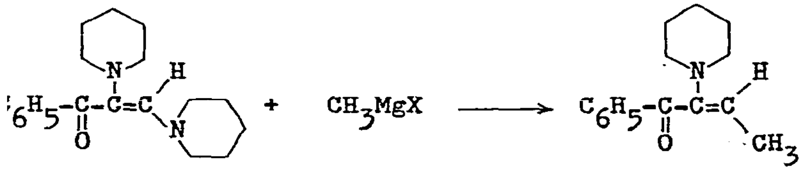




llylic, vinylic and phenyl Grignard reagent add in the 1,4-conju-
ate position exclusively with unsaturated aldimines as studied by euk, Mauzé and Miginiac [235]:

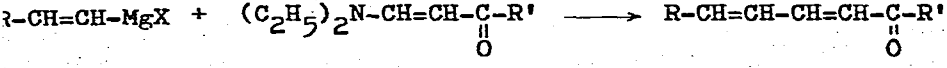
H_3-CH=CH-CH=N-i-C_3H_7 , C_6H_5-CH=CH-CH=N-R (with R = methyl, isopropyl and tert-butyl)

Reactions of enamines with Grignard reagents lead to displacement of the amino group:



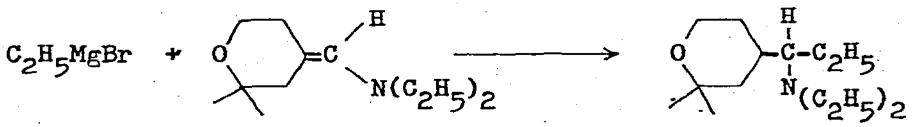
Duhamel, Duhamel and Truxillo [236] as well as Duhamel, Plé and Commare [237].

With vinylmagnesium halides the same type of enamine was studied by Näf and Decorzant [238]:

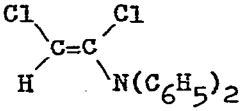


$$R\text{-}CH{=}CH\text{-}MgX + (C_2H_5)_2N\text{-}CH{=}CH\text{-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-}R' \longrightarrow R\text{-}CH{=}CH\text{-}CH{=}CH\text{-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-}R'$$

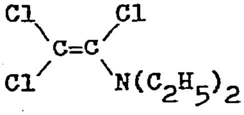
Noravyan, Sarkisyan and Vartanyan observed addition to the C=C double bond in the following reaction of an enamine [239]:



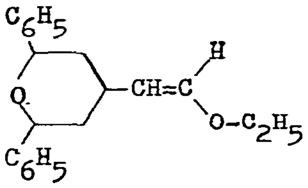
Ficini, Barbara, D'Angelo and Dureault [240] and Ficini together with Dureault [241] reported reactions of isopropylmagnesium chloride and of alkyl-, allyl-, vinyl- and alkynylmagnesium halides with di- and trichloroenamines:



and

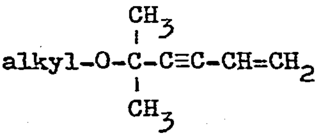


Dorofeenko, Mezheritskii, and Vassermann reacted the following unsaturated ether with arylmagnesium bromides [242]:



Alkynyl and allenic products were obtained in reactions of Grignard compounds with 2-alkynyl ethers:

Badanyan and Sargsyan [243]:

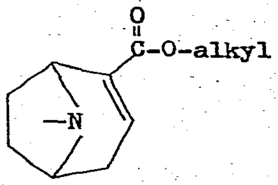


$$\text{alkyl-O-}\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}\text{-C}\equiv\text{C-CH=CH}_2$$

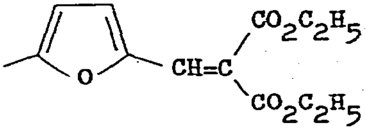
Troyanowsky and Tsamantakis [244]: CH_3-O-CH_2-C≡C-CH_2-Br

Rose and Taylor observed ring opening reactions as well as conjugate addition to the double bond combined with ringopening when Grignard compounds reacted with vinyloxirane [245]:

Anhydroecgonine alkyl esters react with arylmagnesium halides to form products resulting from conjugate addition (Clarke and Daum [246]):

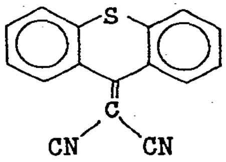


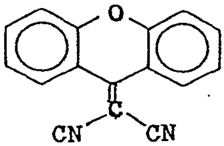
Holmberg, Jalander, Norrgard and Petterson continued their investigations in the field of conjugate addition to furfurylidene malonates [247]:

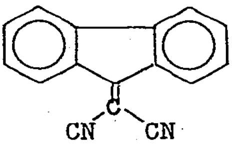


Investigations of Welvart, Cabaret and Carrie on the stereochemistry of reactions of Grignard reagents with unsaturated cyano malonates have already been referred to in Chapter 3C [124].

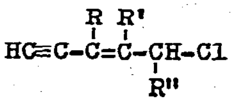
Latif, Mishriky and Mohsen reported more extensively on the reaction of methyl- or isobutylmagnesium halides with substituted cyanonitriles [248]:







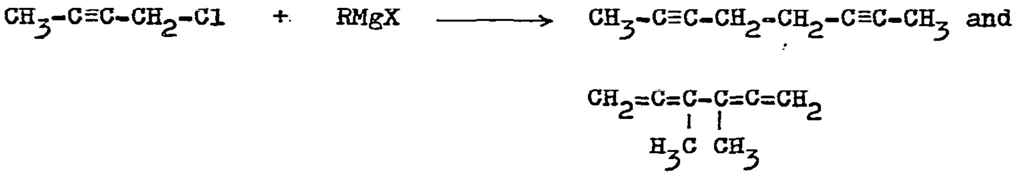
Reactions of unsaturated halides with organomagnesium compounds have already been referred to in previous chapters:



$HC{\equiv}C{-}\overset{R}{C}{=}\overset{R'}{C}{-}\underset{R''}{CH}{-}Cl$; Dulcère, Gore and Roumestant, Chapter 2Biv [34]

Allylic Grignard reagents with allylic halides ; Sonnet, Bierl and Beroza [125]; see Chapter 3C.

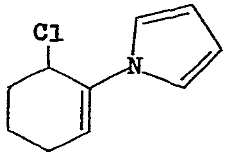
Mkryan, Mkrtchyan, Gasparyan, Voskanyan and Nazaryan studied the reaction of ethyl- and propylmagnesium bromide with 1-chloro-2-butyne [249]



$$CH_3{-}C{\equiv}C{-}CH_2{-}Cl \;+\; RMgX \longrightarrow CH_3{-}C{\equiv}C{-}CH_2{-}CH_2{-}C{\equiv}C{-}CH_3 \text{ and } CH_2{=}C{=}\underset{H_3C}{C}{-}\underset{CH_3}{C}{=}C{=}CH_2$$

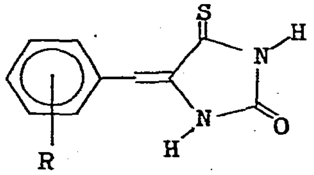
among other products.

