MAGNESIUM

ANNUAL SURVEY COVERING THE YEAR 1977[+]

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I. Introduction 2
II. Preparation of Organomagnesium Compounds 3
  A. Reaction of magnesium metal with organic halogen compounds 3
  B. Other reactions which form organomagnesium compounds 4
  C. Some organomagnesium compounds prepared or studied 9
    1. Halogen-substituted compounds 9
    2. Hydroxy, alkoxy, and acetal-substituted compounds 10
    3. Amino-substituted compounds 11
    4. Carboxy- and other carbonyl-substituted compounds; enolates 12
    5. Unsaturated and polycyclic compounds 12
    6. Heteroaromatic compounds 13
    7. Di-magnesium derivatives and other metal-substituted or metallomagnesium compounds 13
  D. Analysis of organomagnesium compounds 15
III. Spectra, Properties, and Structures of Organomagnesium Compounds 16
  A. Spectroscopic studies 16
  B. Other physical measurements 18
  C. Isomerism in structure and reactions of allylic and related organomagnesium compounds 19
  D. Reversibility in reactions of allylic organomagnesium compounds 24
IV. Reactions of Organomagnesium Compounds with Carbonyl Functions 25
  A. Mechanism of the Grignard addition 25
  B. Stereochemistry of addition to aldehydes and ketones 30
    1. Stereochemistry with aldehydes and acyclic ketones 30
    2. Stereochemistry with cyclic ketones 33
  C. Selective additions to aldehydes and ketones 38
  D. Other additions to aldehydes and ketones 41
  E. Reactions with carboxylic acids and derivatives 45
    1. Open-chain derivatives 45
    2. Lactones, lactams, and cyclic anhydrides 51
V. Addition of Organomagnesium Compounds to Other Unsaturated Functions 54
  A. Reaction with carbon-nitrogen unsaturation 54
  B. Reaction with carbon-carbon unsaturation 60
  C. Reaction with conjugated carbonyl and carboxy derivatives 67
  D. Addition to heteroaromatic compounds 77
  E. Addition to C=S groups 81
  F. Addition to other unsaturated compounds 82

[+] E.A. Hill, Magnesium; Annual Survey covering the year 1976, see J. Organometal. Chem., 158 (1978) 93 - 210.

VI. Displacement Reactions by Organomagnesium Compounds 83
A. Coupling or displacement reactions with organic halides or sulfonates 83
B. Displacement reactions at C-O, C-S, or C-N bonds 92
C. Displacement reactions at sulfur or phosphorous 100
D. Alkylation (displacement) at other elements 102
E. Reaction as a base; metallation 111
VII. Other Reactions of Organomagnesium Compounds 113
A. Rearrangements 113
B. Catalysis of polymerization and other reactions 114
C. Miscellaneous reactions 116
REFERENCES 120

I. INTRODUCTION

The seventh volume of Korte's Methodicum Chimicum, devoted to the preparation of compounds of the main group elements, includes a chapter by Blomberg on magnesium chemistry with a heavy emphasis on organometallic aspects [1].

Review articles published during 1977 which are concerned largely with organomagnesium chemistry include:

*A review by Blomberg and Hartog of the Barbier reaction, which compares its usefulness to the more common Grignard variation and discusses a number of special cases [2].

*A review of organomagnesium rearrangements by Hill [3].

*Another review by Riecke on the preparation and use of reactive metal powders [4].

Other reviews which have a smaller content of organomagnesium chemistry, but which may prove useful for leading references are concerned with: the structure of main group organometallic compounds with electron-deficient bridge bonds [5]; two reviews of syntheses of insect pheremones, with a generous sampling of organomagnesium reactions [6,7]; the synthesis of chiral organotin compounds [8]; potentially dangerous explosive or very vigorous reactions of metal alkyls [9]; metal atom syntheses of organometallic compounds [10]; orthocarbonic acid derivatives [11]; cyclometallation reactions [12]; aryne- and carbene-formation from organoelement compounds [13]; and free radicals in organometallic chemistry [14]; organocopper reagents in organic synthesis [14a]; main group II peroxides [14b]; and reactions of the Me_3SiCl/Mg/donor solvent combination with various substrates [14c].

An undergraduate Grignard reaction laboratory experiment is described [15] The product, 4-methyl-3-heptanol, is an insect pheremone.

Several doctoral theses with heavy content in organomagnesium chemistry appeared in 1978. In addition to new chemistry which they present (covered elsewhere in this survey), they incorporate substantial literature reviews. These include:

*P. Tergis (City University of New York), "Structure of Grignard Reagents in Diethyl Ether" [16].

*T. L. Wiesemann (Georgia Institute of Technology), "Studies Concerning the Nature of Grignard Reactions with Ketones" [17].

*J.-J. Lin (Georgia Institute of Technology), "Organometallic Reagents in Organic Synthesis" (Reduction with magnesium hydride reagents) [18].

*M. P. Siklosi (Purdue University), "Reversible Grignard and Grignard-Type Reactions. Mechanistic Considerations of the Reaction of Allylic Grignard Reagents with Ketones" [19].

*G. A. Mora Lopez (University of Kansas), "Copper Catalyzed Coupling Reactions Between Grignard Reagents and Functionalized Alkyl Halides" [20].

*T. D. Lee (University of Oregon), "Synthesis of Spin-Labelled Derivatives of Lipids, Diacylglycerolphosphatidylcholine and Pyrochlorophyll-A via Grignard and Alkyllithium Additions to Nitrones" [21].

*N.-C. Wang (Memorial University of Newfoundland), "Reactions of Some Metal Derivatives of Pyrrole" [22].

II. PREPARATION OF ORGANOMAGNESIUM COMPOUNDS

A. Reaction of magnesium metal with organic halogen compounds

In a study of Grignard reagent formation from "cage structures" such as 1-bromoadamantane, it was found that improved yields of Grignard reagent (up to 60%) and less adamantane or bi-adamantyl could be obtained using a "static" procedure for the reaction in ether solution. It was proposed that there is a preliminary initiation phase, in which R· ·MgBr pairs lead mostly to the side products and generate active surface magnesium atoms, followed by a second phase in which Grignard reagent is formed along with the byproducts [23].

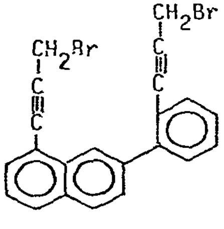
Reduction of cinnamyl chloride with magnesium and HCl in ether led to mixtures of 1- and 3-phenylpropenes which were quantitatively different from those obtained by hydrolysis of the Grignard reagent. A reduction mechanism similar to Grignard reagent formation was proposed, in which a surface organometallic is protonated [24].

Of general interest in organometallic chemistry is a study of the effectiveness of various drying agents. For drying dioxan, lithium aluminum hydride, silica gel, alumina, and calcium sulfate were unexpectedly poor; calcium hydride was rapid and efficient, and potassium hydroxide was surprisingly good [25].

The use of reactive magnesium powders for production of organomagnesium reagents has been reviewed [4], and additional examples of the use of Riecke's magnesium powder have been reported for the "*in situ*" coupling of various alkyl and aryl halides with organotin iodides [26], to reduce coupling during formation of a Grignard reagent from camphenylyl chloride [27], and for preparation of other Grignard reagents.

Two new recipes for production of active magnesium by reduction have appeared. Magnesium halides with potassium graphite in ether or benzene produce magnesium intercalated in graphite, which forms Grignard reagents rapidly at low temperatures or in non-ether solvents [28]. Reduction of $MgCl_2$ in a homogeneous reaction with sodium naphthalene in THF has been recommended for its low cost, ease, and safety [29].

Amalgamated magnesium has been used for *in situ* Barbier-Grignard reaction with methylene iodide [30], for intramolecular coupling of 1 and 2 [31,32], and



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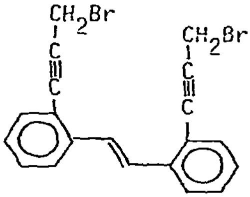

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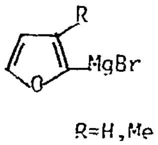
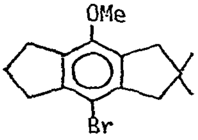


3

for coupling (*in situ*) of methyl chloromethyl ether with silyl chlorides [33]:

$$RSiMe_2Cl \;+\; ClCH_2OMe \;\xrightarrow[HgCl_2]{Mg}\; \underset{\text{(no Fe present)}}{RSiMe_2CH_2OMe} \quad \text{or} \quad \underset{\text{(Fe filings, stirrer or vessel)}}{RSiMe_2OMe \;+\; C_2H_4}$$

A copper-magnesium alloy activated with iodine has been used for formation of 3 [34]. A Grignard reagent has been prepared from 4 by entrainment with ethylene bromide in THF, although metal-halogen exchange with butyllithium failed [35].



4

5

The Grignard reagent from 5 formed in low yield, along with 50-60% of Wurtz product, even with slow addition and a large excess of magnesium [36]. Similarly, 3-bromocyclohexene coupled quantitatively on attempted Grignard reagent formation, even at -50° [37].

Patents have been issued for apparatus for continuous production of Grignard reagents [38,39], and for a large-scale apparatus for their preparation and carbonation with $^{13}CO_2$ [40].

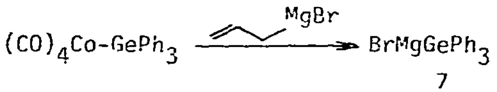
B. Other reactions which form organomagnesium compounds

A number of organomagnesium compounds have been formed by metal exchange reactions. Bis(trimethylsilyl)magnesium has been prepared by exchange of metallic magnesium with the corresponding mercury compound in THF or

DME [41,42]. A crystalline DME complex could be purified by recrystallization and sublimation. It was characterized by hydrolysis with D_2O, by elemental analysis, and by spectroscopic and crystallographic data to be discussed below (sections III A and B). Magnesium-cobalt exchange has also been used for synthesis of silyl- and germylmagnesium derivatives [43]; e.g.

$$(CO)_4Co\text{-}SiPh_3 \;+\; RMgBr \;\rightarrow\; \underset{\underline{6}}{BrMgSiPh_3}$$

(R=Me,Et,allyl)

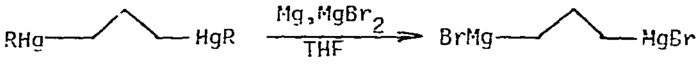


$$(CO)_4Co\text{-}GePh_3 \longrightarrow BrMgGePh_3$$

7

Compounds 6 and 7 were characterized by reaction with H_2O, D_2O, allyl bromide and chlorotrimethylsilane (5 only). A magnesium enolate was made by exchange of $MgBr_2$ with the lithium enolate [44].

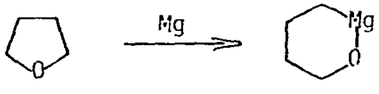
Synthesis of 8 involved three metal exchanges, including



8

It was characterized by carbonation and reaction with Me_3SnCl, Ph_2SiCl_2 and Me_2SiCl_2 [45]. Magnesium bromide-THF complexes were also prepared by exchange of metallic magnesium with $HgBr_2$ [46]. Complexes $MgBr_2\cdot3THF$ and $MgBr_2\cdot4THF$ were obtained by concentration and crystallization above 30° and below 5°, respectively. Recrystallization from methylene chloride gave $MgBr_2\cdot2THF$, and addition of some water gave $MgBr_2\cdot4THF\cdot2(H_2O)$.

Tetrahydrofuran reacts with activated magnesium to produce the magnesium heterocycle 9 [47].



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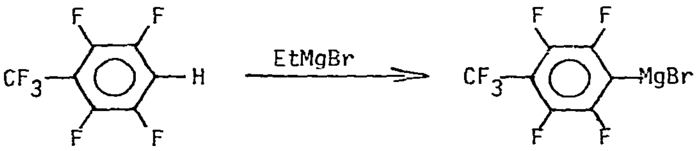
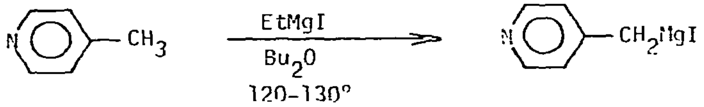
Introduction of magnesium by deprotonation (metallation) is commonplace for terminal alkynes and cyclopentadienes; some other examples of interest include:



[48]



[49]

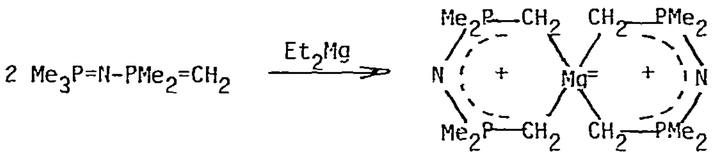
[50]

10

11

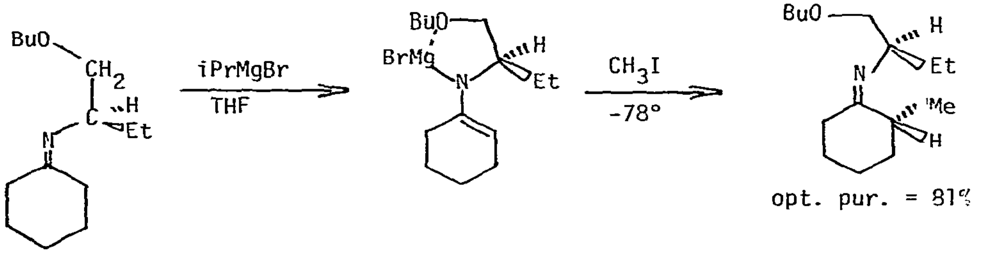
In the last instance metallation occurs cleanly with benzylmagnesium chloride. Reaction of 10 with magnesium metal produces initially 3,5-dichlorophenylmagnesium chloride, which in turn metallates the original chloride to produce 11. Similar reactions were observed with 1,2,3,4-, 1,2,3,5- and 1,2,4,5-tetrachlorobenzene and with pentachlorobenzene.

A chelated ylid complex of magnesium is also formed by deprotonation:



The product distills in vacuum, and was characterized by IR and mass spectrometry [51].

