MAGNESIUM

ANNUAL SURVEY COVERING THE YEAR 1971

CORNELIS BLOMBERG
Department of Chemistry of the Free University
Amsterdam, The Netherlands

Contents

References p. 120

1. INTRODUCTION

1971 Was an important year in the history of organomagnesium chemis-

try: its founder, Victor Grignard, was born in Cherbourg, hundred years ago. The Société Chimique de France dedicated its annual meeting to the French Nobel-Prize winner; Lyon, the city where Grignard discovered "his" reagent in 1900 and where he had worked most of his life, was the center of this celebration in June. It is not surprising than that biographies have appeared on Grignard and his work [1] and [2].

It seems as if the hundredth anniversary of Grignard's birthday has inspired chemists all over the world the be more productive than ever in the field of organomagnesium chemistry: the number of publications has increased considerably as compared with previous years.

Several review articles have been written: Rearrangements of benzylic Grignard compounds on reaction with different substrates [3], Reaction of Group I-IV organometallic compounds with polyhalomethanes [4], Side reactions in alcohol synthesis by the Grignard method [5], The chemistry of allyl and crotyl Grignard reagents [6], α-Haloalkyl and related Grignard compounds [7], and the annual review of recent developments in the chemistry of main group organometallic compounds [8].

A multitude of dissertations, usually containing important literature researches, apart from new chemistry, was published in 1971: Electron exitation in conjugated carbanions and their solvent dependence [9], (X-Ray) Structural studies of organomagnesium compounds [10], Asymmetric Grignard and Meerwein-Pondorf-Verley reductions. Long range asymmetric synthesis and the reduction of perfluoroalkyl carbinol reagents [11], Intramolecular cyclizations of alkynyl Grignard reagents [12], Addition of organomagnesium compounds to isolated double bonds [13], Alkyl-oxygen fission in the reaction of trityl-^{18}O acetate with phenylmagnesium bromide [14], Investigation of the

References p. 120

reaction of α-phenylethyl bromide with ethylmagnesium bromide [15], Studies on the structure and dynamics of selected Grignard reagents [16], Preparation of dialkylmagnesium compounds and intermetallic compounds involving magnesium alkyls [17], Preparation and reactions of complexes of magnesium alkyls and aryls with alkali metal alkyls and hydrides [18], Organostannylmagnesium reagents [19], Structure and reactions of imino Grignard reagents [20], Structural studies of Group II organometallic compounds [21], Ozonization of lithium and magnesium alkyls [22], Inversion studies of organomagnesium compounds [23], Asymmetric reductions of aldehydes by chiral Grignard reagents [24], Bifunctional and cyclic organomagnesium compounds [25], Contribution to the study of reaction mechanisms of organomagnesium compounds [26], Study of physico-chemical properties of organomagnesium compounds [27].

2. PREPARATION AND ANALYSIS OF ORGANOMAGNESIUM COMPOUNDS

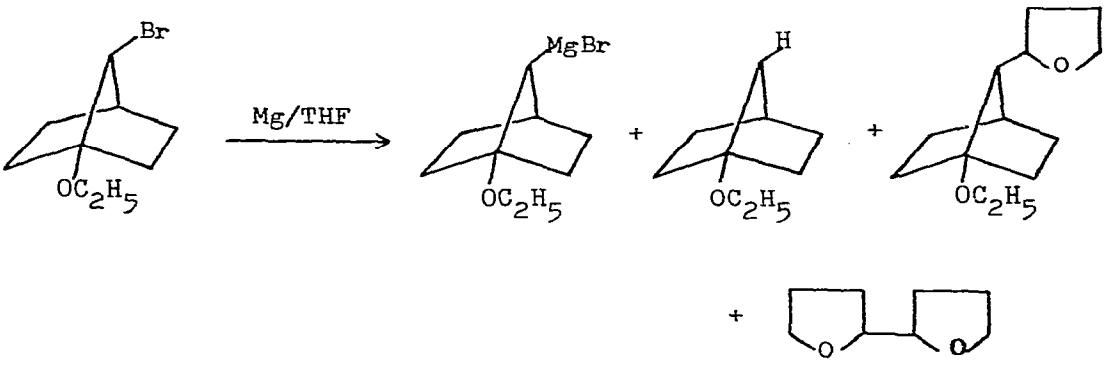
As a warning that not all organomagnesium compounds are as harmless as they are usually considered to be this chapter should start with the report of an explosion that occured during the preparation of a Grignard compound [28]: m-trifluoromethylphenylmagnesium bromide, prepared on a nine mole scale, detonated during the addition of m-trifluoromethylbromobenzene to magnesium in diethyl ether. No satisfactory explanation for the occurence of the violent reaction is apparent.

A. Side reactions during the preparation of Grignard compounds

Several reports have been made on the occurence of side reactions during the preparation of Grignard compounds. Such reactions may shed more light on the still unknown mechanism of the Grignard reac-

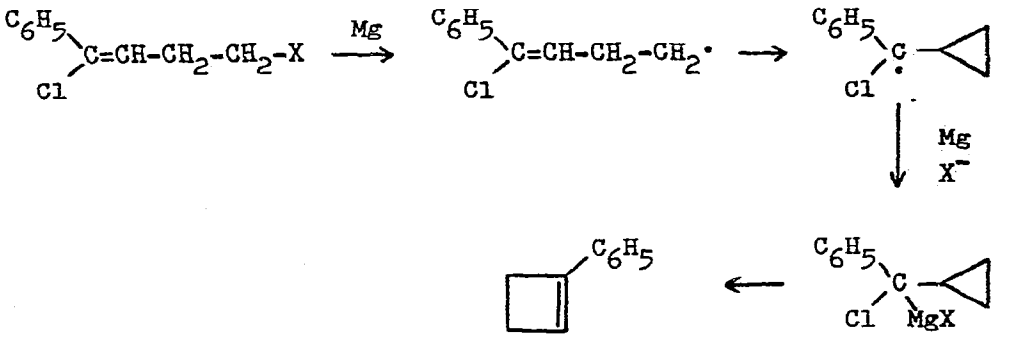
tion. Although it remains questionable whether the formation of all unexpected products has to be attributed to the occurence of what is generally called "highly reactive species", evidence for a radical pathway as at least one of the possible routes for the formation of Grignard compounds was obtained by Bodewitz, Blomberg and Bickelhaupt early 1972 who observed emission and enhanced absorption in the NMR-spectrum, made during the reaction of alkyl halides with magnesium in THF as well as in di-n-butyl ether [29].

Radical intermediates are held responsible by Grootveld, Blomberg and Bickelhaupt for hydrogen abstraction from the solvent during the reaction of 1-ethoxy-7-bromonorbornane with magnesium in THF [30]:

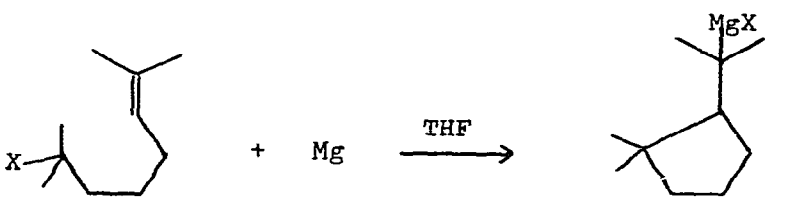


in particular the formation of bitetrahydrofuranyl as well as of 1-ethoxy-7-tetrahydrofuranylnorbornane support the idea that radical intermediates play an important role in the Grignard reaction.

A radical cyclization mechanism appears to be most likely among several other possible mechanisms, suggested by Hill and Engel to rationalize the formation of cyclobutene in the reaction of 1,4-dihalo-1-phenyl-1-butene with magnesium [31]:

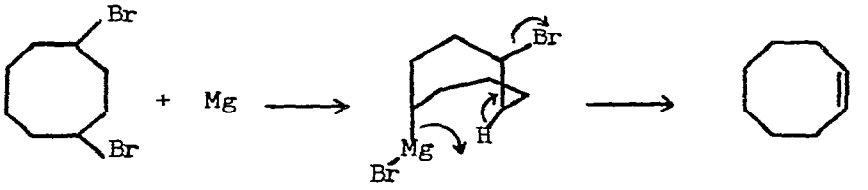


Radicals or unsolvated organomagnesium compounds are also held responsible by Kossa, Rees and Richey for the formation of cyclic products during the preparation of Grignard compounds with 5- or 6- alkenyl halides as the starting materials [32]:



Aleksankin, Fileleeva and Gragerov investigated the reaction of bromobenzene with magnesium in benzene, mixed with diethyl ether, THF or dimethoxyethane; biphenyl was formed in 24%, 13% and 4% yields respectively in the different solvent mixtures [33]. Addition of Cu(II) chloride to these reaction mixtures caused an increase of the yields on biphenyl to 64%, 26% and 16%. Also because of the results, obtained when the reaction was performed in perdeuterated benzene after which deuterium distribution in the products was investigated the authors conclude that biphenyl-formation is caused by radicals.

The formation of cyclooctene and cyclononene in the reaction of the corresponding cyclic 1,4-dibromo compounds with magnesium is attributed by Baird, Reese and Stebles to intramolecular proton abstraction by the monofunctional intermediate Grignard compound the existence of which has not been proved [34]:



Cherkasov, Radchenko and Kupin observed addition to carbon-carbon double bonds (together with rearrangement) of (in situ?) Grignard reagent when bromoethane reacted with magnesium in diethyl ether in the presence of 1-trimethylsilyl-1-butyn-3-ene [35]:

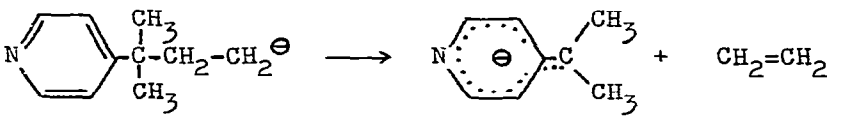
$$C_2H_5\text{-}Br + Mg + (CH_3)_3Si\text{-}C{\equiv}C\text{-}CH{=}CH_2 \longrightarrow \left.\begin{array}{c}(CH_3)_3Si\text{-}C{\equiv}C\text{-}CH_2\text{-}C_3H_7 \\ + \\ (CH_3)_3Si\text{-}CH{=}C{=}CH\text{-}C_3H_7\end{array}\right\} 20\%$$

On hydrolysis a mixture of acetylenic and allenic silyl-compounds was obtained in a total yield of 20%. (The same type of reaction was reported last year for thioethers containing the same type of unsaturated bonds; A.S. 1970).

γ-Tributylstannyloxypropyl bromides, $(C_4H_9)_3Sn\text{-}O\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-}Br$, in which the propyl entity may be substituted with methyl and/or ethyl groups,

on reaction during two hours in refluxing diethyl ether, yield after hydrolyzation the intramolecular substitution reaction product: $(C_4H_9)_3Sn-\overset{|}{C}-\overset{|}{C}-\overset{|}{C}-OH$ [36]. It is not reported at which stage of the whole procedure this substitution reaction takes place; the existence of the expected Grignard compound therefore need not necessarily be precluded.

Fraenkel and coworkers continued their studies on homoconjugation in pyridylalkyl organometallic compounds; for the fragmentation of the expected Grignard compound, probably formed in the reaction of 3-methyl-3-(4-pyridyl-)chlorobutane with magnesium in diethyl ether [37] (see also A.S. 1968) the driving force may lie in the stability of the conjugated departing anion:



In an alternative mechanism it is suggested that the reaction may also proceed by an initial reduction of the pyridine ring, followed by loss of chloride ion and fragmentation.

Fraenkel, together with Pechhold and Adams, report that 3,3-dimethylbromocyclobutane, 2,2-dimethylbromocyclopentane, 2,2-, 3,3- and 4,4-dimethylbromocyclohexane gave only poor yields of the corresponding Grignard reagents and mainly coupling products on reaction with magnesium in diethyl ether, THF and dimethoxymethane [38]. In diglyme however at 60° these halides were smoothly converted to Grignard reagents in nearly quantitative yields.

B. Preparation of Grignard compounds

Of the numerous different types of Grignard compounds, the preparation of which was reported this year, the following will be mentioned:

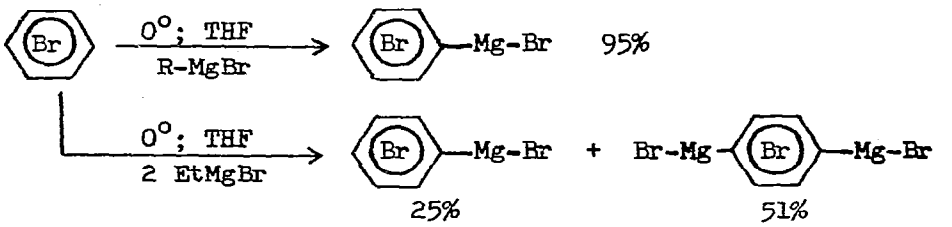
Kinoshita, Imoto and coworkers prepared a polymeric Grignard compound by the reaction (with entrainment) of magnesium with poly-p-vinylbenzyl bromide in THF; an extremely large excess of bromoethane was applied. Addition of carbon dioxide to the reaction mixture yielded poly-p-vinylphenylacetic acid [39]. As reported in a footnote in the same report one of the authors failed in preparing the polymeric Grignard compounds of poly-p-vinylchloro(and -bromo-)benzene.

i. Halide-substituted Grignard compounds

Tamborski and Moore prepared perfluorophenylmagnesium halides by metal-halogen exchange reactions: pentafluoroiodo-(or -bromo or -chloro-)benzene reacted with ethylmagnesium bromide (or chloride) to give high yields of pentafluorophenylmagnesium halides in extremely rapid reactions (quite often within one minute) [40]. Surprisingly enough pentafluorophenylmagnesium chloride, prepared by this reaction is unstable and decomposes almost completely within 24 hours. Even more surprising is the observation that the chloride, prepared by metal-hydrogen exchange (ethylmagnesium chloride added to penta-fluorobenzene) is much more stable: after 24 hours still 50% of the Grignard compound was present in the solution). No explanation could be advanced for these instabilities. p-Dibromotetrafluorobenzene reacted with two molar equivalents of ethylmagnesium bromide to give 93% of the bifunctional Grignard compound. Such bifunctional Grignard compounds were obtained from the meta- and the ortho-isomers in low yields: 4% and 14% respectively.

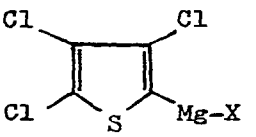
References p. 120

In a preliminary communication by Smith, Moore and Tamborski an improved synthesis of perbromo-mono- and -bifunctional phenyl-Grignard compounds by reaction of hexabromobenzene with phenyl- or ethylmagnesium bromide was reported [41]. Not more than 51% of the parabifunctional Grignard compound could be isolated as well as some meta isomer but no ortho product:



Pentabromophenylmagnesium bromide is less stable at 0° than the fluoro compound. When bromoethane is present in the solution (formed in the exchange reaction) the major pathway of decomposition is the formation of ethylated products.

Bromo 3,4,5-trichlorothiophenemagnesium,



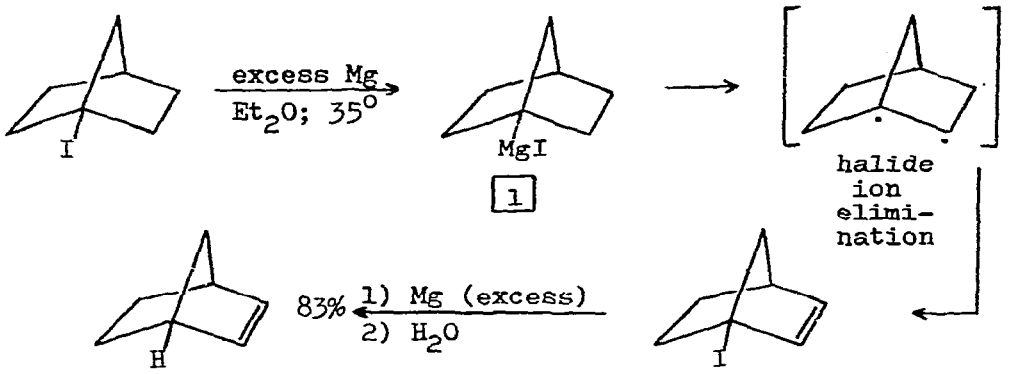
was prepared by Gilman and coworkers by the reaction of tetrachlorothiophene with magnesium (entrain with 1,2-dibromoethane) [42].

Kruglova and Freidlina prepared ω-dichloroaliphatic Grignard compounds by the reaction of $Cl_2CH-(CH_2)_n-Br$ (n = 2, 3 or 5) as well as of $Cl_2C=CH-(CH_2)_3-Br$ with magnesium [43]; the yields varied from 10 - 50 %.

L. Miginiac and Blois prepared 4-, 5- and 6-chloroalkylmagnesium bromides from the corresponding chloroalkyl bromides on reaction

with magnesium in THF [44] (see also Noel, Thesis 1963, and Normant, Noel and coworkers: 1969).

Tatlow, Campbell and coworkers assume the formation of a transient bridgehead biradical in perfluoro[2,2,1]bicycloheptane to rationalize

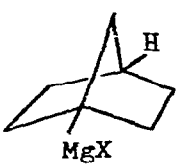


1

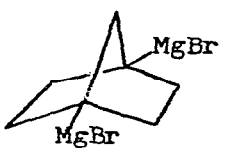
All unmarked substituents are fluoride

the formation of the unsaturated bicyclic compound in the reaction described above [45]. 1-Bromoundecafluorobicyclo[2,2,1]heptane reacts similarly.

In contrast to the perfluoro[2,2,1]bicycloheptylmagnesium iodide [1] the mono- and bifunctional Grignard compounds [2] and [3], prepared from 1-H-4-bromo(or -4-iodo-)decafluorobicyclo[2,2,1]heptane and from 1,4-dibromodecafluorobicyclo[2,2,1]heptane are stable in diethyl ether at reflux temperature [46].



X = Br or I

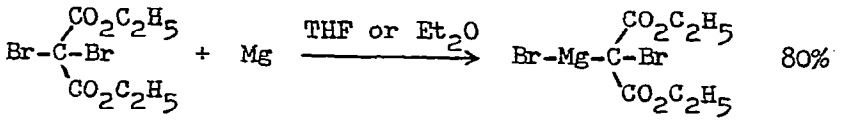


2 3

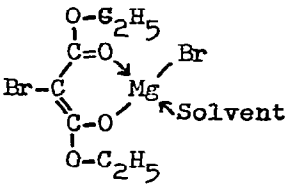
All unmarked substituents are fluoride

The lower stability of the 4-fluoro substituted Grignard reagent may result from an interaction within the central molecular cavity between the dipole, associated with the carbon-fluorine bond, and the carbanionic centre of the carbon-magnesium bond (Campbell, Tatlow and others; A.S. 1967).

Gaudemar and Gaudemar-Bardone report the facile reaction of diethyl dibromomalonate with magnesium in diethyl ether or THF to give a monofunctional Grignard compound [47]:

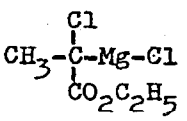


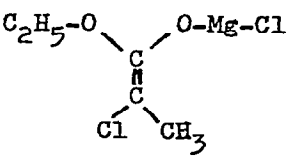
Infrared data suggest the chelated structure



for this peculiar Grignard compound that reacts with aldehydes to give the normal addition reaction products in fair yields (ca. 50%) but fails to react with ketones.

The same type of α-halo Grignard compound which probably also exists in the enolate form was obtained by Blagoev, Momchev, Ivanov and



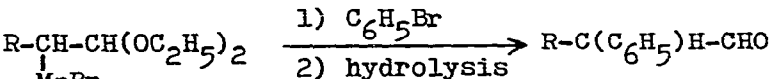


Todorov by the reaction of isopropylmagnesium chloride with α-chloropropionic acid [48].

The preparation (leading to detonation; see the beginning of this chapter) of m-trifluoromethylphenylmagnesium bromide has been reported [28].

ii Alkoxy-substituted Grignard compounds

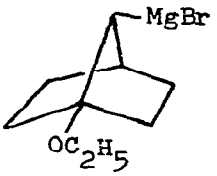
Extremely surprising is the report by Pallaud [49] in which it is stated that 2-bromo-1,1-diethoxyalkanes react with magnesium in THF to form Grignard compounds (entrain reaction) in varying yields as may be concluded from the products obtained on reaction with bromobenzene followed by hydrolysis.



R	Yield: %
H	10
C_2H_5	44
C_6H_{13}	18
C_8H_{17}	12

Furthermore it is surprising to read in the same report that the 2-bromo-1,1-dimethoxy homologues do not react at all with magnesium.

The preparation of bromo 1-ethoxy-7-norbornylmagnesium

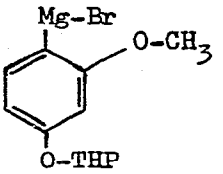


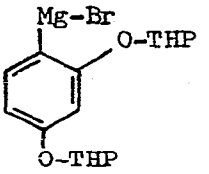
has already been mentioned in the beginning of this chapter [29].

THP-O-$(CH_2)_n$-Mg-Cl (n = 4, 5 or 6) have been prepared and used in synthesis (THP stands for tetrahydropyranyl-) [44].

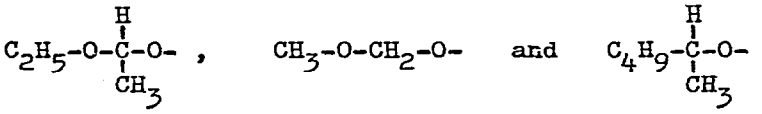
The preparation of aromatic Grignard compounds containing methoxy

as well as tetrahydropyranyl substitutents has been reported [50]





R-substituted phenylmagnesium bromides have been prepared with R-groups such as [51]:

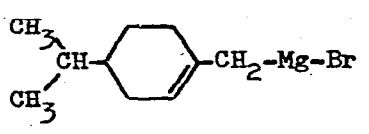


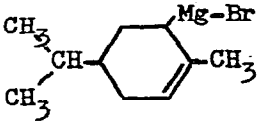
3-Methoxy- as well as 3-t-butoxy-1-propynyl-1-magnesium bromide was prepared from the corresponding 3-alkoxy-1-propyne by reaction with ethymagnesium bromide in THF [52]. The greater solubility of these Grignard compounds in THF as compared to the solubility in diethyl ether (Heilbron, Jones, Lacey; 1946) promotes its application in synthesis.

iii Unsaturated Grignard compounds

The preparation of the 3-alkoxy-substituted acetylenic Grignard compound, R-O-CH_2-C≡C-Mg-Br has been reported above [52].

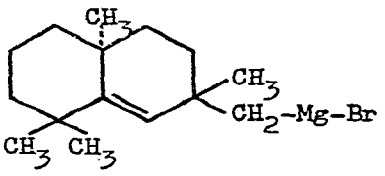
The reaction of 7-bromo-p-menthene-1 as well as of bromocarvomenthene with magnesium is reported to be very sluggish although the corresponding Grignard compounds





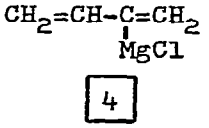
are obtained in good yields; reactions of the two organomagnesium compounds with different substrates give the expected products in poor yields only with the exception of the reaction with allyl bromide (product yields 45 % and 38 % respectively) [53].

The preparation of the neopentyl-type Grignard reagent



has been reported [54] and its reaction with cyclohexanone has been investigated.

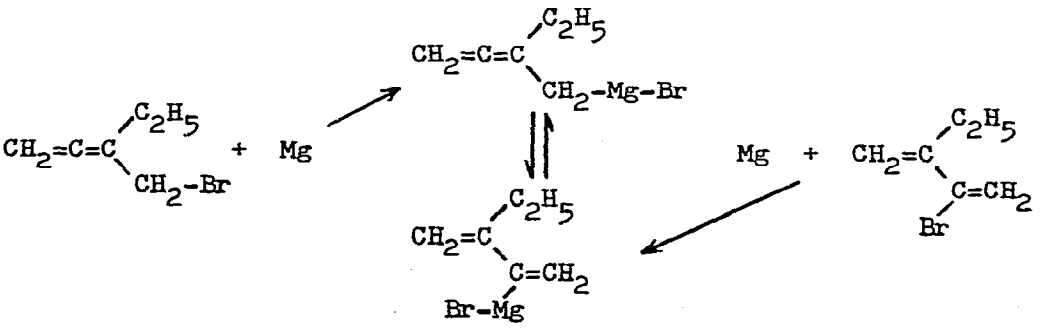
Chloro 1,3-butadienyl-2-magnesium [4] has been prepared in a reaction



[4]

which will be discussed later on in this chapter [55].

Michel, Raffi and Troyanowsky prepared the same type of Grignard reagent which exists in solution in equilibrium with its allenic isomer



in a Grignard reaction with two isomeric unsaturated bromides [56]. On reaction with acetaldehyde two isomeric products are obtained.

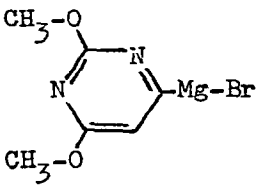
The preparation of 5- and 6-alkenylmagnesium halides has been reported above to be accompanied by ring-closure side-reactions [31]. α-Allenyl- and β-acetylenic-Grignard compounds have been reported by Moreau and Gaudemar [57].

iv Some_other_organomagnesium_compounds

7-Norbornylmagnesium bromide and its reactions with formaldehyde and acetaldehyde has been reported by Belikova, Gazuko and Plate [58]. Guts and Sukhoverkhov prepared several adamantyl- and homoadamantyl-Grignard reagents [59].

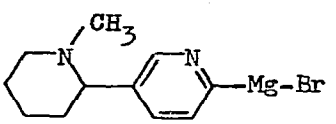
Imidazolyl- and several triazolylmagnesium bromides have been used in reactions with trityl halides [60].

2,4-Dimethoxypyrimidyl-6-magnesium bromide



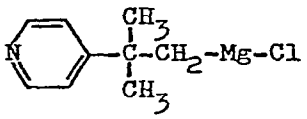
has been prepared and used in reactions with $^{14}CO_2$ [61].

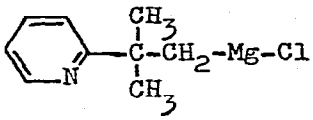
The substituted pyridyl Grignard reagent



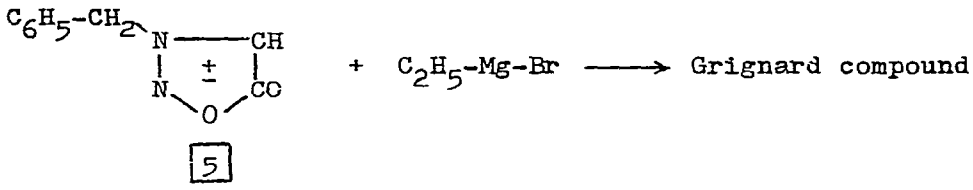
prepared from 6-bromo-N-methylanabasine has been reported [62].

In their study on homoconjugation in pyridyl organometallic compounds (see also in the beginning of this chapter) Fraenkel and coworkers report the preparation of 2-(2-pyridyl)- and 2-(4-pyridyl)-2-methylpropylmagnesium chloride [37]:

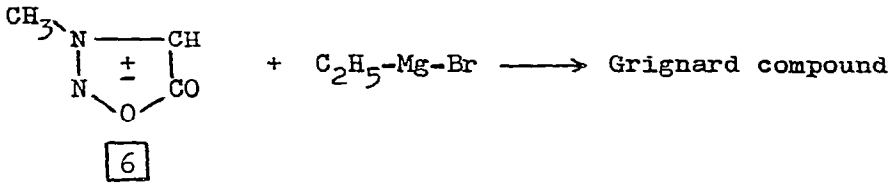




Ethylmagnesium bromide reacts with 3-benzylsydnone [5] and with 3-methylsydnone [6] to form Grignard reagents the structure of which



[5]



[6]

is discussed by the authors [63].

Tin-containing organomagnesium compounds were obtained by Harrison, Zuckerman and Noltes by the reaction of dicyclopentadienyltin(II) and of bis(methylcyclopentadienyl)tin(II) with phenylmagnesium bromide in diethyl ether [64]:

$$(RC_5H_4)_2Sn + C_6H_5MgBr \longrightarrow C_6H_5(RC_5H_4)_2SnMgBr$$

R = H or CH_3

Ashby and coworkers have reported more detailed reaction conditions for the preparation of aliphatic "fluoro-Grignards", R-Mg-F [65] (see also A.S. 1970). The best solvents for the reaction of fluoroalkanes with magnesium appear to be THF and 1,2-dimethoxyethane, the best catalyst is iodine; methyl- and hexylmagnesium fluoride were obtained in 95% yield, ethylmagnesium fluoride in 36% yield only. Under the most

favorable conditions phenyl- and benzylmagnesium fluoride could not be prepared.

Two Russian groups have been working on carboranylmagnesium halides: Stanko and Anorova [66] prepared o-, m- and p-carboranylmagnesium halides as well as 10-chloro-o-carboranylmagnesium bromide and 9-chloro-m-carboranylmagnesium bromide from the corresponding chlorocarboranes.

Zakharkin and coworkers prepared o-carboranylmagnesium halide [67].

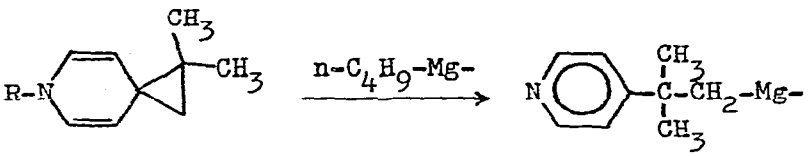
The stability of solutions of magnesium-naphthalene in liquid ammonia, ethylenediamine and HMPT has been studied by Pascault and Gole; changes in the solutions could be observed spectroscopically [68]. Magnesium-naphthalene is very stable in HMPT: at 25° only 8% destruction occurs within 100 hours. In ethylenediamine as well as in ammonia protolysis takes place; in HMPT the reaction is different. The stability of magnesium-naphthalene in liquid ammonia at -60° is remarkable compared with the stability of sodium-naphthalene under the same conditions.

C. New and uncommon reactions for the formation of organomagnesium compounds

Saito reports formation of dicyclopentadienylmagnesium in a smooth reaction between cyclopentadiene and magnesium at 0° with cyclopentadienyltitanium trichloride as a catalyst [69]. It is supposed that the actual catalyst is a titanium-magnesium complex with the formula $Cp_2Ti_2Mg_2Cl_3.2THF$. Other titanium salts like Cp_2TiCl_2 and $TiCl_4.2THF$ were less satisfactory as catalysts.

Baryshnikov and Kvasov studied the composition of the solution and of the precipitate, obtained on addition of dioxane to solutions of phenylmagnesium chloride in toluene or in chlorobenzene [70]. Diphe-

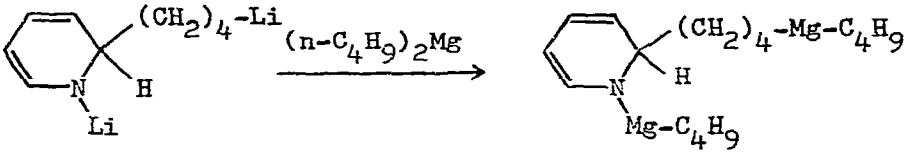
nylmagnesium was the main constituent of the solutions obtained. The reaction of 1-substituted-4-(1,1-dimethylspirocyclopropyl)-1,4-dihydropyridine with butylmagnesium compounds leads to the formation of the organomagnesium compound [7] [37]:



[7] tert. $^{+}$ alkoxides

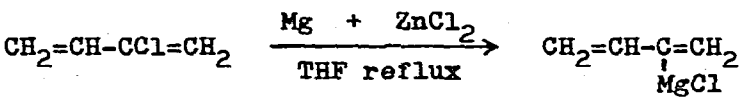
R = CH_3CO-, CH_3CO_2-, $C_2H_5CO_2$- or $C_6H_5CO_2$-.

In the same report by Fraenkel and coworkers the following reaction of a dihydropyridyldilithium compound with di-n-butylmagnesium was mentioned:



there was no change in the nmr spectra of the solution but the organomagnesium compound was thermally much more stable than the lithium compound.

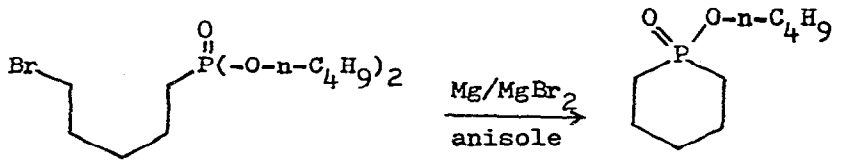
2-Chloro-1,3-butadiene reacts with magnesium in refluxing THF in the presence of a metal salt such as zinc chloride to form a Grignard reagent [55]:



References p. 120

A same type of reaction for the preparation of unsaturated organomagnesium compounds was reported in a Japanese patent; 2-methyl-2,7-octadiene was reacted with magnesium in the presence of zinc chloride to yield an organomagnesium compound [71].

Di-n-butyl-5-bromoamylphosphonate reacts with magnesium in the presence of magnesium bromide in, what is called by the authors " a Grignard-type reaction " to form the cyclization product n-butylpentamethylenephosphinate in 80% yield [72]:



In a German patent Vit claims the preparation of hydrocarbon solutions of alkyl-, aryl- and heterocyclic-Grignard compounds, complexed with magnesium alkoxides having the general formula:

$$Mg(-O-R)_2.nR'-Mg-X$$

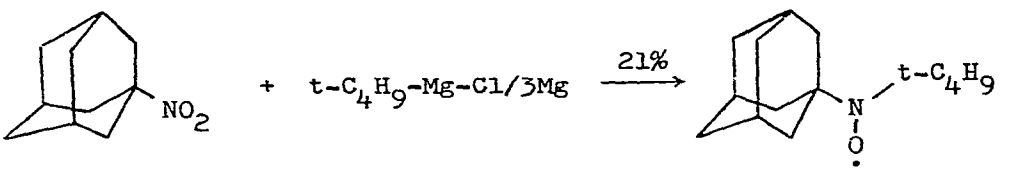
in which n may be 1, 2 or 3 and R is $-CH_2-CH_2-OCH_3$, $-CH_2-CH_2-N(CH_3)_2$, $-(CH_2)_4-O-CH_3$ or $-(CH_2)_2-O-(CH_2)_2-O-CH_3$ [73]. The Grignard compounds are reported to give products in excellent yields when reacted with different substrates.

D. Miscellaneous

The preparation of ethylmagnesium bromide in an optically active bidentate ligand (-)sparteine has been reported [74]; on reaction products could be obtained with optical purities as high as 22%

as the result of asymmetric synthesis due to the presence of the chiral ligand.