Rather unexpected products were isolated by Blazejewski, Cantacuzène and Wakselman in the mixture of products obtained from the reaction of Grignard compounds with the following unsaturated chloroamine [250]:

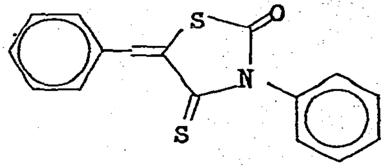


Arylmagnesium halides react with the following benzylidene heterocycles under addition to the exocyclic C=C bonds

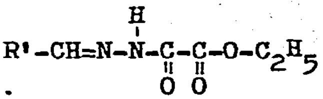
Shalby, Daboun and Boghdadi [251] :



Kassab, Abdallah and Messeha [252]:



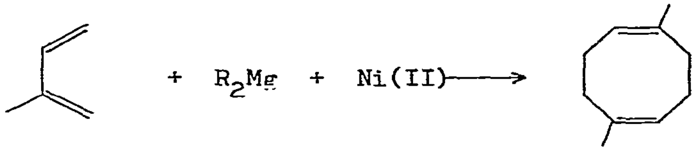
Addition to the C=N bond in the following ester was observed in reactions of aryl-, 2-thienyl and alkyl Grignard reagents [227]:



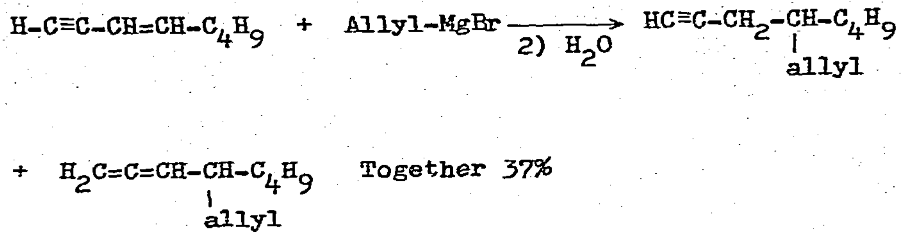
$$R'-CH=N-\overset{H}{\overset{|}{N}}-\underset{O}{\underset{\|}{C}}-\underset{O}{\underset{\|}{C}}-O-C_2H_5$$

5D. Reactions with C-C unsaturated bonds

The preparation of organomagnesium compounds by addition of ethyl- or allylmagnesium bromide to the double bonds in polycyclic unsaturated hydrocarbons has been mentioned in Chapter 2C [63]. Akutagawa, Watanabe, Somya, Yoshida and Komatsu, in a Japanese patent, claim the cyclization of isoprene under the influence of dialkylmagnesium compounds with Ni(II) salts [253]:



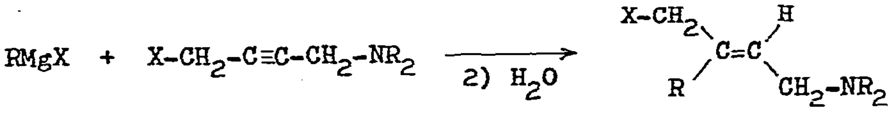
Reactive organomagnesium compounds such as allylmagnesium bromide react with enynes to form products resulting from either carbon-carbon double bond or carbon-carbon triple bond addition, as observed by Courtois, Mauzé and Miginiac [254]:



$$H\text{-}C\equiv C\text{-}CH{=}CH\text{-}C_4H_9 + \text{Allyl-MgBr} \xrightarrow[2)\ H_2O]{} HC\equiv C\text{-}CH_2\text{-}\underset{\text{allyl}}{CH}\text{-}C_4H_9$$

$$+\ H_2C{=}C{=}CH\text{-}\underset{\text{allyl}}{CH}\text{-}C_4H_9 \quad \text{Together } 37\%$$

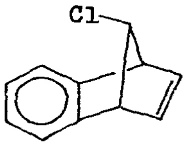
Trans addition to the alkynylic bond was observed by Mornet, Gouin and Bouet [255]:



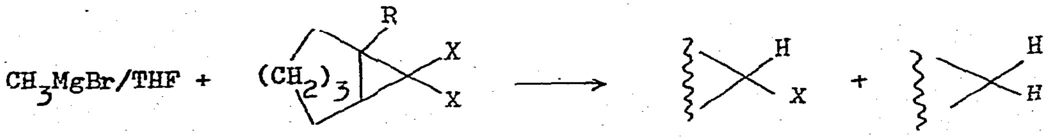
X = OH, NR'_2
OR or SR

5E. Reactions with organic halides

Whereas anti-7-chlorobenzonorbornadiene does not react with phenylmagnesium bromide the syn-isomer reacted very slowly with the same organomagnesium compound (Cristol and Maxwell [256]) to give syn-7-phenylbenzonorbornadiene.

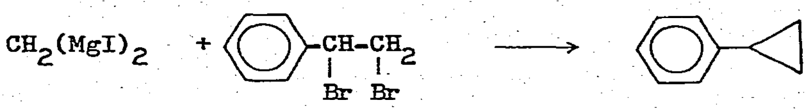


According to Nefedov and Agavelyan methylmagnesium bromide reacts with 2,2-dihalobicyclo[5.1.0] octanes to give both reduction products [257]

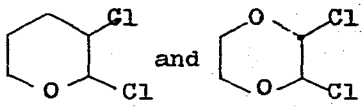


X = Cl or Br

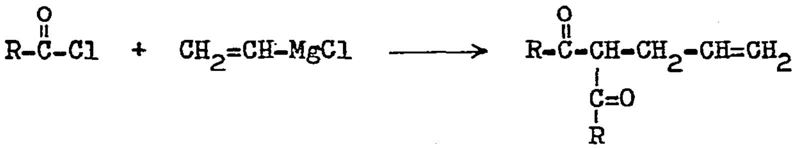
Ohtake and coworkers report the formation of cyclopropylbenzene by the following reaction [36]:



The stereochemical investigations by Arbuzov and coworkers using α-halo cyclic ethers have been referred to in Chapter 5 Introd. [177]:



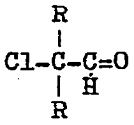
A variety of products was obtained by Suga, Fujita, Watanabe, Takahashi in the reaction of vinylmagnesium chloride with acid chlorides [258]:



$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl \;+\; CH_2{=}CH\text{-}MgCl \longrightarrow R\text{-}\overset{O}{\overset{\|}{C}}\text{-}\underset{\underset{R}{|}}{\underset{C=O}{\underset{|}{CH}}}\text{-}CH_2\text{-}CH{=}CH_2$$

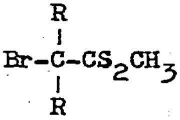
among other products.

Riehl and coworkers reported reactions of alkynylic Grignard reagents with α-chloroaldehydes [194]:



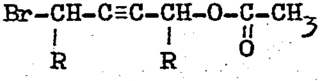
$$Cl\text{-}\overset{R}{\overset{|}{\underset{\underset{R}{|}}{C}}}\text{-}\underset{H}{C}{=}O$$

Arens and coworkers reported reactions of Grignard reagents with α-bromodithio esters [229]:



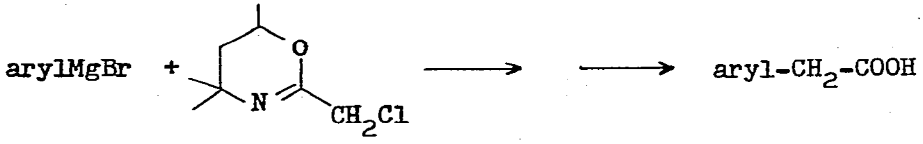
$$Br\text{-}\overset{R}{\overset{|}{\underset{\underset{R}{|}}{C}}}\text{-}CS_2CH_3$$

Perriot and Gaudemar investigated reactions of organomagnesium compounds with bromoalkynyl esters [126] and [222]:



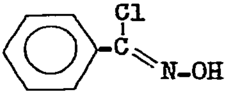
$$Br\text{-}\underset{\underset{R}{|}}{CH}\text{-}C{\equiv}C\text{-}\underset{\underset{R}{|}}{CH}\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_3$$

Aryl Grignard reagents react with 2-chloromethyloxazine to give satisfactory yields of coupling products which ultimately lead to arylacetic acids as reported by Malone and Meyers [259]:

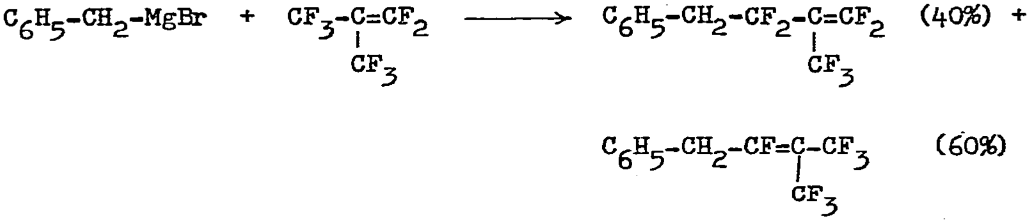


Alkyl Grignard reagents however give an array of products, indicating that this process will not be synthetically useful.