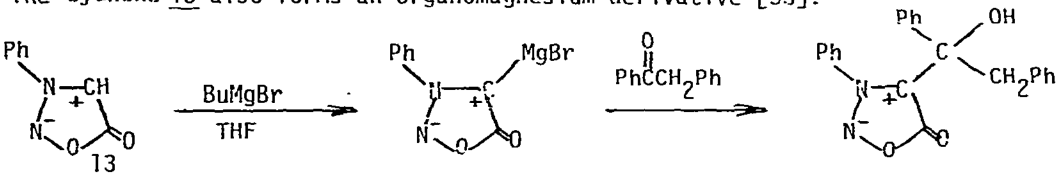
The magnesium derivative from enamine 12 is alkylated stereoselectively in a predictable fashion [52].



opt. pur. = 81%

12

The sydnone 13 also forms an organomagnesium derivative [53]:



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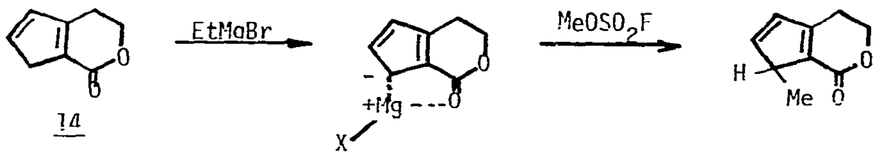
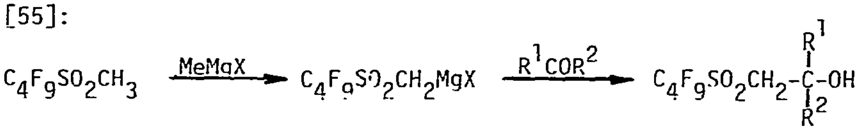
The cyclopentadienylmagnesium derivative of 14 is regioselectively alkylated possibly due to chelation of the magnesium with localization of the charge [54].



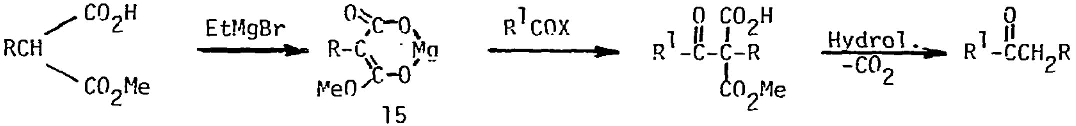
14

Methylperfluoroalkyl sulfones are also converted to organomagnesium derivatives [55]:



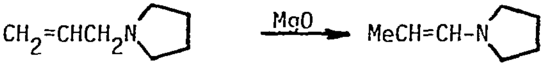
$$C_4F_9SO_2CH_3 \xrightarrow{MeMgX} C_4F_9SO_2CH_2MgX \xrightarrow{R^1COR^2} C_4F_9SO_2CH_2\text{-}\overset{R^1}{\underset{R^2}{C}}\text{-}OH$$

The Ivanov reagent PhCH(MgCl)CO$_2$MgCl was prepared by reaction of phenylacetic acid with isopropylmagnesium chloride [56]. The magnesium enolate 15 provides a useful route to ketones [57,58,59].



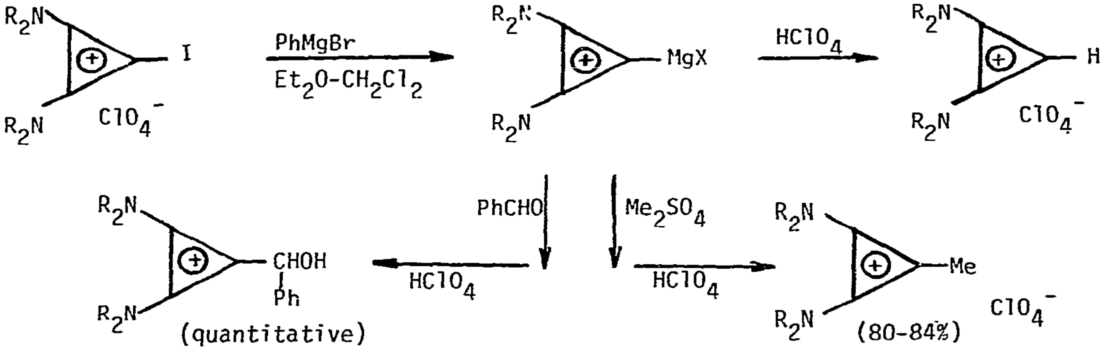
15

The hydrogen exchange of hydrocarbons over MgO appears to correlate with CH acidity; surface magnesium alkyls are effectively the reaction intermediate [60]. The same may be suggested for the isomerization of 16 [61].

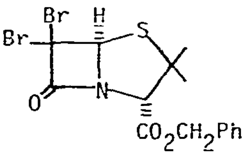


16

Formation of Grignard reagents by magnesium-halogen exchange is common with perfluoro-compounds (e.g., C$_6$F$_5$MgBr) [62]. The iodocyclopropenium ion 17 also exchanges iodine for magnesium, producing a novel Grignard reagent [63].



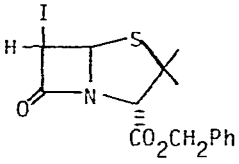
Metal halogen exchange occurs readily with the halogenated penicillinate and cephalosporate esters 18-20. In the case of 18, a 95% yield of a mixture of diastereomeric addition products with acetaldehyde was isolated [64].



18

+MeMgBr

THF,-78°



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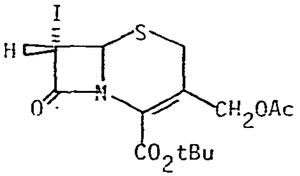
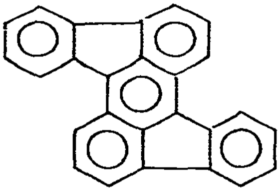


20

The formation and isolation of R_2Mg compounds by precipitation of magnesium halide-dioxanate is reported for $R=Me_3CCH_2-$, Me_3SiCH_2-, and $PhMe_2CCH_2-$. The neopentyl compound is characterized as a trimer soluble in benzene and sublimable in vacuum, but the silyl compound appears to be polymeric [65].

A complex between $U(OiPr)_6$ and three moles of R_2Mg is reported (R=Me, neopentyl, Me_3SiCH_2-). A donor-acceptor structure is proposed in which each magnesium is coordinated to two isopropoxy oxygens [66]. Reaction of magnesium aluminohydride-THF with $AlH_3{\cdot}NMe_3$ and $tBuNH_2$ led to a complex of stoichiometry $(tBuNAlH)_3{\cdot}tBuNMg{\cdot}THF$ [67] (see also section III.B).

Reaction of magnesium with fluorenone at 300° led to the polycyclic product 21. Analogous products are produced from benzofluorenone.



21

The year saw several publications by Ashby's group on the preparation and characterization of alkylmagnesium hydrides and related reagents. Lithium aluminum hydride reacts with Me_2Mg or Ph_2Mg in THF to produce MeMgH or PhMgH in solution. Reaction of active MgH_2 (produced from $LiAlH_4$ and Et_2Mg in 1:1 ratio) with Me_2Mg or Ph_2Mg formed RMgH or RMg_2H_3, depending upon stoichiometry. These were characterized by NMR, ebulliometry, and thermal analysis [70,71,72]. Reaction of "ate-complexes" of Me_2Mg and Me_2Zn with $LiAlH_4$ gave complex hydrides $MgZnH_4$ and $Mg(ZnH_3)_2$, depending upon stoichiometry [73]. The active MgH_2 slurry also reacts exothermically with THF solution of $MgBr_2$ or $MgCl_2$ to produce solutions of HMgX. Disproportionation appears to occur in the solid state [74].

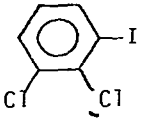
The new magnesium hydride reagents are reported to add to alkenes and alkynes; reduction of carbonyl compounds also occurs, but without unusual stereoselectivity. Reagents of composition HMgOR or H_3Mg_2OR, from reaction of active MgH_2 with ROH or $Mg(OR)_2$ in THF, could be isolated as solids, and appeared from powder diffraction patterns to be compounds rather than physical mixtures. These reagents reduced cyclohexanones with enhanced selectivity to equatorial attack [75]. A preparative procedure for magnesium hydride from butylmagnesium bromide and lithium aluminum hydride has been published [76].

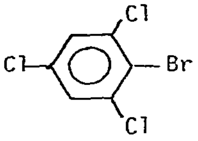
C. Some organomagnesium compounds prepared or studied

In this section, a variety of functionally-substituted organomagnesium reagents or other reagents of less typical structure will be surveyed.

1. Halogen-substituted compounds

Selective formation of aryl mono-Grignard reagents from the following halides and magnesium metal has been reported.





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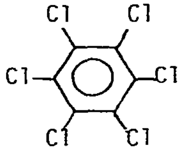
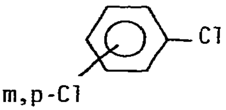


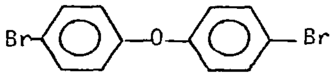
[77]

23

[78]



[78]



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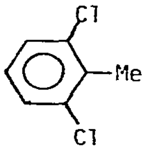
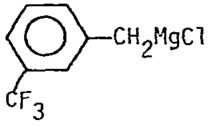
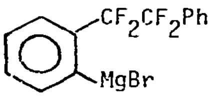


[79]

Formation of 22 in ether required entrainment with ethylene bromide and a 36 hour reaction time. Some di-Grignard reagent and dibromide accompanied 23. Formation of Grignard reagents from some poly-chlorinated benzenes led to metallation of unreacted halide by the initially formed Grignard reagent [50] (see section II.B) Fluorinated Grignard reagents have been prepared:



[80,81]

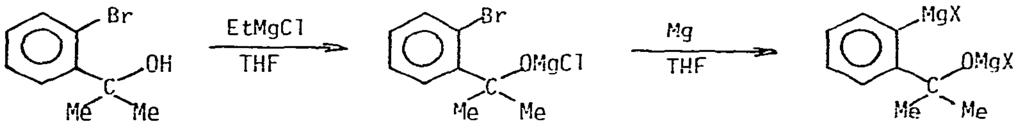


[82]

The latter required entrainment with ethylene bromide and freshly cut magnesium.

2. Hydroxy-, alkoxy-, and acetal-substituted compounds

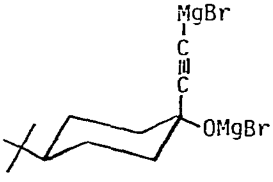
A hydroxy-substituted Grignard reagent was prepared by first converting the OH group to an alkoxide [83]:



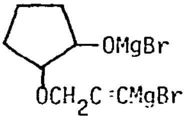
Several organomagnesium compounds were prepared from a hydroxy-substituted acetylene and an excess of a Grignard reagent; e.g.

$BrMgC{\equiv}CCR_2OMgBr$

[84-87]



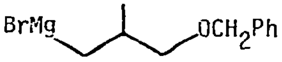
[84]



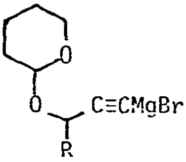
[88]

Reaction with most electrophiles occurs at the C-Mg bond, but both functions may be silylated [85].

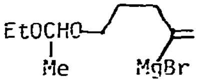
Ether or acetal groups have been used to protect a hydroxyl function, and then removed after formation and reaction of the Grignard reagents. Examples include the following:



(>95% pure enantiomers)
[89]



[90-92]



[93]

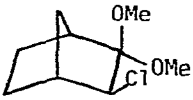
The per-fluorinated β-alkoxy Grignard reagents 24 and 25 may be prepared from the corresponding iodides [94] but reaction of 26 with magnesium led to elimination [25]. Other alkoxy-substituted Grignard reagents include 27 [96] and

$(CF_3)_2CFOCF_2CF_2MgI$

24

$IMgCF_2CF_2O(CF_2)_5OCF_2CF_2MgI$

25



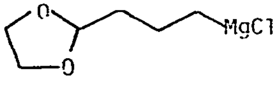
26

$BrMgC{\equiv}C{-}CH{=}CHOMe$

27

a Grignard reagent from ethyl chloromethyl ether [97]. Aryl Grignard reagents with perfluoroalkoxy groups [98] and a variety of other alkoxy groups are routinely prepared.

An aldehyde function protected as an acetal is present in reagents 28-30 [99-101]. With 28 and 29, intramolecular attack on the acetal group (with cyclization to a cyclobutane) is a side reaction competing with normal Grignard reactions. However, it is reported that very concentrated solutions (5 M) are reactive toward carbonyl groups at lower temperature and lead to excellent yields [100].



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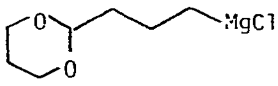

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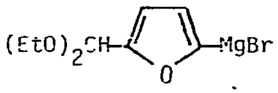
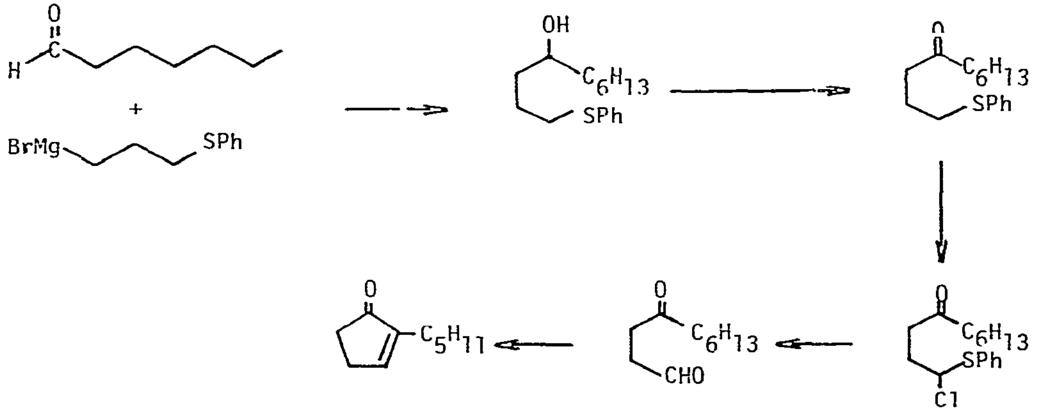


30

Two reports of Grignard reagents with thioether functions may be noted. Grignard reagents PhS$(CH_2)_n$MgBr (n=3,4) are useful for synthetic introduction of a functionalized three- or four-carbon chain [102]. One of several examples is shown:



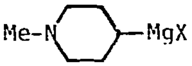
The yield of Grignard reagent from p-methylthiobenzyl chloride is improved with excess magnesium and at high dilution; the yield is lower in THF, or with addition of benzene or toluene to ether [103].