Again a report has appeared indicating the change of the course of reactions with Grignard compounds when excess metallic magnesium, used for the preparation of the reagent is not removed: the presence of a three-fold excess of magnesium in the reaction mixture of t-butylmagnesium chloride and 1-nitroadamantane causes the formation of a radical product, t-butyladamantyl nitroxide in a 21% yield [75]:



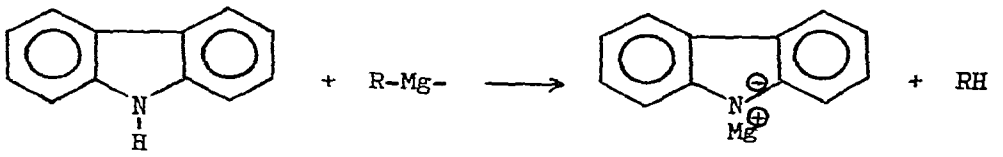
The influence of impurities in magnesium on the course of the reaction of ethylmagnesium bromide with diisopropylacetyl bromide has been investigated by Boussu and Dubois [76]; the results, obtained with magnesium containing 11 ppm impurities don't differ from those obtained with magnesium with 1350 ppm impurities when the solutions are decanted from what the authors call " residual precipitates ". A large difference however was found when these precipitates remained in the reaction mixture: radical reactions, leading to the formation of diketones etc. take place to a larger extent in the reaction mixture containing impure magnesium.

E. Analysis of organomagnesium compounds

A method is described for monitoring the concentration of Grignard

compound in solution during electrolysis in the presence of a lead anode for the production of tetraalkyllead compounds [77].

Fontanille and Tersac report an analytical method for the determination of organomagnesium compounds in very dilute solutions [78]. The method is based on the spectrophotometric determination of the carbazyl-anion, formed on the addition of an organomagnesium com-



pound (10^{-3} - 10^{-6} M) to carbazole.

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

A. Electrochemistry of organomagnesium compounds

The oxidation potentials of several Grignard compounds in THF were determined by Chevrot, Troupel, Folest and Périchon with the aid of a rotating microelectrode (gold, polished or platinized platinum). The reduction power of R-Mg-Cl decreases in the order: t-butyl > ethyl > isopropyl, vinyl > n-butyl > methyl > phenyl [79]. Although the oxidation potentials of each of these Grignard compounds is higher than the reduction potentials of aromatic hydrocarbons, $ArH \rightarrow ArH^{\cdot-}$, the authors observed the formation of the radical anion $ArH^{\cdot-}$ in many cases when ArH (5.10^{-4} - 5.10^{-6} M concentration) was added to a large excess of R-Mg-Cl (6.10^{-1} M). The plot of current against potential shows a reduction wave. Aromatic hydrocarbons such as anthracene or 9,10-diphenylanthracene with reduction poten-

tials lower than -2.7V are not reduced by any of the above mentioned Grignard compounds.

In a second report, the same authors determined the basic behavior of R-Mg-Cl compounds by studying the redox properties of the system H^+/ H_2 at a platinized platinum electrode in THF solutions of R-Mg-Cl [80]. The oxidation of hydrogen in the presence of methyl-, ethyl-, n-butyl- and phenylmagnesium chloride was observed by plotting the current against the potential. Isopropyl- and t-butylmagnesium chloride are more readily oxidized than hydrogen in the presence of these two Grignard compounds so no change is found in the current-potential graphs for these organomagnesium compounds with or without the presence of hydrogen . In order to determine quantitatively the basicities of R-Mg-Cl compounds the change of zero-current potentials of the solutions were measured during the titration of the Grignard compounds with n-butanol. The value of the potential of half-neutralization (expressed in pH units) gives a quantitative classification of the basicity; pH 1/2 values obtained were : CH_3MgCl, 30, C_2H_5MgCl, 27, n-C_4H_9MgCl, 23, C_6H_5MgCl, 23. For comparison: the pH 1/2 value of water in THF (10^{-2} M) in the presence of $Mg(OH)_2$ is 11.

Ducom and Denise measured the electric conductivities of magnesium chloride and bromide, of diethylmagnesium as well as of ethylmagnesium chloride, ethylmagnesium bromide and of n-butylmagnesium bromide in HMPT [81]. In this strongly basic solvent the equivalent conductivity of Grignard compounds can be as high as 20 $\Omega^{-1}.cm^2.mol^{-1}$; the authors propose the following ionization equilibrium:

$$R\text{-}Mg\text{-}X \rightleftharpoons R\text{-}Mg^+ + X^-$$

Magnesium bromide is completely ionized, organomagnesium bromides

are ionized for approximately 30%.

Together with Fauvarque Ducom reports on the electric conductivity of ethylmagnesium bromide in an ether-benzene mixture on addition of HMPT in small portions [82]. There is a considerable increase in the conductivity of the solution after the addition of two molar equivalents of HMPT indicating that the monomeric Grignard compound, solvated by two molecules of the amide, is ionized.

B. Ultraviolet spectra of organomagnesium compounds

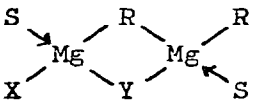
Ebel and Wagner determined the ultraviolet spectra of phenyl-, benzyl-, α,α'-dimethylbenzyl-, benzhydryl-, triphenylmethyl- and phenylallylmagnesium chloride in diethyl ether [83]. λ_{max} increases in this order from 248 to 317 nm; the substitution of an electron-rich substituent -C-Mg- disturbs the phenyl chromophore. For the Mg-Cl substituent overlap is made possible of the valence electrons of the benzylic carbon with the π-system of the chromophore; magnesium influences both the electronegativity of the α-carbon atom and the possibilities for resonance.

Addition of HMPT to the above mentioned solutions shifts the absorption maxima in the ultraviolet spectra to higher wavelengths. When more than two molar equivalents of HMPT have been added ionization of the carbon-magnesium bond is complete and absorption occurs in the visible region of the ultraviolet spectrum at ca. 450 nm, with an exception for phenylmagnesium bromide which remains colorless [84].

C. NMR studies of organomagnesium compounds

Several NMR studies of organomagnesium compounds have appeared dealing with the mechanism and rate of inversion of the carbon magnesium bond as well as with the structure of the compounds in solution.

From their studies of methyl- and t-butylmagnesium compounds Ashby and Parris conclude that, a) the structure of the alkyl group has a profound effect upon the rate of alkyl exchange, b) the presence of a good bridging group such as alkoxide catalyzes alkyl exchange and c) that the solvent plays an important role in the exchange reaction. The " key intermediate " in the exchange reaction should have the following structure:



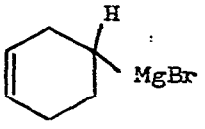
with R= alkyl, X= halide, S= solvent and Y= halide, alkoxide etc. [85].

Fraenkel, Cottrell and Dix published extensively on the mechanism of inversion in primary organomagnesium compounds [86]. Inversion parameters were determined for 2-methyl-1-butylmagnesium compounds as well as for 2,3-dimethyl- and for 2,3,3-trimethylbutyl-1-magnesium compounds; the authors come to the conclusion that there is no significant steric effect on the rates of inversion.

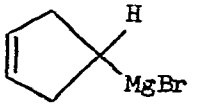
Furthermore, if inversion resulted from any process which polarized the carbon magnesium bond it should be very sensitive to solvent polarity and should be accompanied by large negative entropies of activation; neither of these effects are observed. Actually it has been found that inversion rates in organomagnesium compounds decrease with increasing solvent basicity. Finally, also as the result of the determination of the kinetic order for the inversion, the authors come to the conclusion that dimeric transition states are implicated in the inversion process with (at least) one of the alkyl groups in the bridging position.

References p. 120

Since secondary alkyl groups in organomagnesium compounds do not bridge as easily as primary alkyl groups this should influence the rate of inversion of such compounds; indeed Fraenkel, Pechhold and Adams find that inversion is slow (on a NMR-time scale) for Grignard compounds such as 3,3-dimethylcyclobutylmagnesium bromide, 2,2-dimethylcyclopentylmagnesium bromide, 2,2-, 3,3- and 4,4-dimethylcyclohexylmagnesium bromide in diglyme at temperatures as high as 175° [38]. The maximum reciprocal mean lifetime between inversions at 175° is 1 sec^{-1} while the extrapolated value for 2-methyl-1-butylmagnesium bromide at the same temperature is 1.2×10^{-5} sec^{-1}. Rapid inversion at secondary carbon atoms in cyclic Grignard compounds was found by Maercker and Geuss [87]. The NMR spectrum of 3-cyclohexenylmagnesium bromide [8], shows a broad and unresolved signal at room temperature for the α-proton; fine structure was obtained at lower and at higher temperatures. The occurence of coalescence can only be explained by an inversion at the α-carbon atom.



[8]



[9]

The rapid inversion at this secondary carbon atom has to attributed to the double bond between C-3 and C-4 which enhances the electrophilicity of magnesium, thus increasing the ease of replacement in a S_E2 mechanism. This concept is supported by the NMR spectrum of 3-cyclopentenylmagnesium bromide [9], where the coalescence point has not been reached at -20°.

The rate of inversion is lowered, not only on changing the solvent from diethyl ether to THF, but also on changing to more dilute solu-

tions. This makes an ionization-recombination mechanism for inversion unlikely for these Grignard compounds.

Ashby and coworkers have continued their studies on the Schlenk equilibrium in Grignard solutions with the aid of NMR spectroscopy [85]. Distinction could be made between the signals of CH_3MgBr and of $(CH_3)_2Mg$ (see also A.S. 1969): the temperature dependence of these signals in diethyl ether and in THF was measured. At -26° also the diethyl ether solution of t-butylmagnesium chloride exhibits two signals, which are assigned to the Grignard compound (signal at 9.09) and the diorganomagnesium compound (signal at 9.11). In THF these signals were found at 9.13 and 9.15 respectively and didn't coalesce at + 65°. The authors calculated thermodynamic parameters for the Schlenk equilibrium:

$$(t\text{-}C_4H_9)_2Mg + MgCl_2 \rightleftharpoons 2\ t\text{-}C_4H_9MgCl$$

The equilibrium is statistical in THF and RMgX is favored over R_2Mg at higher temperatures. Coalescence of the signals occur at lower temperatures when alkoxides, formed by air oxidation, are present in solution. The dominant role in deciding the position of the Schlenk equilibrium is played by the solvent, probably due to its ability to solvate the magnesium halide component of the equilibrium. In general the alkyl group has little effect upon the position of the equilibrium; transition metal impurities seem to have little effect upon the rate of alkyl exchange in the Schlenk equilibrium.

Evans and Fazakerley report on the Schlenk equilibrium for a number of Grignard compounds. ("RMgX") : ("R_2Mg") ratios were determined with the aid of NMR spectroscopy and are given for: methyl- and ethylmagnesium bromide, for 2-methylphenyl-, 2-ethylphenyl-, 2-methylnaphthyl-, 2,6-dimethylphenyl-, 2,4,6-trimethylphenyl-, 2-tri-

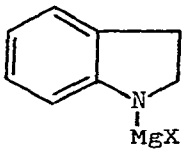
fluoromethylphenyl, 4-fluoro-2-methylphenyl-, 3,5-dideuterophenylmagnesium bromide as well as for 2,6-dimethylphenylmagnesium chloride in THF. The authors did not attempt to make detailed calculations of the rates of alkyl and aryl exchange " largely because of the possibility of catalysis by impurities ". Substitution in the ortho position of aromatic rings by bulky groups results in lower rates of exchange. The more strongly coordinating is the solvent, the slower the rate of exchange for a particular Grignard reagent [88].

In a series of physico-chemical studies by Ducom, that has appeared this year NMR studies have been published on the influence of HMPT on the proton magnetic resonances of solvated Grignard compounds [89]. Distinction can be made between symmetrical and non-symmetrical methyl- and ethylmagnesium compounds; mixtures of R_2Mg and R-Mg-X (X= Br or Cl) show different absorptions. When benzene is used as the solvent and molar equivalents of HMPT were added no distinction could be made between R_2Mg and R-Mg-X with less than two equivalents . Furthermore the alkyl exchange reaction is slowed down when the relative amount of HMPT increases: for methylmagnesium compounds e.g. the coalescence temperature for $(CH_3)_2Mg$ and CH_3-Mg-Br signals is 75° in pure HMPT and only 3° when 2.5 molar equivalents HMPT were present. The authors suggest that there is to be " thought of a reaction of S_E2 type with a transition state much more of the open type than of a closed type ".

In another publication, Ducom concludes from NMR investigations that $(C_2H_5)_2Mg.2HMPT$ is formed when HMPT is added to diethylmagnesium in benzene and more than two molar equivalents of HMPT are present [90] With less than two molar equivalents a monomer-dimer equilibrium exists. For solutions of dimethylmagnesium in toluene and one molar equivalent HMPT different signals were found for bridging and termi-

nal methyl groups at -65°. The coalescence temperature for the two signals is -34°. Parameters are given for the dissociation reaction. No evidence was found for the presence of a trisolvated dimeric species, $(R\text{-}Mg\text{-}X)_2.3HMPT$.

Reinecke, Sebastian, H.W. Johnson Jr. and Pyun report extensively on the NMR spectra of indole-alkali metal and -Grignard reagents [91]. The improved and expanded data in no way alter the previous conclusion that the indole reagents in THF contain no appreciable quantities of C-Mg-X species. The previous conclusion (same authors 1963) of an essentially covalent species such as



as a possible representation of the indole Grignard reagent in THF seems justified.

Contrary to alkali metal indole compounds, even at 60° the NMR spectra of a mixture of indole and indolylmagnesium bromide in THF show two distinct groups of signals, attributable to the separate compounds. With HMPT as the solvent both the alkali metal and the Grignard derivatives of indole display similar time-avarage NMR spectra indicating a rapid exchange. The authors conclude that the unique feature of the indole Grignard reagents appears to be its greater extent of intramolecular association in all solvents except HMPT.

D. Miscellaneous techniques

From the infrared and ultraviolet spectra of cyclopentadienylmagnesium compounds Ford concludes that such compounds consist of deloca-

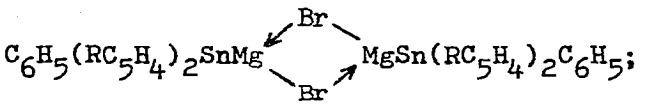
lized cyclopentadienide ions with magnesium located on or near the C_5 axis [92]. Cyclopentadienylmagnesium bromide and chloride probably are ion pairs and dicyclopentadienylmagnesium is probably an ion triplet. The appearance of two peaks in the NMR spectrum of cyclopentadienylmagnesium chloride at -115° indicates that the Grignard compound is composed of two discrete species as discussed under paragraph C of this chapter.

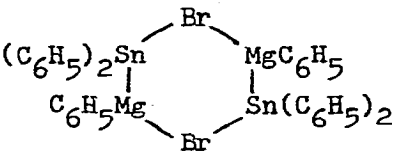
Low temperature NMR, infrared spectral investigations, fractional crystallization as well as dioxane precipitation studies by Ashby and Yu indicate that alkylmagnesium fluorides are dimeric in diethyl ether and in THF [93], probably due to the unusual stability of Mg-F-Mg bridge bonds in the dimeric units:

The ionic dissociation of alkylmagnesium bromides mentioned above in HMPT [81] was confirmed by measurements of the degrees of association by ebuliometric methods.

The solvation of diethylmagnesium by tetramethylethylene diamine, dimethoxyethane, THF and diethyl ether has been studied by Ducom with cryoscopic and NMR spectral techniques [94]. In these solvents an equilibrium exists between a disolvated monomer and a disolvated dimer; constants for such equilibria could be determined and the conclusion was drawn, that in more basic solvents the equilibrium is shifted to the side of the monomer which requires breaking of C-Mg bridge-bonds.

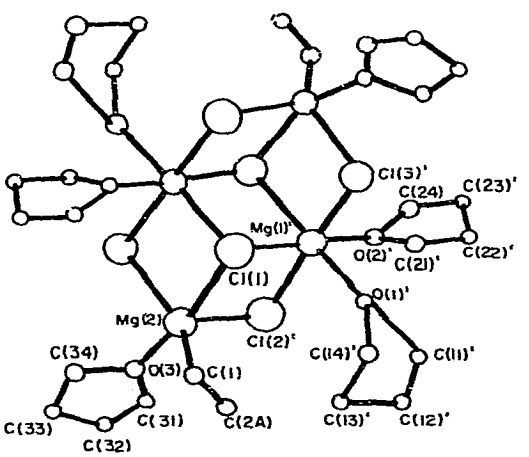
^{119m}Sn Moessbauer spectroscopy has been used to elucidate the structure of $(C_6H_5)_3SnMgBr$, $C_6H_5(C_5H_5)_2SnMgBr$ and of $C_6H_5(CH_3C_5H_4)_2SnMgBr$. The following structures are supposed to be the most reascnable ones for the different compounds [64]:

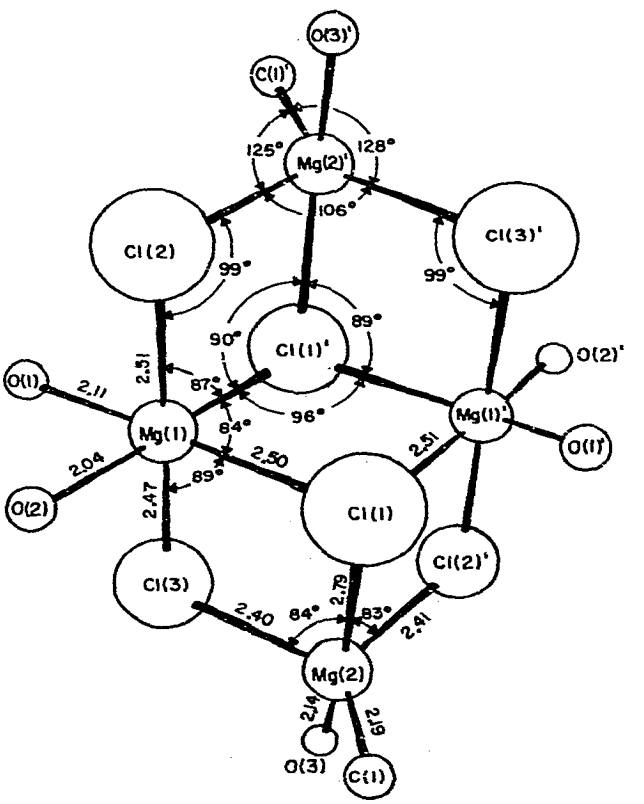




R = H or CH_3

As already partially discussed in last years survey Stucky and Toney resolved the crystal structure of $[C_2H_5Mg_2Cl_3(C_4H_8O)_3]_2$, in which compound penta- and hexa-coordinated magnesium atoms exist [95]. The molecular structure is indicated below together with a structure illustrating selected bond distances and angles:

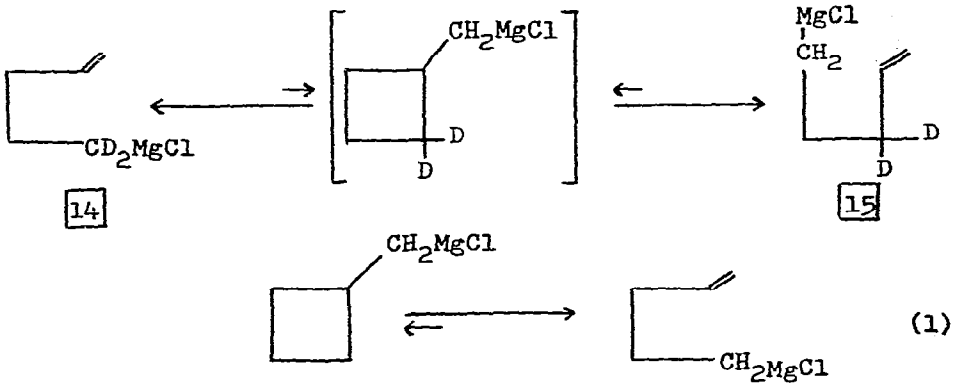




References p. 120

Davies, Roberts and Tudor report that, contrary to earlier reports by El-Fayoumy, Wahab and Roushdy (A.S. 1970) no isomerisation takes place in reactions of n-butyl-, isobutyl- and sec-butylmagnesium halides with boron trifluoride [102].

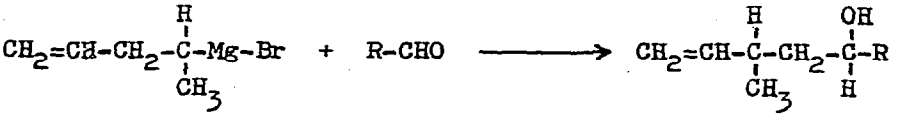
The Grignard reagent [14], prepared from 5-chloro-1-pentene-5,5-d_2 in THF lacks the high-field NMR signal of hydrogens α to a magnesium atom [103]. After heating during several hours at 140° a high-field



14 15 (1)

triplet appears from [15]. From the rate of appearance of these signals Hill and Ni calculated rate constants for ring cleavage reactions as well as a value of 2.5×10^{-3} (at 140°) for the equilibrium constant of equation (1).

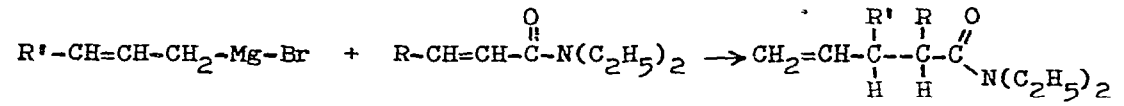
Several publications have appeared on structural changes of unsaturated Grignard compounds in reactions with different substrates. Ph. Miginiac and Couseeran found complete rearrangement of the γ-unsaturated secondary Grignard compound to the primary structure on reaction with an aldehyde in diethyl ether whereas the rearrange-



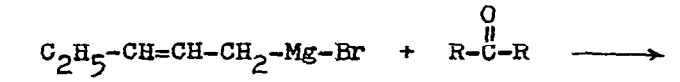
ment was very slow in THF [104]. In THF complete rearrangement was obtained after heating the reaction mixture during three hours. The same rearrangement occurs in reactions with oxygen.

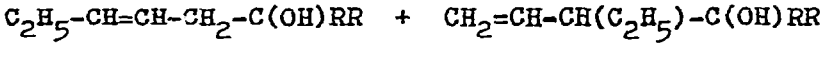
Rearrangement in substituted allylic Grignard compounds has been reported several times this year:

Ph. Miginiac and Daviaud found such rearrangement in the reaction with N,N-disubstituted α-unsaturated amides [105]:



The reaction of ethylallylmagnesium bromide with diisopropyl ketone yields both the unrearranged and the rearranged product but their relative amounts depend strongly on the solvents used (Miginiac and Barbot) [106]:



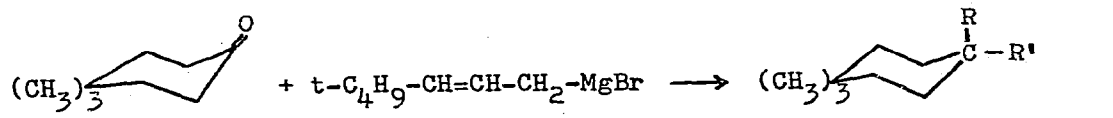


Addition of zinc bromide to the reaction mixture in THF yields the unrearranged product quantitatively. With pentanone-3 however only the rearranged product was obtained, independent of the addition of zinc bromide although the organozinc compound yielded the unrearranged product exclusively.

The mechanistic aspects of the rearrangements during the reactions of substituted allylmagnesium bromides with acetone and epoxycyclohexane will be discussed in chapter 4 A [107].

References p. 120

The reaction of t-butylallylmagnesium bromide with 4-t-butylcyclohexanone was investigated by Chérest and Felkin [108]:



Product a	Product b	Product c
R = $-CH_2-CH=CH-t-C_4H_9$	R = -OH	R = -OH
R' = -OH	R' = $-CH_2-CH=CH-t-C_4H_9$	R' = $-CH(t-C_4H_9)-CH=CH_2$

Ratio a : b : c = 41 : 33 : 26

The reaction of the same t-butylallylmagnesium bromide was found to be very sensitive for steric hindrance in the neighborhood of the carbonyl group (Felkin, Chérest and Frajerman) [109]. The ratio of unrearranged and rearranged products γ, increases in the following order:

	$(CD_3)_2C=O$	$(CH_3)_2C=O$	$(C_2H_5)_2C=O$	$(i-C_3H_7)_2C=O$
γ	3.1	3.4	8	>100

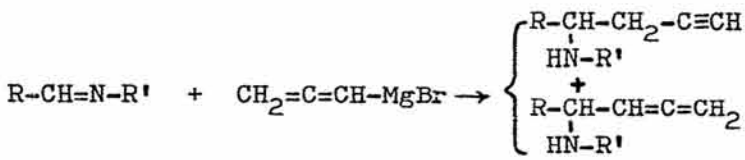
The difference in γ-values for the reaction with acetone and with acetone-d_6 is said to be in harmony with the view that secondary deuterium isotope effects are steric in origin, CD_3 being less bulky than CH_3.

In a comment on this report Kresge and Nowlan point out that hyperconjugative isotope effects are to be expected in this reaction thus making it unlikely that the isotope effect, found by Felkin and coworkers is wholly steric in origin [110].

Allene-propargylic rearrangements during reactions of Grignard compounds prepared from unsaturated bromides have been reported by Gaudemar as well as by Ph. and L. Miginiac this year.

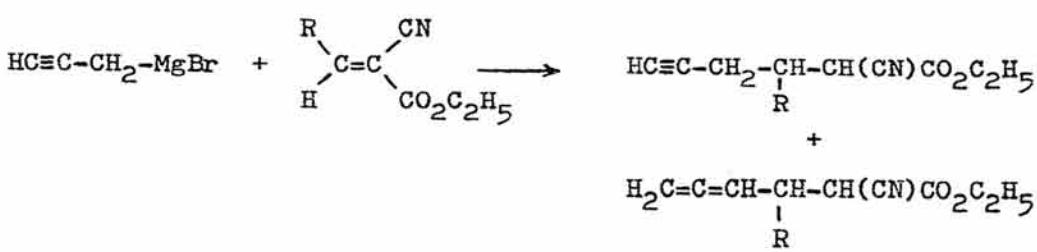
Together with Pierrot, Gaudemar investigated the reaction of allenylmagnesium bromide with bromo-acetylenic esters, with and without cuprous chloride as a catalyst [111].

Together with Moreau, Gaudemar reports on the reaction of aldimines with allenylmagnesium bromide [57]:



The yields of the two products (the allenic form was present in a small excess) were unsatisfactory which had to be attributed to side reactions of unreacted Grignard reagent with the secondary amines formed.

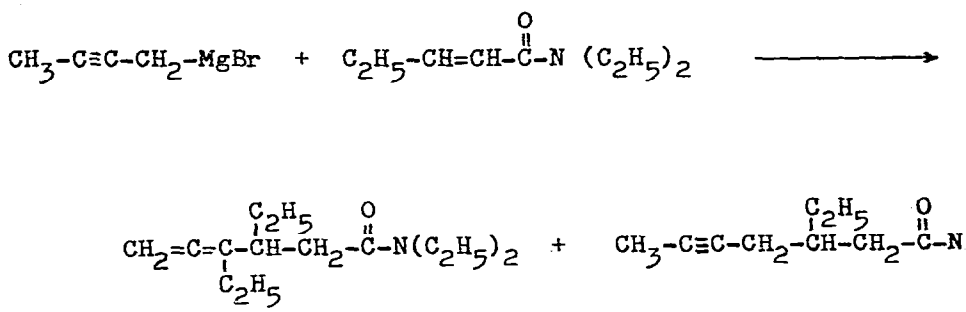
The same type of rearrangement has been observed by Ph. Miginiac, Daviaud and Massy-Barbot in the reaction of propargylmagnesium bromide with propyl- as well as with isopropyl-substituted ethyl ethylidenecyanoacetates [112]:



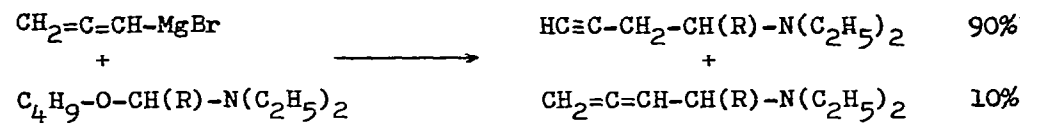
R = n-propyl or isopropyl

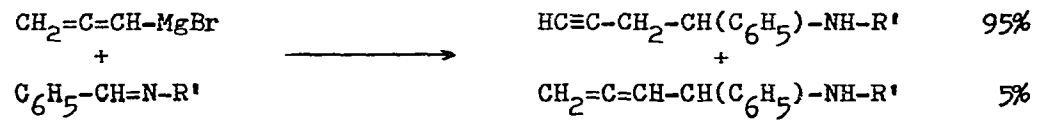
Another example of such a rearrangement was found by Ph. Miginiac

together with Daviaud in the following reaction [105]:

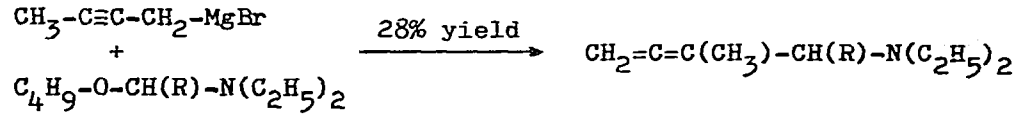


As was found by L. Miginiac and Nivert the main product of the reaction of allenylmagnesium bromide with gem-amino ethers as well as with aldimines is one with acetylenic structure [113]:

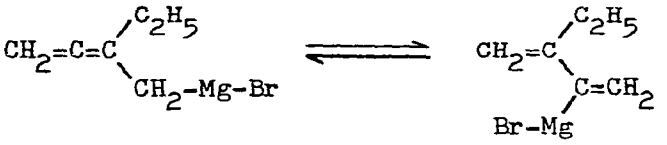




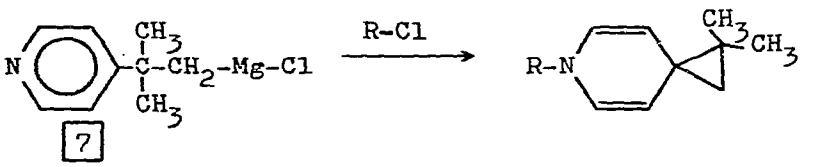
However the Grignard compound derived from 1-bromo-2-butyne yields the allenic product exclusively on reaction with gem-amino ethers:



In chapter 2 B iii the equilibrium between two unsaturated Grignard reagents



has been reported [56]. On reaction with acetaldehyde products were obtained containing both the allenic and the dienylic structure. 2-(4-pyridyl)-2-methyl-1-propylmagnesium chloride [7] treated with acid chlorides or trimethylsilyl chloride undergoes reaction at the nitrogen with quantitative formation of 1-substituted-4-(1,1-dimethylspirocyclopropyl)-1,4-dihydropyridines [37]:

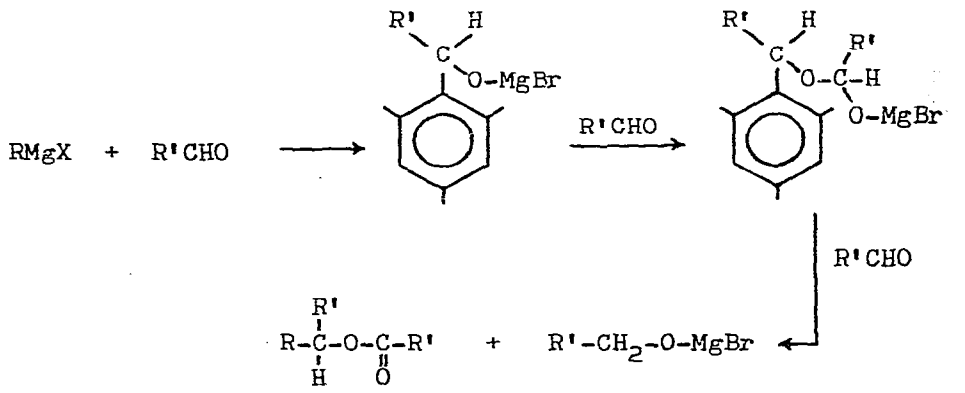


R = $CO_2C_2H_5$, CO_2CH_3, COC_6H_5, $COCH_3$ or $(CH_3)_3Si$

4. MECHANISM OF REACTIONS OF ORGANOMAGNESIUM COMPOUNDS

There seems to be no limitation to the reaction possibilities of organomagnesium compounds; this year too, several new types of reactions with different substrates have been reported and mechanims for such reactions have been proposed. Although most of these reactions will be discussed in the following chapter the report of Rieker, Butsugan and Shimizu seems surprising enough to function as an introduction to this chapter [114]:
sterically hindered phenylmagnesium halides react with a two-fold excess of an "oxidating" aldehyde (which also gives Cannizzaro-reactions), such as formaldehyde or benzaldehyde, to form an ester in

yields as high as 55%. The mechanism given by the authors



includes, among other reactions, an Oppenauer oxidation by the aldehyde. Substituents in the phenyl ring on the 2- and 6-position are essential for this anomalous reaction; phenylmagnesium bromide only yields the normal product(s?).

A. Reactions with carbonyl compounds

i. Addition reactions

The mechanism of the addition reaction of Grignard compounds as well as of dialkylmagnesium compounds with carbonyl groups has been studied with more intensity than ever this year.

El'yanov and Svetlanova conclude from their experimental results (reaction of ethylmagnesium bromide reaction with pinacolone at extremely high pressures; no change was found in the product composition compared to the reaction under normal conditions) that the formation of the transition states in these reactions must involve very similar volume changes [115].

Tuulmets and Luuk describe a new type of stopped-flow apparatus for thermogravimetric measurements of reactivities of organomagnesium compounds with different substrates; they report that the rate of the (second order) reaction of dimethylmagnesium with pinacolone at 20° is 27 ± 4 mole^{-1} sec^{-1} [116].

Since the solvent properties (dielectric constant in particular) have a great influence on the composition of the organomagnesium compounds in solution Tuulmets and coworkers have studied the kinetics of several reactions of organomagnesium compounds in different solvents: with Koppel the reaction of n-propylmagnesium bromide with pinacolone in methylal, diethyl ether of diethylene glycol [117], triethyl amine and N,N-dimethylaniline [118]. With Koppel, Loit and Luuk Tuulmets investigated the reaction of ethyl- and n-propylmagnesium bromides with pinacolone at 20° under pseudo-first order conditions in the binary mixtures of diethyl ether with n-heptane and dichloromethane [119]. The variation of the medium polarity has been carried out by adding non-solvating heptane or dichloromethane to the Grignard reagent in diethyl ether. The relative rate of addition in the reaction of ethylmagnesium bromide with pinacolone increases with increasing medium polarity.