Suprunova and coworkers studied reactions of organomagnesium halides derived from alkoxyalkynes (see Chapter 2Biii) with the following chlorcaldoxime [31]:



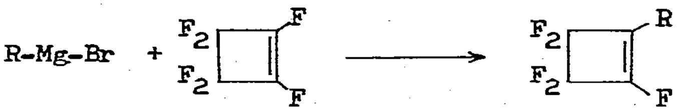
As studied by Rozov, German, Zeifman, Cheburkov and Knunyants benzylmagnesium bromide reacts with perfluoroisobutene as follows [260]



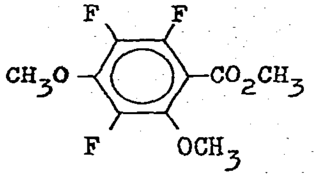
$$C_6H_5\text{-}CH_2\text{-}MgBr \; + \; CF_3\text{-}\underset{\substack{| \\ CF_3}}{C}{=}CF_2 \longrightarrow C_6H_5\text{-}CH_2\text{-}CF_2\text{-}\underset{\substack{| \\ CF_3}}{C}{=}CF_2 \quad (40\%) \; +$$

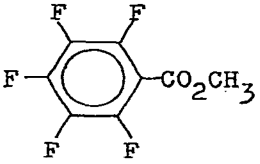
$$C_6H_5\text{-}CH_2\text{-}CF{=}\underset{\substack{| \\ CF_3}}{C}\text{-}CF_3 \quad (60\%)$$

The reaction of an alkylmagnesium bromide with perfluorocyclobutene has been found to favor the formation of a vinylic monoalkyl product

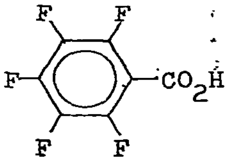


whereas an alkylmagnesium chloride favored the synthesis of a vinylic dialkyl compound (Park, Croft and Anderson [261]).
Grasimova, Baturina, Fomenko, Chertok, Kollegov and Fokin report reactions of phenylmagnesium bromide with aromatic fluorocompounds to form phenyl substituted aromatic derivatives [262] :



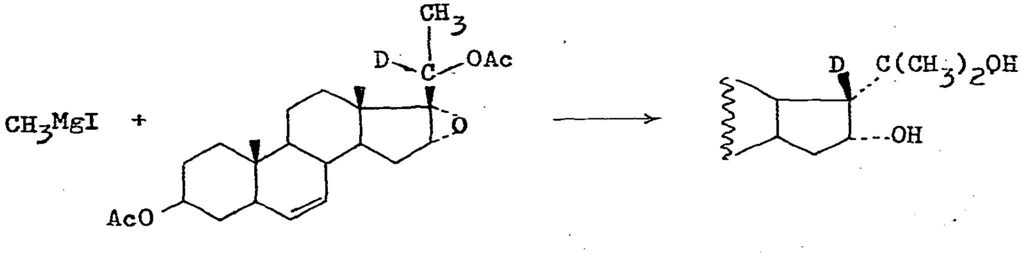


and



5F. Reactions with oxiranes and oxetanes

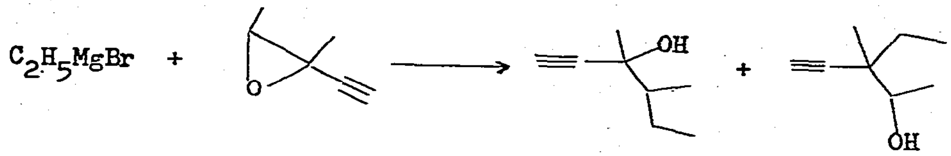
Ilyukhina and Akhrem as well as Ilyukhina, Kamernitskii and Voznesenskaya reported reactions of methylmagnesium iodide with 16,17-epoxypregnenediol diacetates [263] and [264]:



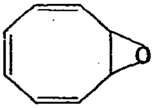
and other stereoisomers

Ohtake and coworkers reported the reaction of diiodomagnesiummethane with phenyloxirane [36].
The reaction of Grignard compounds with vinyloxirane has been referred to in Chapter 5C [245].

Skiba and Tatarchuk reported reactions of alkylmagnesium halides with ethynyloxiranes [265]:

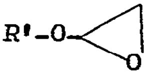


Hambrecht, Straub and Müller reacted organomagnesium compounds with cyclooctatetraene epoxide [266]:

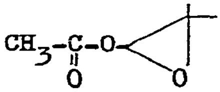


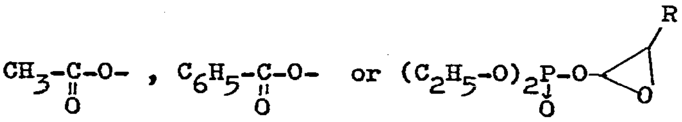
The kinetic studies of Sano and coworkers on the reactions of RMgX with hexyloxirane in diethyl ether and in THF have been mentioned in Chapter 4C [150].

Together with Endo, H. Matsuda and S. Matsuda Sano also studied solvent effects of reactions of RMgX with alkoxyoxiranes of the following type [267]:

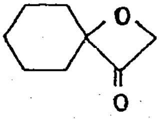


Riehl, Casara and Fougerousse studied reactions of Grignard reagents with differently substituted oxiranes:

with  [268], and

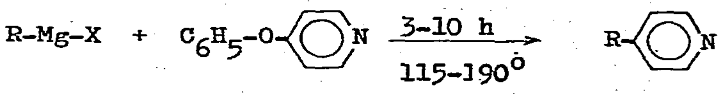
with  [269]

Donnelly, Hoey and O'Donnell investigated the reaction of phenylmagnesium bromide with spirooxetan-3-one [270]:

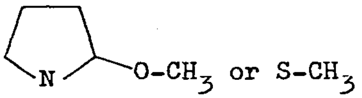


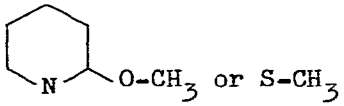
5G. Reactions with ethers, thioethers and acetals

Reactions with 4-pyridyl ethers were investigated by Vompe, Monich and Meshki [271]:

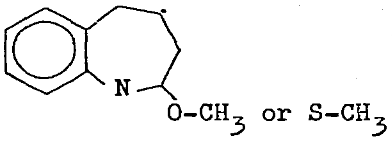


Joshi, Rao and Anand studied reactions of phenyl- or indolylmagnesium bromides with several heterocyclic ethers and thioethers [272]

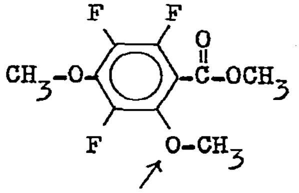




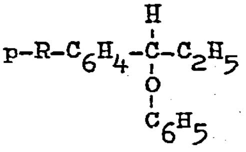
and



Gerasimova and coworkers observed reaction of phenylmagnesium bromide with a methoxy group in the following fluoro ester [262]:

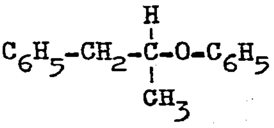


Ether bond cleavage on reaction with methylmagnesium iodide or with phenylmagnesium bromide was observed in the following compounds (Cabiddu, Maccioni, Seccio and Sotgiu [273]):



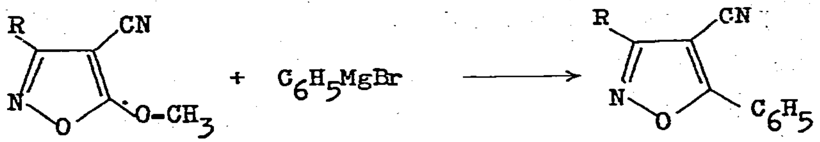
$$p\text{-}R\text{-}C_6H_4\text{-}\overset{\displaystyle H}{\underset{\displaystyle \underset{\displaystyle C_6H_5}{O}}{C}}\text{-}C_2H_5$$

and



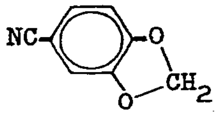
$$C_6H_5\text{-}CH_2\text{-}\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C}}\text{-}O\text{-}C_6H_5$$

Mangiavacchi and Scotton observed the following reaction [274]:

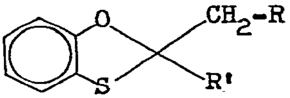


The kinetic investigations by Westera, Blomberg and Bickelhaupt of the reaction of ethylmagnesium bromide with 2-ethyl-1,3-dioxolane in benzene with one molar equivalent of diethyl ether, THF or diisopropyl ether have been mentioned in Chapter 4C [100].

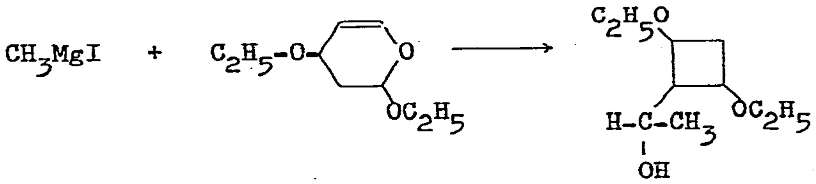
Forrest, Heacock and Forrest observed ring opening of the dioxolane entity in the following compound on reaction with ethylmagnesium bromide [275]:



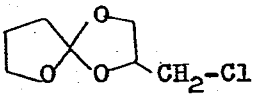
Cabiddu, Bonsignori and Cerioni studied reactions of the following thioketal [276]:



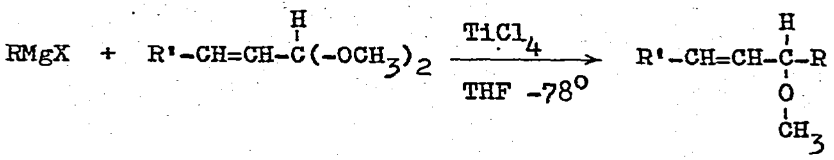
Eskenazi and Maitte reported the following reaction [277]:



Kuznetsov and Myrsina investigated the reaction of Grignard reagents with the following spiroortho esther [278]:



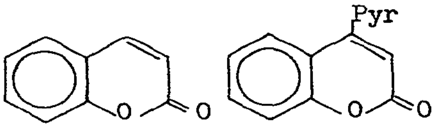
Mukaiyama and Ishikawa reported a facile reaction of Grignard reagents with unsaturated acetals at very low temperatures in the presence of $TiCl_4$ [279]:



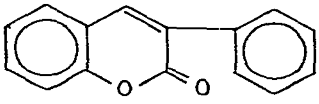
$$\mathrm{RMgX} + \mathrm{R'{-}CH{=}CH{-}\overset{H}{C}({-}OCH_3)_2} \xrightarrow[\mathrm{THF}\ -78^{\circ}]{\mathrm{TiCl_4}} \mathrm{R'{-}CH{=}CH{-}\overset{H}{\underset{\underset{CH_3}{O}}{C}}{-}R}$$

5H. Reactions with heterocyclic compounds

Mono-oxygen heterocycles:



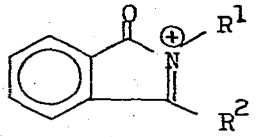
Tickle, Melton and Elvidge [280]



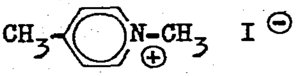
Ivanov and Bozhilova [281]

Depending on the type of Grignard reagent with both heterocycles ring substitution as well as ring opening reactions are observed.

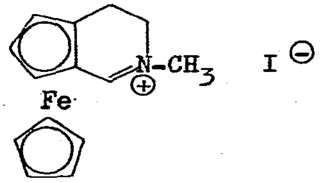
Mono-nitrogen heterocycles:



; Bartfeld, Flitsch and Gurke [282]

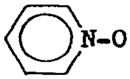


; Thiessen, Lepoivre and Alderweireldt [283]



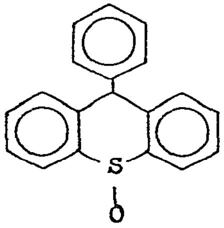
; Yamakawa, Sakaguchi and Osumi [284]

In each of these reactions addition to the heterocyclic ring occurs. Ring opening occurs in the reaction of Grignard compounds with



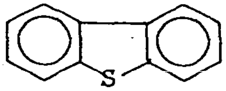
pyridine-N-oxide as observed by Schiess, Monnier, Ringele and Sendi [285].

Mono-sulfur heterocycles:

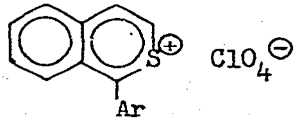


The radical nature of the reaction of phenylmagnesium bromide with 9-phenylthioxanthene-10-oxide was discussed in Chapter 4B [149]:

Hetero ring opening as well as addition was observed by the following type of sulfur heterocycles:

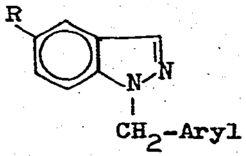


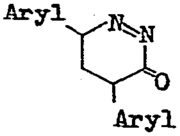
; Hori, Kataoka, Shimizu and Miyagaki [286]



; Hori, Kataoka, Shimizu and Sugai [287]

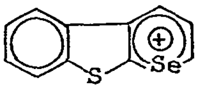
Another ring-expansion was reported by Tertov, Onishenko and Bessonov [300] with 1-benzylindazole derivatives:



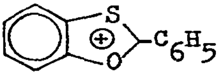


; Baddar, Latif and Nada [301]

Mixed sulfur-selenium and oxygen heterocycles :

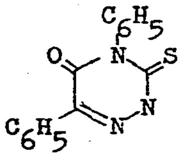


Y $^\ominus$ Tadino, Christiaens and Renson [302]

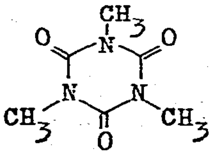


$ClO_4^\ominus$; Degani, Fochi and Tundo [303]

Tri-nitrogen-heterocycles:

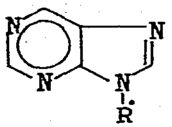


; Mansour, Ibrahim and Eid [304]

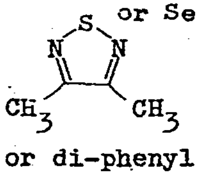


(or C_6H_5) ; Etienne, Lonchambon and Girondeau [305] and Etienne, Bonté, Lonchambon and Roques [306].