3. Amino-substituted compounds

The use of γ-dialkylamino Grignard reagents 31 and 32 (and closely

$Me_2N\text{-}CH_2CH_2CH_2MgCl$

31



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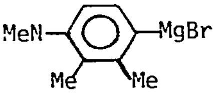


33

related variants) has now become quite commonplace, and references will not be given. Preparation of the reagent 33 required entrainment with ethylene bromide [104].

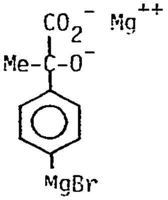
4. Carboxy- and carbonyl-substituted compounds; enolates

The carboxy-substituted Grignard reagents 34 and 35 were prepared by conventional reactions. The carboxy group was protected as an oxazoline in 36, and subsequently regenerated by hydrolysis. An enolate was prepared by reaction of magnesium with 4-bromo-2,2-dimethyl-3-pentanone, and converted to R_2Mg by precipitation with dioxan [108]. Other enolates are noted elswewhere (section II.B).

$BrMgC{\equiv}C(CH_2)_2CO_2MgBr$

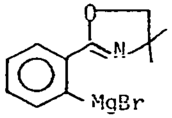
34

[105]



35

[106]

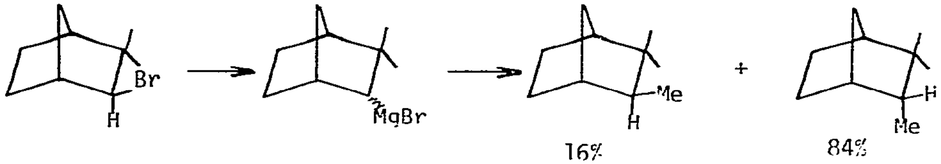


36

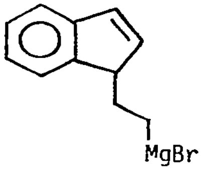
[107]

5. Unsaturated and polycyclic compounds

As noted in section II.A, a high-yield preparation of the 1-adamantyl Grignard reagent has been reported [23]. The Grignard reagent from camphenylyl bromide was characterized stereochemically by a cuprate coupling [27].



The Grignard reagents 37 and 38 have been reported; no competition from metallation of 37 at the indenyl position was noted. A Grignard reagent was prepared from p-vinylbenzyl chloride; the magnesium was activated with ethylene bromide [111]. The secondary benzylic Grignard reagent 39 was prepared and reacted in good yield.



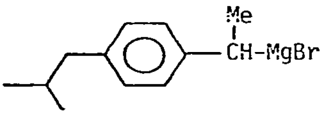
37

[109]

$BrMgC{\equiv}C\text{-}CH{=}CH_2$

38

[110]



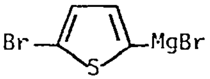
39

[112]

"Allylic isomerism" of allylic, propargyl, or allenic Grignard reagents is covered in section III.D.

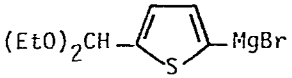
6. Heteroaromatic compounds

A variety of heteroaromatic Grignard reagents have been prepared conventionally and used synthetically. These include the unsubstituted 2-thieny [113,114], 2- and 3-thenyl [114-116], and 2-furyl [34,113] reagents, and reagents 40-48.



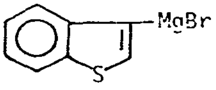
40

[117]



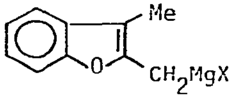
41

[101]



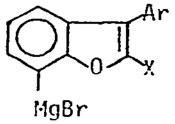
42

[118]



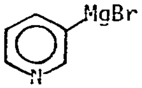
43

[119]



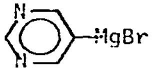
44 [X=H,Br,Me]

[120]



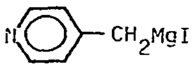
45

[121]



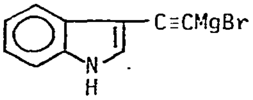
46

[98]



47

[49]



48

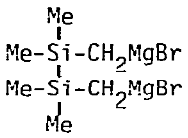
[122]

7. Di-magnesium derivatives and other metal-substituted or metallo-magnesium compounds

The di-Grignard reagents 49 and 50 have been prepared. The former was made via magnesium-mercury exchange; the latter was formed in 60% yield from

49

[45]



$$\begin{array}{c} \mathrm{Me} \\ | \\ \mathrm{Me{-}Si{-}CH_2MgBr} \\ | \\ \mathrm{Me{-}Si{-}CH_2MgBr} \\ | \\ \mathrm{Me} \end{array}$$

50

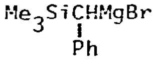
[123]

the dibromide in ether, along with 20% of cyclic coupling product. Di-magnesium derivatives of thiophene and 2,2'-bithienyl were studied [124,125].

Metal- or metalloid-substituted Grignard reagents include 51-56, formed

Me_3SiCH_2MgCl

51
[126]



$Me_3SiCH(Ph)MgBr$

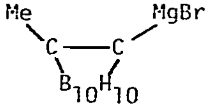
52 (75% in ether)
[127]

$Me_3SiCH{=}CHMgBr$

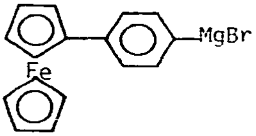
53
[85]

$Me_2AsCH_2CH_2CH_2MgCl$

54
[128]



55
[129]

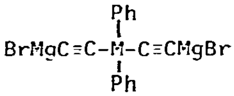


56
[130]

by reaction between the halide and magnesium metal, and 57 and 58 prepared from the corresponding alkyne and a Grignard reagent.

$R_3MC{\equiv}CMgBr$

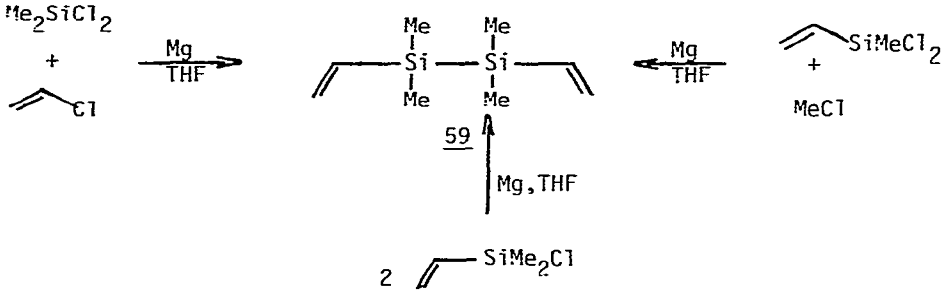
57 (M=Ge,Si)
[131,132]

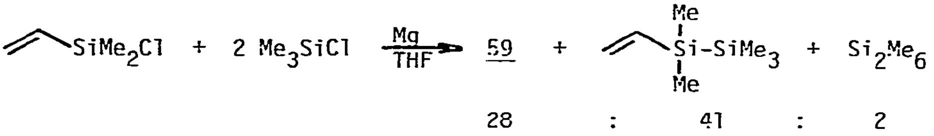


$BrMgC{\equiv}C{-}M(Ph)_2{-}C{\equiv}CMgBr$

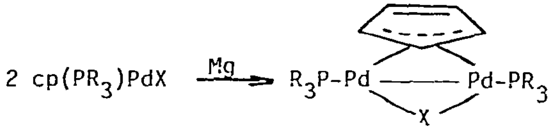
58 (M=Ge,Si)
[132]

Previous mention has been made of the synthesis of (triorgano)silyl or -germyl magnesium derivatives by metal exchange [41-43] (section II.B). It is possible that similar intermediates are involved in the reactions of Me_3SiCl wi various classes of organic compounds in the presence of magnesium metal and a donor solvent [14b], and in the following reactions [133-135]:

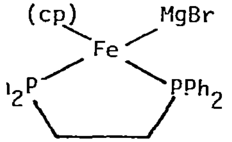




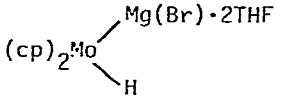
$$2\ R_2SbBr \xrightarrow{Mg} R_2SbSbR_2$$



The "inorgano-Grignard reagents" 60 and 61 have been studied. The former



60
[136,137]

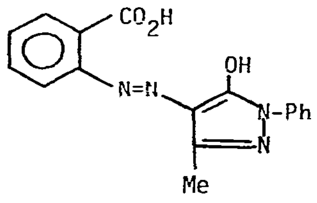


61
[138]

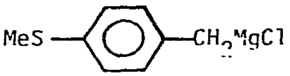
is acylated by benzoylchloride and reacts with alkylbromides to give a mixture of products, including those of alkylation and magnesium-bromide exchange (along with products from the radical derived from the alkylbromide). The latter was characterized by X-ray crystallography, and its reaction with water (cp_2MoH_2), $CO(cp_2MoCO)$, methyl iodide (cp_2MoHI), allyl bromide (cp_2Mo-π-allyl), benzyl halide (cp_2Mo benzyl$_2$), and acetyl chloride ($cp_2MoHCOMe$).

D. Analysis of Organomagnesium Compounds

A new reagent 62 for spectrophotometric magnesium determination has been proposed [139]. In reaction of 63 and 64, a transient color was noted on

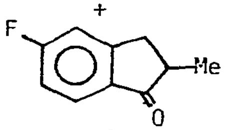


62



63

+



64

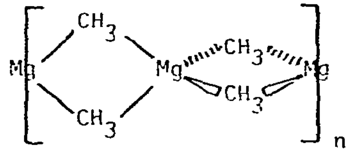
addition of ketone to the Grignard reagent, as long as excess Grignard reagent remained. Titration in this fashion gave a value for Grignard reagent concentration in agreement with other analyses [103].

Voltammetry of Grignard reagents at a silver electrode was studied and used to monitor titrations for Grignard reagent concentration or active hydrogen in solvents [140].

III. SPECTRA, PROPERTIES, AND STRUCTURES OF ORGANOMAGNESIUM COMPOUNDS

A. Spectroscopic Studies

The infrared and Raman spectra of unsolvated $(CH_3)_2Mg$ and $(CD_3)_2Mg$ have been determined at 90 and 300°K [141]. A complete assignement of frequencies was made on the basis of a normal coordinate calculation for an isolated infinite bridged chain structure 65, using 18 force constants. Lack of coincidence between infrared and Raman bands indicated a centrosymmetric unit cell. A relatively large value for the C-Mg force constant may suggest direct metal-metal bonding. Because of extensive coupling, a number of frequencies have a contribution from C-Mg stretching.



65

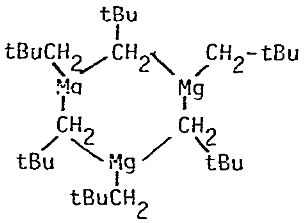
The Raman spectra of $[EtMgBr{\cdot}OiPr_2]_2$, $EtMgBr{\cdot}2\ OEt_2$, $PhMgBr{\cdot}2\ OEt_2$, and $PhMgBr{\cdot}2$ THF have been determined [142]. All have known structures from X-ray diffraction; the first compound is a dimer with bridging bromines, and the others are tetrahedral monomers. The magnesium-bromine and magnesium-carbon stretching frequencies are lowered with increased donor capability of the ether, and consequent greater ionic character of the C-Mg bond. Frequencies of the coordinated ether are similar to those of free ether.

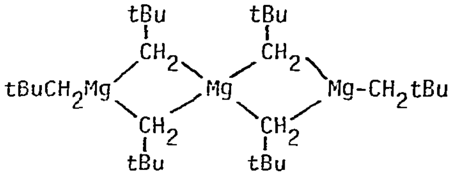
Raman spectra of methyl and ethyl Grignard reagents at various concentrations were interpreted on the basis of associated species with a coordination number of four and bridging halogens. Alkyl bridging was indicated at degrees of association above two. Changes in intensities of ether skeletal bands indicated a change in conformation with coordination [16].

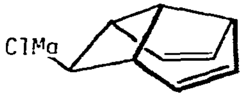
The infrared and Raman spectra of dicyclopentadienylmagnesium have been determined and some new assignments were made [143,144]. The ligand bands are similar to those of other cyclopentadienyl complexes except for lower out-of-plane and higher ring stretching frequencies than in covalent complexes. These differences, and the absence of Raman bands at 1014 and 1400 cm, which are forbidden in free cyclopentadienyl anion, lead to the conclusion that bonding is largely ionic.

An analysis of ^{13}C-H coupling constants for C_1 of isopropyl derivatives, including isopropylmagnesium chloride, has been reported [145]. The one-, two-, and three-bond coupling constants are 120.7, 5.0, and 7.3 Hz, respectively.

NMR spectra of R_2Mg compounds (R=neopentyl, neophyl, or CH_2SiMe_3) have been reported. The solvent-free neopentyl compound is a sublimable trimer postulated to have the structure 66a or b, with proton resonances in benzene at 1.30 and


66a


66b


67

0.40 ppm, and carbon resonances in toluene-d_8 at 36.53 (q), 33.03 (t) and 30.75 ppm. Both broaden at low temperature. ^{1}H-spectra of their ether and TMEDA complexes in benzene are also recorded [65].