The influence of the solvent polarity was also investigated by Tuulmets together with Pilt and Uus in relation to the increased reactivity of arylmagnesium bromide towards pinacolone or benzophenone by substitution in the aromatic ring [120]: p-tolyl- > phenyl- > p-chlorophenylmagnesium bromide.

It has become more and more evident that the addition reaction of organomagnesium compounds to carbonyl groups is extremely complex; apart from radical intermediates that might occur (see next paragraph) several competitive reactions are assumed to take place.

References p. 120

Tuulmets states [121] that the experimental results obtained when the reaction of n-propylmagnesium bromide with pinacolone was studied under pseudo-first-order conditions can not be simply explained on the basis of the simple scheme:

$$R\text{-}Mg\text{-}X + \underset{/}{\overset{\backslash}{C}}{=}O \rightleftharpoons \underset{/}{\overset{\backslash}{C}}{=}O.RMgX + R\text{-}Mg\text{-}X \longrightarrow \text{product}$$

nor by assuming R_2Mg to be the only reactive species:

$$R\text{-}Mg\text{-}R + \underset{/}{\overset{\backslash}{C}}{=}O \rightleftharpoons \underset{/}{\overset{\backslash}{C}}{=}O.R_2Mg \longrightarrow \cdots\cdots$$

A competitive reaction must be

$$X\text{-}Mg\text{-}X + \underset{/}{\overset{\backslash}{C}}{=}O \rightleftharpoons \underset{/}{\overset{\backslash}{C}}{=}O.MgX_2 + R\text{-}Mg\text{-}R \longrightarrow \text{product}$$

The contribution of each of these reactions to the product formation depends on the initial concentration of R-Mg-X, on the solvent (see above) and on the ratio $n = [Br]/[C_2H_5]$.

On the other hand Tuulmets, Luuk and Loit state that the pseudo-first-order rate constants of the reaction of excess ethylmagnesium bromide with pinacolone depends only poorly on the initial concentrations of the reagents [122]. A reaction scheme involving two pathways for the interaction of a ketone with dialkylmagnesium: a) direct reaction, and b) reaction through a ketone magnesium halide intermediate, seems to be the most acceptable to the authors to interpret the kinetic data observed by themselves as well as as reported by others (Billet and Smith, 1968; Ashby, Walker and Neumann, 1970).

Ashby, Laemmle and Neumann observed the rate of disappearance of the

absorption band at 410 nm which appears immediately when methylmagnesium bromide is allowed to react with excess 2-methylbenzophenone and which is attributed to a complex between ketone and CH_3MgBr [123]. The initial rate of product formation was equal to the rate of disappearance of the absorption band; product formation takes place via reaction of CH_3MgBr with ketone in a first order reaction as well as via reaction of $(CH_3)_2Mg$ with ketone (also first order). The same authors reported extensively on the reaction of dimethylmagnesium and 2-methylbenzophenone [124]. It consists of a series of reaction steps:

$$(CH_3)_2Mg + \text{Ketone} \rightleftharpoons \text{Complex} \longrightarrow \text{Product}_1$$
$$\text{Product}_1 + \text{Ketone} \rightleftharpoons \text{Complex}_1 \longrightarrow \text{Product}_2$$
$$\text{Product}_2 + \text{Ketone} \rightleftharpoons \text{Complex}_2 \longrightarrow \text{Product}_3$$

in which the products are $P_1 = (CH_3MgOR)_2$, $P_2 = CH_3MgOR.Mg(OR)_2$ and $P_3 = Mg(OR)_2$ with $R = -C(C_7H_7)(C_6H_5)CH_3$.
Although the formation of P_3 by the reaction of $Complex_2$ with a ketone has to be excluded in the reaction of dimethylmagnesium:

$$\text{Product}_2 \overset{K_2}{\rightleftharpoons} \text{Complex}_2 \xrightarrow{k_{cK}} \text{Product}_3$$

"in no case do the kinetic data allow one to distinguish between the following two mechanisms for the formation of P_3":

$$\text{Complex}_2 \overset{K_2}{\rightleftharpoons} \text{Product}_2 \xrightarrow{k_p} \text{Product}_3$$

which represents a simple bimolecular collision, and

$$\text{Product}_2 \overset{K_2}{\rightleftharpoons} \text{Complex}_2 \xrightarrow{k_c} \text{Product}_3$$

References p. 120

which reaction represents rearrangement of the complex.

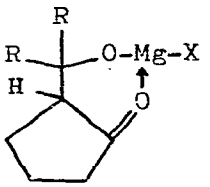
After all that has been reported about rapid equilibria in solutions containing organomagnesium compounds and reaction products the following observations by Gross, Georgoulis and Ziegler seems very surprising [125] : whereas methylmagnesium bromide reacts with di-tert-butyl ketone to give the addition product in almost quantitative yield dimethylmagnesium (as is well known) reacts with only one of its methyl groups to form a methylmagnesium alkoxide. However, addition of magnesium bromide to the product of this "half-way" reaction causes no change at all in the product yield, indicating that the Schlenk-equilibrium is not shifted to the right:

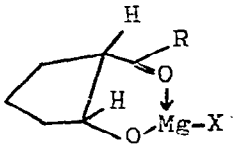
$$CH_3Mg\text{-}O\text{-}C(t\text{-}C_4H_9)_2CH_3 + MgBr_2 \not\rightleftharpoons CH_3MgBr + BrMg\text{-}O\text{-}\underset{CH_3}{C}(t\text{-}C_4H_9)_2$$

Using both a thermogravic technique and the quenching method in a rapid-flow apparatus Tuulmets, Luuk and Vaiga determined the pseudo-first-order rate constants for the reaction of ethylmagnesium bromide with 2-methylpentanone-4, 2,4-dimethyl-3-pentanone, acetone, butanone, 2-hexanone and 2-methyl-3-butanone [126]. The influence of the alkyl groups on the reaction rate was found to be determined above all by their steric parameters E_S^o.

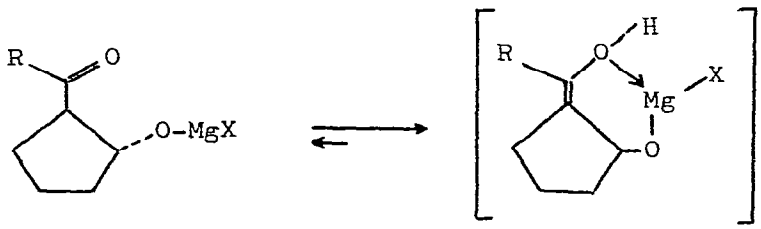
ii. Stereoselectivity of reactions of organomagnesium compounds with carbonyl groups

Reactions of phenylmagnesium bromide as well as of methylmagnesium bromide with β-hydroxycyclopentanes or with cis-β-oxocyclopentanols were stereospecific which was explained by Ghera and Shoua in terms of chelating effects in the intermediates formed:

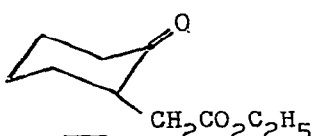




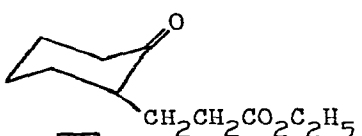
Reactions of the trans-β-oxocyclopentanol with both Grignard reagents resulted in product formation in low yield and low stereoselectivity; This had to be attributed to displacement of the following equilibrium to the right, so that chelation is made possible in the inter-



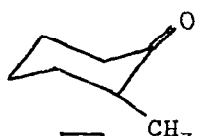
mediate but stereoselectivity is lost in the planar structure. This behavior in reactions of Grignard compounds seems to be specific for the cyclopentane ring; preliminary results with cyclohexane homologues suggest that formation of the chelated ring is more difficult [127]. Indeed Ficini and Maujean didn't notice any influence on the stereoselectivity of the addition reaction of methylmagnesium iodide with substituted cyclohexanones [16] and [17] as compared



[16]



[17]

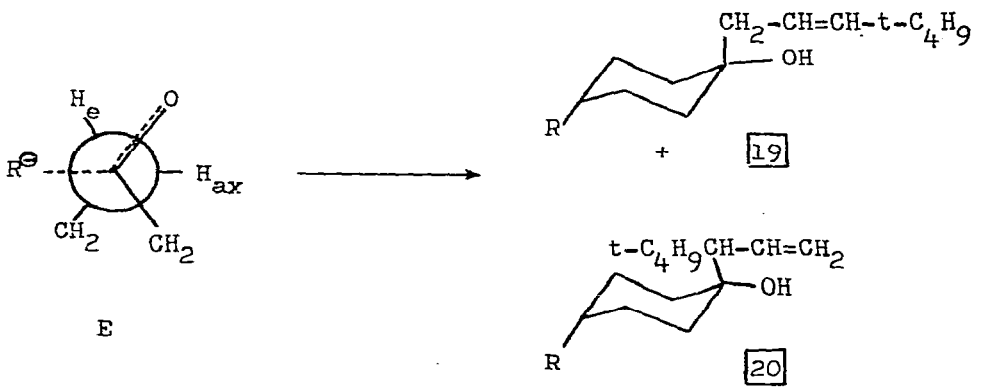


[18]

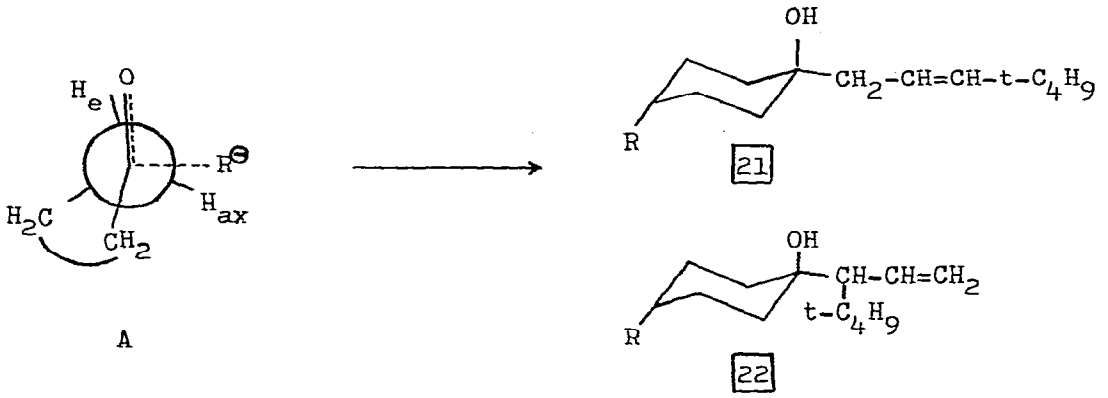
to the same reaction with 2-methylcyclohexanone [18] [128].

References p. 120

The reaction of methyl- or n-propylmagnesium bromide with 2-ethylcyclopentanone yields the trans addition product as the major one (80 : 20) as Chodkiewicz and Battioni report [129]. CH_3-C≡C-Mg-Br however gives the cis alcohol as the main product (cis-trans ratio 64:36). Much less difference in stereoselectivity was found for the addition reactions with 3-methyl- and 3-t-butylcyclopentanone.
As already mentioned in chapter 3E t-butylallylmagnesium bromide in its reactions with ketones is a sensitive measure of steric hindrance in the neighborhood of the carbonyl group [109]. Felkin and Chêrest investigated the factors governing the product formation in the reaction of this Grignard compound with 4-t-butylcyclohexanone [108]. Steric strain in the transition state, leading to the equatorial products [19] and [20] is real (yields [19] : [20] >100):



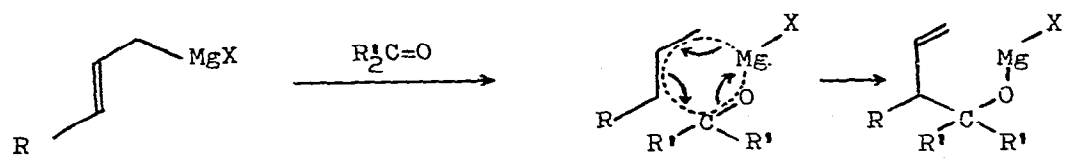
The ratio of the yields on axial products [21] and [22] is extremely small (1.3) from which it follows that the factor which impedes the formation of the axial epimer can not be steric strain involving H_{ax}



and t-butylallyl in the transition state A, nor can it be "product development control" since the less stable product is formed. The steric outcome is best ascribed to the net difference between the steric strain in the transition state E, leading to the equatorial alcohol and the torsional strain in transition state A, leading to the axial alcohol.

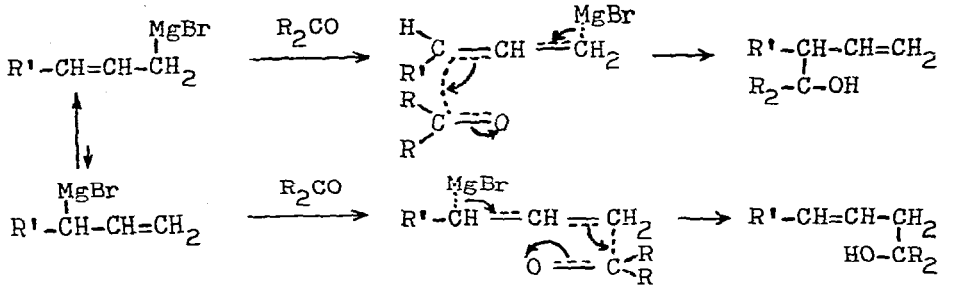
iii. Unsaturated organomagnesium compounds

Competition reactions of allylmagnesium bromide, butenylmagnesium bromide and α,γ-dimethylallylmagnesium bromide with acetone show that these three Grignard compounds have approximately the same reactivity (Felkin, Frajerman and Roussi; see also A.S. 1970) [109]. The S_Ei' mechanism described by the authors to rationalize the formation of the products is the following one:



Felkin, Chêrest and Frajerman point out that the steric strain in the transition state of such reactions might be considerable when

t-butylallylmagnesium bromide is used as the reactant [109]; as already mentioned above this reagent allows the authors to determine steric hindrance in the neighborhood of carbonyl groups:



iv. Reduction, enolization and addition reactions

Details are given of a mechanism, proposed earlier by Nasipuri, Ghosh and Mukherjee for the reduction reaction of organomagnesium compounds and ketones [130]; the following Newman-type formula

viewed along the C··H··C axis differs in two aspects from the transition state proposed by Matthie (1968): a) the model has been twisted along the C··H··C axis to relieve steric and torsional strain, and b) the two oppositely developing dipoles O^- and Mg^+ are loosely bound through space thus avoiding rigidity consequent to a cyclic model.

In accordance with results, previously obtained (together with Denise and Ducom; A.S. 1970) Fauvarque concludes from the results of his studies of the reaction of α-exo-deuterated isobornylmagnesium bromide with phenylisopropyl ketone (reduction of the ketone takes place with formation of phenylisopropyl carbinol) that the mechanism involves a planar cyclic six-membered ring [131].

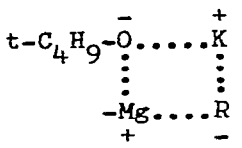
The influence of solvent or additives on the ratio addition/reduction reaction has been studied by several groups:

in the reaction of 2-hexylmagnesium chloride with pinacolone in diethyl ether, triethyl amine or β-phenylethyldimethyl amine Vitt and Khristova found a decrease in reduction products with increasing basicity of the solvent. Furthermore in diethyl ether the authors observed a considerable increase in reduction reaction products when the solutions were diluted [132].

Mme Fauvarque and Ducom compared the reactivities of diethylmagnesium and di-n-butylmagnesium with those of the corresponding Grignard compounds in diethyl ether and in HMPT as the solvent [82]. Combining the results obtained with those from measurements of electric conductivity of the organomagnesium compounds in ether/HMPT mixtures the authors conclude that the ionic form of R-Mg-X causes reduction in the reaction with phenylisopropyl ketone and enolization in the reaction with cyclohexanone.

The rate of the reduction reaction of diethylmagnesium with di-t-butyl ketone decreases with increasing basicity of the solvent (the authors used THF, DME, TMED and HMPT) as was reported by Gross, Georgoulis and Ziegler [133]. In HMPT a small amount of addition reaction occurs (about 2%); this amount is increased to 73% when equimolar amounts of potassium t-butoxide were added! In the "classical" reaction of n-propylmagnesium bromide with diisopropyl ketone

again the addition increases (79%) with increasing amounts of HMPT. The effect of potassium t-butoxide on the product formation in the same reaction mixture was studied: the authors point out two effects of the alkoxide: being a strong base it facilitates enolization of the ketone. Furthermore, by formation of a complex like



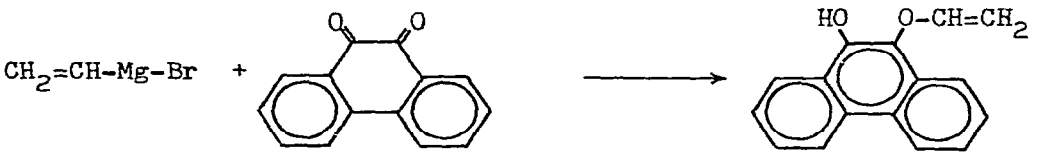
it accentuates the ionic character of the organomagnesium compound and thus promotes the addition reaction.

B. Radical reactions

The occurence of radical intermediates in reactions of organomagnesium compounds with a wide variety of substrates seems well established by now. It is not always clear which reaction conditions or which types of reactants are responsible for the formation of radicals; as already mentioned in chapter 2 D the presence of excess magnesium in the reaction vessel containing 1-nitroadamantane and t-butylmagnesium chloride causes a considerable increase in the formation of the radical product t-butyladamantyl nitroxide [75]. The formation of radical reaction products from reaction mixtures containing metal salts such as cuprous salts (see also chapter 2 D) is not at all surprising anymore.

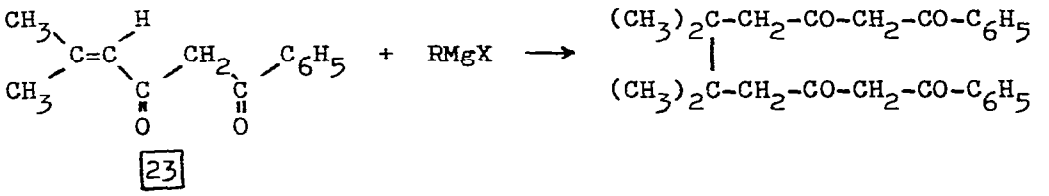
Among the radical reactions mentioned in 1971 the ones in which ketones are involved still are the most surprising; Wege found that vinylmagnesium bromide reacts with 9,10-phenanthrenequinone to form 9-hydroxy-10-vinyloxyphenanthrene in 50% (Blomberg, Grootveld, Ger-

ner and Bickelhaupt obtained 20% of the phenyloxy homologue using phenylmagnesium bromide; A.S. 1970); this product arises from radical intermediates as a result of electron transfer from the Grignard compound to the quinone. No abnormal radical reaction products



were obtained when phenanthrenequinone reacted with ethylmagnesium bromide or with methylmagnesium iodide. The author concludes that it is possible that the nature of the carbon-magnesium bond in the Grignard reagent is an important factor determining the mode of addition [134].

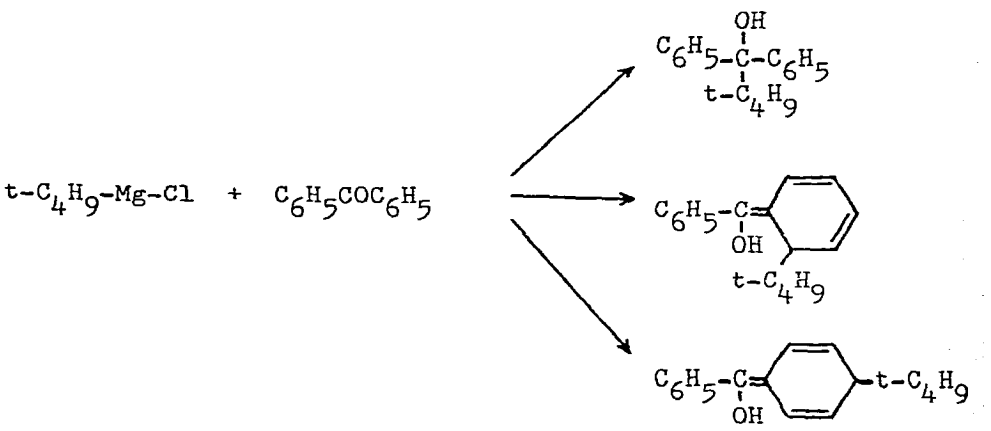
60%, 60% and 65% dimerization reaction products were obtained by Gélin, Gélin and DeHondt in the reaction of the β-diketone [23] with ethyl-, n-propyl- and t-butylmagnesium halides [135]:



The authors assume that the first step in the reaction is the transfer of an electron from the Grignard compound to the ketone followed by dimerization. It is to be noted that no such dimers are obtained in diketones with the phenyl group replaced by methyl; even more surprising, replacement of the cis-methyl group by a hydrogen

also seems to prevent radical formation!

Holm and Crossland added new dimensions to the reactivity of Grignard compounds when they discovered that in diethyl ether benzophenone reacted with t-butylmagnesium chloride to give not only 44% carbonyl addition reaction product (so-called 1,2 addition) but also products resulting from 1,4- and 1,6-addition [136]:

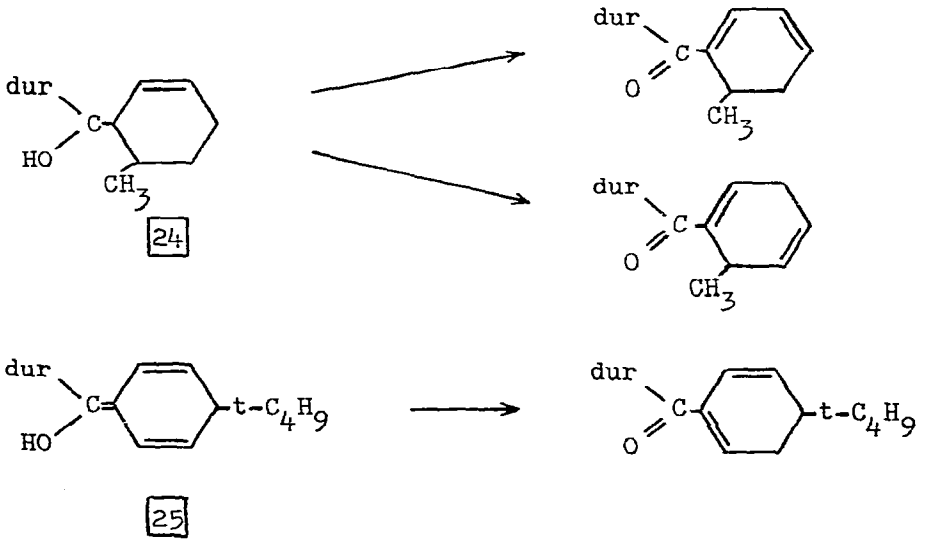


Using substituted benzophenones the authors obtained a variety of 1,2-, 1,4- and 1,6-addition reaction products together with benzopinacols. Measuring pseudo first order rate constants for the reaction of 0.56M t-butylmagnesium chloride with nineteen different benzophenones Holm and Crossland could plot log rate versus σ-substituent values, which resulted in a satisfactory Hammett plot for the sum of the four competing reactions. Steric factors evidently have no influence on the rate of the overall reaction as measured by the disappearance of the substrate. The authors conclude that the reactions are not independent but proceed through a common rate limiting step, most probably the one-electron transfer from the Grignard reagent to the benzophenone to form the ketyl radical anion and the

t-butyl radical. "This would indicate, that the radical path is not a side reaction, but rather constitutes the main, if not the only reaction mechanism".

For methylmagnesium bromide the same authors suggest that it reacts with hindered ketones such as benzoyldurene by the one electron mechanism but with unhindered benzophenones by a different, probably heterolytic mechanism. In this regard it has to be mentioned that Ashby and coworkers in their paper on the kinetics of the reaction of methylmagnesium bromide with benzophenone make the final remark that the absolute amount of free ketyl, formed in the reaction is apparently very small since product studies under the actual conditions gave 100% yield of addition product [123].

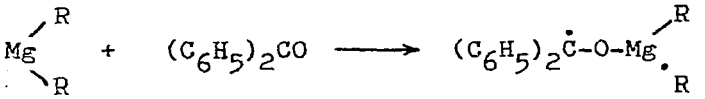
Holm and Crossland clarified the structure of the reaction products from methyl or t-butylmagnesium halides and benzoyldurene [137]. The rather labile enols [24] and [25] rearrange to secondary products:



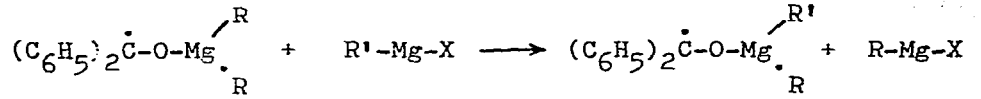
[24] [25]

Although a 1:1 mixture of isobutylmagnesium bromide and β-deutero-

isobutylmagnesium bromide on reaction with benzophenone yields benzhydrol with deuterium incorporation with an apparent isotope effect of 2.7, direct rate measurements of each of the Grignard compounds by Holm showed that the deuterated reagent is virtually as reactive as the non-deuterated [138]. This indicates the existence of a rate determining SET-step, different from the product determining hydrogen/deuterium transfer step. If it is assumed that dialkylmagnesium is the reactive species from which the electron is transferred the following intermediate could be proposed:



which can exchange rapidly with an alkyl group of the Grignard compound as follows:



The biradical intermediate may than collapse to benzhydrol and olefin with different deuterium contents. The formation of 1,4- and 1,6-addition products as mentioned above indicates the participation of a less complex radical species than the dialkylmagnesium "semiradicals"; since a 1,6-attack takes place far from the site of the initial electron transfer, separation of the radical from the magnesium is conceivable.

A single electron transfer reaction was also (tentatively) proposed by Reeve, Brown and Steckel to rationalize the formation of very uncommon products in the reaction of several Grignard compounds with aryl-, alkyl- and alkynyl(trichloromethyl)carbinol tosylates [139]. With phenylmagnesium bromide e.g. the reaction may proceed via the

following steps:

$$C_6H_5MgBr + \underset{\underset{OTs}{|}}{RCHCCl_3} \longrightarrow C_6H_5^{\bullet} + \underset{\underset{OTs}{|}}{RCHCCl_2}^{\bullet} + ClMgBr$$

$$C_6H_5^{\bullet} + C_2H_5OC_2H_5 \longrightarrow \underset{64\%}{C_6H_6} + CH_2\dot{C}H\text{-}O\text{-}C_2H_5$$

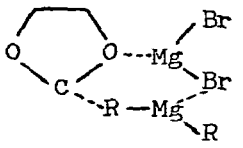
$$CH_3\dot{C}H\text{-}O\text{-}C_2H_5 + C_6H_5MgBr \longrightarrow \underset{13\%}{C_6H_5\text{-}C(CH_3)H\text{-}O\text{-}C_2H_5} + BrMg^{\bullet}$$

$$BrMg^{\bullet} + \underset{\underset{OTs}{|}}{RCHCCl_2}^{\bullet} \longrightarrow TsOMgBr + \underset{42\%}{RCH{=}CCl_2}$$

Diphenyliodonium chloride, bromide, iodide or tetrafluoroborate react with triphenylmethylmagnesium chloride to form radicals (ESR signals) as reported by Levit, Kalibabchuk and Gragerov [140]. Evidently a single electron transfer occurs; diphenyliodonium chloride reacts with methylmagnesium iodide to give methane (containing 5% ethane) which also proves the formation of (methyl) radicals.

C. Miscellaneous reactions

Orlova, Trofimov and Atavin propose the following intermediate in the reaction of a 1,3-dioxolane with a Grignard compound [141]:

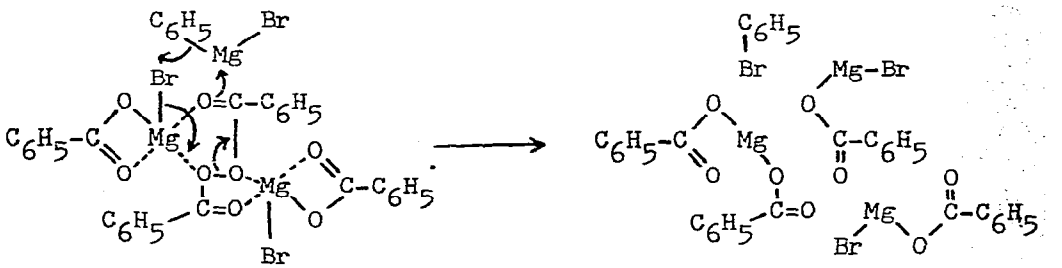


which collapses to give products as a result of cleavage of the

1,2-carbon-oxygen bond.

Complex formation between cyclic acetals and magnesium iodide was investigated by Esofov and Azarova [142]: stable complexes of the type $MgI_2.2L$ have been isolated with the ligand L being 2,2,6-trimethyl-4-ethyl-1,3-dioxane, 2,2,6-trimethyl-4-isopropyl-5-ethyl-1,3-dioxane and 2,2,5,5,6-pentamethyl-4-ethyl-1,3-dioxane. Pyrolysis of these complexes results in the formation of aldehydes, ketones and other products.

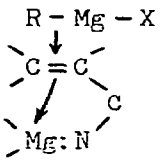
Dubsky and Jacot-Guillarmod investigated the reaction of benzalacetone with butyl- and phenylmagnesium compounds [143]. Conjugate addition to the unsaturated ketone is favorized by participation of monomeric species such as the diorganomagnesium.pyridine complexes. The structure of the complex formed on addition of phenylmagnesium bromide to benzoylperoxide was investigated by Okubo, Maruyama and Osugi [144]. If phenylmagnesium bromide is added slowly and in very small drops the magnesium-bromine bond in the complex is attacked exclusively which leads to the formation of bromobenzene and magnesium salts of benzoic acid



In the reactions of Grignard compounds like n-C_4H_9, C_6H_5-, C_6H_5-C≡C-, -C_4H_9-C≡C-, C_6H_5-CH=CH-, i-C_4H_9-CH=CH- and n-C_4H_9-CH=CH-Mg-Br with

substrates such as carbon dioxide, formaldehyde, trimethylchlorosilane, etc. the nucleophilic reactivity of the Grignard compound decreases in the order : vinyl, aryl, alkyl, acetylenyl Grignard compound as was found by Zakharkin, Gravilenko and Palei [145]. In the metallation reaction with carbon-hydrogen acids such as acetylene the decreasing order of reactivity is: allyl, vinyl, aryl, acetylenyl Grignard compound.

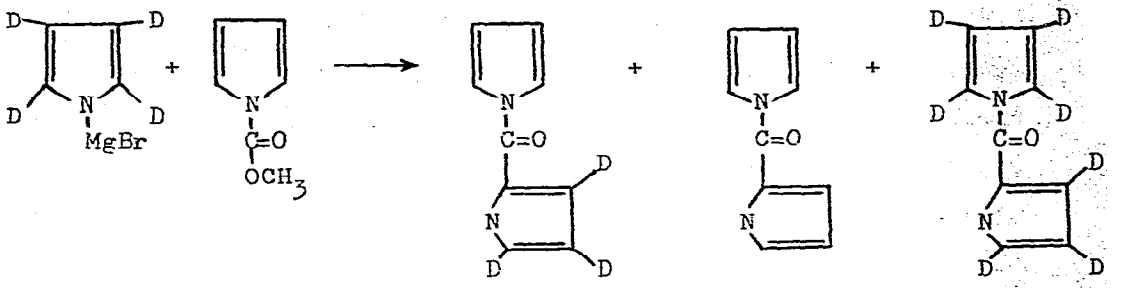
In analogy to the reactions of allylic Grignard reagents with unsaturated alcohols Richey, Erickson and Heyn observed addition of allylic Grignards to ethylenic and acetylenic carbon-carbon bonds in amines such as C_6H_5-CH=CH-CH_2-NH_2, C_6H_5-CH=CH-$N(CH_3)_2$ and C_6H_5-C≡C-CH_2-$N(CH_3)_2$ [146]. No addition occurs to 1-phenyl-1-propene or to 1-phenyl-1-butyne, not even in the presence of one of the amines mentioned above; the authors assume therefore that addition probably is due to complex formation of magnesium to the amine function.



The coordinated magnesium (in analogy to what is suggested for the reaction with unsaturated alcohols) may facilitate the addition of an external Grignard reagent, perhaps by acting as an electrophile.

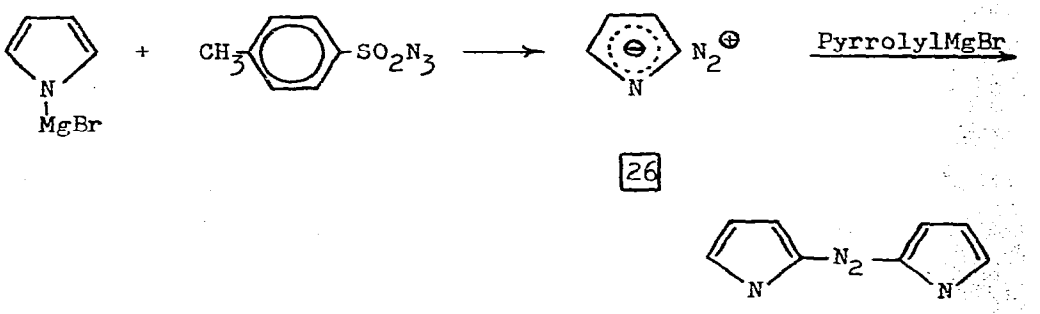
To elucidate the mechanism of the reaction of pyrrolylmagnesium bromide with methyl 1-pyrrolecarboxylate, Loader and Anderson made use of deuterated reagents [100]; pyrrolyl-d_4-magnesium bromide reacts with undeuterated 1-pyrrole carboxylate to form 1,2'-dipyrrolyl ketone

References p. 120

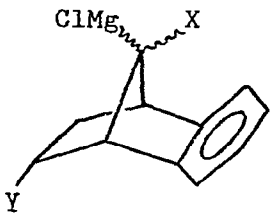


Reaction of 1-pyrrole-(2,3,4,5-d_4)-carboxylate with undeuterated pyrrolyl Grignard reagent resulted in the formation of the d_4-ketone beside other products among which undeuterated ketone. The authors conclude that the reaction proceeds by direct acylation at the 2-position of the Grignard compound rather than by initial substitution onto the 1-position followed by rearrangement to the 2-position. Furthermore at an intermediate stage, ring interchange takes place between the 1-substituted pyrrole ring in the intermediate and unused Grignard reagent.