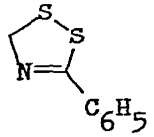
Some other heterocycles:



Higashino, Iwai and Hayashi [307]



; Bertini, De Munno, Menconi and Tissi [308]



; Böhme and Arens [309]

51. Reactions with B, N, Si, P, S, Ge and Cr compounds

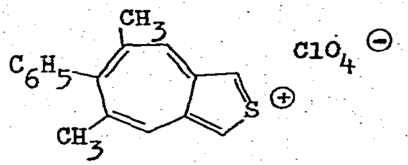
Kacheishvili, Pirtskhalava and Dzhioshvili prepared mixed boron compounds by the following reaction [310]:

$$C_6H_5\text{-}CH{=}CH\text{-}CH_2\text{-}MgCl \;+\; R_3B \longrightarrow R_2B\text{-}CH_2\text{-}CH{=}CH\text{-}C_6H_5$$

Bortovoi prepared mixed amines in high yields as follows [311]:

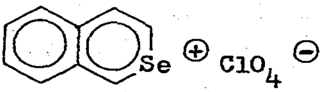
$$C_4H_9\text{-}MgCl \;+\; (C_2H_5)_2N\text{-}Cl \xrightarrow{\text{diethyl ether}} C_4H_9\text{-}N(C_2H_5)_2 \cdot MgCl_2$$

The stereochemical outcome of the reaction of chiral 1-phenylethane diazotate with Grignard compounds has been discussed in the Introduction of Chapter 5 [175].

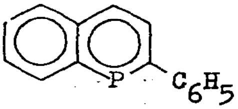


; Hori, Kataoka, Tadashi, Shimizu, Yoshimura [288].

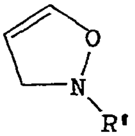
Ring substitution was also observed by Stackhouse, Senkler Jr., Maryanoff and Mislow with the following selenaheterocyclic compound [289] :



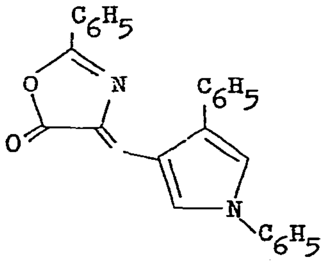
Maerkl and Heier studied reactions of benzylmagnesium bromide with 2-phenyl-1-phosphanaphthalene [290]:



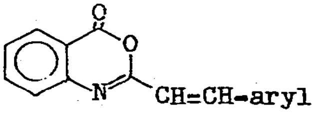
Nitrogen-oxygen heterocycles:



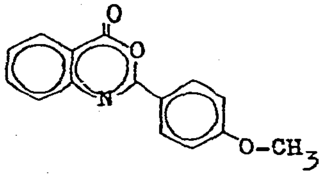
; Adachi, Harada, Miyazaki and Kano [291]



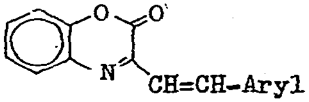
; Elkaschef, Abdel-Megeid and Yassin [292]



; Sammour, Zimaity and Abdo [293]

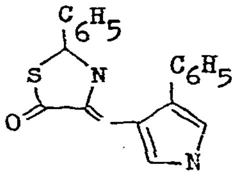


; Zaher, Jahine, Aknookh and Gendy [294]

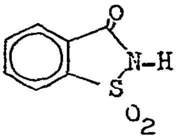


; Khalifa and Abed [295]

Nitrogen-sulfur heterocycles:

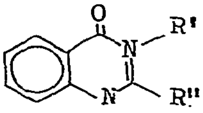


; Elkaschef, Abdel-Megeid and Salah [296



; Abramovich, E.M. Smith, Humber, Purtschert, Srinivasan and Singer [297]

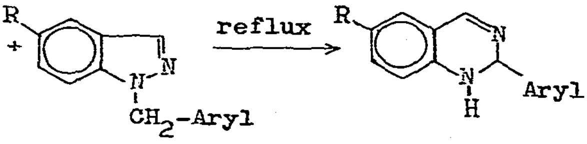
Dinitrogen-heterocycles:



; Elkaschef, Abdel-Megeid and Abdel-Kade [298].

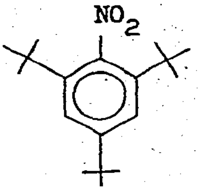
In a Russian Patent Tertov and Onishchenko claim the following ring-enlargement reaction [299]:

C_6H_5MgBr/diethyl ether: DME +



The radical character of the reaction of tri-tert-butyl-nitrosobenzene with Grignard reagents, as studied by Inamoto and coworkers was discussed in Chapter 4B [147].

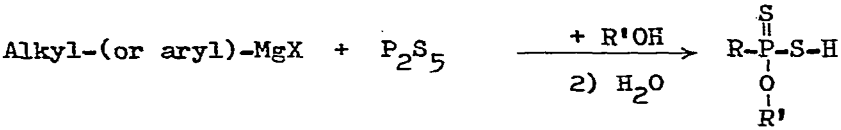
Inamoto, Okazaki and Inagaki studied the reaction of Grignard compounds with tri-tert-butyl-nitrobenzene and observed the formation of products, derived from an attack of the reagent onto the ortho or para position to the nitro group [312]:



Wolfsberger and Schmidbauer reported the formation of trialkyl phosphine [313]

$$\text{alkyl-MgX} \quad + \quad (C_6H_5\text{-O-})_3P \quad \longrightarrow \quad (\text{alkyl})_3P$$

Imamura and Nabekawa and Ohzubo, in a Japanese Patent claim the following reaction [314]:

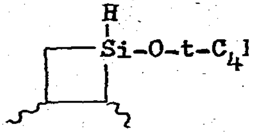


$$\text{Alkyl-(or aryl)-MgX} \quad + \quad P_2S_5 \quad \xrightarrow[2)\ H_2O]{+\ R'OH} \quad R\text{-}\overset{\overset{\displaystyle S}{\|}}{\underset{\underset{\displaystyle R'}{|}}{\underset{\displaystyle O}{\underset{|}{P}}}}\text{-S-H}$$

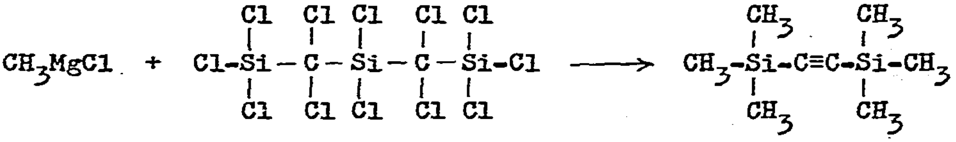
From Corriu's laboratory again a series of investigations on the stereochemical aspects of displacements reactions by means of Grignard reagents on Si have been reported. In Chapter 4C one aspect of this reaction has been referred to [165]. Two other reports were from Corriu together with Chavière, Kpoton and Lanneau [315] and from Corriu together with Moreau [316].

The synthetic aspects of the reaction of Grignard compounds with bis(pentafluorophenyl)methylsilane, reported by Gilman, were mentioned in Chapter 2C [70].