The newly synthesized bis-trimethylsilylmagnesium was characterized spectroscopically. The proton shift was -0.09 ppm in DME, and -0.07 ppm in THF. Crystalline adducts with these ethers (1:1 and 1:2, respectively) are soluble in cyclopentane; chemical shifts are -0.03 and +0.01 ppm. The spectrum of a mixture of magnesium and mercury derivatives indicates rapid exchange at room temperature. but several lines are present at -50°, possibly indicating "ate"-complexes [41]. The molecular ion of the DME complex is observable in the mass spectrum [42].

The proton and carbon NMR spectra of the tricyclic Grignard reagent 67 gave no evidence for homoaromatic delocalization [89a]. The α-C resonance appeared at 48.3 ppm, 20 ppm downfield from the resonance in the hydrocarbon.

The cyclic compound 9 from reaction of magnesium with THF was spectroscopically characterized [47]; the α-protons were at -0.30 ppm (t, J=7 Hz).

Mixtures of Me_2Mg and Me_2Zn (or equivalent solutions prepared from $MgBr_2$ and "ate"-complexes of MeLi with Me_2Zn) give only a single proton NMR resonance over a wide temperature range. Infrared spectra of the solutions indicate the presence of free Me_2Mg and Me_2Zn. It is probable that these solutions contain $MgZnMe_4$ or $Mg(ZnMe_3)_2$ in rapid equilibrium with their monomeric constituents [73].

A variety of spectroscopic and physical techniques was used to characterize new magnesium hydride species. In a solution from $LiAlH_4$ + 4 Me_2Mg, equal areas of the Mg-Me and Al-Me proton resonances and the absence of Al-H IR bands indicated quantitative exchange to produce MeMgH. Further spectroscopic characterization of the same species from Me_2Mg and MgH_2 was reported [70]. IR and NMR spectra of PhMgH and $PhMg_2H_3$, produced similarly from Ph_2Mg and MgH_2 or $LiAlH_4$ in THF, and some other RMgH compounds are also recorded [71,72]. NMR signals of the alkyl groups appear at positions characteristic of other organomagnesium compounds, but the hydride signal is probably masked by the THF solvent. An IR band at 1250-1300 cm^{-1} (~940 with deuterium) appears to be the characteristic stretch of a bridging MgH in dimeric or polymeric species. The infrared spectra of HMgCl and HMgBr also have MgH stretching bands at 1290 and 1260 cm^{-1}, respectively [74].

Two ^{13}C NMR studies of metal enolates of 2,2-dimethyl-3-pentanone have been published [108,146]. A distinction between O- and C-metallation appears possible on the basis of chemical shifts of the carbonyl and α-C resonances, although there are solvent and metal effects reflecting changes in ionic character. The one-bond ^{13}C-H coupling constant and the infrared carbonyl (or C=C) stretching frequencies appear to be less characteristic. The RMgBr and R_2Mg species fall in the O-metal category.

Bromine NOR spectra of magnesium bromide and etherates of some organomagnesium bromides have been reported [147]. Low values of the resonance frequencies show that Mg-Br bonding is largely ionic (estimated -86%). There is little effect of alkyl group structure on the MgBr bond, though some minor variations (such as lower frequency for a THF etherate) are explained on the basis of variation in ionic character. A lower frequency for the dimeric $[EtMgBr \cdot O(iPr)_2]_2$ is ascribed to bridging by the bromine atoms. Two sets of resonances were observed for t-BuMgBr.

The carbon 1s binding energy of dicyclopentadienylmagnesium was determined as 290.12 eV, and compared with a variety of transition metal cyclopentadienyls [148].

B. Other physical measurements

The electrochemical oxidation of Grignard reagents at a silver electrode has been studied [140]. Oxidation of the electrode to an unstable organosilver compound occurs, but the potential of an electrode plunged into a Grignard solution is considered to be an equilibrium potential. Voltammetry at the silver electrode was used to follow reactions between Grignard reagents and a variety of reactants ($AgClO_4$, BuOH, $PhNH_2$).

Several molecular association studies of organomagnesium compounds have been reported. In a careful ebullioscopic study, no difference in association of MgI_2 was found in the presence of metallic magnesium; formation of univalent magnesium in sizeable amounts under these conditions is thus precluded [16]. Di(neopentyl)magnesium was found to be trimeric in benzene solution [65]. Methyl- and ethylmagnesium hydrides are dimeric in dilute solution, and more highly associated at higher concentrations, while phenylmagnesium hydride approaches a monomeric structure at high dilution [70-72]. Chloro- and bromomagnesium hydrides are dimeric in dilute solution [74].

Single crystal X-ray analysis has been used to confirm the structure of the bis(trimethylsilyl)magnesium-DME complex [41]. Magnesium is approximately tetrahedrally coordinated, with a SiMgSi angle of 125°. The Mg-Si and Si-C bond lengths are 2.63 and 1.88Å, respectively, and the chelating DME molecule is in a non-planar skew conformation.

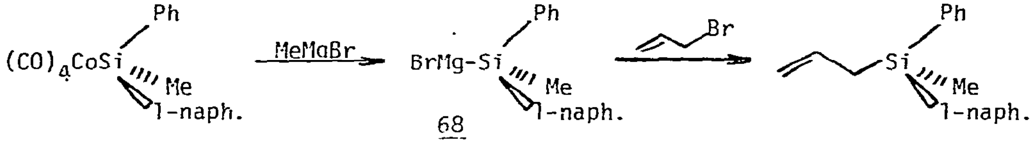
The dimer of pentamethylenemagnesium, $(CH_2)_5Mg \cdot 4THF$, was shown by single crystal electron diffraction to be a 12-membered ring [149]. The conformation of the ring differs somewhat from that of cyclododecane. The THF rings are puckered, and the CMgC bond angle is particularly large at 141.5°.

Crystal structures of two magnesium bromide-THF complexes have been determined [150]. $MgBr_2 \cdot 2THF$ has a polymeric structure in which $MgBr_2$ units form a chain with two bromine bridges between each pair of magnesium atoms. Two THF molecules (trans to each other) complete the distorted octahedral geometry. The complex $MgBr_2 \cdot 4THF \cdot 2(H_2O)$ has a nearly perfect octahedron with water molecules trans; the bromines are outer sphere ions, separated by intermolecular distances. X-Ray powder diagrams of $MgBr_2(THF)_3$ indicate crystallinity, but large crystals were not obtained for a single crystal study.

The X-ray powder diagram of PhMgH, after evaporation of solvent, showed bands characteristic of $Ph_2Mg \cdot 2THF$, and $MeMg_2H_3$ gave a powder pattern corresponding to MgH_2 [72]. Powder diagrams and TGA and DTA studies of thermal decomposition were used to establish the existence of $Mg(ZnH_3)_2$ as a discrete compound [73], but solid HMgBr and HMgCl had powder diagrams identical with $MgBr_2 \cdot 3THF$ and $MgCl_2 \cdot 2THF$ [74].

A complex $(t\text{-}BuNAlH)_3 \cdot tBuNMg \cdot THF$ was shown by X-ray studies to have a cubic structure, with briding nitrogens occupying alternate corners, and with the THF coordinated to the magnesium [67].

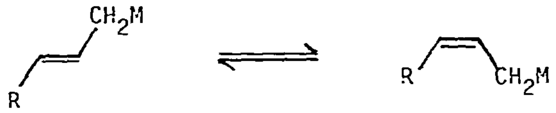
The chiral silylmagnesium compound 68, prepared from an optically active precursor, had a small rotation, but was converted to product with 70% over-all retention of configuration [43].



Atomization energies of several metal cyclopentadienyls (including cp_2Mg were calculated by a virial statistical method [151].

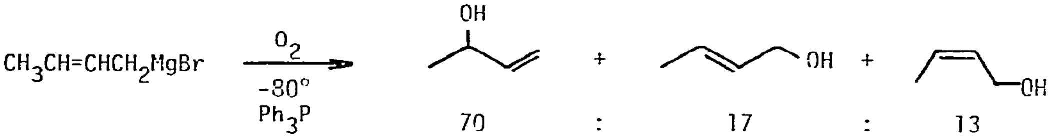
C. Isomerism in structures and reactions of allylic and related organomagnesium compounds

Earlier studies have indicated a preferred cis geometry for substituted allylic organometallic compounds. Since the cis preference increases with the

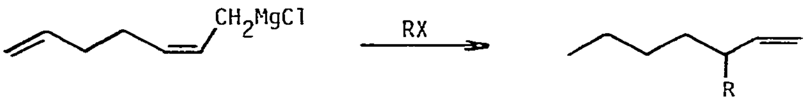


electropositivity of the metal, it has been proposed that the preference is characteristic of the carbanion. It has now been found by measurement of gas phase acidities with ion cyclotron resonance mass spectrometry that the gas phase butenyl anion is 0.2 kcal/mol more stable in the trans configuration [152]. This result casts doubt upon the interpretation of the solution organometallic results.

Oxygenation of the butenyl Grignard reagent yields a mixture of alcohols. The distribution of the initially-formed hydroperoxides was reflected by the products from trapping by phosphine; increased amounts of the secondary alcoho under other conditions resulted from isomerization or parasitic loss of the primary hydroperoxide [153].



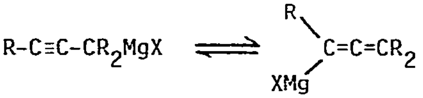
Coupling of Grignard reagent 69 with allylic halides gave products of reaction at the internal carbon [154]:



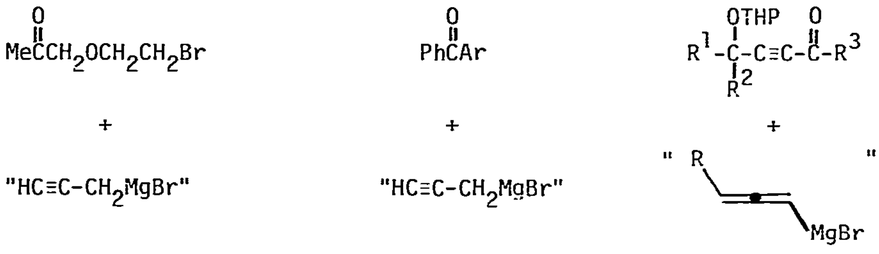
69

Reaction of the 3-methyl-2-butenyl Grignard reagent with an epoxide is noted in section VI.B [155]. Allylic isomerism in addition to carbon-carbon multiple bonds is important in some reactions discussed in section V.B.

"Allylic isomerism" of propargyl Grignard reagents may lead to acetylenic or allenic products. Most frequently, acetylenes are obtained in additions to simple carbonyl compounds. Several examples following this course are:



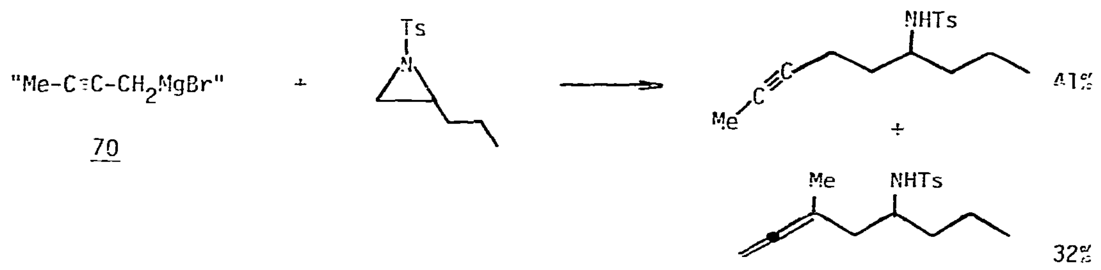
$$\text{R-C}\equiv\text{C-CR}_2\text{MgX} \rightleftharpoons \text{(R)(XMg)C=C=CR}_2$$



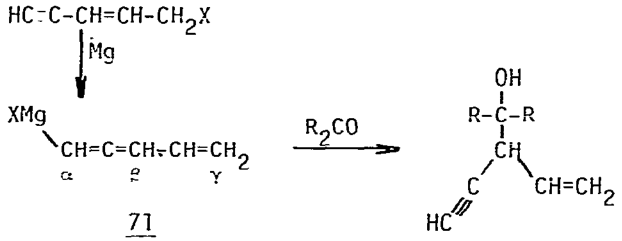
[156] [157] [158]

A number of similar additions to di-aldehydes were used in syntheses of macrocyclic aromatic compounds [159,160] (see section IV.D).

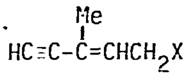
The "2-butynyl" Grignard reagent 70 led to a mixture of acetylenic and allenic products in reaction with a tosylaziridine [161].



The "vinylallenic" Grignard reagent 71 is hydrolyzed by water to the corresponding vinylallene, but gives acetylenic products with most ketones [162] When a vinyl ketone was used, Cope rearrangement of the product to a ketone



provided a useful synthetic sequence. Similar results were obtained with related Grignard reagents from halides 72-74.