The reaction of pyrrolylmagnesium bromide with toluene-p-sulfonyl azide yields 2,2'azopyrrole (15% yield) which supports a mechanism in which 26 is formed as the intermediate [101]:



From the reaction of (substituted) cyclopentadienylmagnesium bromide (or chloride) with benzyne no products could be isolated which could have been formed by a stepwise nucleophilic addition reaction of the Grignard compound (Ford; See also A.S. 1970) [147]. The simplest mechanism which accounts for the formation of the intermediate Grignard reagents [27] is [3 + 2] cycloaddition of benzyne to cyclopenta-



X= CH_3, $Si(CH_3)_3$ or H
Y= H or CH_3

[27]

dienyl anions which may also be called $\pi^4s + \pi^2s$ cycloaddition.

Finally, in this chapter dealing with mechanisms of reactions of organomagnesium compounds a series of papers by Tamura and Kochi need special mention. These authors have reinvestigated the well-known Kharasch reaction of Grignard compounds with alkyl halides in the presence of metal salts and paid special attention to the formation of organometallic intermediates.

With silver salts the authors propose the following catalytic mechanism [148]:

$$R'MgX + AgX \longrightarrow R'Ag + MgX_2$$

$$R'Ag, RAg \longrightarrow R\text{-}R,\ R'\text{-}R,\ R'\text{-}R' + 2\ Ag$$

$$Ag + R\text{-}X \xrightarrow{\text{slow}} R\cdot + AgX$$

$$R\cdot + Ag \longrightarrow RAg, \text{ etc}$$

The oxidative dimerization of Grignard reagents with $AgNO_3$ was unique in that less than stoichiometric amounts of silver(I) were required

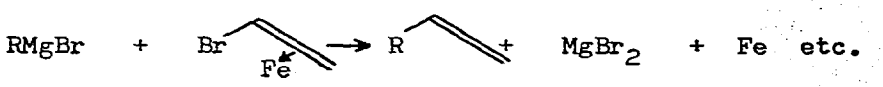
since nitrate was capable of reoxidizing silver. With $LiNO_3$, nitrogen dioxide or nitromethane only catalytic amounts of AgBr were required. Coupling reactions by silver and copper, despite their similarity, occur by fundamentally different mechanisms; the authors propose the following mechanism for the copper catalyzation [149]:

$$\begin{aligned} RMgBr &+ Cu^{I}Br \longrightarrow RCu^{I} + MgBr_2 \\ RCu^{I} &+ R'Br \xrightarrow{slow} R\text{-}R' + Cu^{I}Br, \text{ etc.} \end{aligned}$$

The catalysis by iron takes place via a mechanism which is a combination of those proposed for silver and copper [150] and [151]:

$$\begin{aligned} RBr &+ Fe \longrightarrow R\cdot + FeBr \\ R\cdot &+ Fe \longrightarrow RFe \\ R'MgBr &+ FeBr \longrightarrow R'Fe + MgBr_2 \\ RFe, R'Fe &\longrightarrow RH, R'H, R(-H), R'(-H) + 2Fe, \text{ etc.} \end{aligned}$$

The authors in particular studied the coupling reaction with alkenyl halides and found these reactions to proceed stereospecifically, e.g. with cis- and trans-propenyl bromide; alkenylation proceeds therefore via a Fe-assisted displacement of the alkenyl halide by the Grignard reagent:

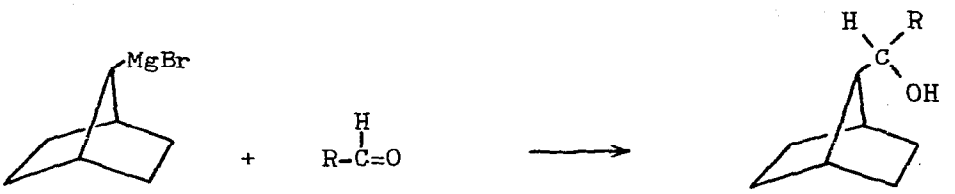


In another paper this year the authors report the results of studies of the reaction of Grignard compounds with metal halides in which those of Co(II), Ni(II), Pd(II) and Mn(II) are included beside the metal salts mentioned above; the reactions are coupling, disproportionation and exchange reactions with olefins [152].

5. REACTIONS OF ORGANOMAGNESIUM COMPOUNDS

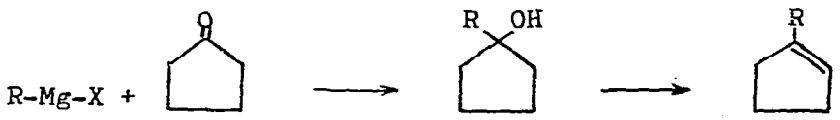
A. Reactions with aldehydes and ketones

Belikova, Gazuko, Plate and Sterin obtained the expected carbinols in 32% and 36% yields when bromo 7-norbornylmagnesium reacted with formaldehyde or acetaldehyde in diethyl ether [58]:



R = H or CH_3

Mosumzadze, Gurbanov, Shabanov and Dzharadova obtained alkyl-substituted cyclopentenes by dehydration of the carbinols, obtained in the reaction of alkylmagnesium halides with cyclopentanone in diethyl ether [154]:



R = CH_3-, C_2H_5-, n-C_3H_7-, i-C_3H_7- and n-C_4H_9-

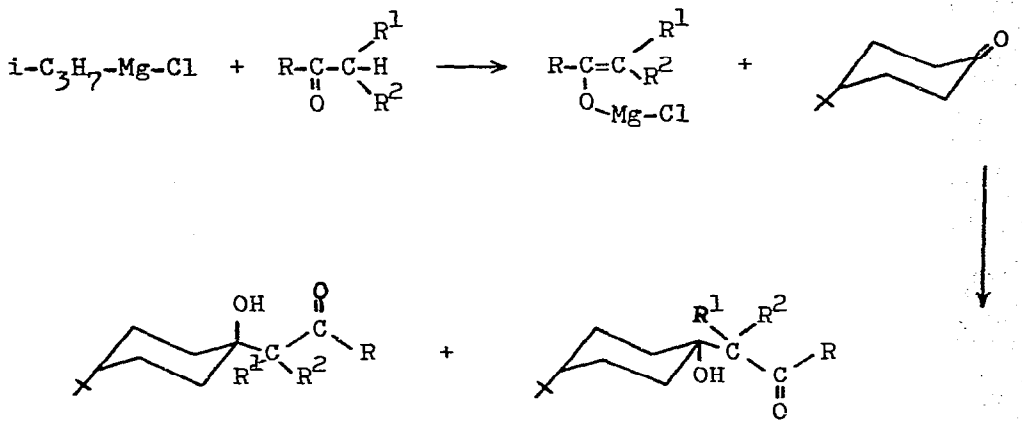
Ethylmagnesium bromide, prepared in benzene and an optically active amine ((-) sparteine) reacts with benzaldehyde and acetophenone to give the expected carbinols in 15% and 11% yield respectively with 22% and 0% optical purity [74].

The stereochemical aspects of the reaction of organomagnesium compounds with substituted cyclic ketones have been studied by several groups and some of the mechanistic implications were mentioned in chapter 4 A ii. The following reports will therefore be mentioned

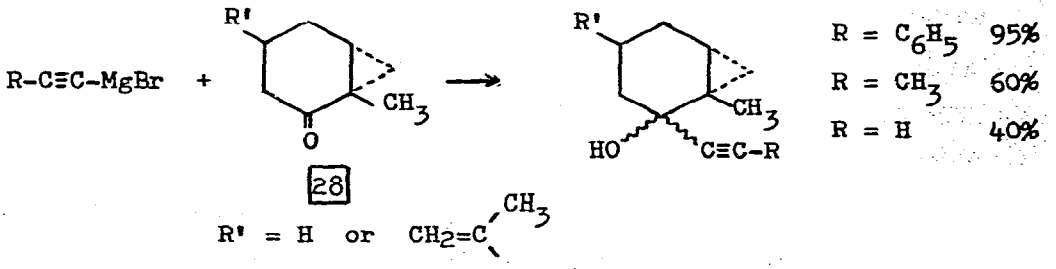
only briefly:

Jones, Kauffman and Goller compared the stereochemistry of addition and reduction reactions of n-propylmagnesium reagents with those of the corresponding cadmium and zinc reagents in their reactions with 4-t-butylcyclohexanone [155].

Cantagrel and Maroni-Barnaud determined the cis/trans ratios in the ketoalcohols, obtained in the interesting reaction of the chloromagnesium enolates of sterically hindered ketones with 4-t-butylcyclohexanone [156]:



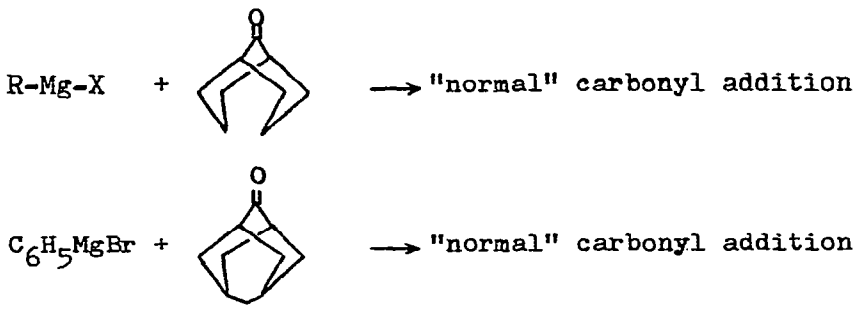
Rocquet, Sevin and Chodkiewicz report that alkylmagnesium halides don't add to the carbonyl double bond in the cyclic ketone [28] but that yields as high as 95% were observed in the addition reaction of acetylenic Grignard compounds and the same ketone [157]:



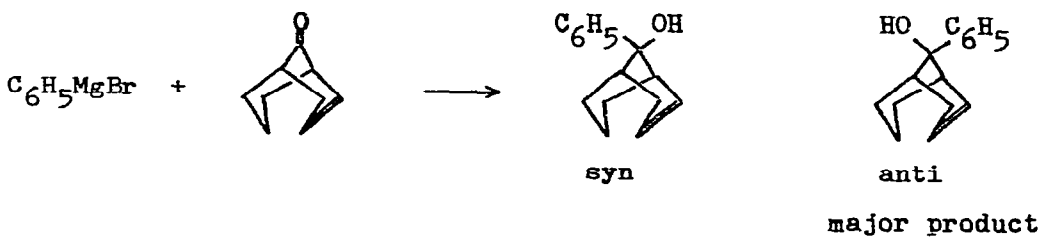
28

R' = H or $CH_2=C(CH_3)$

Baiocchi and Giannangeli investigated the reactions of Grignard compounds with polycyclic ketones as depicted in the following equations (including adamantone) [158]:



The stereochemical aspects were studied of the reaction of phenylmagnesium bromide with bicyclo[3,3,1]non-2-en-9-one:



syn anti

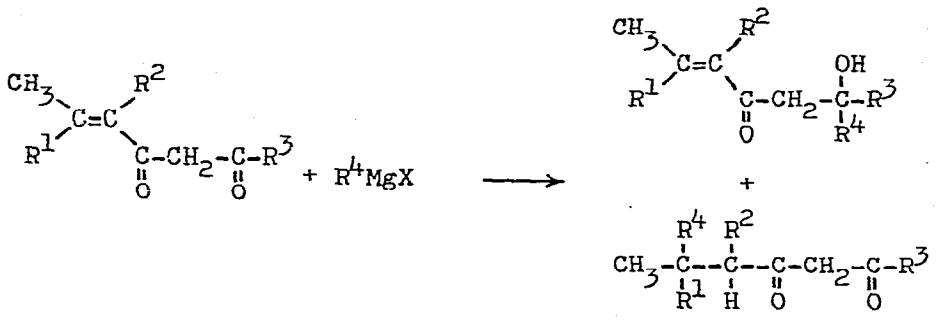
major product

Several reports have appeared dealing with reactions of organomagnesium compounds with diketones:

Barabás and Balaban give detailed reports of the reaction of benzylmagnesium chloride with acetylacetone resulting in the formation of both the mono- and the diaddition product [159] (preliminary reports were given by the same authors in 1967 and 1969 and by Canonne and coworkers in 1966 and 1967).

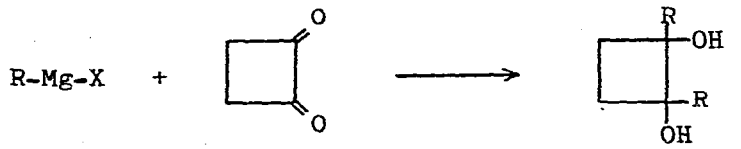
As already mentioned in chapter 4 B aliphatic Grignard compounds may react with unsaturated β-diketones via radical intermediates

[135]. With several substituents however conjugate addition may also occur as indicated:

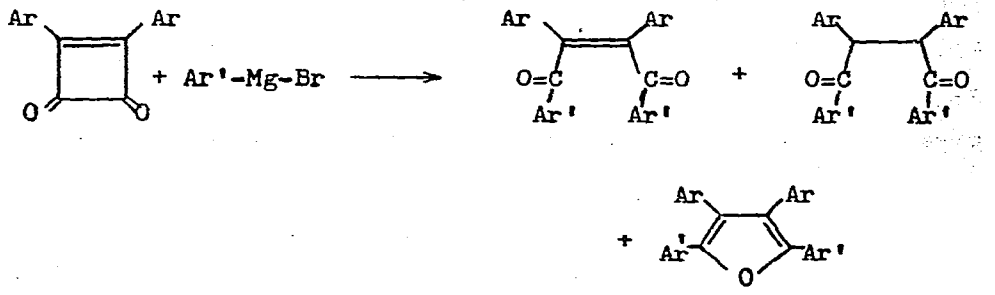


Addition to the carbonyl double bond takes place with ethyl- and phenylmagnesium bromides and with R^1 and R^3 being methyl groups and R^2 being hydrogen. For R^1 is methyl, R^2 is hydrogen and R^3 is phenyl addition to the carbonyl double bond takes place only with phenylmagnesium bromide.

Methyl- and ethylmagnesium compounds react with cyclobutadione in a normal fashion to give the diaddition products [160]:



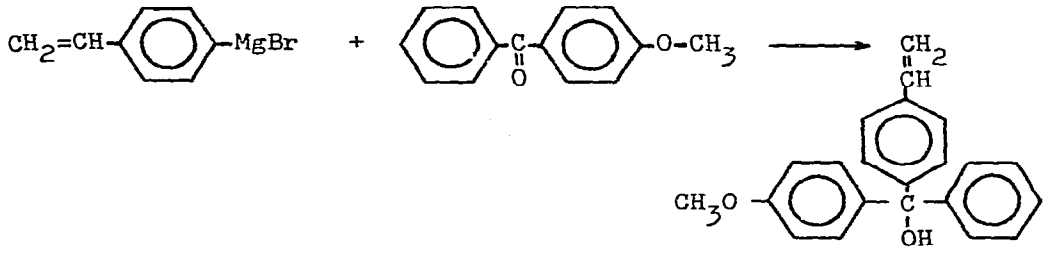
Ried and Lantzsch observed an unexpected ringscission in the reaction



in which Ar is either phenyl or p-tolyl and Ar' is phenyl, p-tolyl or p-anisyl [161]. With aliphatic Grignard compounds a complicated mixture of products is obtained.

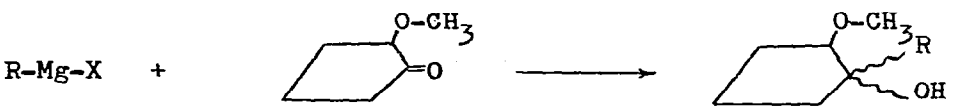
Several reactions were reported of alkoxy-substituted ketones and organomagnesium compounds:

Potapov, Kochetkova and Shabarova reported the following reaction



the product of which was used for polymerization reactions [162].

Guillerm-Dron, Capmau and Chodkiewicz observed the formation of trans products in the reaction of aliphatic and β-unsaturated Grignard compounds (propargylic and allylic) with 2-methoxypentanone whereas



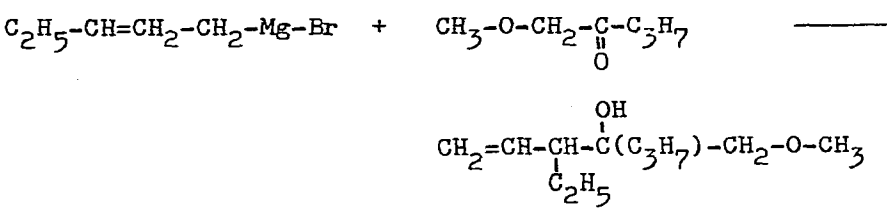
the cis products were preferentially formed in reactions with acetylenic Grignard compounds [163].

The reaction of Grignard compounds of different types (including aliphatic Grignard compounds as well as unsaturated Grignard compounds such as CH_3-O-CH=CH-C≡C-MgBr) with the vinyloxy ketone: CH_2=CH-O-CH_2CH(CH_3)-CO-CH_3 leads to the expected addition reaction

References p. 120

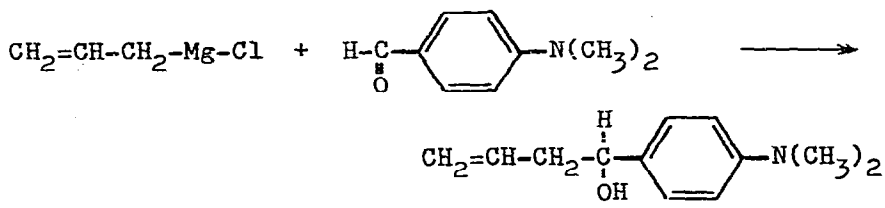
products in yields varying from 40 - 85% [164].

Rearrangement is observed in the reaction of ethylallylmagnesium bromide with 1-methoxy-2-pentanone as was found by L. Miginiac and Lanoiselee [165]:

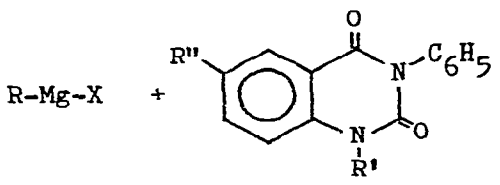


In several publications amino carbonyl compounds were used in reactions with Grignard reagents:

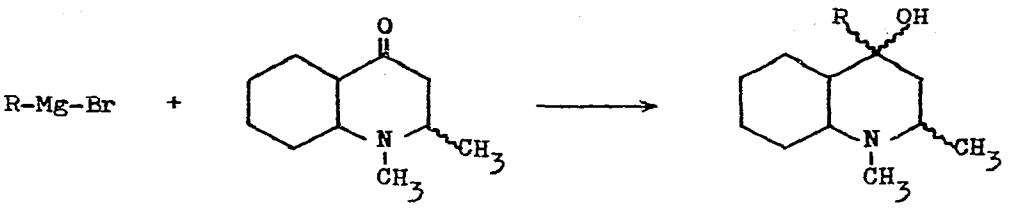
Allylmagnesium chloride in diethyl ether mixed with an emulsion of p-dimethylaminobenzaldehyde yields the "normal" butenol [166]:



The reaction of methyl-, ethyl-, phenyl- and p-anisylmagnesium bromide with 3-phenyl-2,4-(1H,3H)-quinazolinedione has been reported: [167]:

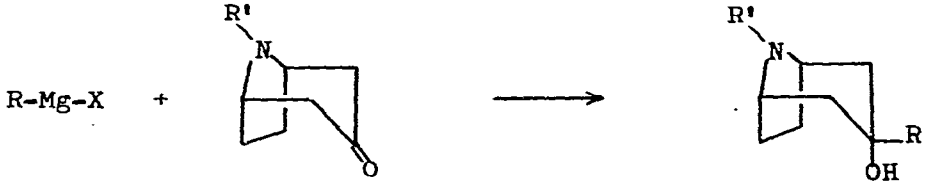


Akhrem, Ukhova and Uskova investigated the reaction of ethynyl- and of vinylmagnesium bromide with 1,2-dimethyldecahydro-4-quinolone; the steric effect of the C-2 methyl group on the product formation

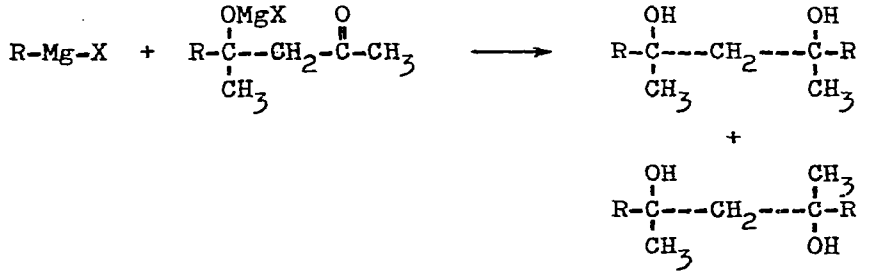


is discussed [168].

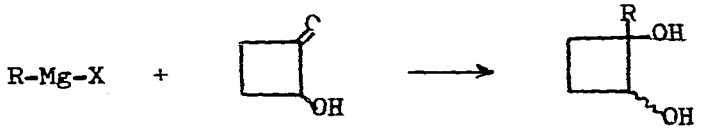
N-substituted tropines were obtained by Fischer and Mikite by the reaction of Grignard compounds with N-substituted tropinones [169]:



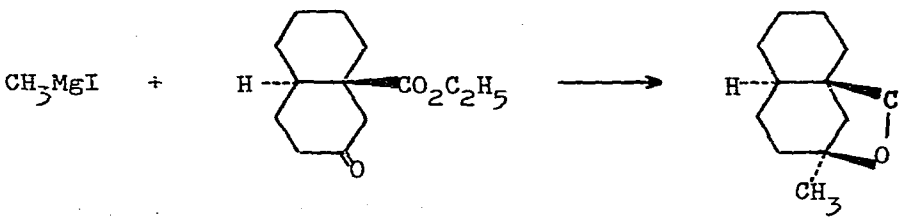
Michel and Canonne studied the stereochemistry of the reaction of two equivalents of R-Mg-X with acetyl-acetone in which reaction an intermediate is formed which can be regarded as the bromomagnesium alkoxide of a β-hydroxyketone [170]:



2-Hydroxycyclobutanone reacts with several Grignard compounds to form cyclobutanediols [160]:

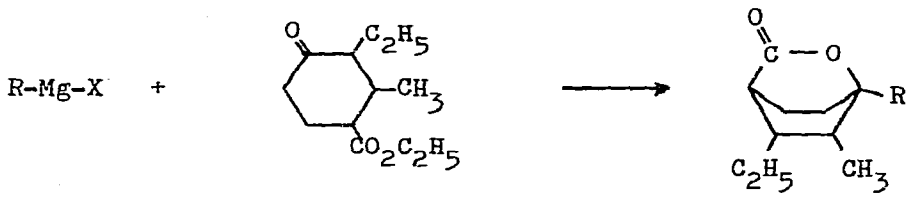


The following two reports of reactions of Grignard compounds with keto esters are given in equations only:



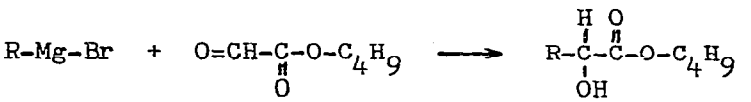
[171]

and



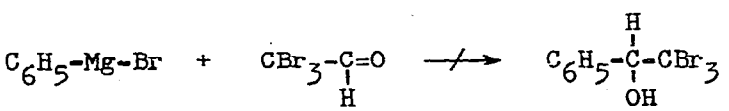
[50]

Two reports from Akimova and Orlikova deal with the reaction of n-butylglyoxylate with Grignard compounds; addition to the aldehyde function takes place [172] and [173]:

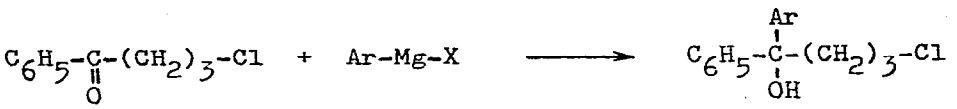


R = n-C_4H_9- or iso-C_4H_9-

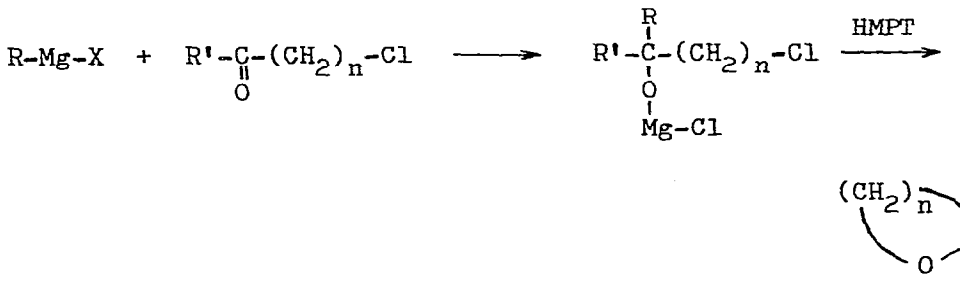
Reactions of organomagnesium compounds with halogen substituted aldehydes and ketones have also been reported several times in 1971: although phenylmagnesium bromide reacts with chloral to give 60% of the expected carbonyl addition product bromal fails to react with the the same Grignard reagent [174]:



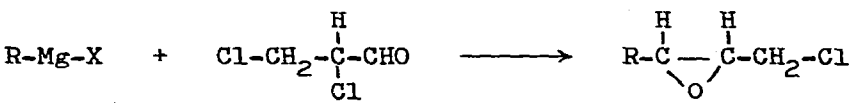
Reactions of aromatic Grignard compounds with fluorinated dimethoxybenzoic esters, leading to the formation of fluorinated dimethoxybenzophenones are discussed by Lubemets, Gerismova and Fokin [175].
The reaction of an aromatic Grignard compound with a γ-chloro ketone



was mentioned in a Russian patent [175].
Several reactions of chlorinated ketones with Grignard compounds were reported by Combret, Larchevêque and Leroux [176]:



on addition of HMPT to the reaction mixture cyclization occurs due to the enhanced nucleophilicity of the alkoxide in this solvent. The authors report the preparation of a multitude of oxetanes, oxolanes, oxanes and oxepanes. Applying α-alkoxy-Grignard compounds with chloro-substitution such as $Cl-CH_2-CH_2-O-CH_2-Mg-Cl$ the authors synthesized a number of dioxanes by the same methods!
Chloroepoxides were obtained by Shigo and Shinichi by the reaction of Grignard compounds with 2,3-dichloro-1-propanal:

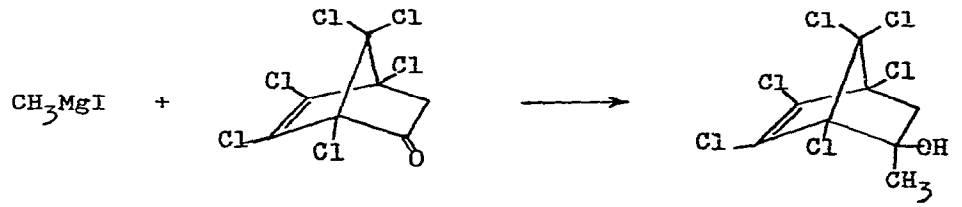


with R is methyl (27 % yield), R is ethyl (39 % yield) and R is

styryl (12 % yield) [177].

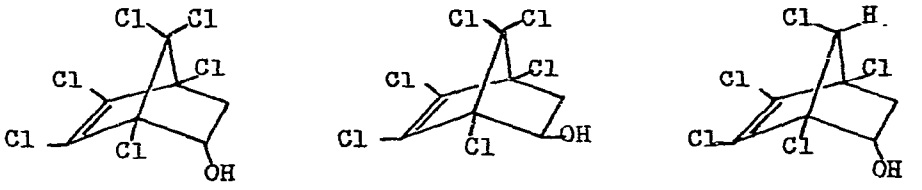
Davies, Masson and Parrott investigated the reaction of methyl-, ethyl- and isopropylmagnesium halides with 1,4,5,6,7,7-hexachloronorborn-5-en-2-one [29] [178]:

methylmagnesium iodide yields products derived from endo-attack exclusively (as does lithiumaluminum hydride in a reduction reaction):



[29]

Reactions of ethylmagnesium bromide and isopropylmagnesium chloride with [29] gave no tertiary alcohols but the following three products:



[30] [31] [32]

With ethylmagnesium bromide only 4-8% of [32] is formed whereas with isopropylmagnesium chloride [32] is formed in yields as high as 34%. The authors suggest that this great difference might be related to the degree of association of the Grignard reagents concerned: ethylmagnesium bromide being monomeric can only form [32] in a two-step

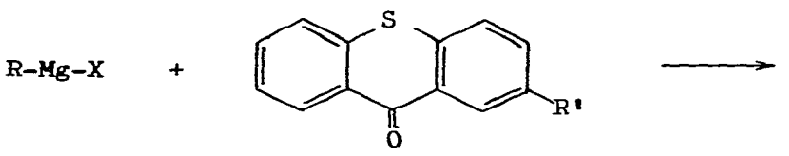
mechanism whereas in the case of the reaction of the dimeric isopropylmagnesium chloride with [29] the reaction might proceed via a single step mechanism.

Finally in this paragraph reactions of Grignard compounds with the following carbonyl compounds have to be mentioned:

Horspool, Stanley, Sutherland and Thomson reacted methyl-, ethyl- and phenylmagnesium halides with ferrocenylmethyl ketone [179].

The stereoselectivity of the reaction of Grignard compounds with ferrocenyl ketones, substituted in the α-position by substituents such as hydroxymethyl and dimethylaminomethyl was investigated by Moise, Tirouflet and Sautrey [180].

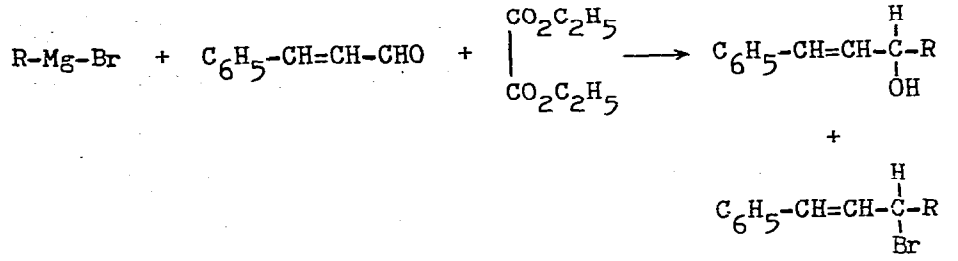
The following reaction with a substituted cyclic thia ketone was reported:[181] :



with R is cyclopropyl or allyl and R' is chlorine or SO_2-N(-CH_3)$_2$.

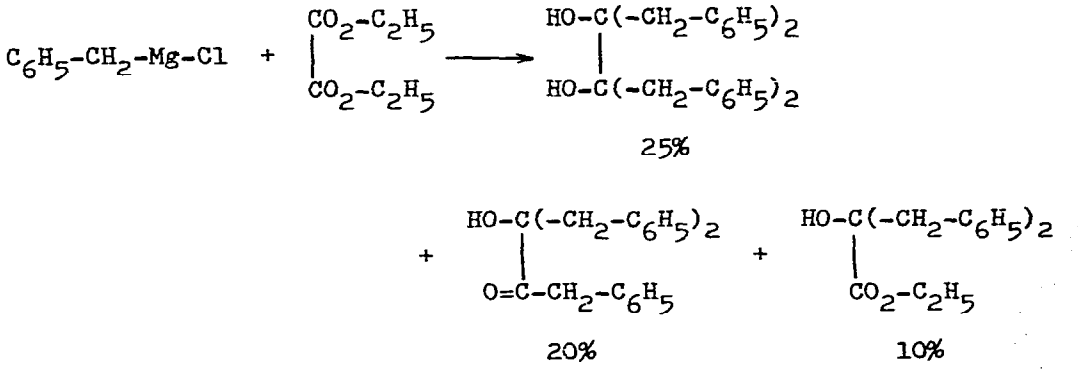
The reaction of methylmagnesium bromide with a steroidal ketone of complicated structure, sapogenoic acid ester, was reported by Barton, Kulkarni and Sammes [182].

Of the following report unfortunately the original print is difficult to obtain which is to be regretted because of the surprising information in the abstract: although phenyl-, p-tolyl-, ortho- as well as para-anisylmagnesium bromide react with cinnamaldehyde to give the "normal" products in fair yields (50% to 85%) addition of diethyl oxalate to the reaction mixture causes the formation of the corresponding bromide in high yields [183]:

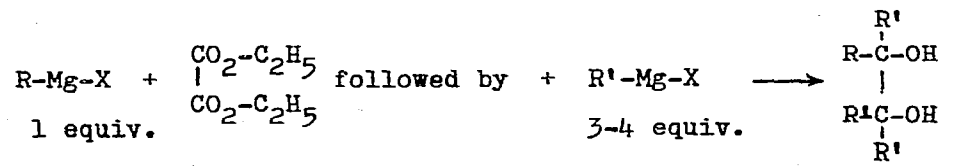


B. Reactions with esters, lactams, imines, lactones etc.

An excess of benzylmagnesium chloride reacts with diethyl oxalate to give the normal reaction product in 25% yield beside a product, resulting from the reaction with only one of the ester groups (10%) and a keto alcohol (20%) [184]:



Mixed vicinal diols were obtained by Lapkin, Svinina, Karavanov and Skvortsova by the two-step addition of different Grignard compounds to diethyl oxalate [185]:



R = 3,4-dimethylphenyl-, naphthyl-, n-hexyl-, n-heptyl-, n-octyl- and n-nonyl-

R' = n-propyl-, phenyl- and p-tolyl-

As already reported in chapter 5 A n-butyl glyoxylate reacts faster with its aldehyde function than with the carboxylate group when isobutyl- or n-butylmagnesium halides are added to it in diethyl ether [172] and [173].

Emptoz, Huet and Jubier investigated the composition of the products obtained on reaction of a Grignard reagent with an ester or an other acid derivative in HMPT [186]. Almost exclusive formation of ketone is observed in the reaction of isopropylmagnesium halide with aliphatic acid esters:

$$i\text{-}C_3H_7\text{-}Mg\text{-}X + R\text{-}CO_2\text{-}CH_3 \xrightarrow{HMPT} R\text{-}\underset{\underset{O}{\|}}{C}\text{-}i\text{-}C_3H_7$$

R = n-C_3H_7 : 45 % yield; R = i-C_4H_9 : 51 % yield
R = s-C_4H_9 : 65 % yield; R = t-C_4H_9 : 27 % yield

With derivatives of benzoic acid n-butylmagnesium bromide gives not only the corresponding ketone but also products resulting from reactions with the intermediate ketone, i.e. addition and reduction reactions. Since the ratio of these two reactions is constant (about 1 : 2 - 1 : 3) with ethyl benzoate, benzoyl chloride and benzoic acid anhydride it is unlikely that other reaction mechanisms are to be assumed for the formation of the alcohols.