The stereochemistry of displacement reactions on silicon in the following sila-cyclobutane was studied by Dubac, Mazzerolles and Serres [317]:



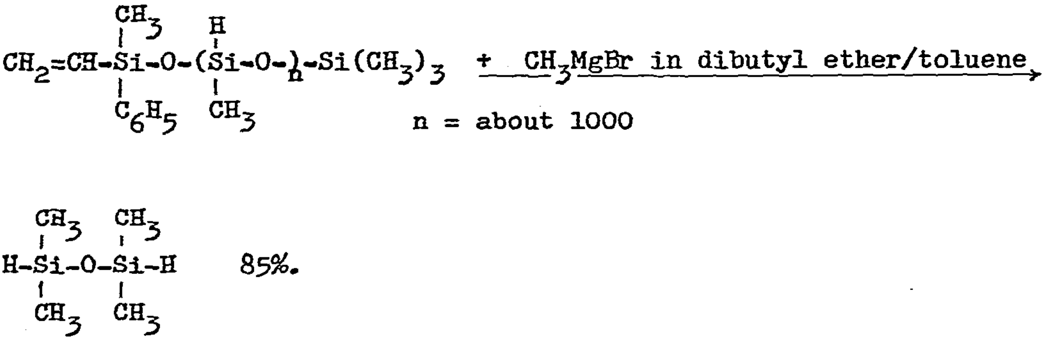
Fritz and Bosch continued their series of publications on the poly methylation of polychlorosilanes with the aid of methylmagnesium chloride [318]:



$$CH_3MgCl + Cl\text{-}\overset{Cl}{\underset{Cl}{Si}}-\overset{Cl}{\underset{Cl}{C}}-\overset{Cl}{\underset{Cl}{Si}}-\overset{Cl}{\underset{Cl}{C}}-\overset{Cl}{\underset{Cl}{Si}}\text{-}Cl \longrightarrow CH_3\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}C{\equiv}C\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}CH_3$$

among other products

In a German patent the following reaction is claimed by Takamizawa, Shinohara and Nishimura [319]:



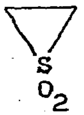
$$CH_2{=}CH\text{-}\overset{CH_3}{\underset{C_6H_5}{Si}}\text{-}O\text{-}(\overset{H}{\underset{CH_3}{Si}}\text{-}O\text{-})_n\text{-}Si(CH_3)_3 \;\; \underrightarrow{+\;\; CH_3MgBr \text{ in dibutyl ether/toluene}}$$

n = about 1000

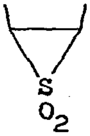
$$H\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}H \qquad 85\%.$$

The reaction of Grignard reagents with alkynylsulfoxides, leading to the formation of alkynylmagnesium halides has been mentioned in Chapter 2C [66].

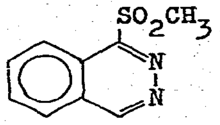
Vilsmayer, Tropitzsch and Vostrowsky reported reactions of Grignard compounds with 1,1-thiirane dioxides[320]:



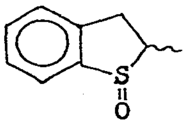
and



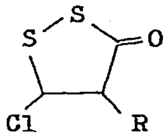
Oishi, Osumi and Hayashi reported the formation of unexpected products in the reaction of Grignard reagents with the following sulfur compound [321]:



Anderson, Caret and Karup-Nielsen studied the stereochemical aspects of reactions of methylmagnesium compounds with the following cyclic sulfoxide [322]:



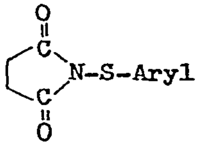
Cleavage of the sulfur-sulfur bond in the following compound was observed by Boberg, Ghoudikian and Khorgami [323]:



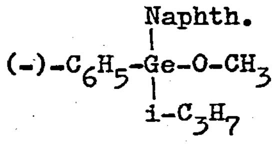
Lazar and Vinkler reported the following reaction [324]:

$$C_6H_5\text{-}S\text{-}SO_2\text{-}Cl \;+\; C_6H_5\text{-}MgBr \xrightarrow{-78^\circ} C_6H_5\text{-}S\text{-}SO_2\text{-}C_6H_5$$

Furukawa, Suda and Hayashi studied reactions of the following thioaryl imides [325]:

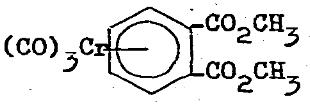


Carrê and Corriu studied the stereochemistry of reactions of Grignard compounds with chiral germanes [326]:



$$(-)\text{-}C_6H_5\text{-}\overset{\text{Naphth.}}{\underset{i\text{-}C_3H_7}{Ge}}\text{-}O\text{-}CH_3$$

Reaction of the following chromium derivative with methylmagnesium iodide leads to the formation of the di-methyl-ketone [327]



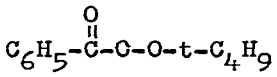
5J. Reactions with oxygen and peroxides

The radical nature of reactions of a meta-cyclophane Grignard reagent with oxygen or with tert-butyl hydroperoxide as studied by Parham and Montgomery has been referred to in Chapter 4B [145]. The same is true for the reaction of several different Grignard compounds with tert-butyl peroxide as studied by Kochi, Nugent and Bertini [146].

Chemiluminescence studies by Bolton and Kearns in reactions of aryl Grignard reagents with either oxygen [156] or peroxides [157] have been discussed in Chapter 4C.

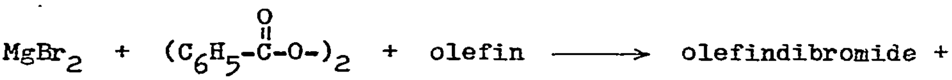
In Chapter 4C furthermore mention has been made of the mechanistic investigations by Okubo, Saito and Tomiyoshi of the reaction of phenylmagnesium bromide with some peroxides having oxygen- and nitroge atoms adjacent to the peroxide function [154].

In a Japanese Patent Kimura, Masuda and Gunjima report reactions of aryl Grignard compounds with the following peroxide [328]:



$C_6H_5-\overset{O}{\overset{\|}{C}}-O-O-t-C_4H_9$

Okubo, Kusakabe, Hiwatashi and Kishida studied the reaction of magnesium bromide with a mixture of an olefin and benzoyl peroxide [329]:



$$MgBr_2 + (C_6H_5-\overset{O}{\overset{\|}{C}}-O-)_2 + \text{olefin} \longrightarrow \text{olefindibromide} +$$

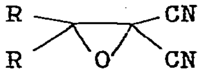
Mg-benzoate both in almost quantitative yield.

5K. Reactions with nitriles and isonitriles

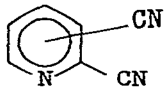
In Chapter 4C mention was made of kinetic investigations by Chastrette and coworkers of the influence of salts on the rates of reactions of Grignard reagents with benzonitriles [158].

Reactions of methyl- or isobutylmagnesium halides with unsaturated dinitriles, leading to reduction as well as to coupling products, as studied by Latif and coworkers have already been mentioned in Chapter 5C [248].

Other dinitriles investigated were:



; Moisan and Robert [330]

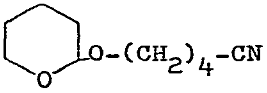


(in 3-, 4-, 5- and 6-position)

; Skala, Kuthan, Dedina and Schraml [331].

Riobe studied reactions of

$HO-(CH_2)_4-CN$ and



with large excesses of Grignard reagents [332].

Walborsky together with Niznik and Morrison [333] and together with Periasamy [334] studied reactions of Grignard reagents with isonitriles not containing α-hydrogens. Reactions proceed by an α-addition to produce metallo aldimines.

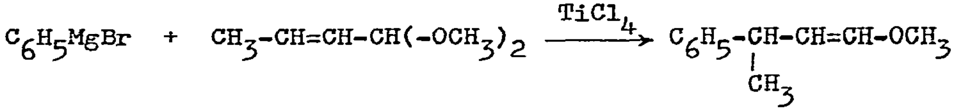
5L. Reactions with or in the presence of metal salts

Metal salts may change the reactivity of organomagnesium compounds in an unexpected manner. More and more publications appear each year dealing with this subject; in particular copper(I), nickel and cobalt are used for many different types of reactions.