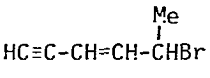


$HC{\equiv}C\text{-}\overset{Me}{C}{=}CHCH_2X$

72

$CH_3C{\equiv}C\text{-}CH{=}CHCH_2Cl$

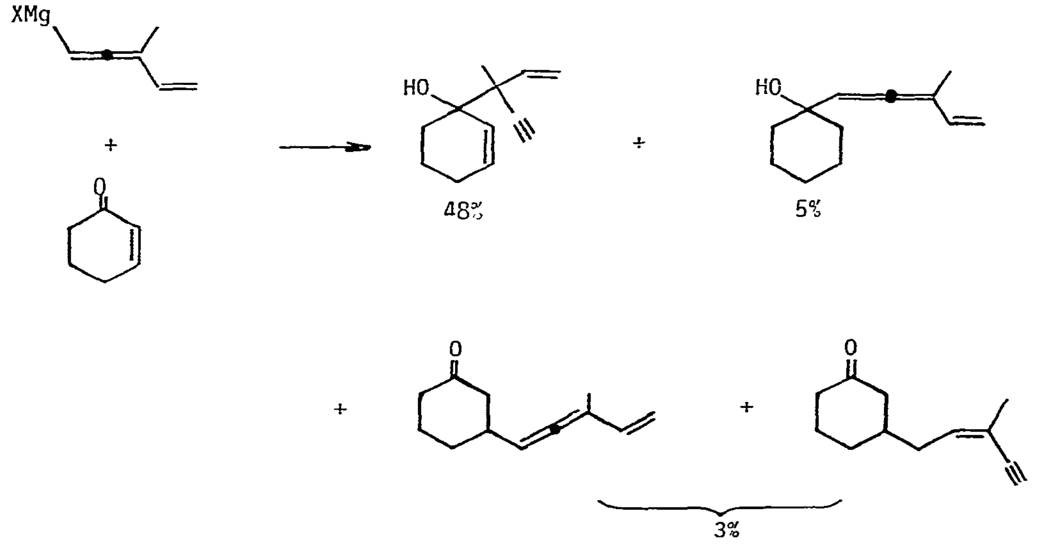
73

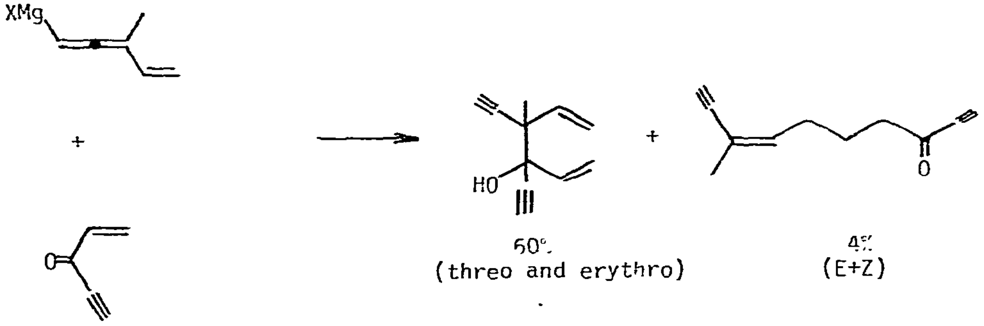


$HC{\equiv}C\text{-}CH{=}CH\text{-}\overset{Me}{C}HBr$

74

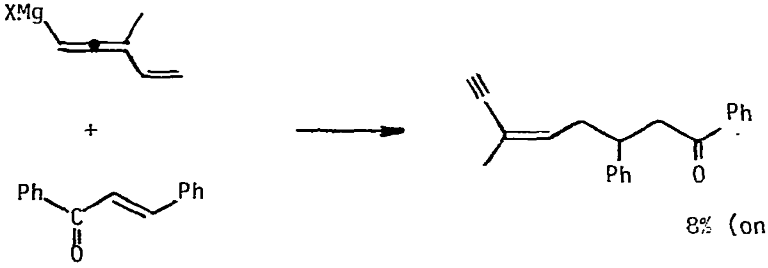
More varied results were obtained in several cases:





60%
(threo and erythro)

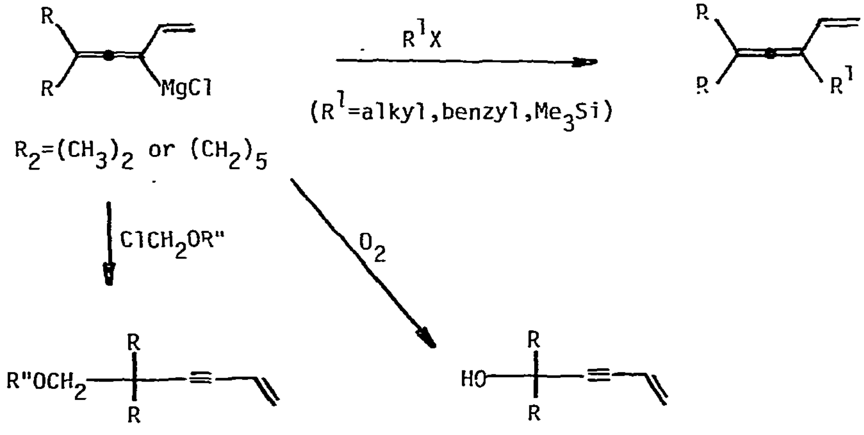
4%
(E+Z)



8% (only product)

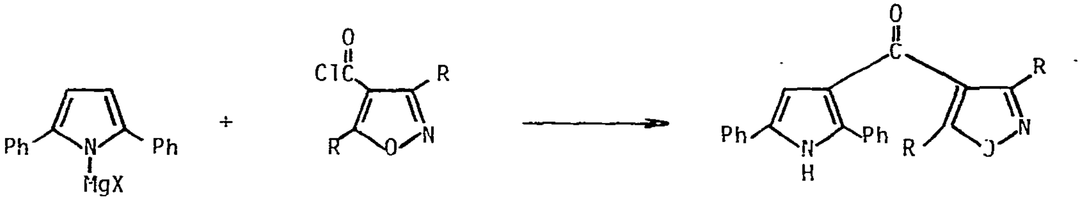
It was concluded that the β-position (see structure 71) is generally the most reactive, giving only 1,2 addition; the γ-position gives only 1,4 addition, while the α-position gives both simultaneously. Trends with variation in substitution on the ketone were explained by differences in hard/soft character.

An isomeric vinylallenic type of organomagnesium structure is alkylated and oxygenated with the following results [163-165]:

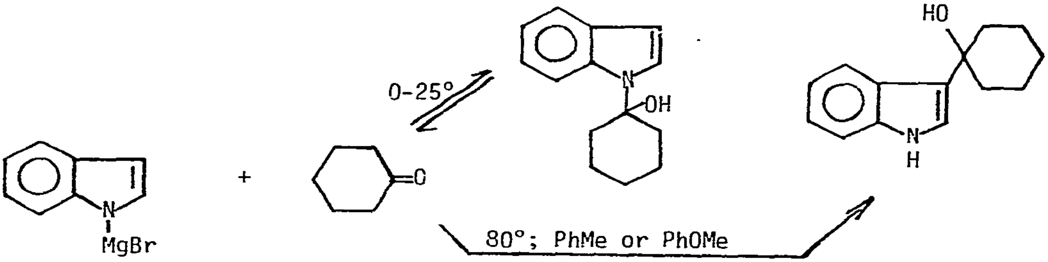


Some of the alkylations giving allenic product were catalyzed by CuCl [163,164].

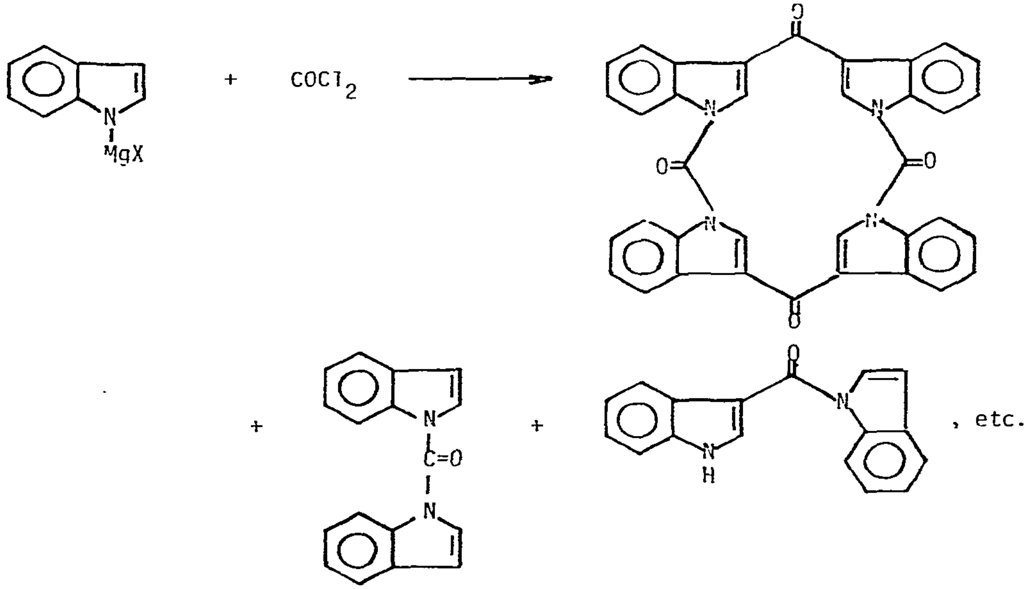
Pyrrolyl and indolyl Grignard reagents have the same sort of structural ambiguity as allylic organometallics, and the same potential for reaction at more than one position. Methylation of pyrrolylmagnesium bromide with methyl iodide occurred on carbon in ether solution, but on nitrogen in the presence of HMPA. Acylation with acid chlorides, anhydrides, phosgene or carbon dioxide normally occurs predominantly on carbon also. However, N-acylation is favored by use of TMEDA as solvent, by electron withdrawing functional groups, or on reaction with esters, isocyanates, carbodiimides or dimethylcyanamide. The N-acylated product may isomerize on heating to the C-acylated [22,166]. A more complex example giving C-acylation is [167]:



Isomerization of a ketone addition product of the indolyl Grignard reagent has been found [168]:

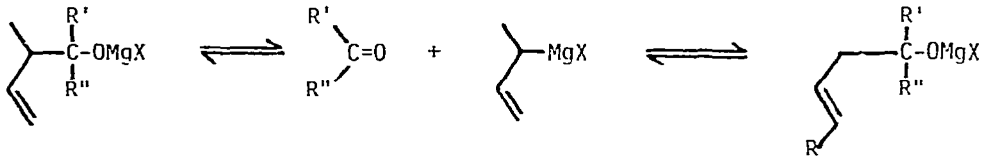


Reaction of the indolyl Grignard reagent with phosgene gave a mixture of products with C- and N-acylation [169]. High temperatures favored the macrocyclic product. Analogous products were obtained with oxalyl chloride.



D. Reversibility in reactions of allylic organomagnesium compounds

The reversibility of addition of allylic Grignard reagents to hindere ketones was studied by several techniques including isomerization of the adduct

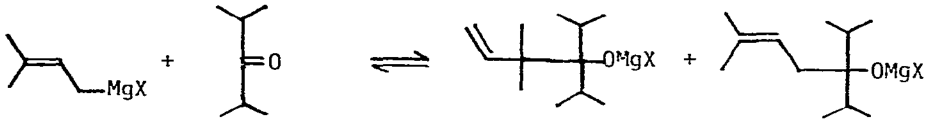


75

76

and trapping or enolization of the ketone [19]. It was concluded that the addition occurs via competing six- and four-center transition states.

Reversibility has also been studied in the reaction [170]:



77

78

The fraction of "linear" product 78 increases with time, while the total yield remains constant. In THF, it increases from about 20% initially to nearly 100% after 96 hr at 20°. The ketone intermediate in the isomerization was also trapped by allylmagnesium bromide. Formation of the less-hindered 78 is effectively irreversible.

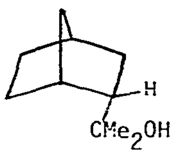
It has also been pointed out that rearrangements of the type 75→76 or 77→78 are formally sigmatropic rearrangements [171]. They are subject to cation- and solvent-effects (Mg<Li<Na<K and Et_2O<THF<crown ether in HMPA) similar to [3.3]-sigmatropic shifts of the type:

IV. REACTIONS OF ORGANOMAGNESIUM COMPOUNDS WITH CARBONYL FUNCTIONS

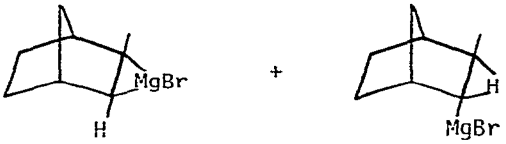
A. Mechanism of the Grignard addition

Two studies have been reported of the reaction of norbornyl Grignard reagents with carbonyl compounds. Addition of norbornylmagnesium bromide to formaldehyde appears to occur with retention of configuration. Two reagents which were >95% *endo* and 43% *endo* led to addition products with the same stereochemical composition. The addition of 5 mol % $FeCl_3$ had no effect, except for a decrease in yield. From the complete retention observed, it was concluded that a single electron transfer process to produce an intermediate norbornyl radical could not be involved. With other carbonyl compounds, clearcut results could not be obtained because of large proportions of reduction side reaction, particularly from the *exo* Grignard reagent [173].

In a similar study, *endo*-2-norbornylmagnesium bromide gave the *endo* isomer 79 as the sole addition product with acetone. Little or no addition of the *exo*-Grignard reagent occurred. In an effort to circumvent the reduction side reaction, a camphenylyl Grignard reagent 80 was prepared. Unfortunately, no addition product was obtained. The Grignard reagent was eventually destroyed by protolysis (enolization?). Reaction with benzophenone appeared to occur selectively with the *endo* isomer, but reaction was not complete. An electron transfer mechanism was suggested [27].