Coutrot, Combret and Villiéras found a facile route to α-chloroepoxiketones by reaction of Grignard compounds with α-chloroglycidic esters [187]. The results are:

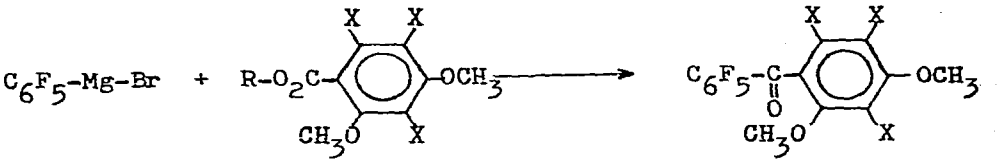
$$RMgBr + (CH_3)_2CH\text{-}\underset{\diagdown O \diagup}{CH}\text{—}C(Cl)CO_2CH_3 \xrightarrow{-78^\circ} (CH_3)_2\underset{\diagdown O \diagup}{CH}\text{—}C(Cl)\text{-}\underset{\underset{O}{\|}}{C}\text{-}R$$

R	CH_3	C_2H_5	$(CH_3)_2CH$	C_6H_5	cy-C_6H_{11}
Yield in %	55	72	50	31	56

References p. 120

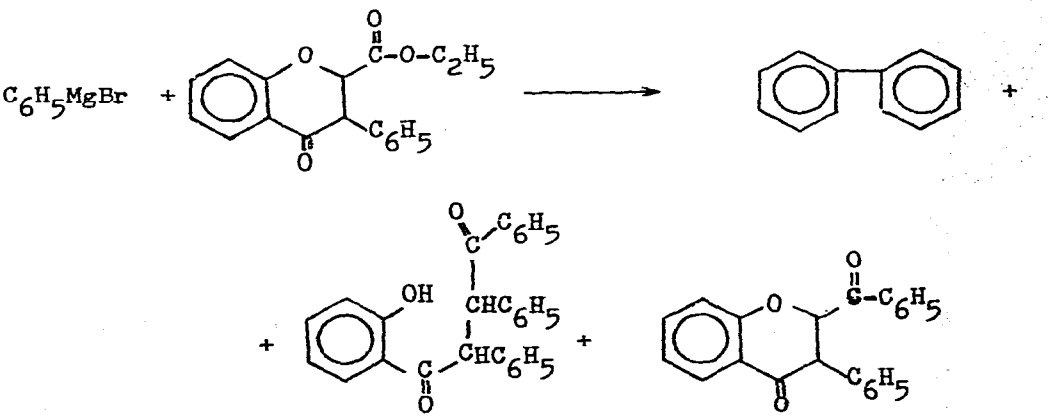
The authors report that at elevated temperatures (-50°) the chloro epoxy ketone reacts further with Grignard compounds to give tertiairy alcohols. Several other substituents were introduced in the glycidic ester and the product yields were determined. No such reactions were found with the much more reactive bromo glycidic esters. The major product in this case is a bromo diketone.

According to Lubemets, Gerisimova and Fokin aromatic fluorinated ketones are formed by the following reactions [188]:



with X = H or F

The reaction of phenylmagnesium bromide with ethyl 3-phenylchromon-2-carboxylate yields a variety of products among which biphenyl, 2-benzoyl-3-phenylchromon and 2,3,4-triphenyl-1-(o-hydroxyphenyl)-2-butene-1,4-dion were mentioned by Holmberg and Jalander [189]:



Extending their investigations on the reactivity of the alkoxyimino-group versus Grignard compounds, Pornet and Mme. L. Miginiac added the iminocarbonate $C_6H_5-N=C(O-C_2H_5)_2$ to organomagnesium halides [190]; the following types of reactions were observed:

$$R-Mg-X + C_6H_5-N=C(O-C_2H_5)_2 \longrightarrow C_6H_5-N=C(R)-O-C_2H_5 \quad a$$

$$R-Mg-X + C_6H_5-N=C(O-C_2H_5)_2 \longrightarrow C_6H_5-N=CR_2 \quad b$$

$$R-Mg-X + C_6H_5-N=C(O-C_2H_5)_2 \longrightarrow C_6H_5-\underset{\underset{H}{|}}{N}-CR_3 \quad c$$

Isopropylmagnesium halides do not react at all with the iminocarbonate; n-butylmagnesium bromide gives not more than 21% of a product resulting from type a reaction; the same type of reaction product was obtained with phenylmagnesium bromide, however in 78% yield. Allylic Grignard compounds gave high yields of products resulting from reactions of type c. When the allyl- group is substituted with R rearrangement occurs resulting in the formation of several isomeric products.

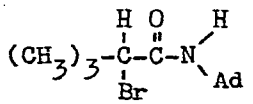
Phenylmagnesium bromide reacts with 1-adamantyl-3-t-butylaziridinone to form an α-aminoketone, as reported by Lengyel, Mark and Troise [191]

$$(CH_3)_3C-CH\begin{array}{l}\diagdown\\ \diagup\end{array}\begin{array}{l}N\\ |\\ Ad.\end{array}\!\!>C=O + C_6H_5MgBr \longrightarrow (CH_3)_3C-\underset{\underset{NHAd}{|}}{CH}-\overset{\overset{O}{\|}}{C}-C_6H_5$$

Ad. represents an adamantyl-1 group

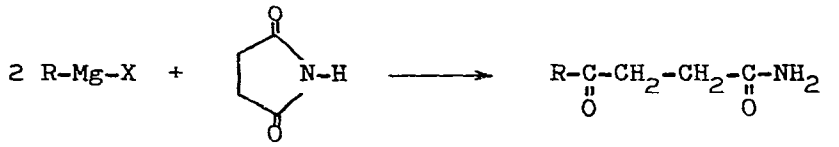
Thin layer chromatography of the crude product indicated the presence

of



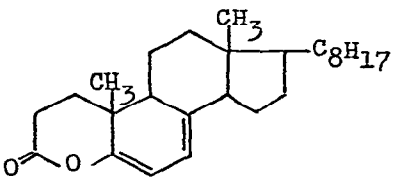
which type of product is claimed by Talaty and coworkers (A.S. 1970) to be the only reaction product of both alkyl and aryl Grignard reagents with α-lactams. In a control experiment by Lengyel c.s. it was shown that the α-bromoamide was formed exclusively in 90% yield in the reaction of magnesium bromide with the α-lactam under investigation.

Sekiya and Terao report the following ring-opening reaction [192]:

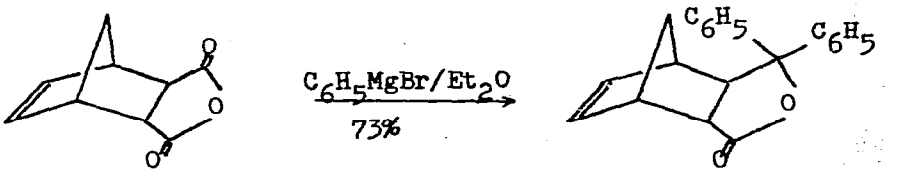


in which the group R can be alkyl as well as aryl.

A variety of products was obtained by Whitehurst and Overnell from the reaction of methyl-, ethyl- and isopropylmagnesium halides with the steroid A-ring lactone [193]:



Sugita and Tamura report the following reaction with exo-cis-bicyclo [2,2,1]hept-5-ene-2,3 dicarboxylic acid anhydride [194]



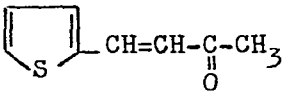
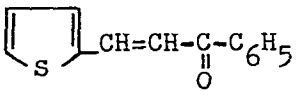
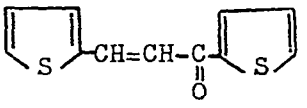
The endo-isomer gives the same reactions but the yields were poor in that case.

C. Reactions with unsaturated ethers, esters, ketones, etc.

Reactions of organomagnesium compounds with unsaturated ketones may lead to 1,2- as well as to 1,4-addition reactions.

Conjugate addition of phenylmagnesium bromide to 1-benzylidene-2-acenaphthenone, accompanied by reaction with the ether solvent has been reported by Tsuge and coworkers [195] (see also A.S. 1969).

Churkin and Putokhin investigated the reaction of several Grignard compounds with unsaturated thienyl ketones such as

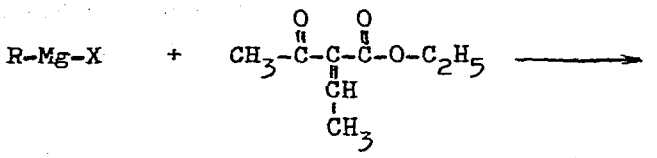
and observed 1,2- as well as 1,4-addition: the relative amount of 1,2-addition reaction product decreases in the series methyl > 2-thienyl > β-naphthyl. With the latter compound no reaction occurred at all [196] and [197].

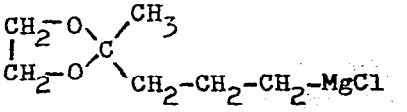
Reactions of diphenyl- and di-n-butylmagnesium pyridine complexes with benzalacetone have been mentioned in chapter 4 C [143].

Marets and H. Rivière obtained enolates from the reaction of phenylmagnesium bromide with α,β-unsaturated ketones [198]. The configuration of the enolacetates, obtained on acetylation depends on the substitutent in the α position of the unsaturated starting ketone.

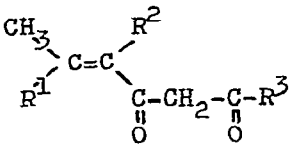
The reaction was studied of several different Grignard reagents with ethylideneacetylacetonate by Kutznetsov and Guznenok [199]:

References p. 120



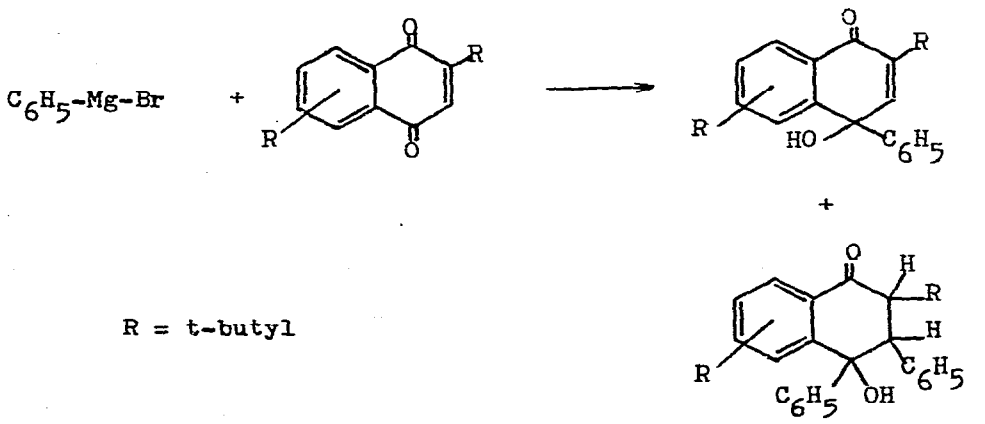
R = isopropyl, n-decyl, phenylethynyl and 

The radical type reaction as well as the normal 1,2-addition reaction of Grignard compounds with the unsaturated diketone



which also undergoes 1,4-addition has been reported in chapters 4B and 5A [135].

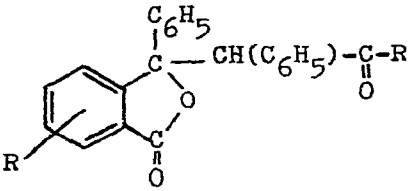
According to Crawford phenylmagnesium bromide reacts with 2,6- as well as with 2,7-di-t-butyl-1,4-naphthoquinone to give the expected mono- and diaddition products [200]:



R = t-butyl

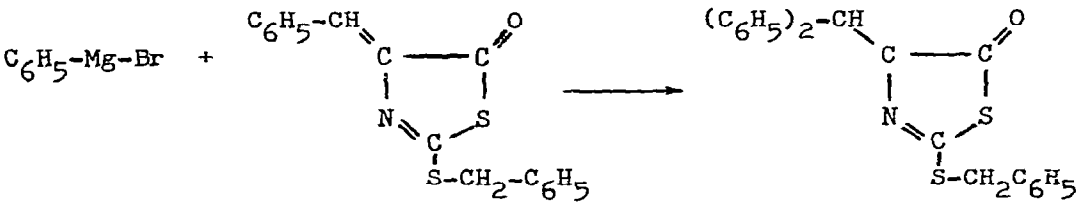
50% and 60%

If the solvent ether is evaporated from the reaction mixture before hydrolysis with ammonium chloride has taken place 30% and 50% of the phthalides :

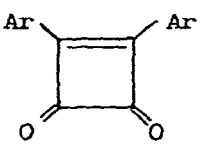


are obtained!

Mustafa, Harhash, Elmagdi and Abd El-All observed exo-cyclic conjugate double bond addition in the reaction of phenylmagnesium bromide with 2-benzylthio-4-benzylidene-2-thiazoline-5-one [201]:

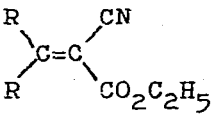


The peculiar ring scission in the reaction of aromatic Grignard compounds with the unsaturated cyclic diketone



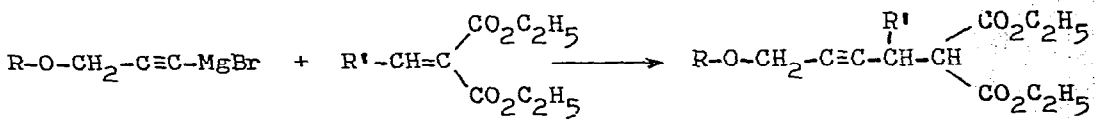
as reported by Ried and Lantzsch [161] has been mentioned already in chapter 5 A.

Several reports have appeared concerning conjugate addition of Grignard compounds to double bonds in unsaturated esters; the reaction (accompanied by rearrangement) of propargylic Grignard compounds with alkylidenecyanoacetates

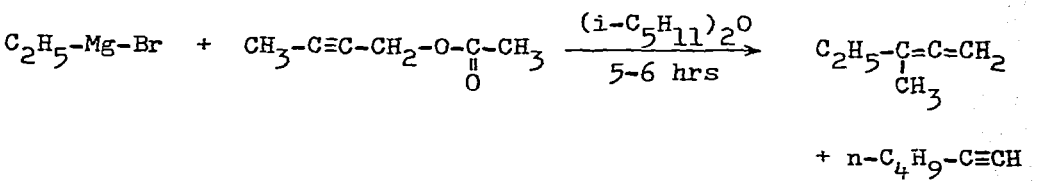


as reported by Miginiac and co-workers has been mentioned in chapter 3 E [112].

Frangin, Couffignal and Gaudemar report conjugate addition of 3-alkoxy-1-propynylmagnesium bromide in the reaction with diethyl alkylidenemalonate [52]:



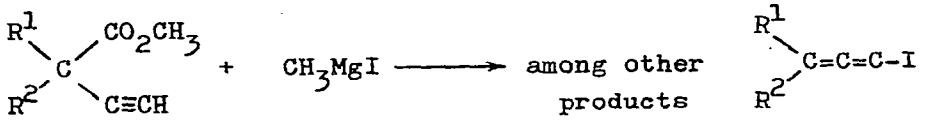
But-2-ynyl acetate reacts with Grignard compounds under substitution of the acetoxy group by the group R of the organomagnesium compound, as was reported by Voskanyan, Piruzyan, Gasparyan and Mkryan [202]; rearrangement of the alkynyl entity to an allenic structure takes place partially. As an example the following reaction is given:



The main product is methylethylallene (92%); 1-hexyne is formed for 8% only. The authors report that also 2-butyn-1-ol is formed as a minor product.

The same type of reaction was investigated by Gore and Roumestant [203]; 1,1-disubstituted prop-2-ynyl acetates react with methylmag-

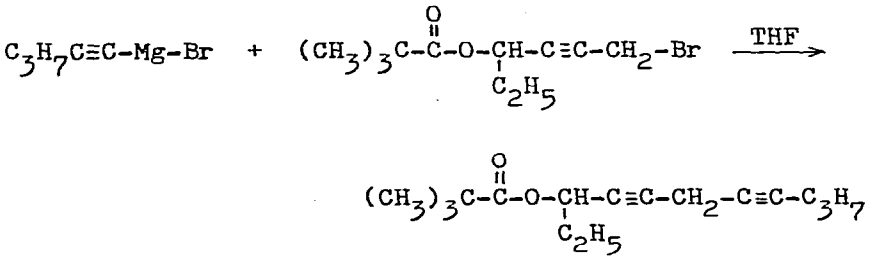
nesium iodide to form the products of the type mentioned above together with iodoallenes:



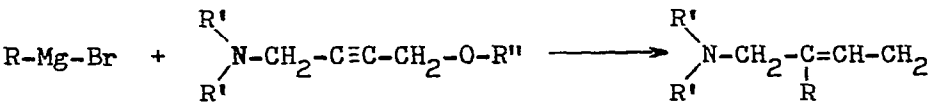
The yield of iodoallenes is increased to 50 % when four molar equivalents of magnesium iodide are added!

Conjugate addition was also observed in the reaction of Grignard compounds with (-)menthyl iminoglyoxylates as reported by Fiaud and Kagan [204]:

The following reaction in which an unsaturated ester is involved was reported by Pierrot and Gaudemar [111]:



The reaction of 1-N,N-dialkylamino-4-alkoxy-2-butyne with aliphatic Grignard compounds leads to addition to the acetylenic triple bond under displacement of the alkoxy group as reported by Mkryan, Gasparyan and Melkonyan [205]:



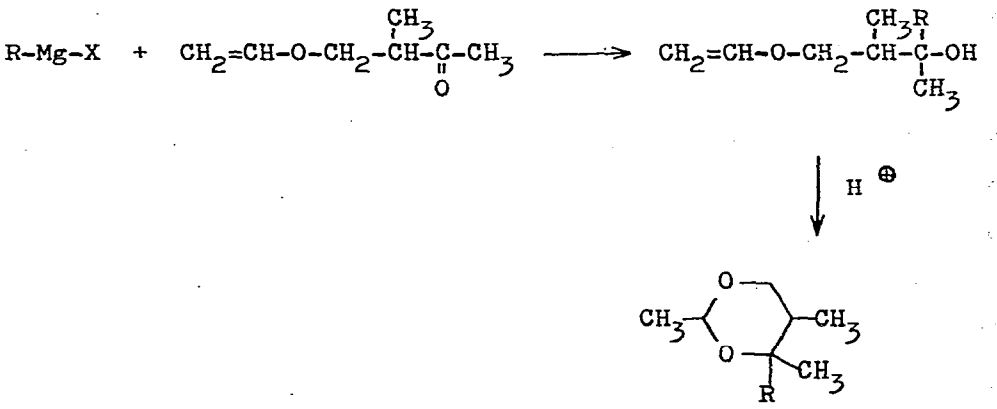
R is methyl, ethyl or n-propyl

R' is methyl or ethyl

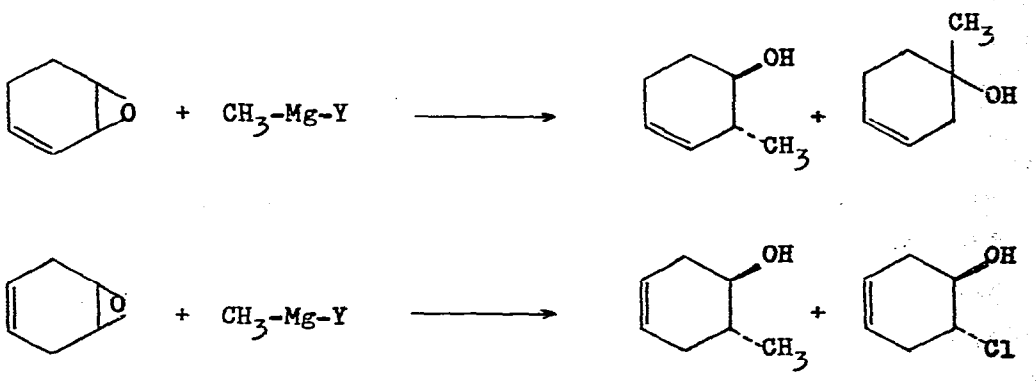
R'' is methyl, ethyl, n-propyl or n-butyl

References p. 120

The reaction of Grignard compounds with vinyloxy ketones as mentioned in paragraph 5 A is applied by the authors to prepare substituted 1,3-dioxanes [164]:



The reaction of cyclohexadiene monoepoxides, as investigated by Rickborn and Staroscick may yield several products, depending on the type of organomagnesium compound used [206]:



Y is methyl or chlorine

1,3-Cyclohexadiene monoepoxide reacts with dimethylmagnesium to give the trans methylcyclohexenol exclusively, whereas methylmagnesium

chloride gives 19% 4-methyl-1-cyclohexene-4-ol as a byproduct together with 70% of the trans methylcyclohexenol. 1,4-Cyclohexadiene monoepoxide reacts with methylmagnesium chloride to give 4-chloro-1-cyclohexene-5-ol as a byproduct.

The mechanistic aspects of the reaction of (mainly aliphatic) Grignard compounds with 4-substituted 1-halo-2-butyne have been studied by Gêlin, Gêlin and Albrand [207]. Chloro- as well as bromo-4-butyne-2-ol-1 react as follows:

$$X\text{-}CH_2\text{-}C{\equiv}C\text{-}CH_2\text{-}OH + R\text{-}Mg\text{-}X \longrightarrow CH{=}C{=}\overset{\overset{R}{|}}{C}\text{-}CH_2\text{-}OH + R\text{-}CH_2\text{-}C{\equiv}C\text{-}CH_2\text{-}OH$$

The authors investigated more closely the conditions required to promote the formation of one of the two possible products.

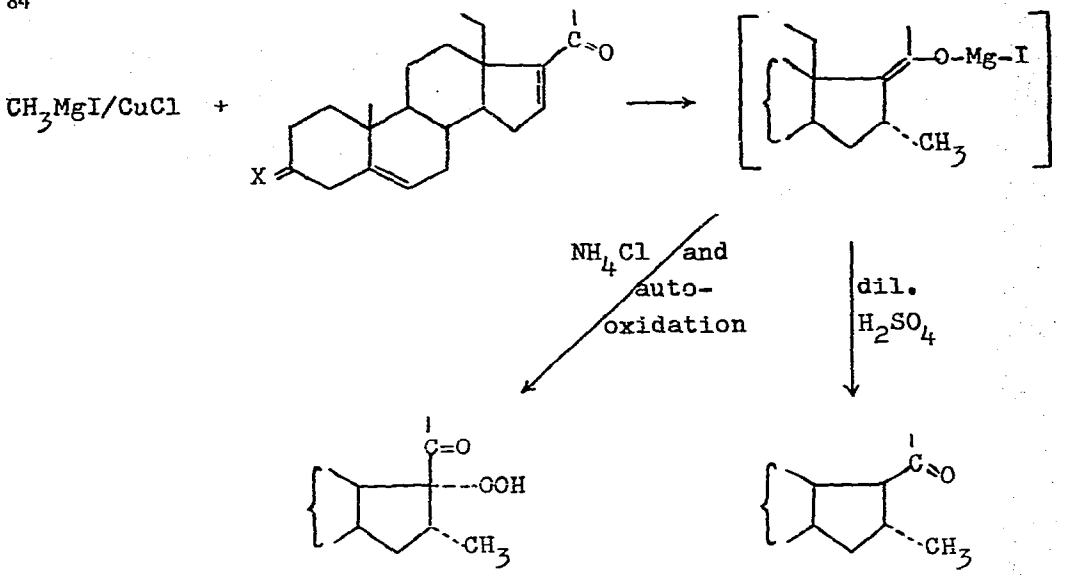
In principle the same sort of reactions takes place when the hydroxy group is replaced by CH_3CO_2- or by CH_3O-; no reaction occurs with $Cl\text{-}CH_2C{\equiv}C\text{-}CH_2\text{-}n\text{-}C_4H_9$.

Pornet and Mme. L. Miginiac investigated the reaction of organomagnesium compounds with the imino ether $C_6H_5\text{-}N{=}CH\text{-}O\text{-}C_2H_5$ [208]; two possible reactions are mentioned:

$$C_6H_5\text{-}N{=}CH\text{-}O\text{-}C_2H_5 + R\text{-}Mg\text{-}X \longrightarrow \begin{cases} C_6H_5\text{-}N(X\text{-}Mg)\text{-}\overset{\overset{R}{|}}{C}(H)\text{-}O\text{-}C_2H_5 \\ C_6H_5\text{-}N{=}C(X\text{-}Mg)\text{-}O\text{-}C_2H_5 \xrightarrow{-C_2H_5OMg} C_6H_5\text{-}N{=}C \end{cases}$$

The reaction leading to the formation of isonitriles is best carried out with aminomagnesium compounds such $(i\text{-}C_3H_7\text{-})_2N\text{-}Mg\text{-}Br$.

Finally the reaction of methylmagnesium iodide/Cu(I)chloride with 18-methyl steroids as reported by Kerb and Wiechert needs to be mentioned [209]:



D. Reactions with double bonds

Addition reactions of organomagnesium compounds with carbon-carbon double bonds are rather exceptional although under special conditions they may occur to give products in good yields.

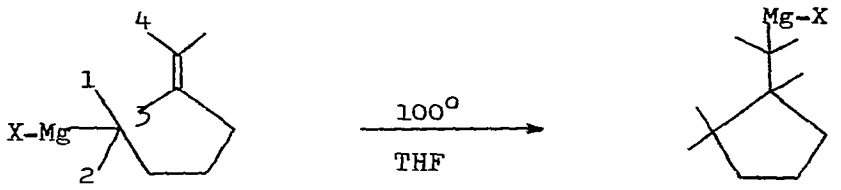
Two U.S. patents protect the industrial preparation of higher homologues of R-Mg-X and R-Mg-R by addition to ethylene or to isobutylene (see also A.S. 1970 for the German Patent of the same reaction) [210] and [211].

The addition of (in situ) ethylmagnesium bromide to double bonds in 1-trimethylsilyl-1-butyn-3-ene when the Grignard compound is prepared in the presence of the unsaturated compound is mentioned in chapter 2 A [35].

The mechanism of the alkyl-olefin exchange reaction or of the olefin insertion that occur between Grignard compound and olefins under the catalytic influence of anhydrous nickel chloride involves nucleo-

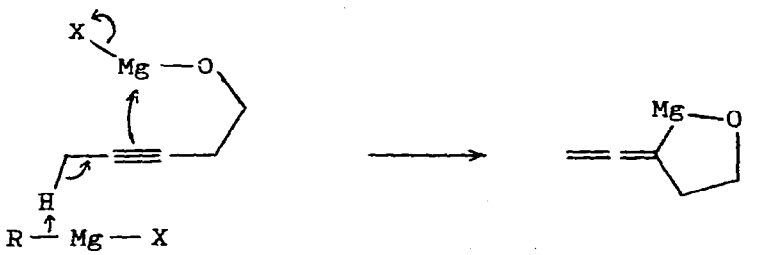
philic attack of a hydrogen atom or of a phenyl group on a π-complexed olefin within an organonickel intermediate as already suggested in earlier papers by the same authors (Farady and Marko) [212] (see A.S. 1969).

Intramolecular cyclization by addition of carbon-magnesium bonds to ethylenic double bonds was studied by Kossa, Rees and Richey [32]:



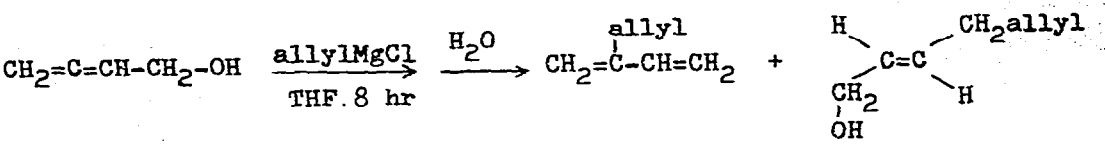
The influence of methyl substituents in positions 1,2, 3 and 4 was pronounced: 1 or 1,2 substitution facilitates cyclization, 3 and 4 substitution retards cyclization. The same sort of reaction was applied to six-membered ring compounds.

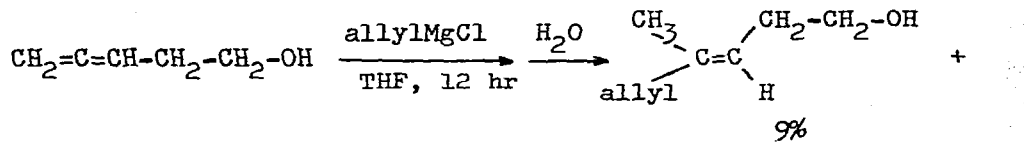
The stereochemistry of the addition reaction of Grignard reagents to alkynols (see A.S. 1969) was studied by Von Rein and Richey [213]; the mechanism for the addition reaction which proceeds preferentially in a trans fashion is closely related to the mechanism of the addition reaction of Grignard compounds to unsaturated amines, as mentioned in chapter 4 C [146].Cis addition may result, at least partially, by addition to an allenol formed by isomerization of the alkynyl reactant perhaps by a mechanism such as

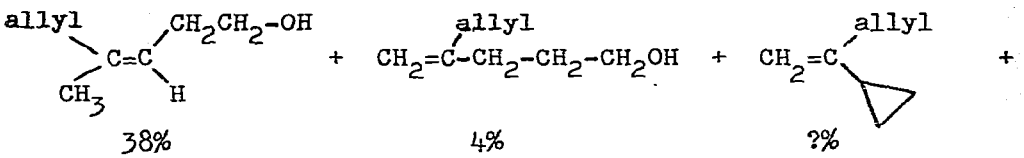


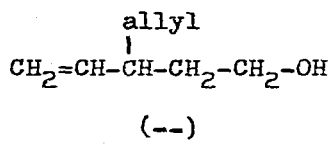
References p. 120

Finally Richey and Szucs investigated the products formed in the addition reaction of allyl Grignard reagents to allenols [214];





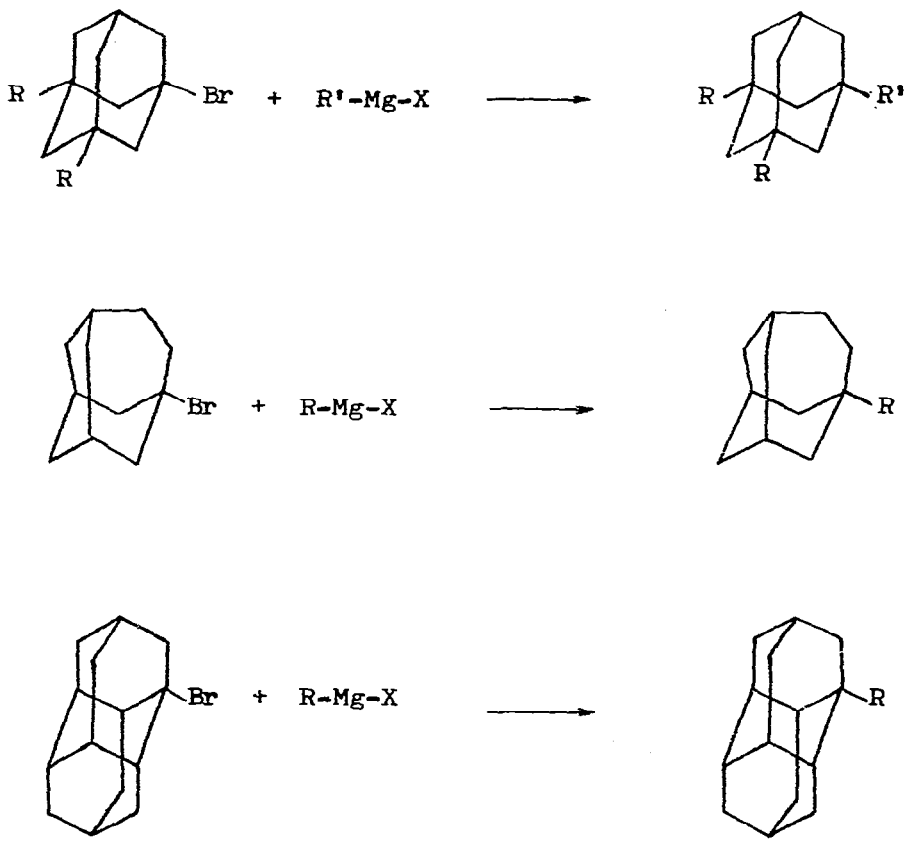




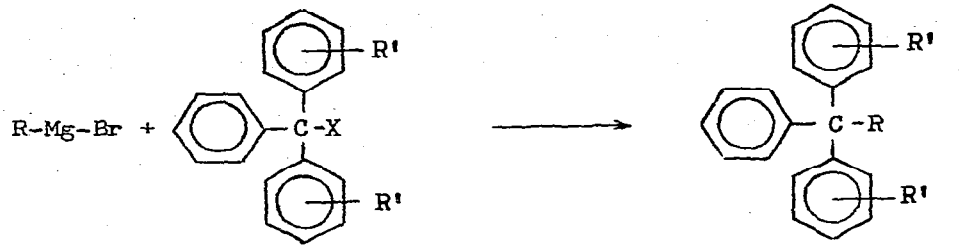
The yields were different for reactions in diethyl ether. The addition products reported could not have been formed from addition to alkynols which are produced in the reaction mixture by isomerization of the allenols, probably by a mechanism related to the mechanism mentioned above for the reverse isomerization reaction. Crude kinetic observations by the authors indicate that the addition of allylmagnesium chloride to the allenol is at least ten-fold faster than to the corresponding alkynol.

E. Reactions with organic halides and halogens

According to a report by Osawa, Majerski and Von R. Schleyer bridgehead alkylated adamantyl derivatives can be prepared in excellent yield by direct coupling of the corresponding bromides with Grignard compounds [215]; the reaction may also be applied to the homoadamantyl and to the diamantyl series. A two- or three-fold excess of the Grignard compound is used in most of the cases.



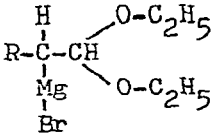
Imidazolyl-, 1,2,4-triazolyl- and 1,2,3-triazolylmagnesium bromides react with triphenylmethyl halides in a normal coupling reaction which gives products in almost quantitative yields [60]:



R = imidazolyl-, 1,2,4- and 1,2,3-triazolyl-

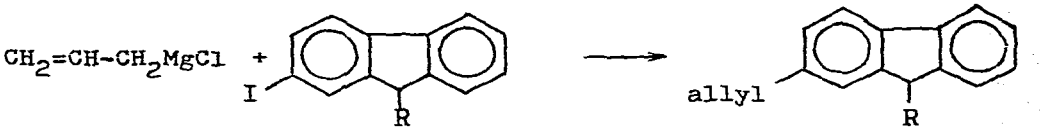
R' = m-NO_2, p-F, p-$(CH_3)_2N$, o-Cl and o,o-diCl

The reaction of the unexpectedly stable Grignard compound



with bromobenzene has been reported in chapter 2 B [49].