Regarding the reactivity of organomagnesium compounds towards unsaturated organic compounds the dimerization of isoprene by R_2Mg in the presence of nickel salts, as studied by Akutagawa and coworkers has been mentioned in Chapter 5D [253].

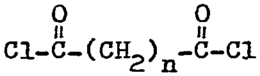
Conjugate addition to unsaturated ketones has been investigated by Akhrem, Levina, Titov, Khripach, Bubnov and Mikhailov who used CuBr as the catalyst [335], as well as by Alexandre and Rouessac who applied CuI together with diisopropyl sulfide in reactions of vinylmagnesium bromide with unsaturated ketones [336].

Conjugate addition of phenylmagnesium bromide to unsaturated ketals in reactions catalyzed by $TiCl_4$ were reported by Mukaiyama and Ishikawa [279]:

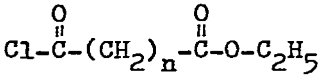


$$C_6H_5MgBr + CH_3-CH=CH-CH(-OCH_3)_2 \xrightarrow{TiCl_4} C_6H_5-\underset{\underset{CH_3}{|}}{CH}-CH=CH-OCH_3$$

The use of copper(I) salts in the coupling reaction of a Grignard reagent with acid chlorides was reported by Ford and Dubois:



$$Cl-\overset{\overset{O}{\|}}{C}-(CH_2)_n-\overset{\overset{O}{\|}}{C}-Cl \quad (\, n = 1, 2, 4, 5, 8) \text{ and }$$

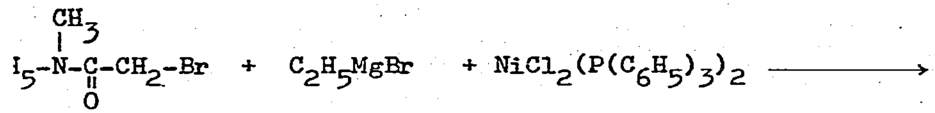


$$Cl-\overset{\overset{O}{\|}}{C}-(CH_2)_n-\overset{\overset{O}{\|}}{C}-O-C_2H_5$$

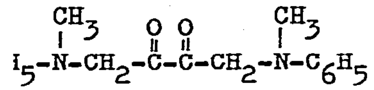
were reacted with tert-butylmagnesium chloride and with isopropylmagnesium iodide [337] (Ford).

Sterically hindered $R-\underset{\underset{O}{\|}}{C}-Cl$ + C_2H_5MgBr + Cu(I) chloride was studied by Dubois and Boussu [338]. See also Chapter 4C [166].

The reaction of ethylmagnesium bromide with a α-bromoanilide in the presence of catalytic amounts of a Ni(II) complex leads to unexpected products as observed by Mori and Nishimura [339]:



$$\text{I}_5\text{-N(CH}_3\text{)-C(=O)-CH}_2\text{-Br} + C_2H_5MgBr + NiCl_2(P(C_6H_5)_3)_2 \longrightarrow$$



$$\text{I}_5\text{-N(CH}_3\text{)-CH}_2\text{-C(=O)-C(=O)-CH}_2\text{-N(CH}_3\text{)-C}_6\text{H}_5$$ (38%) among other products

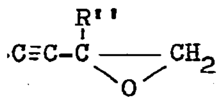
lliéras, Disnar and Normant [43] discussed the formation of reac-
re organo metallics by the reaction of α,α-dichloroesters with
;anomagnesium compounds in the presence of CuI.
uquet and Schlosser reported the following reaction [340]:

$$\text{IgBr} + R\text{-}SO_3\text{-}C_6H_4\text{-p-}CH_3 \xrightarrow[Li_2CuCl_4]{THF\ ,\ -78^{\circ}} R\text{-}R'.$$

: same catalyst was applied by Friedman and Shami to accomplish
ıctional multicarbon homologation by the following coupling reac-
ın [341]:

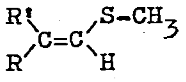
$$\text{;X} + Br\text{-}(CH_2)_n\text{-}Br \xrightarrow{Li_2CuCl_4} R\text{-}(CH_2)_n\text{-}R \quad n = 3, 4, 5, 6 \text{ or } 10$$

ıctions of 7-chlorobenzonorbornadiene with phenylmagnesium bromide
THF, as discussed in Chapter 5E, were also performed in the pres-
:e of CuBr [256] (Cristol and Maxwell).

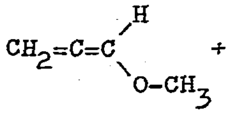


+ RMgBr/10% Cu(I) ; Vermeer, Meyer, De Graaf and Schreurs [347]

·C≡C-S-CH$_3$ + RMgBr/Cu(I) ⟶



; Vermeer, De Graaf and Meyer [348].



$+ \quad RMgX/Cu(I) \longrightarrow R\text{-}CH_2\text{-}C{\equiv}C\text{-}H$ (75-94%); Vermeer an

Meyer [349].

$C_6F_5\text{-}C{\equiv}C\text{-}MgBr \quad + \quad Br\text{-}t\text{-}C_4H_9$ or $Cl\text{-}Si(CH_3)_3$, catalyzed by CuI gives

the coupling products in moderate to good yields, as published by Bogoradovskii, Zavgorodnii, Mingoleva and Petrov [350].

Corriu and coworkers published several papers on the stereochemistr of Ni and Ti catalysed reactions of Si- and Ge derivatives:

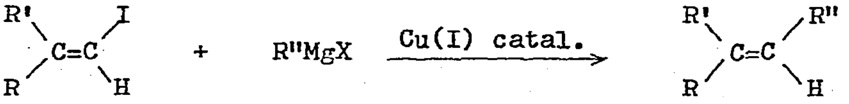
Corriu and Meunier reported on the stereospecific reduction of alkoxy-, chloro- and fluorosilanes, involving the catalytic activation of a Grignard reagent by Cp_2TiCl_2 [351].

Colomer, Corriu and Meunier studied the substitution and reduction reaction mechanisms of organosilanes by Grignard reagents in the presence of nickel complexes [352].

The formation of an optically active "germanium"-Grignard compound by the reaction of a chiral germane with benzylmagnesium chloride, activated by Ni(II) complexes has been referred to in Chapter 2Biv [53].

Ohbe, Doi and Matsuda [342] as well as Ohbe, Tagaki and Matsuda [343] studied the mechanism of the Ni, Co and Fe catalyzed reactions of alkylmagnesium halides with allyl and crotyl halides.

Alkylation of vinylic iodides by Grignard compounds in the presence of Cu(I) salts gives alkenes with retention of configuration as published by J.-F. Normant, Commercon, Cahiez and Villiéras [344]:

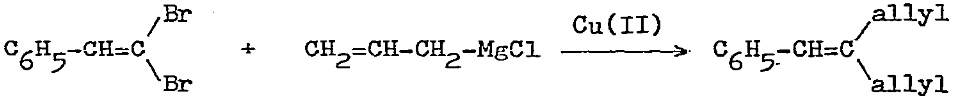


In a German Patent Vonlautem and Donzel claim the coupling of cyclohexylmagnesium bromide with vinyl chloride to give excellent yields when catalyzed by Fe(III) or Ni(II) complexes [345].

Colomer and Corriu report the formation of an effective reductor for vinyl and aryl bromides by combination of isopropylmagnesium bromide and dicyclopentadienyltitanium dichloride [65]. Olefins and acetylenes undergo competitive reduction and isomerization by this reagent.