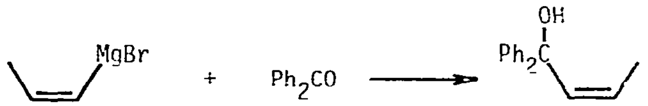


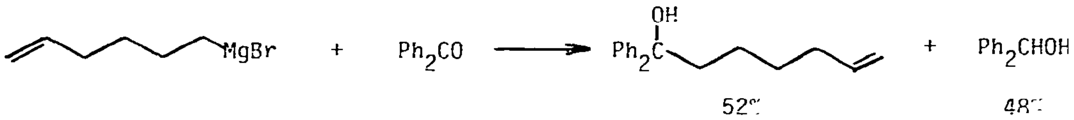
79

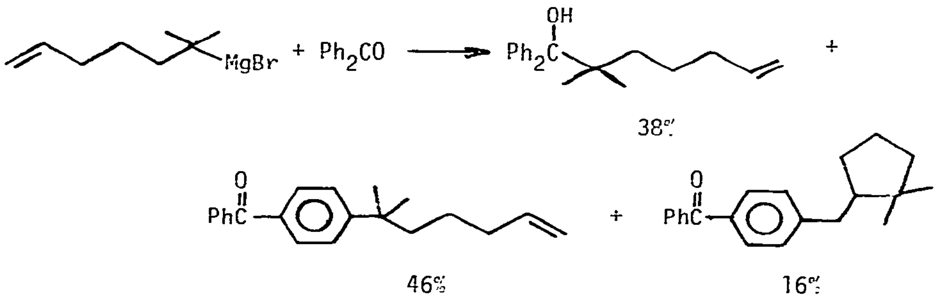


80

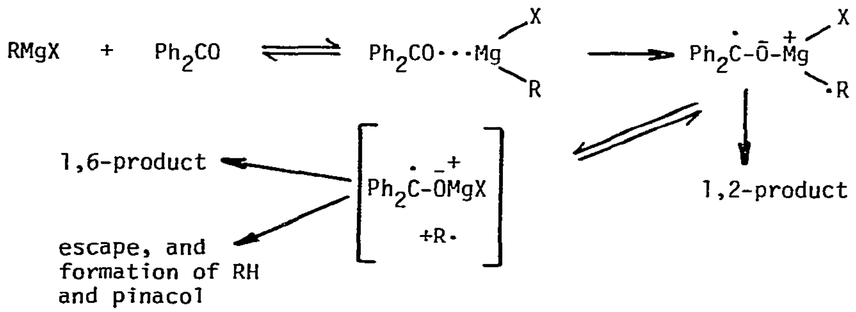
The question of "single electron transfer" *vs.* "polar" addition mechanisms has been explored using several radical probes in the Grignard reagent R-group [173]:



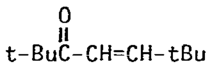




Lack of _cis_-_trans_ equilibration of the propenyl group or cyclization of the hexenyl groups appears to eliminate the possibility of a _free_ radical as a reaction intermediate in the 1,2-additions. However, cyclization of the tertiary hexenyl group is significant in the 1,6-addition. It was concluded that _if_ the reaction occurs by an electron transfer mechanism, then the alkyl group must remain bound to magnesium after the transfer, and that collapse to product occurs more rapidly than isomerization. A ketyl intermediate formed by electron transfer cannot be free either; although p-dinitrobenzene prevents pinacol formation, it did not affect the ratio of 1,2- to 1,6-addition. The following mechanistic scheme was proposed:



A thesis has been presented which describes mechanistic studies, many of which have been published previously, on reactions of methyl and *tert*-butyl Grignard reagents with benzophenone, 2-methylbenzophenone, fluorenone, and acetone [17]. Effects of redox potentials, solvent, magnesium purity, method of reagent preparation, and metal catalysis on the competing pinacol formation were studied. Reduction of benzophenone by traces of a magnesium hydride species was demonstrated. Reactions of methyl, *tert*-butyl and allyl Grignard reagents with *cis*- and *trans*-81 were reported. Isomerization of starting material provides a probe for radical anions, and p-dinitrobenzene is a trap for such intermediates.



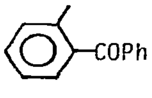
$\text{t-Bu}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-CH=CH-tBu}$

81

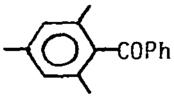
It was concluded that most probably reactions of allyl and *tert*-butyl reagents are "polar" and SET, respectively; methyl is questionable, with a polar mechanism preferred.

A theoretical contribution to the question of the addition mechanism has also been made [174]. A four-center 2+2 cycloaddition reaction is formally forbidden. However, it was concluded on the basis of all-valence-electron SCF-ZDO calculations that interaction of vacant metal orbitals with the π-electrons provides a lower-energy highest occupied molecular orbital (HOMO), permitting a favorable non-radical reaction path. Model systems for calculations were addition of AlH, BH or TiH bonds to ethylene and HMgCl to HCN.

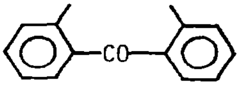
Ketyl radicals resulting from single electron transfer between a Grignard reagent and carbonyl component have been detected and studied by EPR in a number of cases. From well-resolved spectra of radical anions generated from 82 or 83 with phenylmagnesium bromide, the electron configurations were calculated; a non-planar structure was concluded. Ketyl radicals from 84 and 85 gave EPR spectra with poorer resolution [175].



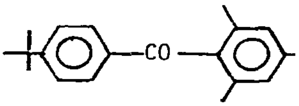
82



83

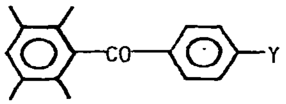


84



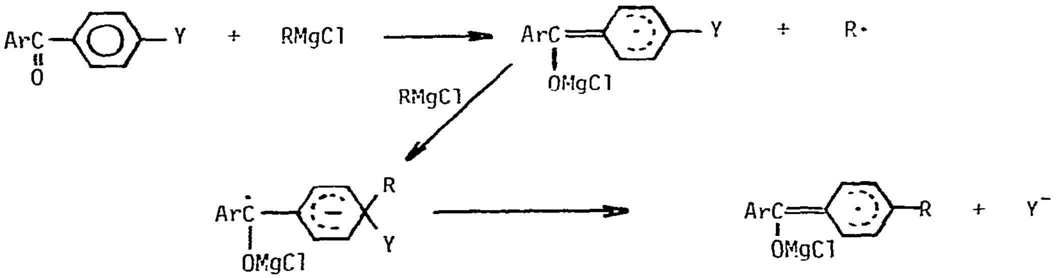
85

Reactions of 86 with Grignard reagents were studied by EPR [176]. With an

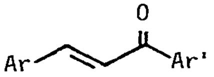


86 (Y=OMe, CN)

excess of benzylmagnesium chloride, the solution went through a series of color changes, eventually producing a good yield of product after 1 hr at room temperature. A maximum radical concentration of ~6% was observed after 30 min. After the color change, the EPR spectrum indicated the presence of the radical anion of 86 (Y=benzyl). Similar results (but lower maximum radical concentration) were found for t-butylmagnesium chloride; phenylmagnesium bromide gave a higher radical concentration, but only starting material was recovered. A mechanism proposed was:

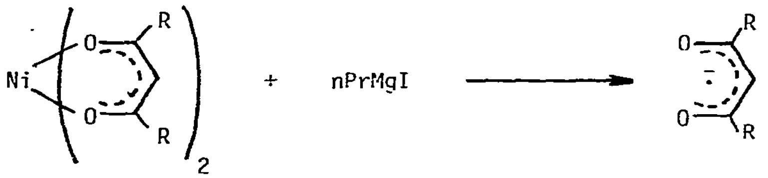


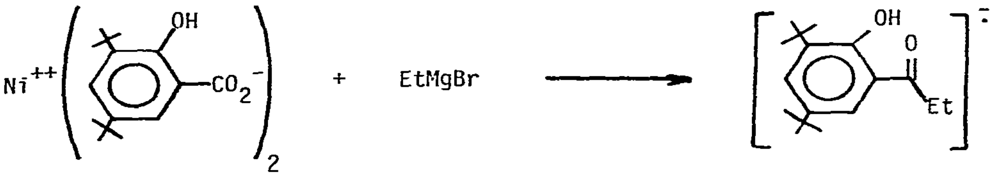
Reactions of 87 were also studied. All substrates gave conjugate addition with phenylmagnesium bromide, but no observable ketyls; a ketyl was observed in the reaction of o-tolylmagnesium bromide with 87 (Ar=mesityl, Ar'=Ph).



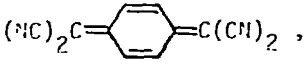
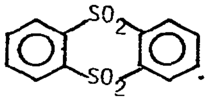
87

A number of other anion-radical observations were reported from Grignard reagents and an electron-acceptor, facilitated by nickel compounds [177]. Examples included are:



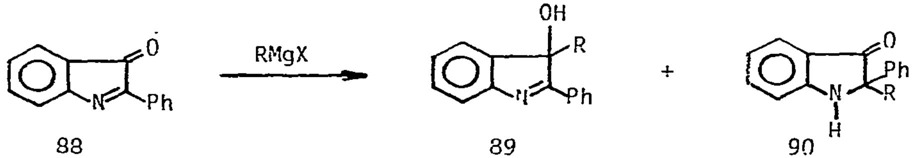


and reactions of n-PrMgI in the presence of $NiBr_2$ with:

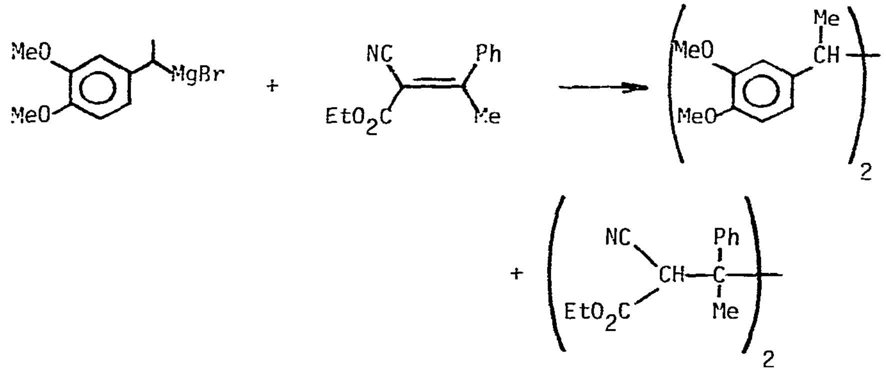
Ph_2CO ,  ,  , TCNE , 

Chemically induced dynamic nuclear polarization (CIDNP) during the reaction of tert-butylmagnesium chloride with o-bromobenzoyl chloride in DME indicates the involvement of radical intermediates. Polarization was observed in the ketone product and in coupling and disproportionation side-products from t-butyl radicals. In the presence of styrene, polarization from encounter pairs was eliminated, and new polarized signals from addition to styrene were seen. Comparison with similar experiments using unsubstituted benzoyl chloride favors polarization from $ArCOCl^{\overline{\cdot}}$ radical (as opposed to only $Ar\dot{C}O$) [178].

Electron transfer processes have been invoked to explain results in other reactions of Grignard reagents with carbonyl compounds. In addition of various Grignard reagents to 88, it is proposed that 89 is the product of nucleophilic attack, while 90 is produced via electron transfer. The proportion of electron transfer product decreased in the order tBu>iPr>Et~Me [179]. Dimerization products in the following and some related reactions may be ascribed to radicals coming from electron-transfer [180]:



88 89 90

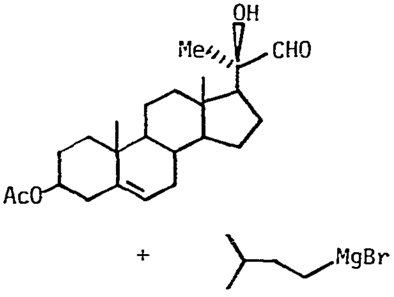


B. Stereochemistry of addition to aldehydes and ketones

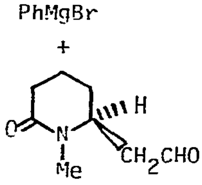
1. Stereochemistry with aldehydes and acyclic ketones

Addition of Grignard reagents to carbonyl compounds in optically active 2-methyltetrahydrofuran led to products of low optical purity (maximum of 11% from PhMgBr + pivalaldehyde). Addition of ethyl ether reduced the extent of asymmetric induction, possibly by preferentially coordinating to the magnesium. Partial kinetic resolution of 2-bromo-1-phenylpropane was obtained by recovery of unreacted halide from formation of the Grignard reagent (2.1% optical purity at 50% of reaction) [81].

Little or no stereoselection was observed in the following additions to aldehyde groups:

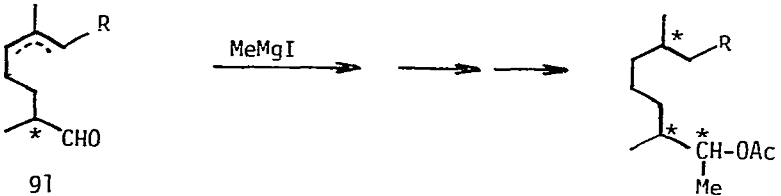


[182]



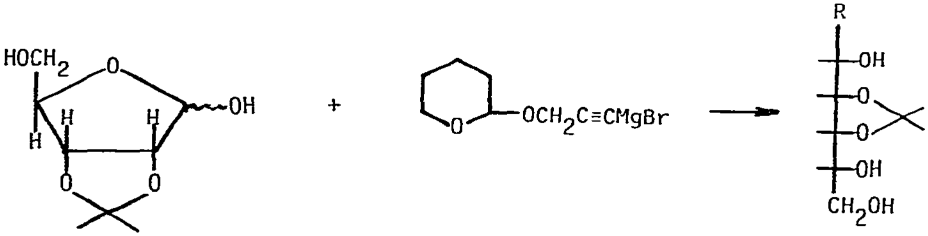
[183]

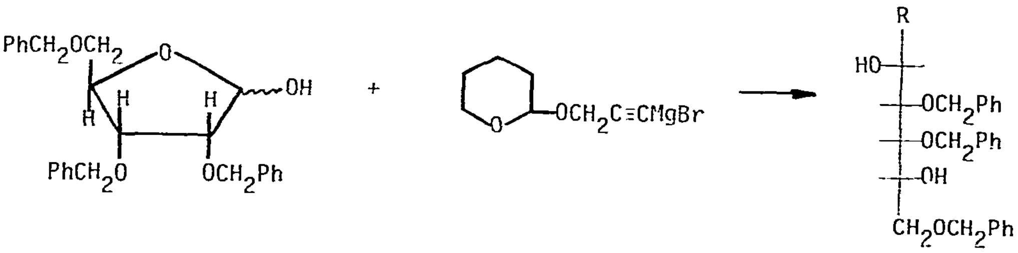
However a single major stereoisomer appears to have resulted from 91 [184].