The reaction of allylmagnesium halides with iodofluorene leads to the formation of 2-allyl-fluorenes [216]:



where R may be methyl, ethyl, n-propyl and n-butyl.

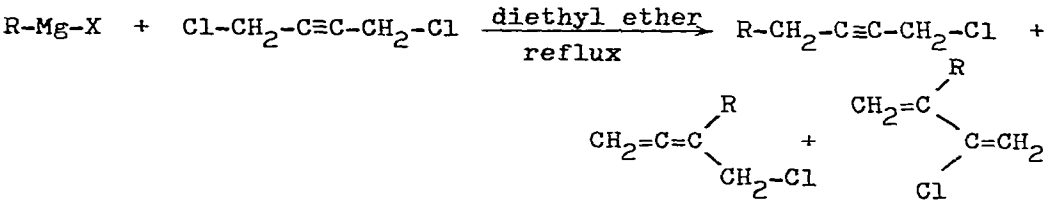
According to Barisova, Zavarykina, Kron, Kron and Stepanov the reaction of phenylmagnesium bromide with hexachlorocyclopentadiene does not lead to the formation of products resulting from substitution of chlorine at the sp^3 hybridized C-atom [217]. An unanalyzed mixture of products was obtained instead.

The reaction of allyl chloride with dicrotylmagnesium may result in the formation of several products: beside the expected cis- and trans

heptadienes-1,5 and the 3-methyl-hexadiene-1,5 (resulting from rearranged crotyl groups) Brisset, Czernecki and Georgoulis observed the formation of considerable amounts of octadienes, evidently resulting from coupling of the crotylmagnesium compound with crotyl halides formed in a functional exchange reaction between allyl chloride and the organomagnesium compound [218].

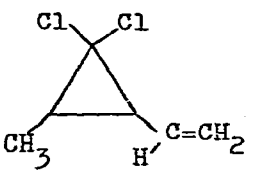
The reaction of the Grignard compounds prepared from 7-bromo-p-menthene-1 and from bromocarvomenthene with allyl bromide has been mentioned in chapter 2 B iii [53].

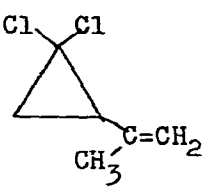
Iossiphides, Michel and Troyanowsky found several different products from the reaction of 1.4-dichlorobutyn-2 with Grignard compounds; the corresponding products from the dibromo homologues were much less stable [219]:



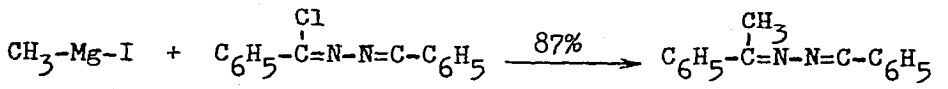
R = ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-octyl cyclohexyl or benzyl

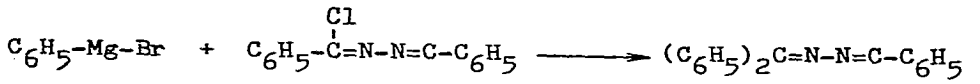
Slobodin and Egenburg report on the reaction of ethylmagnesium bromide with vinylic dichlorocyclopropanes [220] such as



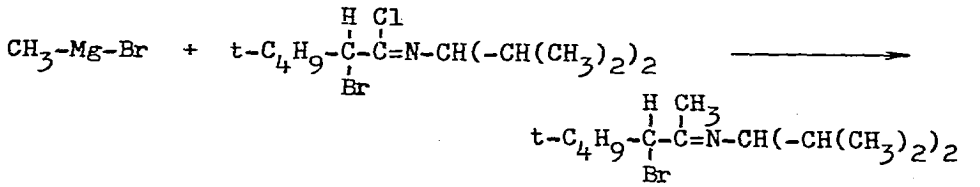


Methylmagnesium iodide reacts smoothly with the chloroazine showed in the following equation to give the methyl substituted azine in good yields whereas the phenyl homologue is obtained in poor yields only from phenylmagnesium bromide [221]:

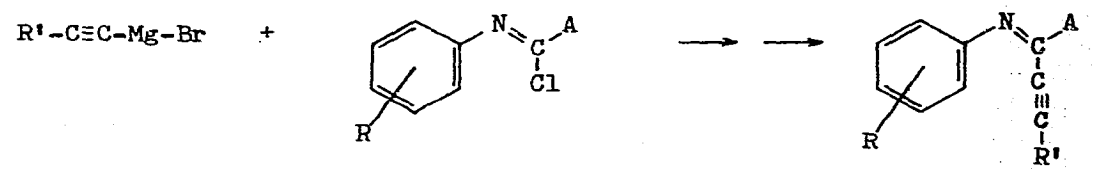




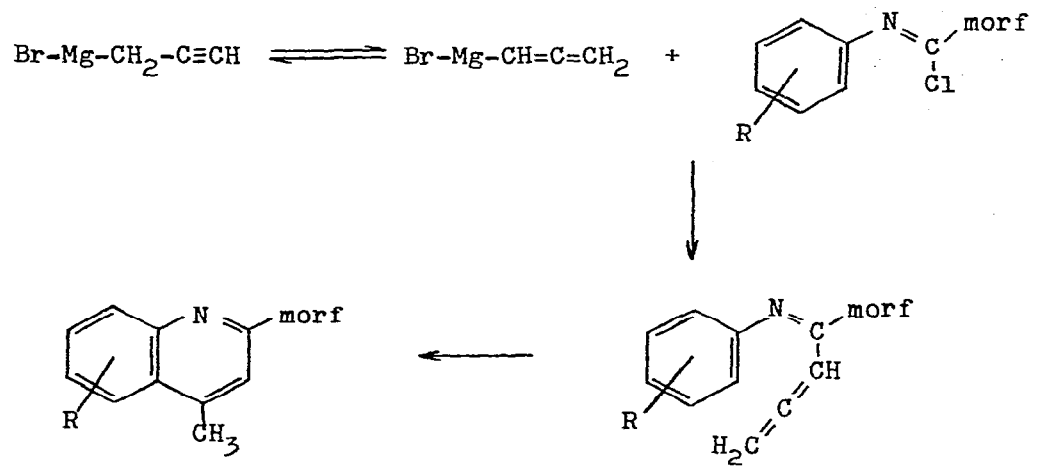
Nucleophilic displacement of chlorine by methyl is reported in the reaction [222]:



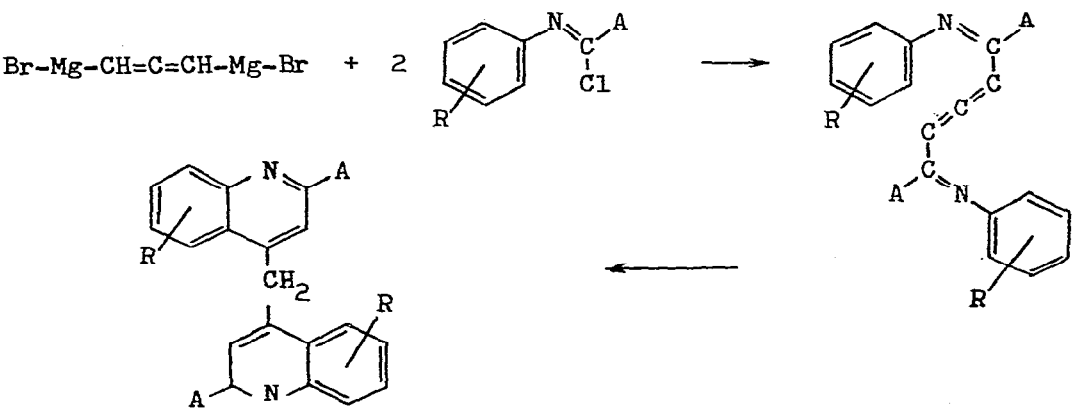
Ried and Weidemann investigated the reaction of acetylenic Grignard compounds with N-arylsubstituted chloroamidines [223]:



with R' being H or C_6H_5 or cy-C_6H_{11}, R being H or c-CH_3 or p-Cl and with A being -$N(CH_3)_2$ or morpholino. The product of the reaction of propargylmagnesium bromide with the same chloroformamidine could not be isolated but cyclized directly to form 2-morpholino-lepidine:

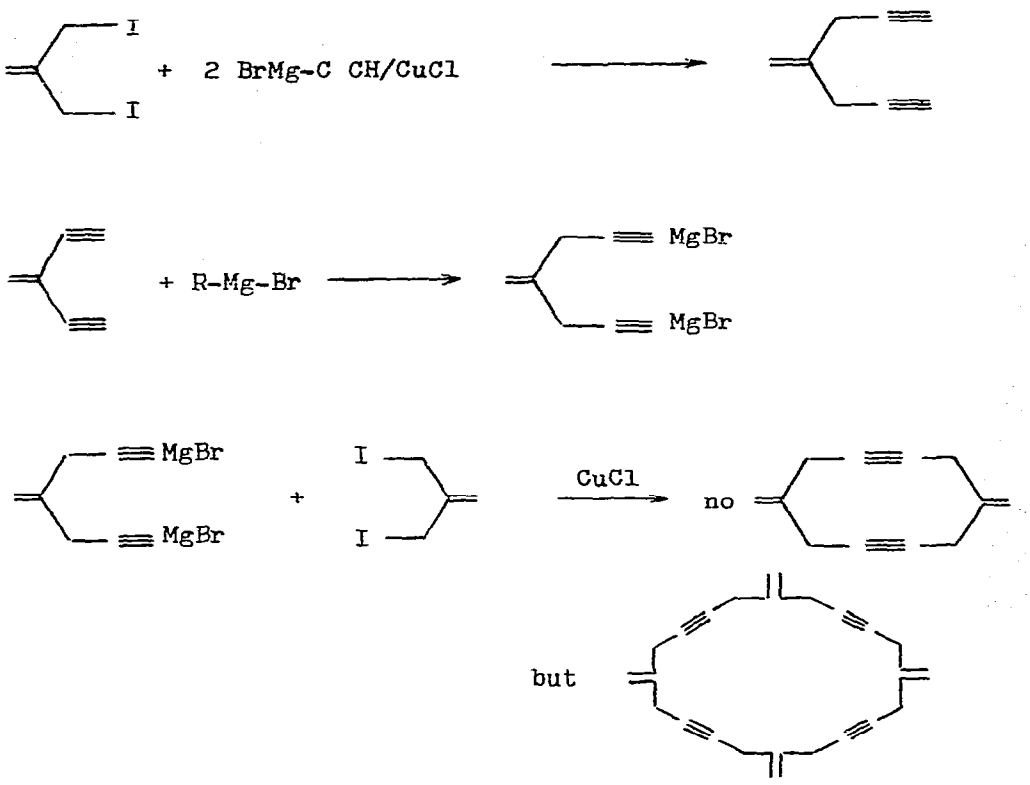


The following side reaction takes place in which the bis-magnesium derivative of allene is involved:



Several reports have appeared concerning the reaction of organomagnesium compounds with organic halides catalyzed by metal salts; a discussion of the systematic study of the Kharasch reaction by Tamura and Kochi is given in chapter 4 C [148] - - - [153].

Looker and Sondheimer synthesized a 20-membered cyclic tetraacetylene in the following sequence of reactions [224]:



The preparation of sterically hindered ketones by the reaction of organomagnesium halides with acid chlorides, catalyzed by cuprous salts has received due attention this year again. The influence of impurities in the magnesium, used for the preparation of the Grignard compound, on the course of the reaction and on the stability of the intermediate organocopper compounds has been discussed in chapter 2 D [76]. In a second paper the same authors, Dubois and Boussu, investigated the stabilities of the organocopper intermediates, their nature and their influence on the formation of reaction products [225]; the organocopper compounds formed on addition of cuprous halide to ethylmagnesium halide in diethyl ether have the formula

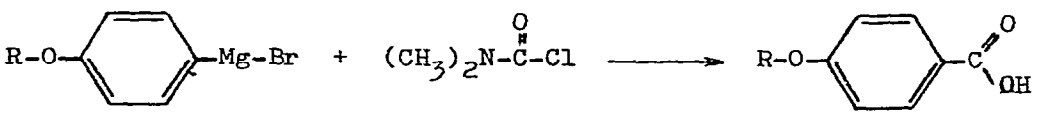
$$EtCu.MgXX'$$

and its stability is optimal in case both X and X' is I.

In the reaction with di-isopropylacetyl chloride the amount of products formed in radical-type reactions depends directly on the rate of decomposition of the organocopper intermediate! In case a small, catalytic amount of cuproushalide is used in the reaction, the supernatant solution, obtained after the precipitate has been removed, still contains organocopper compounds and the reaction proceeds in the same way as in the case of addition of stoichiometric amounts of cuprous salts and filtering off the precipitate formed. The authors conclude that the organocopper compound is regenerated continuously during the reaction with the acid chloride.

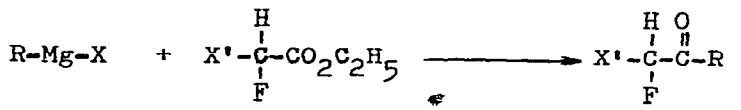
Finally, in a paper with Lion, Dubois and Boussu investigated the precise optimal conditions, required for the preparation of ketones by the reaction of organomagnesium (as well as organolithium) compounds with acid chlorides in the presence of cuprous halides [226].

The reaction of dimethylcarbamoyl chloride with aromatic Grignard compounds leads to the formation of benzoic acids and not to the amides [227]:

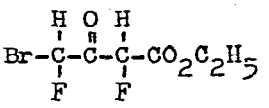


R = alkyl, cycloalkyl or aralkyl

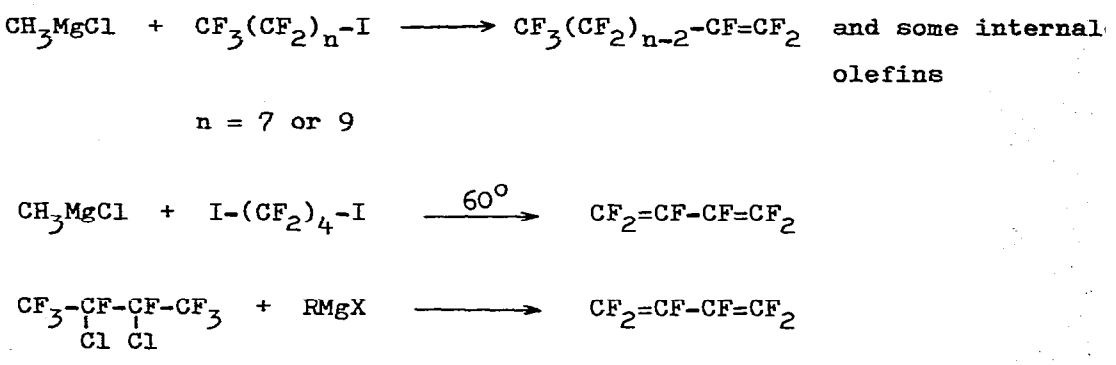
Elkik, Le Blanc and Hamid-Assadi Far observed a decreased reactivity of fluorine substituted in esters when a geminal halo atom was present [228]:



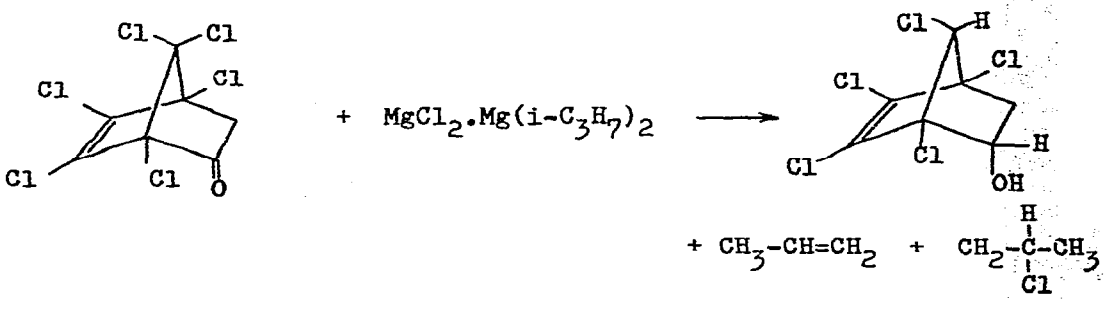
in which reactions for X' is Cl the following R groups have been used : benzyl, isobutyl and cyclohexyl, whereas for X' is Br R was benzyl, isobutyl, n-heptyl and phenyl. For X = X' = Br and R is isobutyl the main product of the reaction was



The reaction of perfluoroalkyl halides with Grignard reagents at elevated temperatures leads almost exclusively to the formation of elimination reaction products [229]; Lo reports the following reactions:



The reaction of isopropylmagnesium compounds with the C-7 chlorine atom in 1,4,5,6,7,7-hexachloronorborn-5-en-2-one probably according to the scheme:



has been reported in chapter 5 A [178].

n-Heptylmagnesium bromide reacts with bromine or with iodine in THF or diethyl ether to form n-heptyl halide and only in small amounts side reaction products such as R-R and 1-heptene, according to Zakharkin, Gravilenko and Palei [145].

Stanko and Anorova investigated the reaction of o-carboranylmagnesium halides with carbon tetrachloride in THF [66]; the main product is the chlorination product C-chlorocarborane. m- And p-carboranylmagnesium bromide do not react with carbon tetrachloride in THF! In the same report the authors mention their results obtained in the chlorination of o- and p-carboranylmagnesium halides in THF. It is to be pointed out that o- as well as p-carboranylmagnesium bromide react with chlorine to give 49% and 78% yield of C-bromo carboranes!

Zakharkin, Zhigareva and Potvisotskaya too investigated the products formed on reaction of carboranylmagnesium halides with carbon tetrachloride [67]. Carboranylmagnesium iodide, prepared by the addition of ethylmagnesium iodide to carborane, reacts with carbon tetrachloride to form not only chlorocarborane but also iodocarborane. The amount of iodide formed depends on the presence of ethylmagnesium iodide or magnesium iodide in the solution. In the same sense the authors found that phenylmagnesium iodide reacts with carbon tetrachloride to form both chlorobenzene and iodobenzene in a 4:6 ratio.

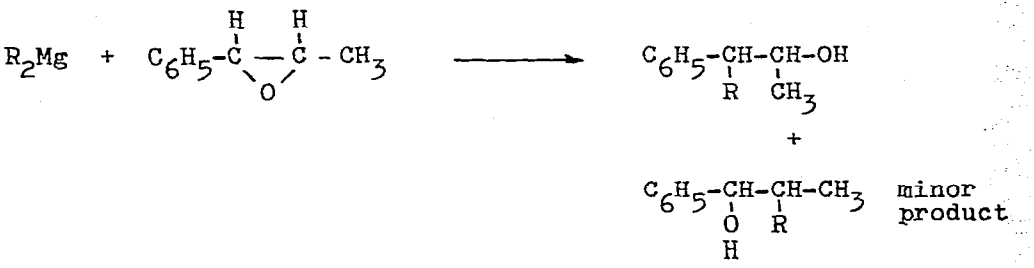
F. Reactions with epoxides

The studies of the reaction of cyclohexadiene monoepoxides with Grignard compounds, reported by Rickborn and Staroscik [206], were already discussed in chapter 5 C.

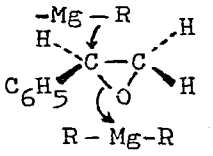
The mechanistic aspects of the reaction of allylmagnesium halides

with epoxides, which occur with inversion of configuration, have been studied by Felkin, Frajerman and Roussi [107].

Cis- as well as trans-1-phenyl-1,2-epoxypropane react with dimethyl- and diethylmagnesium mainly with attack on the benzylic carbon atom as Namy, Abenhaim and Boireau again found in their studies [230]. Utilizing optically active epoxides the authors conclude that the trans-epoxide reacts much faster than the cis-epoxide and furthermore that inversion takes place at the benzylic carbon atom.

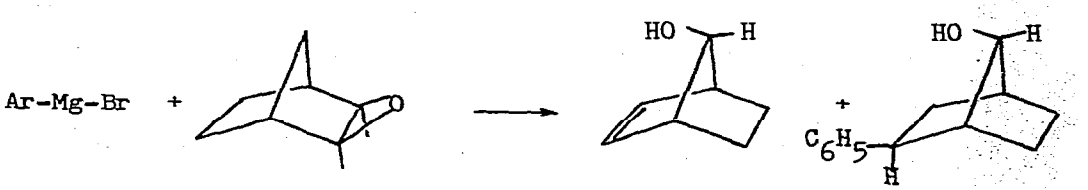


The reaction might take place via the following mechanism:



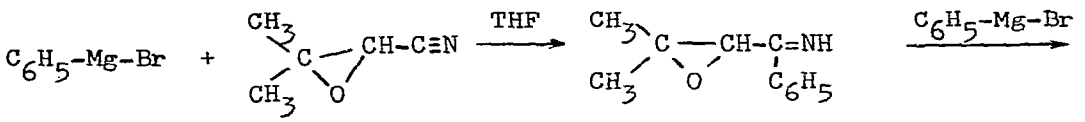
The same authors investigated also the reaction of allylmagnesium compounds with the same epoxides [231].

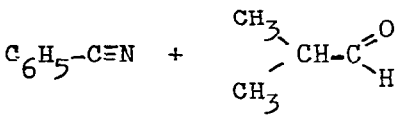
According to Gerteisen and Kleinfelter phenyl- and o- as well as p-tolylmagnesium bromide react with norbornene-2,3-exo-oxide to give a 3 : 1 mixture of 7-syn-norbornenol and 2-exo-aryl-7-syn-norbornanol [232]:



7-syn-norbornenol was also formed in reactions of methylmagnesium iodide with the same epoxide although in some of the experiments also a few other products were isolated from the reaction mixture. For the formation of one of the products the authors propose an intermediate complex formation between magnesium iodide and the epoxide.

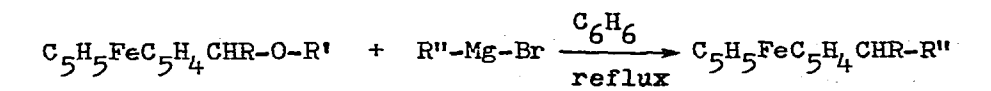
J. Normant and Cantacuzene report that the reaction of phenylmagnesium bromide with cyano epoxy-compounds leads to attack on the nitrile carbon atom when THF is used as the solvent [233]. Reaction of the product with Grignard compounds leads to the formation of aldehydes:





G. Reactions with ethers, acetals and ortho esters

Although in general ethers do not react easily with organomagnesium compounds it seems that reactions of methylferrocenyl ethers with Grignard compounds lead to the formation of alkyl-substituted ferrocenes in high yields [234]: Combs, Willis, Giles and Stephens report that methyl ethers of hydroxymethylferrocene undergo the following reaction:



References p. 120

Yields obtained were for R'' = methyl, 90%, R'' = vinyl, 66%, R = allyl, 60%, R = phenyl, 85%.

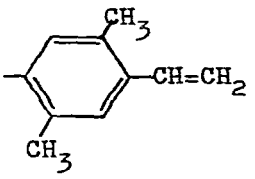
Two reports have appeared this year on the reaction of R-Mg-X with gem-aminoethers: the report by Mme L. Miginiac and Nivert in which also rearrangement of the propargylic Grignard reagent occurs was discussed in chapter 3 E [113].

Tanimoto, Mouri and Okano reported the following reactions [235]:

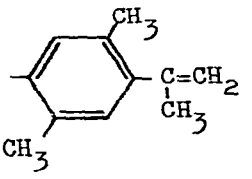
$$R'\text{-}Mg\text{-}X + i\text{-}C_4H_9\text{-}O\text{-}CH_2\text{-}N(R)_2 \longrightarrow R'\text{-}CH_2\text{-}N(R)_2$$

with R is CH_3, C_2H_5 or $i\text{-}C_3H_7$

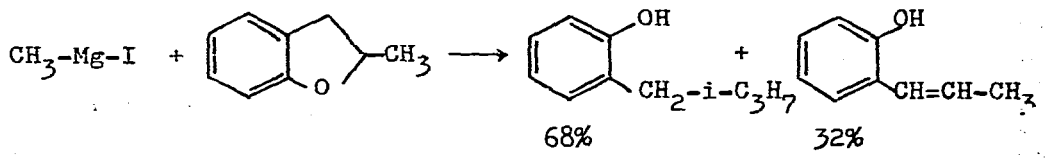
and R' may have the following structures:



or

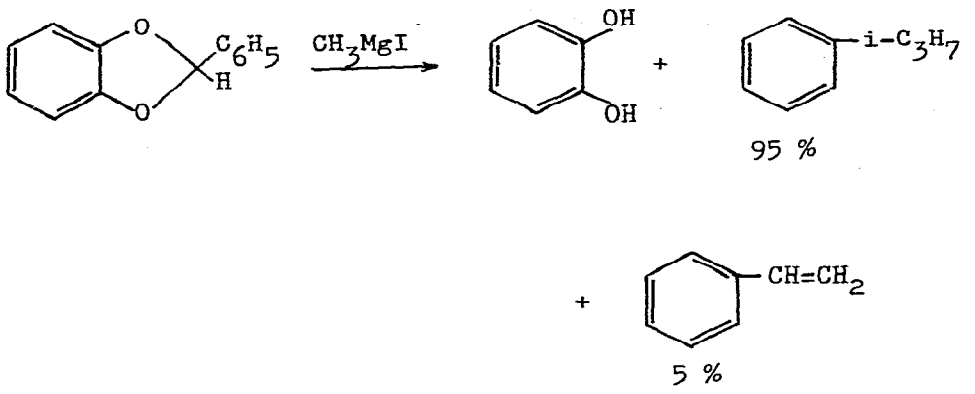


The cleavage of the heterocyclic ring in 2,3-dihydrobenzofuran has been studied by Cabiddu, Maccioni and Secci [236]; saturated



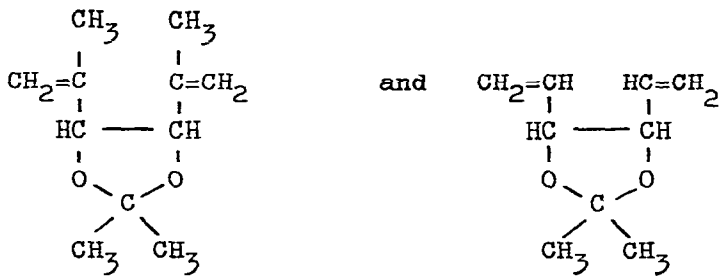
as well as unsaturated products are formed, depending on the substituents in the ring system.

In the same publication the authors report their results obtained with the reaction of Grignard reagents with 1,3-benzodioxolanes;



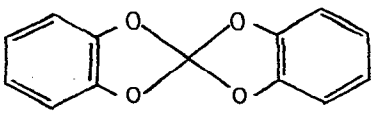
As already reported in chapter 4 C the mechanism of the cleavage of the 1,3-dioxolane ring by the attack of a Grignard compound has been studied [141]; the same sort of ring cleavage reaction was studied by heating the complex formed from magnesium iodide and substituted 1,3-dioxanes, as also mentioned in chapter 4 C [142].

Ring cleavage reactions of several Grignard compounds with substituted 1,3-dioxolanes have also been studied by Mousset [237]. Dioxolanes of the following type were used by this author:

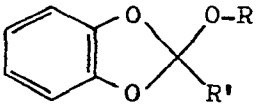


Cabiddu, Gelli and Sotgiu studied the reaction of Grignard compounds with cyclic ortho-esters, ortho-carbonates as well as with

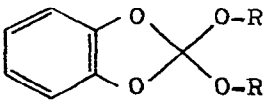
the related thio compounds such as [238]



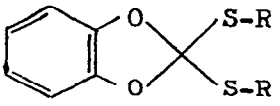
33



34



35

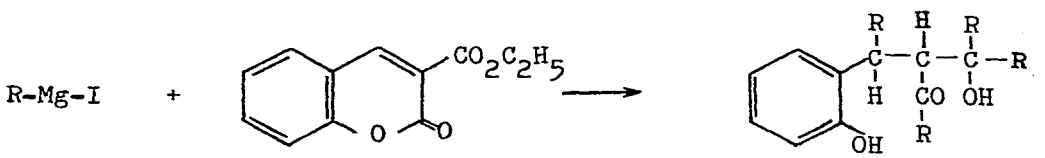


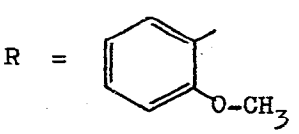
36

33 reacts to form tetrasubstituted methanes $C(R)_4$; 34 may react to form ethers $R''_2(CR'(OR))_2$ as well as unsaturated products; 35 may react under formation of ketals $R'_2C(-OR)_2$ and 36 finally gives thioketals in good yields.

H. Reactions with heterocyclic compounds

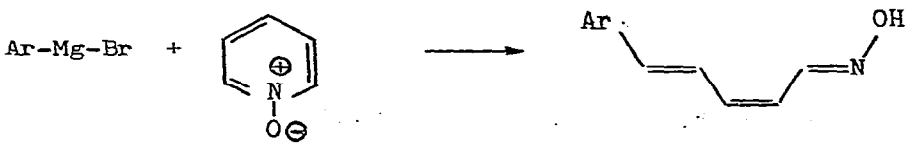
The reaction of 3-carbethoxy coumarin with o-methoxyphenylmagnesium iodide was investigated by Holmberg and Johansson [239]; among other reactions ring scission may take place:



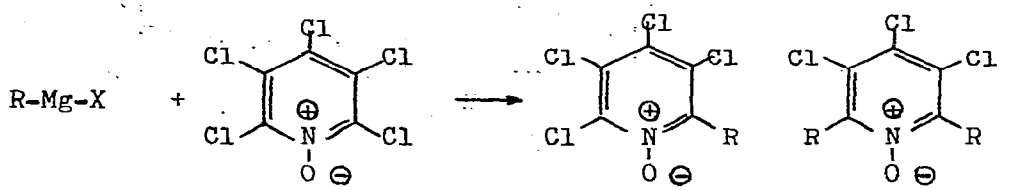


Benzyl as well as triphenylmethyl pyridinium salts react with Grignard compounds to form 1,2- and 1,6-dihydropyridines as the result of nucleophilic addition reactions on the ring [240].

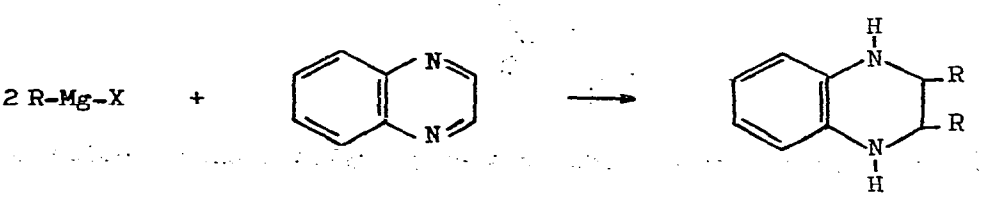
Reaction of aromatic Grignard reagents, including phenyl-, perdeuterated phenyl-, p-tolyl-, p-anisyl or 2-thienylmagnesium halides with pyridine 1-oxide does not lead to addition reaction products (as reported by Kato and coworkers; 1965) but to ring scission products as was demonstrated by Van Bergen and Kellogg [241]:



The reaction of methyl-, ethyl- or phenylmagnesium halides with pentachloro-pyridine 1-oxide results in the formation of 2- as well as of 2,6-disubstituted trichloro-pyridine 1-oxides [242]:



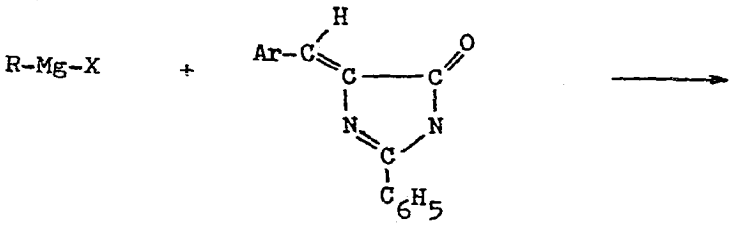
Marxer, Salzmann and Hofer found that 3-dimethylaminopropylmagnesium chloride reacts with quinoxaline to form a disubstitution product [243];



References p. 120

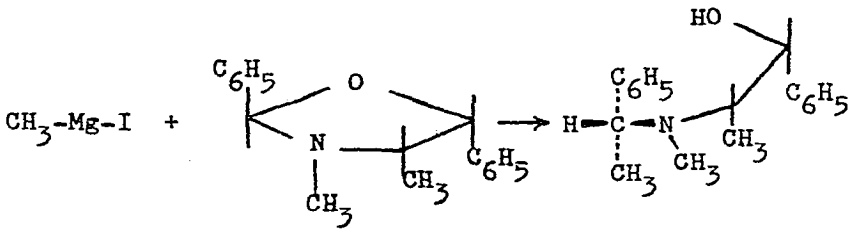
the authors also investigated the reactions of quinoxalinone.

In two publications Asker, Harhash and Kassab report their results obtained in reactions of Grignard compounds with 4-arylidene-2-phenyl-1-substituted-2-imidazolin-5-ones [244] and [245];

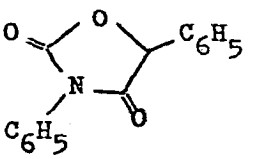


addition occurs to the exocyclic double bond.

The reaction of methylmagnesium iodide in diethyl ether with the optically active oxazolidine, obtained by condensation of benzaldehyde with (-)ephedrine proceeds in a stereospecific manner according to Neelakantan [246];



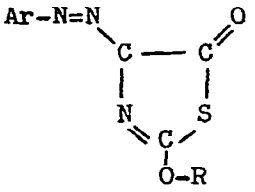
The reaction of Grignard compounds with 3,5-diphenyl-2,4-oxazolidinedione:



leads to ring cleavage products when phenylmagnesium bromide is

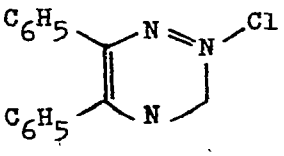
used and mainly to carbonyl addition reaction products with methylmagnesium bromide [247].

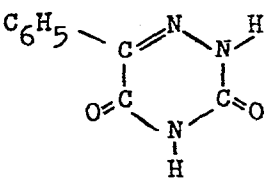
4-(Arylazo)-2-alkoxy-2-thiazoline-5-one reacts with ethyl-or phe-



nylmagnesium bromide under ring cleavage [248].