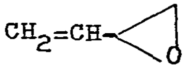
Coupling of Grignard reagents with aromatic halides proceeds in excellent yields when $NiCl_2$, complexed with diphenylphosphine derivatives, is used as the catalyst (Kumada and coworkers [127]).

Dibromostyrene is coupled with allylic organometallics as reported by Klein and Levene [346]:



$$C_6H_5\text{-}CH{=}C(Br)_2 + CH_2{=}CH\text{-}CH_2\text{-}MgCl \xrightarrow{Cu(II)} C_6H_5\text{-}CH{=}C(allyl)_2$$

Other unsaturated compounds, treated with Grignard reagents in the presence of catalysts were the following:

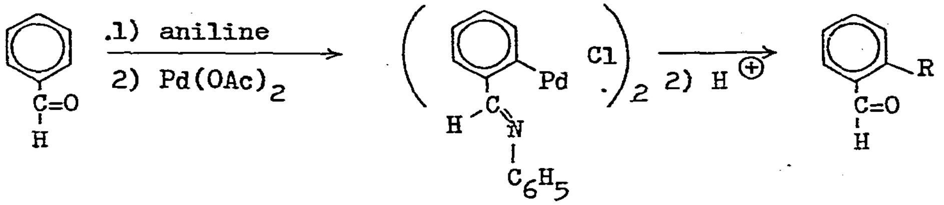


Copper(II) acetate promotes conjugate addition. as observed by Rose and Taylor [245]

Carrê and Corriu published another paper on the stereochemistry of reactions of Grignard compounds with Ge-H bonds, catalyzed by Ni(II) complexes [353].

Modifaction of the reactivity of Grignard reagents towards diethyl oxalate by the addition of cadmium chloride has earlier been mentioned in Chapter 5B (Karavanov et al [211]).

Murahashi, Tanba, Yamamura and Moritani report ortho-substitution in benzaldehyde by the following reaction [354]:



5M. Organomagnesium compounds as polymerization catalysts

Olefin polymerization

Akutagawa, Moriya and Komatsu in a Japanese Patent claim the trimerization of isoprene under the influence of organomagnesium compounds and other additives [355]. The product formed is trans, tran trans-1,5,9-trimethyl-1,5,9-cyclododecatriene.

Butadiene polymerization with the aid of $(s\text{-}C_4H_9)_2Mg$ in hydrocarbon medium was reported by Kamiensky and Merkley [356] and by Kamiensky and Eastham [357].

Hargis and Livigni reported diene-styrene copolymerization with the aid of di-n-butylmagnesium [358].

The polymerization properties of RMgBr/HMPA mixtures in reactions with styrene has been discussed in Chapter 3C (Tomoi and Kakiuchi [121] and [122]).

Polyethylene formation and otherwise polyolefin formation has been reported many times:

Creemers who used di-n-butylmagnesium together with $TiCl_4$ and organoaluminum compounds [359].

Durand and Mangin who applied n-butylmagnesium chloride together with $TiCl_4$ and other additives [360], [361] and [362]; the same is rue for publications by Avaro and Mangin [363].

atsumura, Kazuo, Kuroda, Matsuzaki and Mitsuyoshi used mixtures f RMgX and Ti alkoxides for olefin polymerization [364].

kada, Morinaga and Taguchi (and in the last reference given together with Tsubaki, Iwabuchi and Iida) used RMgX together with siloxanes and other additives for olefin polymerization [365], [366] 367] and [371].

uck, Grant, Butcher and Timms [368] as well as Fletcher and Haward [369] used $TiCl_4$ as an additive for polymerization of ethylene.

atsuura, Kuroda, Kanagawa and Matsuzaki used approximately the same mixture of reagents for ethylene-propylene copolymerization [370].

Metacrylic esters polymerization was studied by Matsuzaki, Konoi, Yamawaki and Rung [372]; ethyl and methyl α-chloroacrylates were polymerized by organomagnesium compounds treated with esters, ketones and epoxides, as studied by Uryn, Ohaku and Matsuzaki [373].

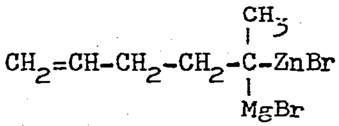
Methacrylonitrile polymerization was reported by Natta, Mazzanti and Dall'Asta [374].

Trioxane polymerization was reported by Glavchef, Kabaivanov and Natov [375].

Guillot reported polymerization of alkylene oxides by R_2Mg/aminopropanediol [376].

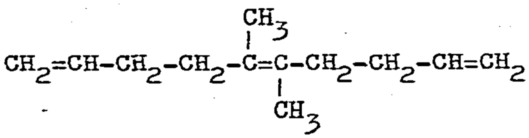
5N. Miscellaneous

Addition reactions of allylic zinc compounds to the double bond of vinylic magnesium compounds lead to the formation of



$CH_2{=}CH{-}CH_2{-}CH_2{-}\underset{MgBr}{\overset{CH_3}{C}}{-}ZnBr$

which at the boiling point of THF leads to the formation of zinc, magnesium bromide and a triene as reported by Frangin and Gaudemar [377]:

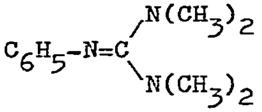


$$CH_2=CH-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}}=\underset{\underset{CH_3}{|}}{C}-CH_2-CH_2-CH=CH_2$$

(51% yield)

Pornet and L. Miginiac reported reactions of different types of organomagnesium halides with

guanidines:

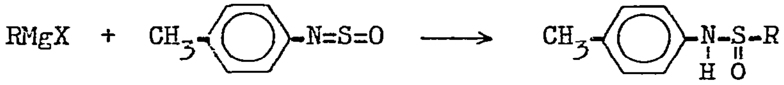


[221], as well as with

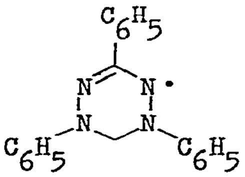
carbodiimides: R-N=C=N-R [378].

Work of Holm, Holm and Huge-Jensen, dealing with reactions of organomagnesium compounds with alkyl- and aryl cyanates has been dealt with in Chapter 4C [59], [160] and [161].

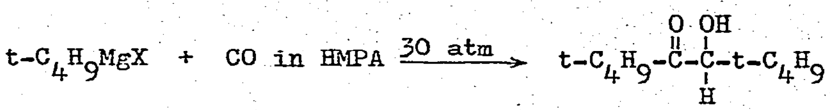
Bowles and Katzenellenbogen published the following method for the preparation of alkyl sulfinyltoluidine [379]:



Miura, Morimoto and Kinoshita reported reactions of alkylmagnesium bromides with 1,3,5-triphenylverdazyl [380]:



Sprangers, Van Swieten and Louw reported the formation of a variety of products on reaction of alkylmagnesium halides with carbon monoxide [381] in HMPA:



$$t\text{-}C_4H_9MgX \;+\; CO \text{ in HMPA} \xrightarrow{30\ \text{atm}} t\text{-}C_4H_9\text{-}\overset{O}{\overset{\|}{C}}\text{-}\underset{H}{\overset{OH}{C}}\text{-}t\text{-}C_4H_9$$

Similar reactions with primary alkyl halides gave ketones.

Semenenko, Bulychev and Bitsoev reported the preparation of mixed magnesium, aluminum, lithium hydrides by reaction with magnesium chloride of $LiAlH_4$ etc. [382].

Jezowska-Tzrebiatowska and Sobota reported on the reactivity of the system $TiCl_4$-Mg-THF;

first on its reactions with carbon dioxide which lead to the formation of formic acid [383];

secondly on its reactions with hydrogen and carbon dioxide [384].

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