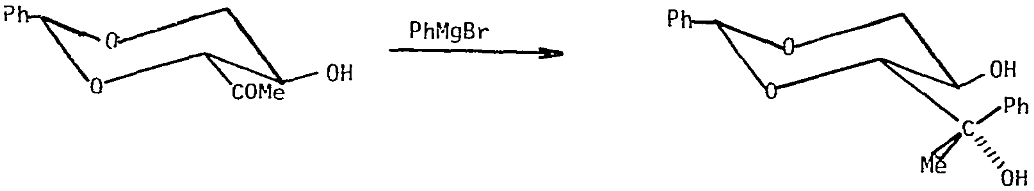


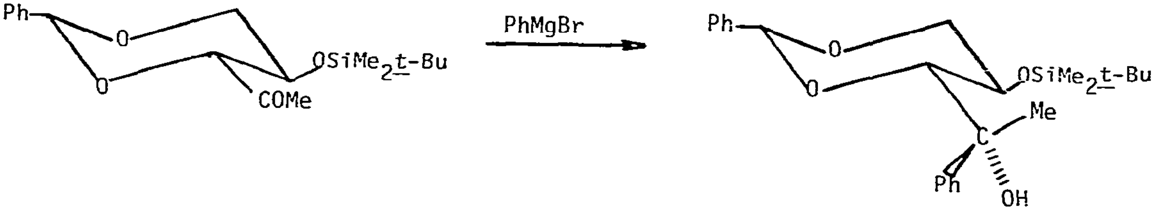
91

In examples from carbohydrate chemistry, different protected derivatives led to opposite stereochemistry in the major diastereomer produced [90,185]:

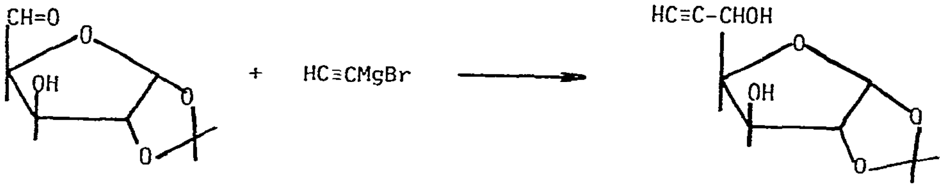




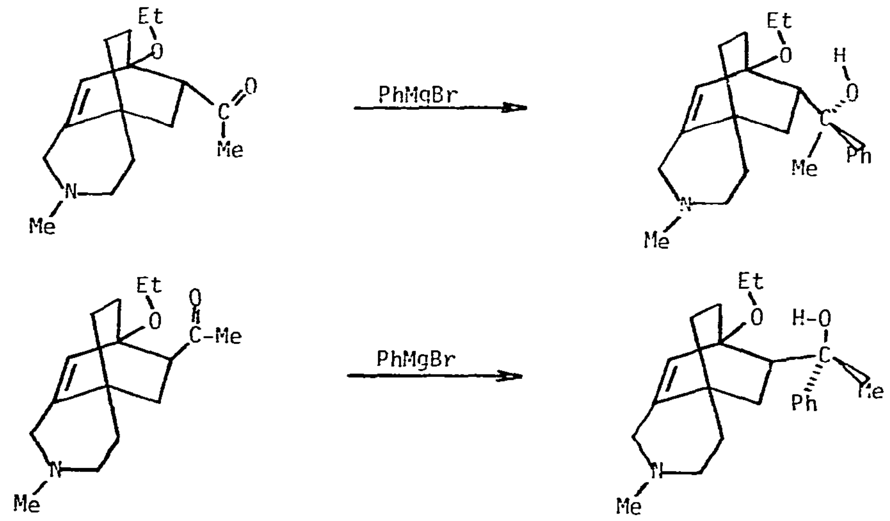




The following reaction produced a mixture of diasteromers in a 14:11 ratio [186]:

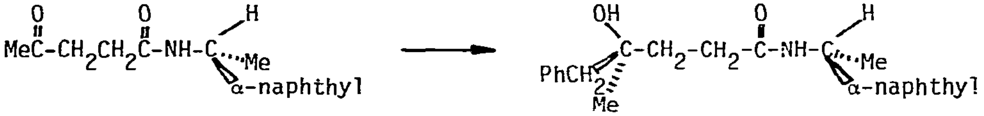


High stereospecificity in the following additions was explained by coordination of magnesium to the bridgehead ethoxy group [187]:



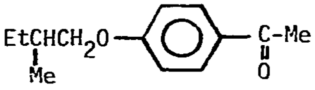
Asymmetric induction from the chiral phosphorous center, possibly also resulting from coordination of magnesium between the two oxygens, led to formation of the less stable erythro diastereomer [188]. The rather distant

chiral center in amide 92 had a sufficiently large effect to direct a 3:1 preference for one diastereometer [189].



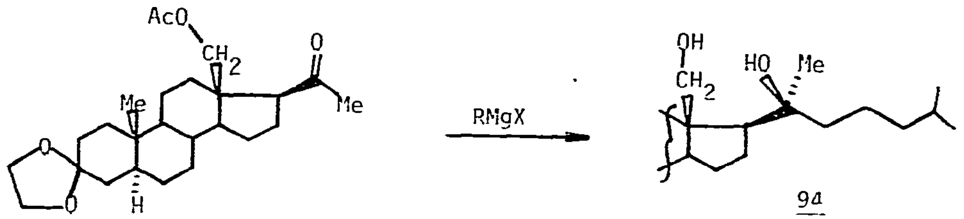
92

It is also claimed that the remote chiral group in 93 induces a chiral preferenc in additions of various Grignard reagents [189a].

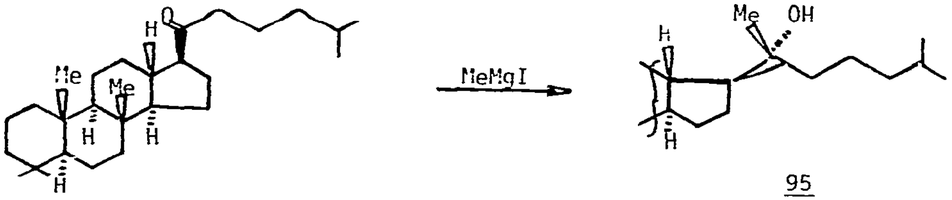


93

Two examples of asymmetric synthesis of steroidal derivatives are shown:



94 [190]

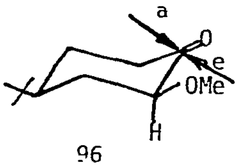


95 [191]

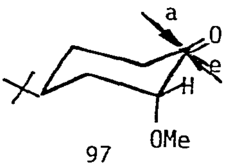
In the first reaction, 94 was the only product isolated, but the second proceeded with a lower stereoselectivity. Diastereomer 95 predominated in a 2:1 ratio, while an 8:11 ratio was obtained from the corresponding methyl ketone with isohexylmagnesium bromide.

2. Stereochemistry with cyclic ketones

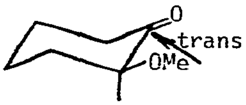
The stereochemistry of addition of a variety of Grignard reagents to 2-methoxycyclohexanones 96-98 was studied [192]. Equatorial and axial attack



96



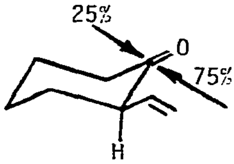
97



98

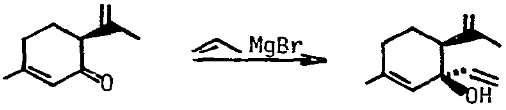
occur to extents of 89-91% and 65-80% with 96 and 97, respectively. Alkynyl Grignard reagents had an increased tendency to axial attack. With the conformationally mobile 98, addition *trans* to methoxy produced the major product (73-91%), with alkynyl reagents being closer to 50%.

Additions to 99-102 also occurred principally from the side *trans* to the 2-substituent.

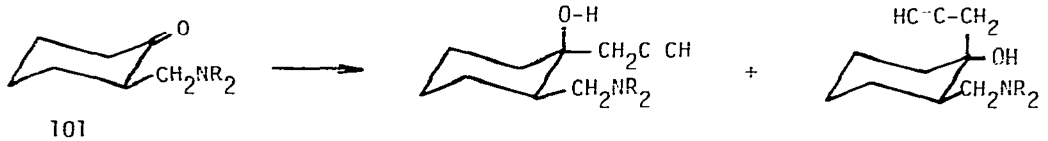


+. MeMgI

99 [193]



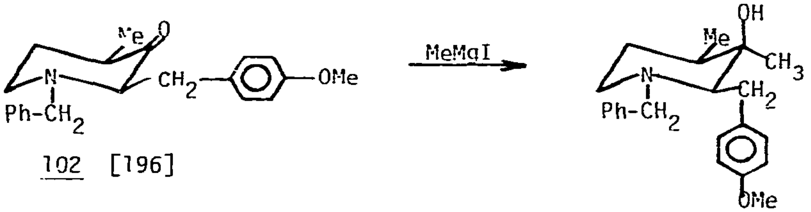
100 [194]



101

+ $HC\equiv C-CH_2MgBr$
[195]

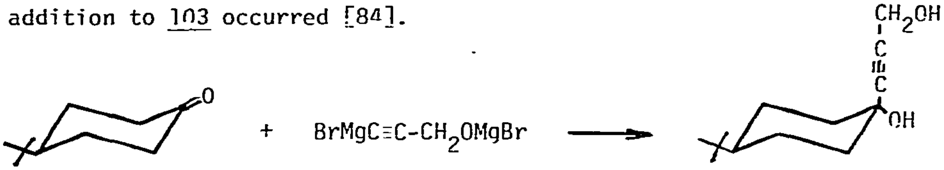
R=Me 80 : 20
R=Et 70 : 30



102 [196]

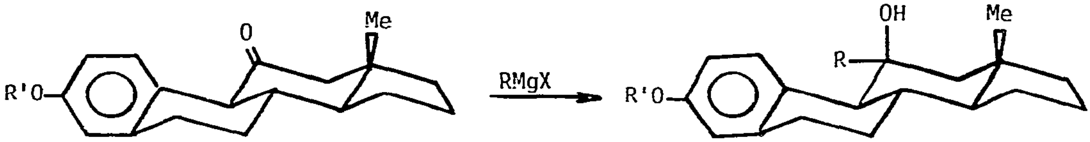
(only isomer reported)

However, addition of phenylmagnesium bromide to a series of 4-n-alkylcyclohexanones produced nearly equal amounts of *trans*- and *cis*-isomers [197]. Axial addition to 103 occurred [84].



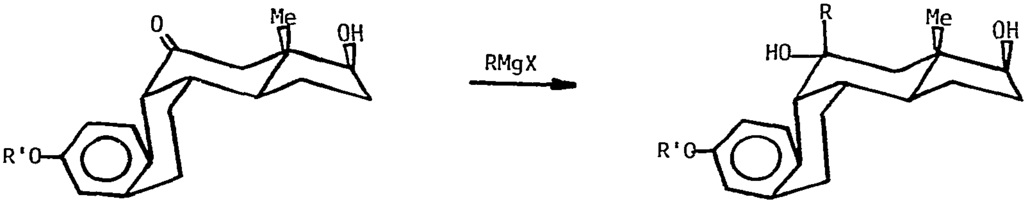
103

Stereochemical results with fused six-membered rings are shown for 104-108. Coordination by phosphorous may direct the addition in 108.



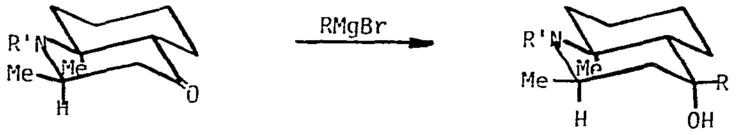
104 [198]

R=Me,allyl



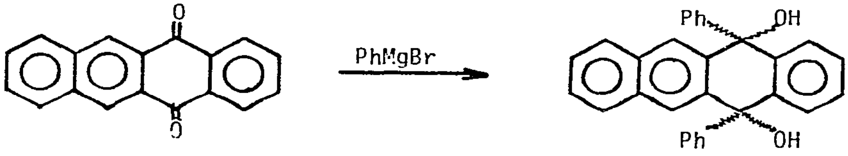
105 [198]

R=allyl
(R=Me; only enolization)



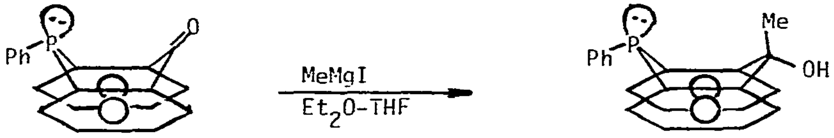
106 R'=H, Me
[199]

R=Et, H_2C=CH-, HC≡C-



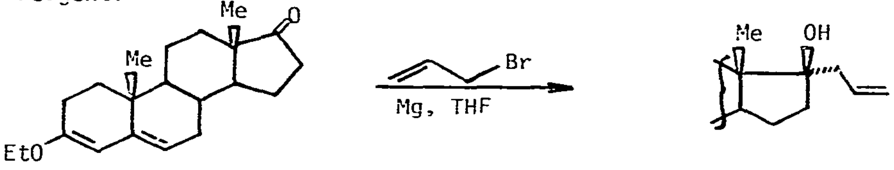
107 [200]

trans:cis = 5:1

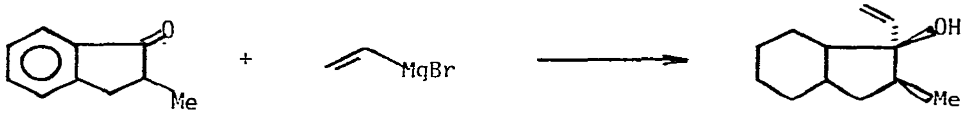


108 [201]

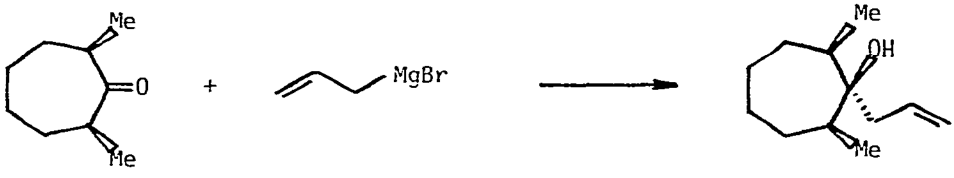
Additions to 109-112 appear to reflect steric effects on approach of the reagent.