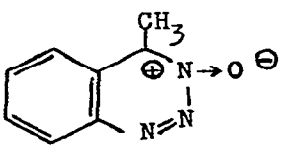
Reactions of triazines and dioxotetrahydrotriazines with Grignard





compounds have been investigated by Mustafa, Mansour and Zaher [249].

Igeta, Tsuchiya and Nakai investigated the reaction of phenylmagnesium bromide with 5,6-benzo-4-methyl-1,2,3-triazine 3-oxide [250]:

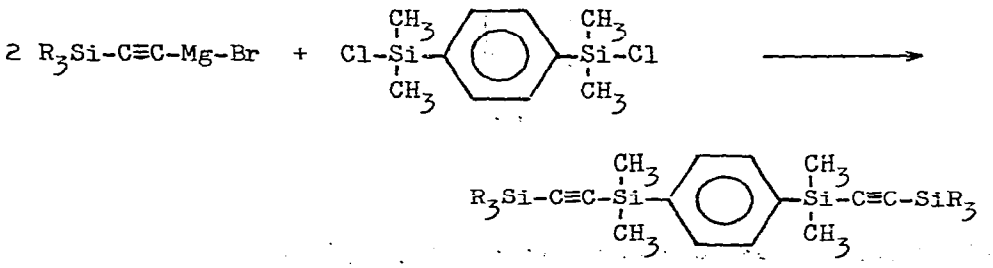


a variety of products, mainly resulting from ring opening reactions was obtained.

References p. 120

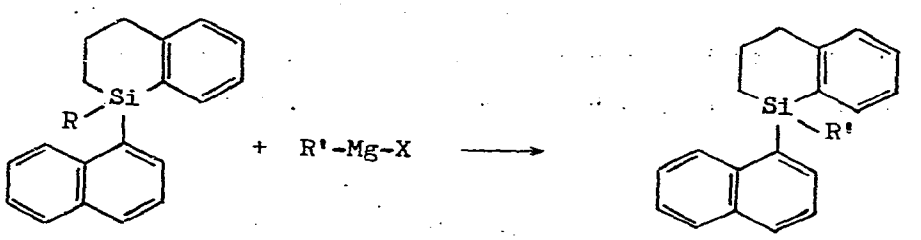
I. Reactions with silicon, phosphorus, sulfur and boron compounds

Reaction of Grignard compounds with chlorosilanes was used by Gverdtsiteli, Melua, Doksopulo and Chagelishvili in the synthesis of the following type of compounds [251]:



$R_3 = (C_2H_5)_3$; $(CH_3)_2C_6H_5$ or $(CH_3)_2C_2H_5$

In a U.S. patent the preparation of organosiloxanes is claimed by the reaction of organomagnesium halides with siloxanes [252].
Corriu and coworkers in a series of papers investigated the stereochemistry of the reaction of organomagnesium compounds with optically active silanes. Together with Masse and Royo, Corriu found that methylmagnesium compounds as well as allylmagnesium compounds react with [37] with retention of configuration when use was made

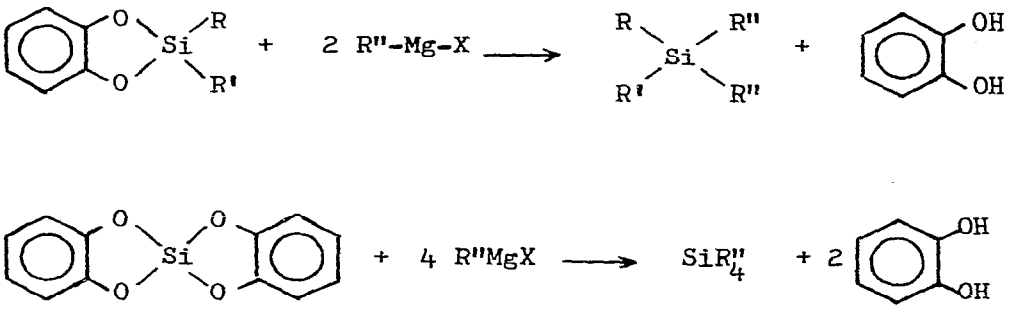


[37] R = O-CH_3 or F

of strongly solvating solvents [253]. Inversion occurs when magnesium bromide was present in the reaction mixture.

Together with Lanneau and Leard Corriu studied the nucleophilic substitution reaction of organomagnesium halides with (-),(-)menthoxy-α-naphthylphenylsilane [254]: chiral organosilanes are reported to be formed.

Cabiddu, Maccioni and Secci studied the reactions of organomagnesium halides with the silicon analogues of the dioxolanes and cyclic ortho-esters the reactions of which are reported in chapter 5 G [255].



Métras, Lahournère and Valade proved that the reaction of sterically hindered Grignard reagents with tetrachlorosilane proceeds via the reduction of the chloro compound to $HSiCl_3$, followed by alkylation; the final product is a dialkylmonochlorosilane [256].

In two other publications the authors further worked out the mechanism and the experimental conditions for such reduction reactions. Métras, Valade, Lacout-Loustalet and Dupin working with sterically hindered Grignard compounds at 160° (!!) proved that, in general, organochloro- as well as organoalkoxysilanes are reduced; the ratio of the two possible reduction reaction products varies with the reaction conditions. The general reaction scheme is [257]:

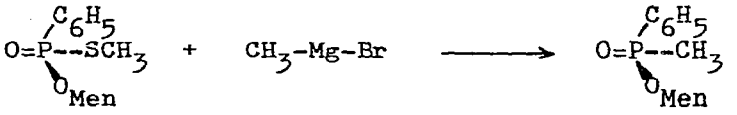
References p. 120

$$R\text{-}Mg\text{-}X + R'_n\text{-}Si\text{-}Z_{4-n} \longrightarrow RR'SiH_2 + R_2R'SiH$$

$Z = Cl$ or $-O-CH_3$

In a third paper the same authors point out that the reduction of triorganosilanes of the type R_3SiZ (with $Z = Cl$ or $-O-CH_3$) at elevated temperatures proceeds either by direct reduction by the Grignard compound or by magnesium hydride, formed by thermal decomposition of Grignard reagents such as t-butylmagnesium chloride [258].

Donohue, Mandel, Farnham, Murray, Mislow and Benschop proved that displacement of a thiomethyl group in the reaction of methylmagnesium bromide with menthyl S-methyl phenylphosphonothioate :



proceeds with retention of configuration [259]
Several phosphines were synthesized by Timokhin, Grechkin Tran'kova and Yakutina according to the following reaction [260]:

$$R\text{-}PCl_4 + R'\text{-}Mg\text{-}X \longrightarrow R\text{-}PR'_2$$

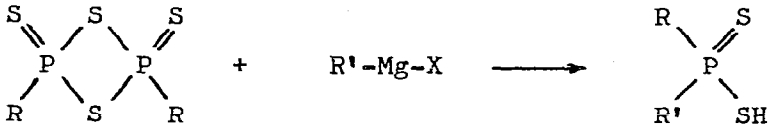
$R = C_6H_5$ or $C_6H_5\text{-}CH{=}CH_2$
$R' = C_2H_5$, $i\text{-}C_3H_7$, $n\text{-}C_4H_9$ and other groups

Timokhin, Grechkin and Kalabina investigated some reactions of Grignard compounds with adducts of triphenylphosphine oxide [261]; reaction of phenyl- or butyl-magnesium bromide with the trichloro

derivative yielded triphenylphosphine

$$R\text{-}Mg\text{-}Br + (C_6H_5)_3POPOCl_2^{\oplus}\ Cl^{\ominus} \longrightarrow (C_6H_5)_3P$$

whereas no reaction occurs with the adduct with trimethylchlorosilane. The following reaction, as investigated by Diemert and Kuchen [262]

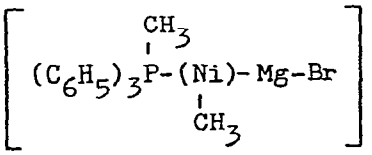


was applied to compounds with R is p-anisyl or methyl and R' is methyl, ethyl, allyl and phenyl.

The reaction of methylmagnesium bromide with the adduct of triphenylphosphine and nickel(II) chloride, as investigated by Swierczewski, Green, Smith and Felkin [264]

$$((C_6H_5)_3P)_2NiCl_2 + CH_3\text{-}Mg\text{-}Br \longrightarrow C_6H_6 + C_6H_5\text{-}CH_3 + (C_6H_5\text{-})_2 + (C_6H_5)_2PCH_3 + C_6H_5P(CH_3)_2$$

leads, after six days to a 70% yield of biphenyl. A phosphorane intermediate, proposed by the authors suggests an uncommon magnesium-nickel bond

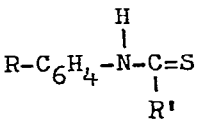


Jarvie and Skelton found that organomagnesium halides react with organic disulfides as follows [265]:

$$R\text{-}Mg\text{-}X + R'\text{-}S\text{-}S\text{-}R' \longrightarrow R'\text{-}S\text{-}R + R'\text{-}S\text{-}Mg\text{-}X$$

The monosulfide is formed quantitatively; apparently there are no side reactions as in the comparable reactions with peroxides (see the following paragraph). A radical process is proposed to rationalize the formation of the products (supported by private information from A.G. Davies who detected these radicals by means of their ESR signals).

Ginwala and Trivedi studied the reaction of several aliphatic Grignard compounds with substituted phenylisothiocyanates and obtained products with the structure



in yields as high as 90 % [266].

Finally in this chapter reactions have to be mentioned of organomagnesium compounds with boron derivatives; as is already reported in chapter 2 E, Davies, Roberts and Tudor found no isomerisation in the aliphatic group during the reaction of n-butyl, isobutyl and sec-butyl Grignard compounds with boron trifluoride [102].

Reaction of the chloro-substituted Grignard compounds, prepared by Miginiac and Blois [44], with trimethoxyborane

$$Cl\text{-}(CH_2)_n\text{-}Mg\text{-}Br + B(OCH_3)_3 \longrightarrow Cl(CH_2)_n\text{-}B(OCH_3)_2$$

yields chloro-substituted boranes.

B-alkyl or B-aryl substituted borazines react with Grignard compounds with displacement of the substituents as was found by Adcock and La-

gowsky [267]. Phenylmagnesium bromide e.g. reacts with hexamethylborazine to give $(CH_3)_3N_3B_3(CH_3)_2C_6H_5$, $(CH_3)_3N_3B_3CH_3(C_6H_5)_2$ and $(CH_3)_3N_3B_3(C_6H_5)_3$ as well.

J. Reactions with oxygen and peroxides

As already noted in Chapter 3 E γ-unsaturated Grignard compounds rearrange on reaction with oxygen and a mixture of products is obtained [104].

Okubo, Maruyama and Osugi investigated the reaction of Grignard compounds with benzoyl peroxide and observed the formation of complexes containing solvent molecules as well as the peroxide [268]. The mechanism of the reaction of another Grignard molecule with this complex has been discussed in chapter 4 C [144].

Jarvie and Skelton [265] investigated the reaction of several organomagnesium halides with t-butyl- and n-butyl peroxide: the two main products of the reaction are ether and alcohol. n-Butylmagnesium chloride on reaction with t-butyl peroxide yields almost 70% t-butyl-n-butyl ether and more than 100% t-butyl alcohol (!?):

$$(t\text{-}C_4H_9\text{-}O\text{-})_2 + n\text{-}C_4H_9\text{-}Mg\text{-}Cl \longrightarrow t\text{-}C_4H_9\text{-}O\text{-}n\text{-}C_4H_9 + t\text{-}C_4H_9OH$$

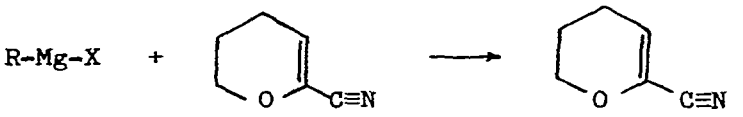
x10^3 mole	4	24	2.70	5.2

A radical process is proposed to account for the different products formed as well as of the varying yields in which they were obtained. Herbstman (Diss. 1963) stated that primary Grignard reagents give the highest yields of ethers whereas tertiairy Grignards give predominantly alcohols. The authors could confirm this and make the remark: this is understandable, as we proceed along the series of Grignard reagents, primary, secondary, tertiairy, the radicals gene-

rated should compete more effectively with the solvent in hydrogen donation to the tertiairy radicals and disproportionation should increase relative to combination.

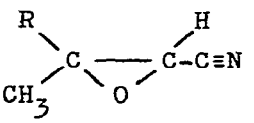
K. Reactions with nitriles and isonitriles

Riobe studied the following reactions [269]:



R = methyl, ethyl or phenyl

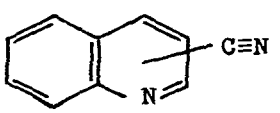
The reaction of Grignard compounds with epoxy nitriles

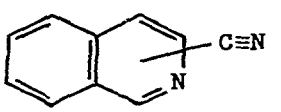


R = methyl or phenyl

was discussed in paragraph 5 F [233].

The reaction of Grignard compounds with nitriles of quinoline or isoquinoline might lead either to attack at the cyano-carbon atom or to attack at the hetero ring, depending on the position

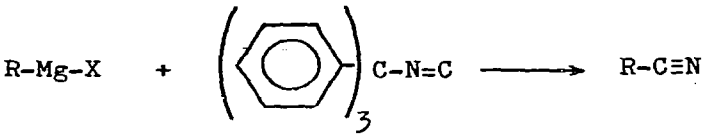




of the nitrile group [270].

As reported by Walborsky, Niznik and Periasamy triphenylmethyl iso-

trile reacts with Grignard reagents to form the corresponding nitriles in varying yields [271]:



R = cyclopropyl, cyclohexyl and mesityl

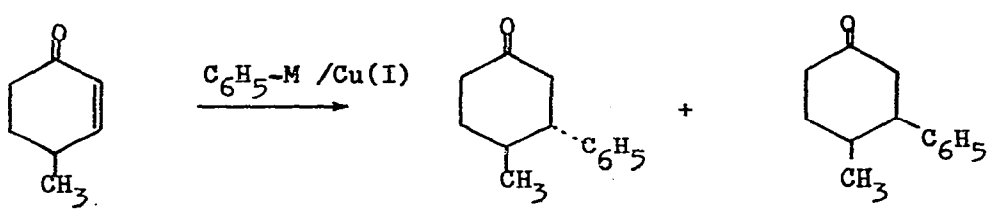
L. Reactions with or in the presence of metal salts

In the previous chapters several types of reactions have been mentioned where metal salts were added together with different substrates and their influence on the course of the reaction has been studied.

Silver salts were used in the reaction of Grignard reagents with organic halides [148] and [153].

In the same sort of reactions iron salts have been applied [149], [151], [152] and [153].

A number of publications deal with the influence of cuprous salts on the course of the reaction of Grignard reagents with acid chlorides [76], [225] and [226]; Luong-Thi and Mme. Rivière found that in such reactions, mixtures of phenylmagnesium bromide and cuprous iodide are as reactive as the lithium reagent mixed with cuprous iodide [272]. The same was found for the reaction with β-unsaturated ketones:



97 : 3

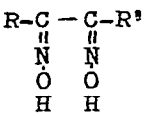
Not more than 2% of the 1,2-addition reaction product was formed whereas phenylmagnesium bromide without cuprous iodide gives the 1,2-addition reaction product almost exclusively.

The reaction of phenylmagnesium bromide with unsaturated ketones in the presence of cuprous salts, leading to the formation of enolates, has been mentioned in chapter 5 C [198].

The use of cuprous salts in the reaction of Grignard reagents with organic halides has been mentioned in chapter 5 E [150], [152] and [153] for aliphatic organic halides and [224] for acetylenic halides.

The reaction of allenic Grignard compounds with bromo esters in the presence of cuprous chloride was mentioned in chapter 3 E [111].

The reactivity of copper, nickel and platinum salts of 1,2-dioximes towards methylmagnesium bromide was investigated by Uhlig and Dorn [273]; the oximes were of the following types:



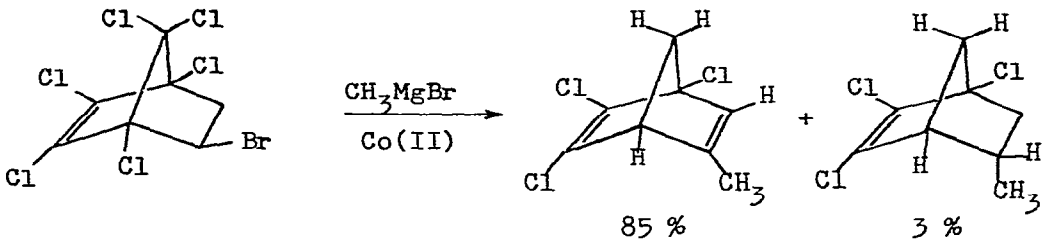
with R and/or R' = methyl, ethyl, dimethylaminomethylene and diethylaminometylene.

The reaction of Grignard compounds with nickel salts was mentioned in chapter 4 C [152]; exchange of alkyl groups as catalyzed by nickel halides was discussed in paragraph D of this chapter [212]. The possible formation of an intermediate "Nickel-Grignard" in the reaction of methylmagnesium bromide with the adduct of triphenylphosphine and nickel chloride was mentioned in chapter 5 I [264].

As Nakaya, Arabori and Imoto found manganese(II) and (III) as well as cobalt(II) and (III) acetylacetonates react with phenylmagnesium bromide to form biphenyl and (in some cases) acetophenone [274].

Alexander, Davies, Hey and Done studied the Kharasch reaction of

methylmagnesium iodide with several polychlorinated 5-bromonorbor-2-nenes [275]; using cobalt (II) chloride as the catalyst a variety of products was obtained possibly via radical intermediates. Those products in which a methyl group (from the Grignard reagent) was introduced contained two or three chlorine atoms less than the starting bromides e.g.



For several reduction products the authors suggest cobalt hydride as the hydrogen source (as was proposed by Abraham and Hogarth (1968); cobalt hydride might be a constituent of the "black materials" formed in the reaction of methylmagnesium iodide and cobalt salt. These "black materials" may also contain adsorbed hydrogen which would be an alternative or additional reducing agent. Tungsten(VI) chloride, WCl_6, catalyzes the disproportionation reaction of Grignard reagents with olefins in a homogeneous system [276]. E.g. 2-pentene in benzene is isomerized to a mixture of cis- and trans-2-pentenes within 60 minutes after which 31% 2-butenes, 65% 2-pentenes and 4% 3-hexenes could be isolated from the reaction mixture.

M. Organomagnesium compounds in polymerization reactions

Among the numerous reports on the application of organomagnesium

compounds in polymerization reactions the following drew special attention:

Isotactic polymers were obtained from methyl methacrylate as well as from methyl α-chloroacrylate when polymerized with the product from the reaction of ethylmagnesium bromide with phenylstyryl ketone [277]

Ethylmagnesium-N,N-di-n-butylamide, C_2H_5-Mg-N(-n-C_4H_9)$_2$, was used as the catalyst for the polymerization of acrylonitrile [278].

In an other report the polymerization of acrylonitrile is realized by dipyridylmagnesium or by ethylpyridylmagnesium in dimethylformamide at -60° [279].

Joh, Kurihara and Tomita report the polymerization of methacrylonitrile by dipiperidylmagnesium or by diethylmagnesium [280]; as chain regulators primary or secondary amines were added.

α-Naphthylmagnesium bromide, didecyl-, diphenyl-, di-m-tolyl-, di-p-tolyl- as well as di-α-naphthylmagnesium were used, mixed with titanium(IV) iodide, as catalysts for the polymerization of 1,3-butadiene and for benzene-isoprene [281].

Magnesium chloride or magnesium bromide, mixed with aminotitanium compounds and organoaluminum compounds, is reported to be an active catalyst in the polymerization of ethylene [282].

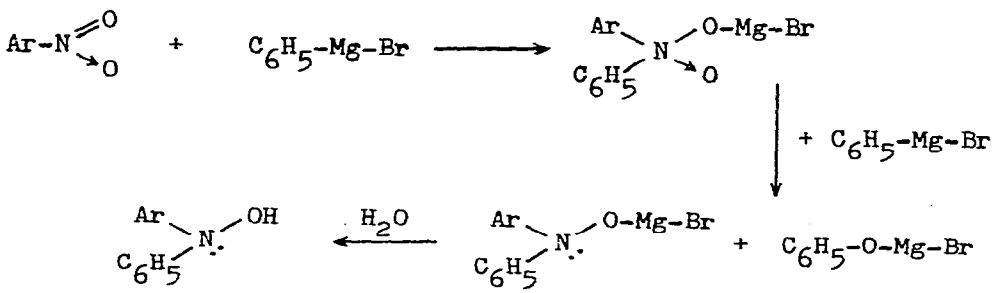
NMR and visible spectrum data suggest that RMgX (R = phenyl or benzyl) is changed to a carbanion on addition of more than two molar equivalents HMPT and that the polymerization of styrene by this species is initiated by the addition of the carbanion to styrene monomer [283]; the formation of carbanions by addition of HMPT to Grignard solutions is discussed in chapter 3 B [83] and [84].

Stafford studied the kinetics of the polymerization of propylene oxide by organomagnesium compounds such as diethylmagnesium as a

diethyl ether-dioxane complex, magnesium bromide as a diethylether complex and ethylmagnesium bromide as a diethyl ether complex [284]. The polymerization of vinylphosphonate is reported: with dialkylmagnesium polymerization occurs in benzene at 80° whereas in a mixture toluene/THF the reaction takes place at -10° [285].

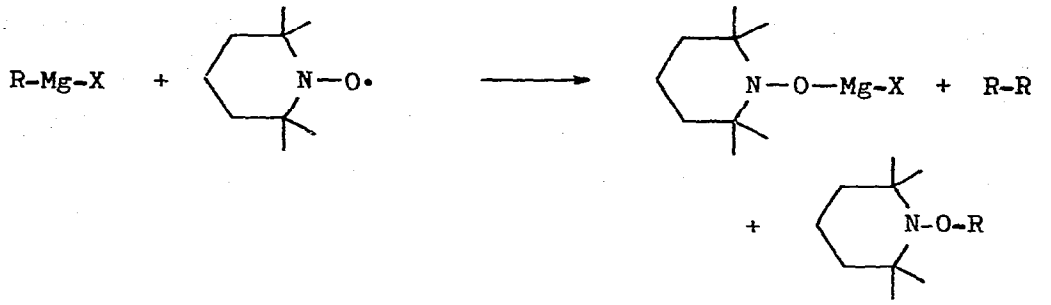
N. Miscellaneous

A second report has appeared in 1971 on the reaction of Grignard compounds with organic nitro compounds (for the first report see chapter 2 D; [75]): Yost, Gutmann and Muscoplat investigated the reaction of phenylmagnesium bromide with aromatic nitro compounds such as 2-nitrofluorene, 3-nitrofluorene, 4-nitrobiphenyl and 4-nitro-p-terphenyl [286]. In each case diarylhydroxylamines were the main products:



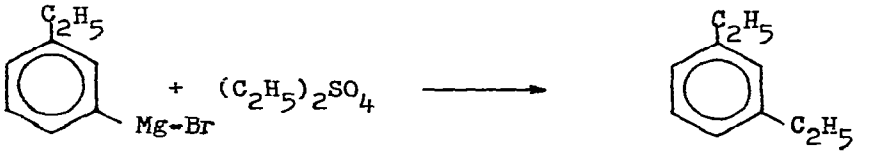
The mechanism of the second step in this sequence of reactions is discussed by the authors; oxidation of a second Grignard molecule takes place under the formation of phenol.

The reaction of Grignard reagents R-Mg-X, with R = phenyl, cyclohexyl, ethyl or methyl, with N-oxyl free radicals leads to the for-

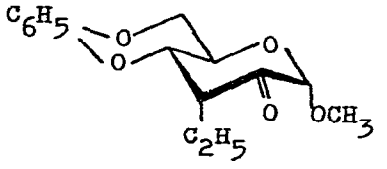


mation of several products among which dimerization products R-R according to Sholle, Golubev and Rozantsev [287].

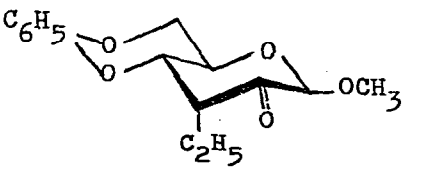
Diethylsulfate reacts with m-ethylphenylmagnesium bromide to form m-diethylbenzene [288]:



Inch, Lewis and Williams continued their investigations of the reaction of Grignard reagents with keto sugars; the configurations of the preponderant products formed by reaction of methyl 4,6-O-benzylidene-3-deoxy-3-C-ethyl-α-D-ribo as well as -arabo-hexopyranosid-2-uloses [38] and [39] with different Grignard reagents are not



[38]



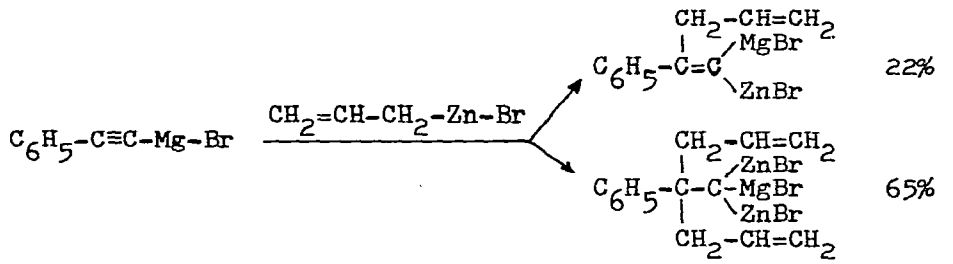
[39]

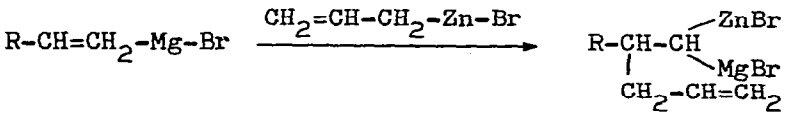
necessarily the same [289]. In their investigations the authors used phenyl and methyl Grignard compounds.

Cooper, Inch and Sellers got only low optical yields in the reaction of ethynylmagnesium bromide, complexed with 1,2:5,6-di-O-isopropylidene-D-glucofuranose (see also Inch and coworkers A.S. 1969) with cyclohexylphenyl ketone (3% optical yield); also other reactions leading to alkynyl carbinols of the same type gave poor optical yields as compared to previous results. The authors state that the variable optical yields "serve to demonstrate further the complexity of the coordination effects between sugars and Grignard reagents" [290].

In an extension of his studies on asymmetric reductions to more groups possessing C_{3v} symmetry Mosher, together with Biernbaum, investigated the asymmetric reduction of phenyl trimethylsilyl ketone and phenyl triphenylsilyl ketone [291]. The highest stereoselectivity in this series was 33%.

Gaudemar found that allylzinc bromide forms several addition reaction products when it is added to unsaturated Grignard compounds as is indicated in the following reactions [292]:





Yields varying from 24% for R = CH_3 to 58% for R= n-C_3H_7

The following reports might be of interest for organomagnesium chemists too:

McCreary and Thorn determined the vapor pressure equation for magnesium [293]:

$$-R\ln p = 34.435\ T^{-1} - 26.258$$

The crystal structure of magnesium amide, $Mg(-NH_2)_2$ was determined by Jacobs by means of X-ray analysis [294].

David, Laurent and Lang report that the crystal structure of magnesium nitride, Mg_3N_2 is isotypic with the structure of magnesium phosphide [295].

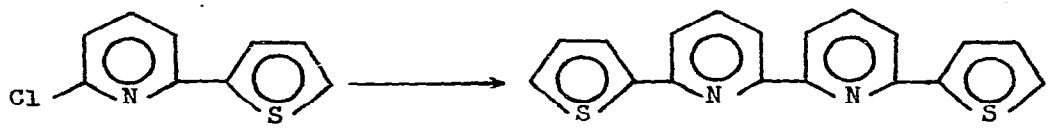
The addition of boranes to solutions of Grignard compounds in THF has a marked influence on the magnesium deposited from this solution on electrolysis [296]; the white, ductile metal obtained was at least 99% pure!

Binks and Lloyd investigated the formation of pinacol from acetone with magnesium amalgam [297]. Different solvents were used as well as different mercury salts; the stoichiometry of the reaction is 1 acetone to 1 magnesium.

Ashby and Srivastava investigated the reduction of diethylmagnesium with aluminum hydride [298]; several mixed magnesium-aluminum compounds were isolated.

James applied the mixed magnesium aluminum hydride, $Mg(AlH_4)_2$, in reduction reactions of organic compounds such as nitrobenzene, benzamide etc. [299]. In some instances yields were as high as 100%.

Kauffmann, Wienhöfer and Woltermann used a mixture of magnesium and cuprous chloride in the following Ullmann-type reaction to prepare the tetra-arene 40 in low yields [300]:

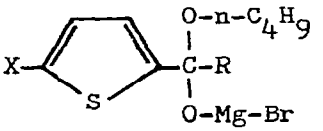


40

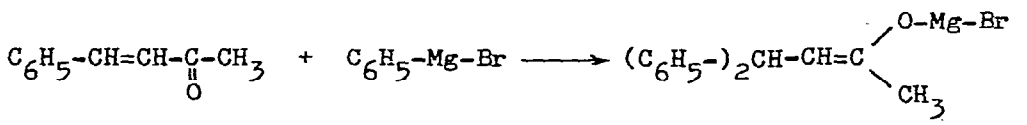
Several reports have appeared on reactions and properties of magnesium alkoxides:

Leroux, Larchevêque and Combret used n-butoxymagnesium halide in reactions with different halides as well as in different solvents for ether synthesis in Williamson-type reactions [301]. In general only reasonable yields were obtained in HMPT as the solvent although even than the results were varying.

In a series of papers on the reduction of halogenated ketones by halomagnesium alcoholates Lapkin and coworkers studied the thermal stabilities of the reaction products with the following structure [302]

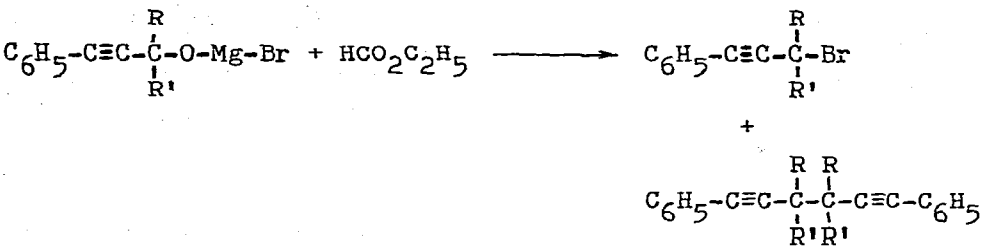


Acylation of halomagnesium alkoxides, obtained by the reaction of Grignard compounds with ketones as in the following example [303]



was investigated by both Angibeaud and Lagrange [303] as well as by Cardillo, Casnati, Malatesta and Pochini [304]; a remarkable solvent dependence of O- and C-acylation was observed.

It is reported by Rybakova that acetylenic alkoxides react with diethyl oxalate or with ethyl formate as follows [305]:



In some instances, e.g. with R = R' = phenyl the bromide was obtained in yields as high as 78%; with R = methyl and R' = n-butyl the dimerization product was obtained in 72% yield.

Finally Mme Miginiac and Courtois reported that contrary to allyllithium, allylmagnesium bromide does not react at all with cinnamylic quaternary ammonium salts like $C_6H_5-CH=CH-CH_2-\overset{\oplus}{N}(C_2H_5)_3I^{\ominus}$ [306].

REFERENCES

1 C.A. Russell, May & Baker Lab. Bull. 9 (1971) 92

2 H.A.M. Snelders, Chem. and Techn. (Amsterdam), 26 (1971) 418

3 I. Partchamazad, Quart. Bull. Fac. Sci. Tehran Univ. 2 (1970) 5

4 S.F. Zhil'tsov and O.N. Druzhkov, Usp. Khim. 40 (1971) 226; Chem. Abstr. 75 (1971) 5986i

5 N.I. Novikov and V.I. Esafov, Uch. Zap. Ural. Gos. Univ. 71 (1969) 35; Chem. Abstr. 75 (1971) 76035j.

6 R.A. Benkeser, Synthesis (1971) 347

7 J. Villiêras, Organometal. Chem. Rev. A, 7 (1971) 81

8 D.J. Cardin, M.F. Lappert, J.D. Smith and D.R.M. Walton, Ann. Rep. Progr. Chem. Sect. B, 67 (1970) 271

9 B. Wagner, Diss. Ruprecht-Karl-University, Heidelberg (1969)

10 J.D. Toney, Diss. Abstr. Int. B. 31 (1970) 607

11 R.W. Ridgway, Diss. Abstr. Int. B. 31 (1970) 593

12 A.M. Rothman, Diss. Abstr. Int. B. 31 (1970) 1839

13 J.H. Merkley, Diss. Abstr. Int. B. 31 (1970) 2570

14 R.D. Shupe, Diss. Abstr. Int. B. 31 (1970) 4594

15 G. Witz, Diss. Abstr. Int. B. 31 (1970) 5278

16 N.K. Robertson, Diss. Abstr. Int. B. 31 (1970) 1181

17 D.D. Malpass, Diss. Abstr. Int. B. 32 (1971) 175

18 R.C. Arnott, Diss. Abstr. Int. B. 32 (1971) 817

19 W.H. Decker, Diss. Abstr. Int. B. 32 (1971) 161

20 H.M. Rowe-Anderson, Diss. Abstr. Int. B. 32 (1971) 841

21 C.D. Whitt, Diss. Abstr. Int. B. 32 (1971) 810

22 P.K. Sysak, Diss. Abstr. Int. B. 32 (1971) 1467

23 C.E. Cottrell, Diss. Abstr. Int. B. 32 (1971) 2065

24 D. Clark, Diss. Abstr. Int. B. 32 (1971) 823

25 H.C. Holtkamp, Thesis Vrije Universiteit, Amsterdam, 1971

26 J.F. Fauvarque, Thesis Paris, Reg. No. CNRS: A.O. 5399

27 J. Ducom, Thesis Paris, Reg. No. CNRS: A.O. 5201

28 J.C. Appleby, Chem. Ind. (London) (1971) 120

29 H.W.H.J. Bodewitz, C. Blomberg and F. Bickelhaupt, Tetrahedron Lett. (1972) 281

30 H.H. Grootveld, C. Blomberg and F. Bickelhaupt, Tetrahedron Lett. (1971) 1999

31 E.A. Hill and M.R. Engel, J. Org. Chem. 36 (1971) 1356

32 W.C. Kossa Jr., T.C. Rees and H.G. Richey Jr., Tetrahedron Lett. (1971) 3455

33 M.H. Aleksankin, L.I. Fileleeva and I.P. Gragerov, Ukr. Khim. Zh. 37 (1971) 390; Chem. Abstr. 75 (1971) 118047x

34 M.S. Baird, C.B. Reese and M.R.D. Stebbles, J. Chem. Soc. D. (1971) 1340

35 L.N. Cherkasov, S.I. Radchenko and B.S. Kupin, Zh. Obshch. Khim.

41 (1971) 936

36 B. Delmond and J.C. Pommier, J. Organometal. Chem. 26 (1971) C7

37 G. Fraenkel and J.W. Cooper, J. Amer. Chem. Soc. 93 (1971) 7228

38 G. Fraenkel, E. Pechhold and D.G. Adams, J. Org. Chem. 36 (1971) 1368

39 T. Doi, N. Kunieda, M. Kinoshita and M. Imoto, Mem. Fac. Eng. Osaka City Univ. 11 (1969) 69; Chem. Abstr. 75 (1971) 130158s

40 C. Tamborski and G.J. Moore, J. Organometal. Chem. 26 (1971) 153

41 C.F. Smith, G.J. Moore and C. Tamborski, J. Organometal. Chem. 33 (1971) C21

42 M.T. Rahman, M.R. Smith Jr., A.F. Webb and H. Gilman, Organometal Chem. Syn. 1 (1971) 105

43 N.V. Kruglova and R.K. Freidlina, Izv. Akad. Nauk. SSSR, Ser. Khim (1971) 1028

44 L. Miginiac and J. Blois, J. Organometal. Chem. 29 (1971) 349

45 S.F. Campbell, J.M. Leach, R. Stephens, J.C. Tatlow and K.N. Wood, J. Fluorine Chem. 1 (1971) 103

46 S.F. Campbell, J.M. Leach, R. Stephens and J.C. Tatlow, J. Fluorine Chem. 1 (1971) 85

47 F. Gaudemar-Bardone and M. Gaudemar, Bull. Soc. Chim. Fr. (1971) 3316

48 B. Blagoev, M. Momchev, D. Ivanov and K.T. Todorov, Dokl. Bolg. Akad. Nauk. 24 (1971) 879; Chem. Abstr. 76 (1972) 45880x

49 R. Pallaud and Le Ngoc Lang, C.R. Acad. Sci. Sér. C, 273 (1971) 418

50 G. Karmas (Ortho Pharmaceutical Corp.) Fr. 1.596.554 (1970); Chem Abstr. 74 (1971) 141296r

51 B. Sundbeck, A.L. Abramo, R. Bjorklund, B. Borretzen and K.G. Olson (Aktiebolag. Ferrosan) Fr. 2.030.939 (1970); Chem. Abstr.

74 (1971) 110414u.

52 Y. Frangin, R. Couffignal and M. Gaudemar, Bull. Soc. Chim. Fr. (1971) 246

53 A. Gaiffe and J. Castanet, C.R. Acad. Sci. Sér. C, 272 (1971) 96

54 M. Ito, K. Abe, H. Takeshita and M. Yatagai, Bull.Chem. Soc. Jap. 44 (1971) 2168

55 N. T. Sultanov, S.D. Mektiev, T.G. Efendieva, S.Y. Kodzhaeva, M.A. Alieva, M.M. Balakiskieva and F.A. Mamedov, U.S.S.R. 280.476 (1968); Chem. Abstr. 74 (1971) 142040q

56 E. Michel, J. Raffi and C. Troyanowsky, C. R. Acad. Sci. Sér. C, 272 (1971) 1643

57 J.L. Moreau and M. Gaudemar, Bull. Soc. Chim. Fr. (1971) 3071

58 N.A. Belikova, I.V. Gazuko, A.F. Plate and K.E. Sterin, Vestn. Mosk. Univ. Khim. 12 (1971) 119; Chem. Abstr. 74 (1971) 111647 q

59 S.S. Guts and V.D. Sukhoverkhov, Vestn. Kiev. Politkh. Inst. Ser. Khim. Mashinostr. Tekhnol. (1969) 80; Chem. Abstr. 75 (1971) 76230u

60 W. Draber and K.H. Buechel, Ger. Off. 1.940.628 (1971); Chem. Abstr. 74 (1971) 125697f

61 J. Filip, Radioisotopy 11 (1970) 427.

62 M. Goshaev, O.S. Otroshchenko and A.S. Sadykov, Mauch. Tr. Samarkand Univ. 167 (1969) 175; Chem. Abstr. 74 (1971) 142110n

63 C.V. Greco and B.P. O'Reilly, Tetrahedron Lett. (1971) 3057

64 P.G. Harrison, J.J. Zuckerman and J.G. Noltes, J. Organometal. Chem. 31 (1971) C23

65 E.C. Ashby and S.H. Yu, J. Org. Chem. 36 (1971) 2123

66 V.I. Stanko and G.A. Anarova, Zh. Obshch. Khim. 41 (1971) 1521

67 L.I. Zakharkin, G.G. Zhigareva and L.S. Podvisotskaya, Izv. Akad. Nauk. SSSR, Ser. Khim. (1971) 2312

68 J.P. Pascault and J. Gole, J. Chim. Phys. Physicochim. Biol. 68 (1971) 198

69 T. Saito, J. Chem. Soc. D. (1971) 1422

70 Y. Baryshnikov and A.A. Kvasov, Tr. Khim. Khim. Tekhnol. (1970) 105; Chem. Abstr. 75 (1971) 63860z

71 T. Moroe, A. Komatse and S. Akutagava, Japan 71 03,770 (1971); Chem. Abstr. 75 (1971) 20583u

72 J.B. Lambert and W.L. Oliver Jr. Tetrahedron 27 (1971) 4245

73 J. Vit (Nat. Pat. Dev. Corp.) Ger. Offen. 2,112,644; Chem. Abstr. 76 (1972) 85912r

74 H. Nozaki, T. Aratani, T. Toraya and R. Noyori, Tetrahedron 27 (1971) 905

75 C. Morat and A. Rassat, Bull. Soc. Chim. Fr. (1971) 891

76 M. Boussu and J.-E. Dubois, C.R. Acad. Sci. Sér. C. 273 (1971) 1270

77 E.E. Johnson, U.S. 3,572,932 (1971); Chem. Abstr. 75 (1971) 20582t

78 M. Fontanille and G. Tersac, Bull. Soc. Chim. Fr. (1971) 2066

79 C. Chevrot, M. Troupel, J.C. Folest and J. Périchon, C.R. Acad. Sci. Sér. C 273 (1971) 493

80 C. Chevrot, J.C. Folest, M. Troupel and J. Périchon, C.R. Acad. Sci. Sér. C 273 (1971) 613

81 J. Ducom and B. Denise, J. Organometal. Chem. 26 (1971) 305

82 J. Fauvarque and J. Ducom, C.R. Acad. Sci. Sér. C 273 (1971) 268

83 H.F. Ebel and B.O. Wagner, Chem. Ber. 104 (1971) 307

84 H.F. Ebel and B.O. Wagner, Chem. Ber. 104 (1971) 320

85 E.C. Ashby and G.E. Parris, J. Amer. Chem. Soc. 93 (1971) 1206

86 G. Fraenkel, C. Cottrell and D.T. Dix, J. Amer. Chem. Soc. 93 (1971) 1704

87 A. Mârcker and R. Geuss, Angew. Chem. Internat. Edit. 10 (1971) 270

88 D.F. Evans and G.V. Fazakerley, J. Chem. Soc. A (1971) 184

89 J. Ducom, Bull. Soc. Chim. Fr. (1971) 3518

90 J. Ducom, Bull. Soc. Chim. Fr. (1971) 3523

91 M.G. Reinecke, J.F. Sebastian, H.W. Johnson Jr. and C. Pyun, J. Org. Chem. 36 (1971) 3091

92 W.T. Ford, J. Organometal. Chem. 32 (1971) 27

93 E.C. Ashby and S. Yu, J. Organometal. Chem. 29 (1971) 339

94 J. Ducom, Bull. Soc. Chim. Fr. (1971) 3529

95 G.D. Stucky and J.D. Toney, J. Organometal. Chem. 28 (1971) 5

96 K. Ohkubo and F. Watanabe, Bull. Chem. Soc. Jap. 44 (1971) 2867

97 M. Astier and P. Millie, J. Organometal. Chem. 31 (1971) 139

98 M. Yang, M. Ando and K. Takase, Tetrahedron Lett. (1971) 3529

99 C.E. Loader and H.J. Anderson, Canad. J. Chem. 49 (1971) 45

100 C.E. Loader and H.J. Anderson, Canad. J. Chem. 49 (1971) 1064

101 Z. Yoshida, H. Hashimoto and S. Yomeda, J. Chem. Soc. D (1971) 1344

102 A.G. Davies, B.P. Roberts and R. Tudor, J. Organometal. Chem. 31 (1971) 137

103 E.A. Hill and H.-R. Ni, J. Org. Chem. 36 (1971) 4133

104 Ph. Miginiac and B. Cousseran, J. Organometal. Chem. 28 (1971) C5

105 G. Daviaud and Ph. Miginiac, Tetrahedron Lett. (1971) 3251

106 F. Barbot and Ph. Miginiac, C.R. Acad. Sci. Sér. C 272 (1971) 1686

107 H. Felkin, Cl. Frajerman and G. Roussi, Ann. Chim. (Paris) 6 (1971) 17

108 M. Chêrest and H. Felkin, Tetrahedron Lett. (1971) 382

109 M. Chêrest, H. Felkin and Cl. Frajerman, Tetrahedron Lett. (1971) 379

110 A.J. Kresge and V. Nowlan, Tetrahedron Lett. (1971) 4297

111 P. Pierrot and M. Gaudemar, C.R. Acad. Sci. Sêr. C 272 (1971) 698

112 G. Daviaud, M. Massy-Barbot and Ph. Miginiac, C.R. Acad. Sci. Sêr. C 272 (1971) 969

113 C. Nivert and L. Miginiac, C.R. Acad. Sci. Sêr. C 272 (1971) 199

114 A. Rieker, Y. Butsugan and M. Shimizu, Tetrahedron Lett (1971) 1905

115 B.S. El'yanov and T.B. Svetlanova, Izv. Akad. Nauk. SSSR, Ser. Khim. (1971) 2102

116 M. Luuk and A. Tuulmets, Reakts. Sposobnost. Org. Soedin 8 (1971) 485; Chem. Abstr. 76 (1972) 45355e

117 J. Koppel and A. Tuulmets, Reakts. Sposobnost. Org. Soedin 7 (1970) 1187; Chem. Abstr. 75 (1971) 19401b

118 J. Koppel and A. Tuulmets, Reakts. Sposobnost. Org. Soedin 7 (1970) 1178; Chem. Abstr. 75 (1971) 19403d

119 J. Koppel, J. Loit, M. Luuk and A. Tuulmets, Reakts. Sposobnost. Org. Soedin 8 (1971) 1155

120 A. Pilt, H. Uus and A. Tuulmets, Acta et Commentationes Univ. Tartuensis, 289 (1971) 131

121 A. Tuulmets, Abstr. Pap. V Int. Conf. Organometal. Chem. Moscow 1971, p. 234 (English translation)

122 J. Loit, M. Luuk and A. Tuulmets, Reakts. Sposobnost. Org. Soedin 8 (1971) 237; Chem. Abstr. 76 (1972) 13409j

123 E.C. Ashby, J. Laemmle and H.M. Neumann, J. Amer. Chem. Soc. 93 (1971) 4601

124 J. Laemmle, E.C. Ashby and H.M. Neumann, J. Amer. Chem. Soc.

93 (1971) 5120

125 C. Georgoulis, B. Gross and J.C. Ziegler, C.R. Acad. Sci. Sér. C, 273 (1971) 292

126 J. Vaiga, M. Luuk and A. Tuulmets, Reakts. Sposobnost. Org. Soedin 8 (1971) 27; Chem. Abstr. 76 (1972) 3043w

127 E. Ghera and S. Shoua, J. Chem. Soc. D (1971) 398

128 J. Ficini and A. Maujean, Bull. Soc. Chim. Fr. (1971) 219

129 J.P. Battioni and W. Chodkiewicz, Bull. Soc. Chim. Fr. (1971) 1824

130 D. Nasipuri, C.K. Ghosh, P.R. Mukherjee and S. Venkataraman, Tetrahedron Lett. (1971) 1587

131 J.F. Fauvarque, C.R. Acad. Sci. Sér. C 272 (1971) 1053

132 S.V. Vitt and E.I. Khristova, Izv. Akad. Nauk. SSSR. Ser. Khim. (1971) 833

133 C. Georgoulis, B. Gross and J.C. Ziegler, C.R. Acad. Sci. Sér. C 273 (1971) 378

134 D. Wege, Austral. J. Chem. 24 (1971) 1531

135 R. Gélin, S. Gélin and A. DeHondt, Tetrahedron Lett. (1971) 4669

136 T. Holm and I. Crossland, Acta Chem. Scand. 25 (1971) 59

137 I. Crossland and T. Holm, Acta Chem. Scand. 25 (1971) 1158

138 T. Holm, J. Organometal. Chem. 29 (1971) C45

139 W. Reeve, R. Brown and T.F. Steckel, J. Amer. Chem. 93 (1971) 4607

140 A.F. Levit, N.N. Kalibabchuk and I.P. Gragerov, Dokl. Akad. Nauk SSSR 199 (1971) 1325

141 S.E. Orlova, B.A. Trofimov and A.S. Atavin, Mater. Konf. Vop. Str. Reakts. Sposobnosti Atsetalei, 2nd (1967) Edited by V.I. Ivanov. Chem. Abstr. 75 (1971) 140081a

142 V.I. Esafov and V.I. Azarova, Zh. Obshch. Khim. 41 (1971) 1787

143 G.J. Dubsky and A. Jacot-Guillarmod, Helv. Chim. Acta 54 (1971) 1571

144 M. Okubo, K. Maruyama and J. Osugi, Bull. Chem. Soc. Jap. 44 (1971) 1365

145 L.I. Zakharkin, V.V. Gravilenko and B.A. Palei, Zh. Obshch. Khim 40 (1970) 2669

146 H.G. Richey Jr., W.F. Erickson and A.S. Heyn, Tetrahedron Lett. (1971) 2183

147 W.T. Ford, J. Org. Chem. 36 (1971) 3979

148 M. Tamura and J. Kochi, J. Amer. Chem. Soc. 93 (1971) 1483

149 M. Tamura and J. Kochi, J. Amer. Chem. Soc. 93 (1971) 1487

150 M. Tamura and J. Kochi, J. Amer. Chem. Soc. 93 (1971) 1485

151 M. Tamura and J. Kochi, J. Organometal. Chem. 31 (1971) 289

152 M. Tamura and J. Kochi, Bull. Chem. Soc. Jap. 44 (1971) 3063

153 M. Tamura and J. Kochi, Synthesis 6 (1971) 303

154 M.M. Morsumzade, P.A. Gurbanov, A.L. Shabanov and F.F. Dzharadov Tr. Azerb. Inst. Nefti. Khim. (1969) 27; Chem. Abstr. 74 (1971) 111815

155 P.R. Jones, W.J. Kauffman and E.J. Goller, J. Org. Chem. 36 (1971) 186

156 R. Cantagrel and Y. Maroni-Barnaud, C.R. Acad. Sci. Sér. C 272 (1971) 1558

157 F. Rocquet, A. Sevin and W. Chodkiewicz, C. R. Acad. Sci. Sér. C 272 (1971) 417

158 L. Baiocchi and M. Giannangeli, Boll. Chim. Farm. 110 (1971) 207 Chem. Abstr. 75 (1971) 129386h

159 A. Barabas and A.T. Balaban, Tetrahedron 27 (1971) 5495

160 J. Conia and J.P. Barnier, Tetrahedron Lett. (1971) 4981

161 W. Ried and R. Lantzsch, Chem. Ber. 104 (1971) 679

162 V.K. Potapov, M.N. Kochetkova and Z.A. Shabarova, Zh. Obshch. Khim. 41 (1971) 240

163 D. Guillerm-Dron, M.L. Capmau and W. Chodkiewicz, C.R. Acad. Sci. Sér. C 273 (1971) 759

164 Y.M. Skvortsov, A.N. Volkov, E.B. Oleinikova and M.F. Shostakovskii, Zh. Org. Khim. 7 (1971) 232

165 L. Miginiac, M. Lanoiselee, Bull. Soc. Chim. Fr. (1971) 2716

166 F.U. Lisenko, Izv. Vyssh. Ucheb. Zaved. Khim., Khim. Tekhnol. 14 (1971) 242; Chem. Abstr. 74 (1971) 141142n

167 M.A.F. Elkaschef, F.M.E. Abdel-Megeid, K.E. Mokhtar and K.E.M. Zaki, J. Chem. Soc. C (1971) 1055

168 A.A. Akhrem, L.I. Ukhova and N.F. Uskova, Izv. Akad. Nauk. SSSR Ser. Khim. (1970) 2305

169 J. Fischer and G. Mikite, Acta Chim. (Budapest) 68 (1971) 253; Chem. Abstr. 75 (1971) 20720m

170 J. Michel and P. Canonne, Canad. J. Chem. 49 (1971) 4085

171 A. Das Gupta, Indian J. Chem. 9 (1971) 85

172 L.N. Akimova, Zh. Org. Khim. 7 (1971) 464

173 L.N. Akimova and N.L. Orlikova, Vestn. Mosk. Univ. Khim. 12 (1971) 748; Chem. Abstr. 76 (1972) 85327d

174 W. Reeve, Synthesis (1971) 132

175 E.S. Lavrinovich, U.S.S.R. 297, 626 (1971); Chem. Abstr. 75 (1971) 88289h

176 J.C. Combret, M. Larchevêque and Y. Leroux, Bull. Soc. Chim. France (1971) 3501

177 T. Shigo and Y. Shinichi, Yuki Gosei Kagaku Kuokai Shi, 29 (1971) 530; Chem. Abstr. 76 (1972) 34603h

178 D.I. Davies, P. Mason and M.J. Parrott, J. Chem. Soc. C (1971) 3428

179 W.M. Horspool, P. Stanley, R.G. Sutherland and B.J. Thomson, J. Chem. Soc. C (1971) 1365

180 C. Moise, J. Tirouflet and D. Sautrey, C.R. Acad. Sci. Sér. C 271 (1970) 951

181 L. Fontanella, L. Mariani, E. Occelli, B. Rosselli del Turco, and A. Diena, Farmaco Ed. Sci. 26 (1971) 489; Chem. Abstr. 75 (1971) 76536y

182 D.H.R. Barton, Y.D. Kulkarni and P.G. Sammes, J. Chem. Soc. C (1971) 1149

183 M.N. Rybakova, Uch. Zap. Perm. Univ. 207 (1970) 283; Chem. Abstr 76 (1972) 24819u

184 L. Lepage-Lomme and Y. Lepage, C.R. Acad. Sci. Sér. C 272 (1971) 2205

185 I.I. Lapkin, T.A. Svinina, N.A. Karavanova and L.S. Skvortsova, Zh. Org. Khim. 7 (1971) 2487

186 G. Emptoz, F. Huet and A. Jubier, C.R. Acad. Sci. Sér. C 273 (1971) 1543

187 Ph. Coutrot, J-Cl. Combret and J. Villiéras, Tetrahedron Lett. (1971) 1553

188 E.G. Lubemets, T.N. Gerisimova and E.P. Fokin, Zh. Org. Khim. 7 (1971) 805

189 G.A. Holmberg and L. Jalander, Acta Acad. Abo, Math. Phys. 30 (1970) 9; Chem. Abstr. 75 (1971) 110141c

190 J. Pornet and L. Miginiac, C. R. Acad. Sci. Sér. C 273 (1971) 1763

191 J. Lengyel, R.V. Mark and C.A. Troise, Synth. Comm. 1 (1971) 153

192 M. Sekiya and Y. Terao, Chem. Pharm. Bull 19 (1971) 391

193 J.S. Whitehurst and J. Overnell, J. Chem. Soc. C (1971) 378

194 K. Sugita and Sh. Tamura, Nippon Kagaku Zasshi 92 (1971) 570; Chem. Abstr. 76 (1972) 72174 b

195 O. Tsuge, I. Shinkai and M. Tashiro, Kogyo Kagaku Zasshi 72 (1969) 1680; Chem. Abstr. 74 (1971) 42202a

196 Y. D. Churkin and N.I. Putokhin, Khimia (1969) 116; Chem. Abstr. 75 (1971) 76496 k

197 Y. D. Churkin and N.I. Putokhin, Khimia (1969) 125; Chem. Abstr. 75 (1971) 140594r

198 J.P. Marets and H. Riviere, Bull. Soc. Chim. Fr. (1970) 4320

199 N.V. Kuznetsov and N.K. Guznenok, Ukr. Khim. Zh. 37 (1971) 684; Chem. Abstr. 75 (1971) 150990k

200 H.M. Crawford, J. Org. Chem. 36 (1971) 3533

201 A. Mustafa, A.H. Harbash, M.H. Elnagdi and F. Abd El-All, Justus Liebigs Ann. Chem. 748 (1971) 70

202 E.S. Voskanyan, E.V. Piruzyan, S.M. Gasparyan and G.M. Mkryan, Arm. Khim. Zh. 24 (1971) 638; Chem. Abstr. 76 (1971) 3365c

203 J. Gore and M.L. Roumestant, Tetrahedron Lett. (1971) 1027

204 J.C. Fiaud and H.B. Kagan, Tetrahedron Lett. (1971) 1019

205 G.M. Mkryan, S.M. Gasparyan and N.K. Melkonyan, Zh. Org. Khim. 7 (1971) 27

206 B. Rickborn and J. Staroscik, J. Amer. Chem. Soc. 93 (1971) 3046

207 R. Gelin, S. Gelin and M. Albrand, Bull. Soc. Chim. Fr. (1971) 4146

208 J. Pornet and Mme. L. Miginiac, Tetrahedron Lett. (1971) 967

209 U. Kerb and R. Wiechert, Justus Liebigs Ann. Chem. 752 (1971) 78

210 L.H. Shepard Jr. (Ethyl Corp.) U.S. 3.597.488 (1971); Chem.

Abstr. 75 (1971) 88751c

211 L.H. Shepard Jr. (Ethyl Corp.) U.S. 3.597.487 (1971); Chem. Abstr. 75 (1971) 118398n

212 L. Farady and L. Marko, J. Organometal. Chem. 28 (1971) 159

213 F.W. Von Rein and H.G. Richey Jr., Tetrahedron Lett. (1971) 3777

214 H.G. Richey Jr. and S.S. Szucs, Tetrahedron Lett. (1971) 3785

215 E. Osawa, Z. Majerski and P. von R. Schleyer, J. Org. Chem. 36 (1971) 205

216 O.G. Akperov, D.A. Burdzaliev, Uch. Zap. Azerb. Gos. Univ. Ser. Khim. Nauk. (1969) 67; Chem. Abstr. 74 (1971) 141365n

217 G.A. Borisova, T.S. Zavarykina, A.A. Kron, V.A. Kron and D.E. Stepanov, Izv. Nauch.-Issled. Inst. Nefta-Uglekhim. Sin. Irkutsk Univ. 12 (1970) 63; Chem. Abstr. 75 (1971) 34947c

218 A. Brisset, S. Czernecki and C. Georgoulis, C.R. Acad. Sci. Sér. C 272 (1971) 115

219 J. Iossiphides, E. Michel and C. Troyanowsky, C.R. Acad.Sci. Sér. C 272 (1971) 1566

220 Y. M. Slobodin and I.Z. Egenburg, Tr. Sev.-Zapad. Zaoch. Politekh. Inst. (1969) 39; Chem. Abstr. 75 (1971) 118001c

221 D.R. Taylor, W.T. Flowers, A.E. Tipping and C.N. Wright, J. Chem. Soc. C (1971) 1986

222 H. Quart, E. Schmitt and R. Frank, Angew. Chem. Int. Ed. Engl. 10 (1971) 651

223 W. Ried, Chem. Ber. 104 (1971) 3329

224 B. Looker and F. Sondheimer, Tetrahedron 27 (1971) 2567

225 J.-E. Dubois and M. Boussu, C.R. Acad. Sci. Sér. C 273 (1971) 1101

226 J.-E. Dubois, M. Boussu and C. Lion, Tetrahedron Lett (1971) 829

227 A. Gaiffe and J. Arbelet, C.R. Acad. Sci. Sér. C 272 (1971) 410

228 E. Elkik, M. Le Blanc and Hamid-Assadi Far, C.R. Acad. Sci. Sér. C 272 (1971) 1895

229 E.S. Lo, J. Org. Chem. 36 (1971) 364

230 J.L. Namy, D.Abenhaim and G. Boireau, Bull. Soc. Chim. Fr. (1971) 2802

231 D. Abenhaim, J.L. Namy and G. Boireau, Bull. Soc. Chim. Fr. (1971) 3254

232 D.C. Kleinfelter and T.J. Gerteisen, J. Org. Chem. 36 (1971) 3255.

233 J.M. Normant and J. Cantacuzene, Tetrahedron Lett. (1971) 2405

234 W.D. Stephens, C.S. Combs, T.C. Willis and R.D. Giles, J. Org. Chem. 36 (1971) 2027

235 S. Tanimoto, Z. Mouri, M. Okano, Yuki Gosei Kagaku Kyokai Shi 29 (1971) 313; Chem. Abstr. 76 (1972) 60107u

236 S. Cabiddu, A. Maccioni and M. Secci, Ann. Chim.(Rome) 61 (1971) 432

237 G. Mousset, Bull. Soc. Chim. Fr. (1971) 4097

238 S. Cabiddu, G. Gelli and F. Sotgiu, Ann. Chim. (Rome) 61 (1971) 634

239 G.A. Holmberg and J.E. Johansson, Acta Acad. Abo, Math. Phys. 30 (1970) 8; Chem. Abstr. 75 (1971) 140634h

240 R.E. Lyle and E. White, J. Org. Chem. 36 (1971) 772

241 T.I. Van Bergen and R.M. Kellogg, J. Org. Chem. 36 (1971) 1705

242 H. Suchitzky and F. Binns, J. Chem. Soc. C (1971) 1223

243 A. Marxer, U. Salzmann and F. Hofer, Helv. Chim. Acta 54 (1971) 2507

244 W. Asker, A.H. Harhash and N.A.L. Kassab, J. Prakt. Chem. 313 (1971) 585

245 W. Asker, A.H. Harhash and N.A.L. Kassab, J. Prakt. Chem. 313 (1971) 594

246 L. Neelakantan, J. Org. Chem. 36 (1971) 2256

247 I. Renvall, Acta Acad. Abo, Math. Phys. 30 (1970) 8; Chem. Abstr. 75 (1971) 5764k

248 A.H. Harhash, M.H. Elgadi and E.A.A. Hafez, J. Prakt. Chem. 313 (1971) 706

249 A. Mustafa, A.K. Mansour and H.A.A. Zaher, J. Prakt. Chem. 313 (1971) 699

250 H. Igeta, T. Tsuchiya and T. Nakai, Tetrahedron Lett. (1971) 3117

251 I.M. Gverdtsiteli, M.S. Melua, T.P. Doksopulo and V.A. Chagelishvili, Soobshch. Akad. Nauk. Gruz. SSR 62 (1971) 317; Chem. Abstr. 75 (1971) 49206j

252 B. Suresh and W.J. Considine, U.S. 3,584,027 (1971); Chem. Abstr. 75 (1971) 49862v

253 R. Corriu, J. Masse and G. Royo, J. Chem. Soc. D. (1971) 252

254 R. Corriu, G.F. Lanneau and M. Leard, J. Chem. Soc. D (1971) 1365

255 S. Cabiddu, A. Maccioni and M. Secci, Gazz. Chim. Ital. 101 (1971) 512

256 F. Mêtras, J.C. Lahournère and J. Valade, J. Organometal. Chem. 29 (1971) 41

257 M.B. Lacout-Loustalet, J.P. Dupin, F. Mêtras and J. Valade, J. Organometal. Chem. 31 (1971) 187

258 M.B. Lacout-Loustalet, J.P. Dupin, F. Mêtras and J. Valade, J. Organometal. Chem. 31 (1971) 337

259 J. Donohue, N. Mandel, W.B. Farnham, R.K. Murray, K. Mislow and H.P. Benschop, J. Amer. Chem. Soc. 93 (1971) 3792

260 B.V. Timokhin, E.F. Grechkin, N.A. Tran'kova and O.A. Yakutina, Zh. Obshch. Khim. 41 (1971) 103; Chem. Abstr. 75 (1971) 20512v

261 B.V. Timokhin, E.F. Grechkin and A.V. Kalabina, Zh. Oshch. Khim. 40 (1970) 2517; Chem. Abstr. 75 (1971) 6065v

262 K. Diemert and W. Kuchen, Angew. Chem. Int. Ed. Engl. 10 (1971) 508

263 O.N. Grishina, L.M. Kosova and S.M. Klyuchanskaya, Zh. Obshch. Khim. 41 (1971) 1995; Chem. Abstr. 76 (1972) 34354 c

264 G. Swierczewski, M.L.H. Green, M.J. Smith and H. Felkin, J. Chem. Soc. D (1971) 158

265 A.W.P. Jarvie and D. Skelton, J. Organometal. Chem. 30 (1971) 145

266 K.K. Ginwala and J.P. Trivedi, J. Indian Chem. Soc. 48 (1971) 791; Chem. Abstr. 76 (1972) 33918c

267 J.L. Adcock and J.J. Lagowski, Inorg. Nucl. Chem. Lett. 7 (1971) 473

268 M. Okubo, K. Maruyama and J. Osugi, Bull. Chem. Soc. Jap. 44 (1971) 125

269 O. Riobe, C.R. Acad. Sci. Sér. C 272 (1971) 1045

270 A. Ide, K. Matsumori, K. Ishizu and H. Watanabe, Nippon Kagaku Zasshi, 92 (1971) 83; Chem. Abstr. 76 (1972) 24515s

271 H.M. Walborsky, G.E. Niznik and M.P. Periasamy, Tetrahedron Lett. (1971) 4965

272 N.T. Luong-Thi and H. Rivière, Tetrahedron Lett. (1971) 587

273 E. Uhlig and D. Dorn, Z. Chem. 11 (1971) 187

274 T. Nakaya, H. Arabori and M. Imato, Bull. Chem. Soc. Jap. 44 (1971) 1422

275 D.I. Davies, R. Alexander, D.H. Hey and J.N. Done, J. Chem. Soc. C (1971) 2367

276 M.L. Khidekel, V.I. Ma'rin, A.D. Shebaldova, T.A. Bol'shinskova and I.V. Kalechits, Izv. Akad. Nauk. SSSR, Ser. Khim. (1971) 663

277 D.S. Breslow and A. Kutner, J. Polym. Sci. Part B 9 (1971) 129

278 N. Teranishi and Y. Jo, Japan 7040,062 (1970); Chem. Abstr. 74 (1971) 112656c

279 Y. Jo, T. Yoshihara, Y. Imai and S. Kurihara, Japan 7110, 181 (1971); Chem. Abstr. 75 (1971) 21500b

280 Y. Jo, S. Kurihara and T. Tomita, J. Polym. Sci. Part A-1 9 (1971) 1463

281 W. Nudenberg, D.B. Merrifield and E.A. Delaney, Ger. Offen. 1,645,489 (1971); Chem. Abstr. 75 (1971) 37612a

282 U. Giannini, P. Longi, D. Deluca and B. Pivotto, Ger. Offen. 2.030.753 (1971); Chem. Abstr. 74 (1971) 112626t

283 M. Tomi, H. Kakiuchi, Kogyo Kagaku Zasshi 73 (1970) 2367; Chem. Abstr. 75 (1971) 6423k

284 J.W. Stafford, Makromol. Chem. 147 (1971) 219

285 O.A. Bragina and E.F. Grechkin, Vysokomol Soedin Ser. B 13 (1971) 710; Chem. Abstr. 76 (1972) 601773

286 Y. Yost, H.R. Gutmann and C.C. Muscoplat, J. Chem. Soc. C (1971) 2119

287 V.D. Sholle, V.A. Golubev and E.G. Rosantsev, Dokl. Akad. Nauk. SSSR 200 (1971) 137

288 A.V. Strashnenko and E.S. Endel'man, Metody Poluch. Khim. Reaktivov Prep. 18 (1969) 118; Chem. Abstr. 74 (1971) 141126k

289 T.D. Inch, G.J. Lewis and N.E. Williams, Carbohydr. Res. 19 (1971) 17

290 D.B. Cooper, T.D. Inch and D.J. Sellens, Tetrahedron Lett. (1971) 2329

291 M.S. Biernbaum and H.S. Mosher, J. Org. Chem. 36 (1971) 3168

292 M. Gaudemar, C.R. Acad. Sci. Sér. C 273 (1971) 1669

293 J. McCreary and R.J. Thorn, High Temp. Sci. 3 (1971) 300

294 H. Jacobs, Z. Anorg. Allg. Chem. 382 (1971) 97

295 Y. Joh, S. Kurihara and T. Tomita, J. Polym. Sci. Part A-1 9 (1971) 1463

296 A. Brenner and J.L. Sligh, Trans. Inst.-Metal. Finish 49 (1971) 71; Chem. Abstr. 75 (1971) 44208b

297 J. Binks and D. Lloyd, J. Chem. Soc. C (1971) 2641

298 E.C. Ashby and S.C. Srivastava, Inorg. Chem. 10 (1971) 186

299 B.D. James, Chem. Ind. London (1971) 227

300 Th. Kauffmann, E. Wienhöfer and A. Woltermann, Angew. Chem. Int. Ed. Engl. 10 (1971) 741

301 Y. Leroux, M. Larchevêque and J.C. Combret, Bull. Soc. Chim. Fr. (1971) 3258

302 I.I. Lapkin, E.V. Dormidontova, Y.P. Dormidontov, P.A. Sentebov and L.D. Parfenova, Khim. Geterosikl. Soedin. 7 (1971) 1171; Chem. Abstr. 76 (1972) 46021e

303 P. Angibeaud and M.J. Lagrange, C.R. Acad. Sci. Sér. C 272 (1971) 1506

304 B. Cardillo, G. Casnati, V. Malatesta and A. Pochini, Rend. Ist. Lomb. Sci. Lett. A 104 (1970) 404; Chem. Abstr. 75 (1971) 19451t

305 M.N. Rybakova, Uch. Zap. Perm. Univ. 207 (1970) 278; Chem. Abstr. 76 (1972) 24821p

306 G. Courtois and L. Miginiac, C.R. Acad. Sci. Sér. C 273 (1971) 68