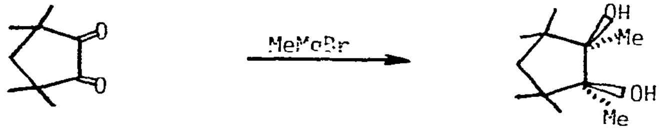
109 [202]



110 [203]

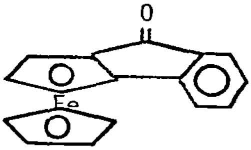


111 [204]

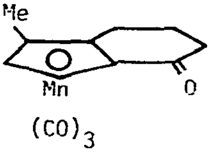


112 [205]

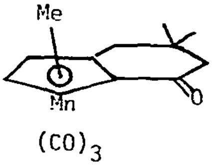
Additions to 113-116 all occurred exclusively from the exo-side with methyl, phenyl and thienyl Grignard reagents [206]. Addition of methyl Grignard reagent



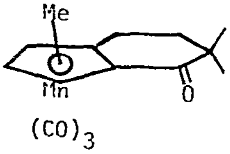
113



114

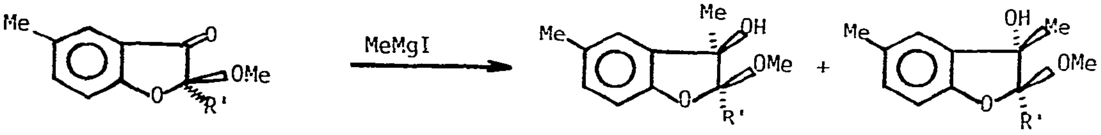


115



116

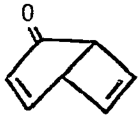
to 117 (R'=Ph) gave a 60:40 mixture of isolated trans and cis isomers. However,



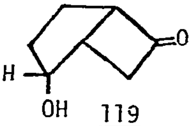
117

only one isomer (of undetermined stereochemistry) was isolated in addition of benzylmagnesium chloride, or addition of either reagent to 117 (R=Me) [207].

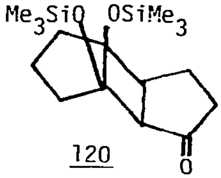
Addition from the less hindered exo side led to the sole product (or sole reported product) in the reactions of 118-122.



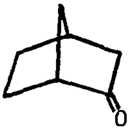
118
\+ PhMgBr
[208]



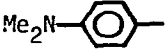
119
\+ MeMgX
[209]

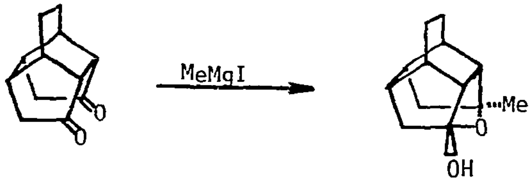


120
\+ MeMgBr
[210]



121
\+ RMgX [211]
R = cyclopropyl, C_6H_5,



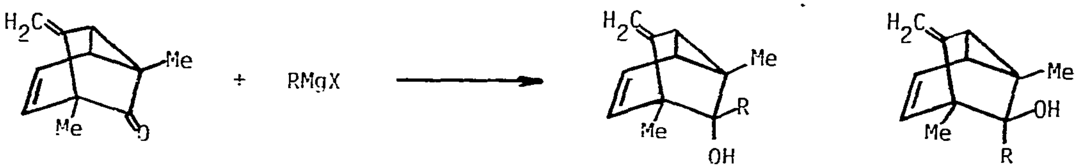


122
[212]

Mixtures of products as shown were reported from 123-125.

123 [213]

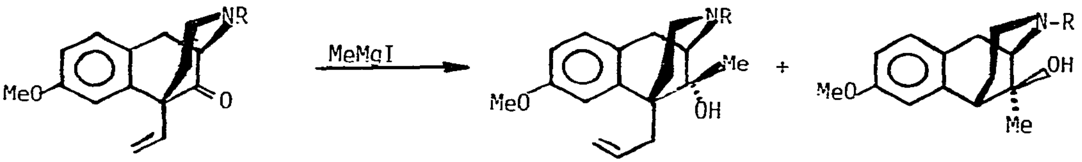
76% 24%



124 [214]

MeMgI 100% --

EtMgBr 94% 6%



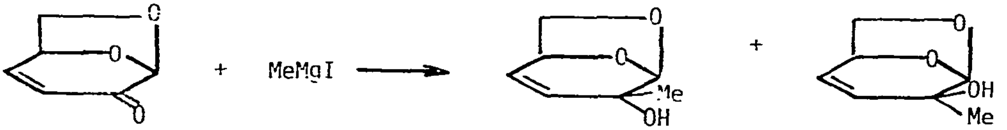
125 [215]

in Et_2O 55% : 45:

in pet. ether >95% : --

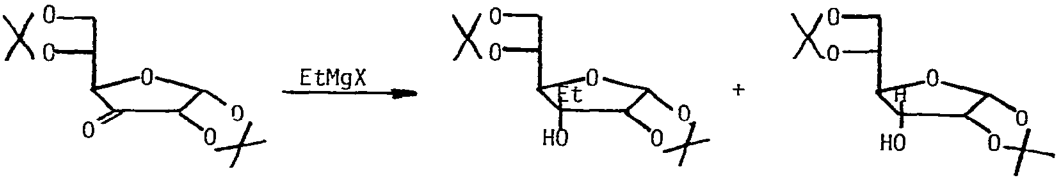
Complexing of magnesium to the nitrogen in the ring was believed to account for the solvent effect with 125.

Addition to carbohydrate derivatives 126 and 127 has been studied:



126 [216] 56% 6%

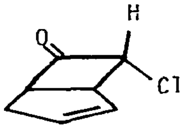
+ 1,4-adduct
6%



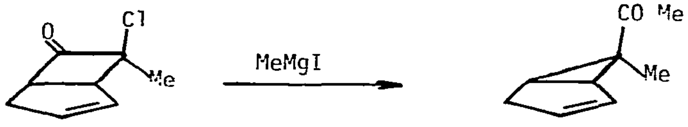
127 [217]

With 127, addition predominates (up to 63%) in ether, while reduction is more important (60-65%) in THF. Lower yields of the epimeric secondary alcohol and starting material (via enolization) were found, but none of the epimeric tertiary alcohol is formed. Cyclohexylmagnesium bromide gives mostly reduction. With phenyl Grignard reagents, the same epimer predominates, but some of the minor one is also present.

Reaction of MeMgI with 128 gave only straightforward addition from the *exo*-side. Rearrangement occurred in the addition to 129. It was proposed that Grignard addition occurred principally from the *endo*-side (because of the polar effect of chlorine) followed by rearrangement with loss of chloride [218].



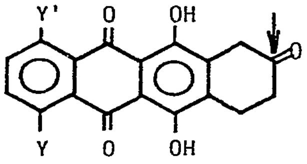
128



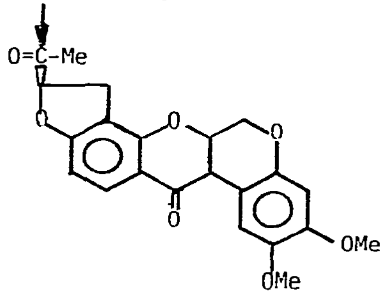
129

C. Selective additions to aldehydes and ketones

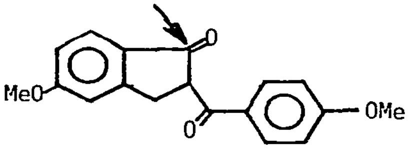
Selective reaction at one carbonyl group (as indicated) is illustrated by the following examples:



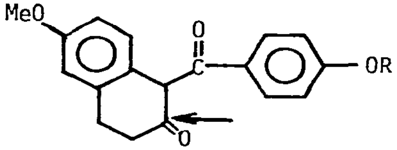
(Y,Y'=H, OMe, OH)
+ HC≡CMgBr or $H_2C{=}CHMgBr$
[219,220]



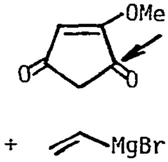
+ MeMgI
[221]



+ PhMgBr
[222]

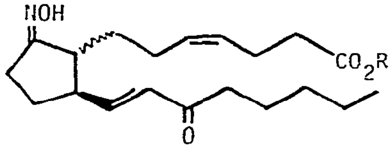


+ PhMgBr
[223]

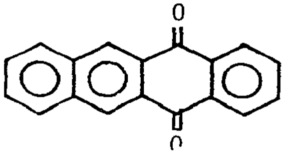


[224]

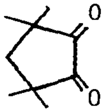
Conversion of a diketone to the mono-oxime 130 served to protect the cyclopentanone while addition to the conjugated ketone function was carried out [225]. In related substrates, selective reaction at this carbonyl group occurred without the need for protection [226]. With 131 and 132, addition of one or two moles



130 + HC_2MgBr



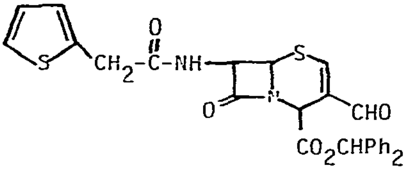
131 + PhMgBr
[200]



132 + MeMgBr
[205]

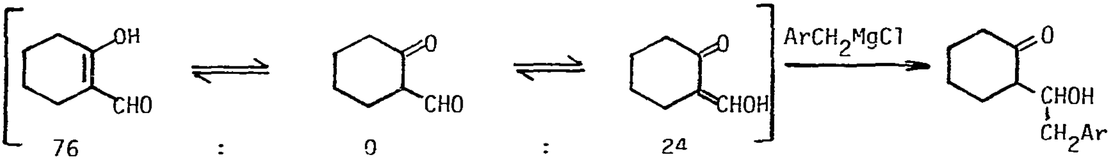
of Grignard reagent can be selected.

The aldehyde group in 133 reacts in preference to other sites [227,228].



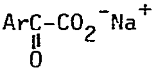
133

Addition to the tautomeric mixture below gave a 47% yield of a single pure

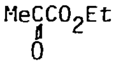


product resulting formally from reaction at the aldehyde [229].

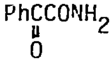
Preferential reaction at an aldehyde or ketone group in the presence of a carboxy or carboxy derivative is standard. Of numerous references to α-keto derivatives, the following examples are cited:



$ArC(=O)-CO_2^-Na^+$



$MeC(=O)CO_2Et$

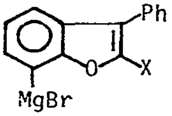


$PhC(=O)CONH_2$

+ n-alkyl MgX
(3-fold excess)

(57-98%)
[230]

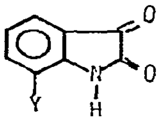
+



(X = H, Me, Br)
[120]

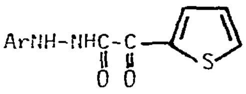
+ RMgBr

(60-86%)
[231]



+ RMgX

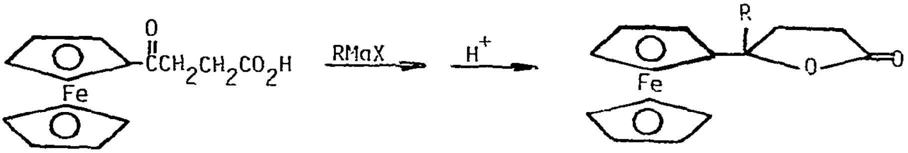
[232,233]



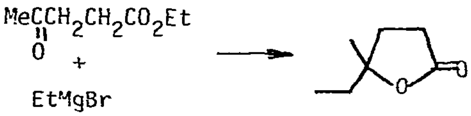
+ PhMgBr

[234]

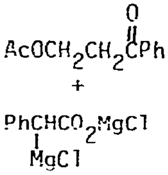
Some other representative examples include:



[235]

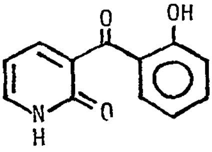


[236]



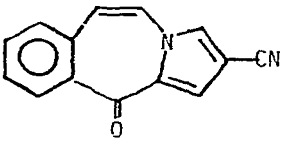
$$\mathrm{AcOCH_2CH_2\overset{\overset{\large O}{\|}}{C}Ph} \quad + \quad \mathrm{Ph\underset{\underset{\large MgCl}{|}}{C}HCO_2MgCl}$$

[56]



+ PhMgBr

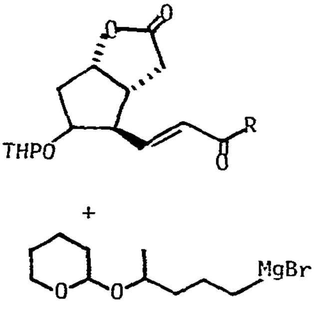
[237]



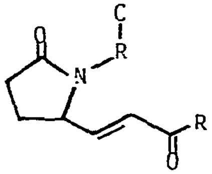
+ $Me_2NCH_2CH_2CH_2MgCl$

[238]

Additional examples are found in prostanoid syntheses.

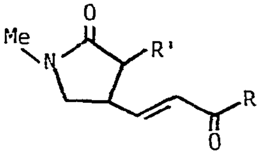


[239]



+ MeMgX

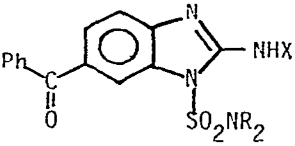
[240,241]



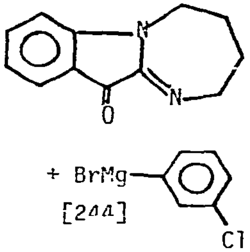
+ MeMgI

[242]

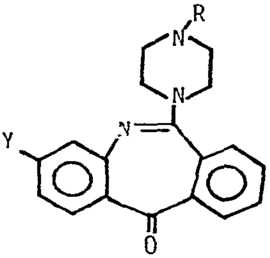
Addition to a carbonyl group in the presence of carbon-nitrogen unsaturation is reported for the following:



+ MeMgBr
[243]



[244]



+ MeMgI
[245]

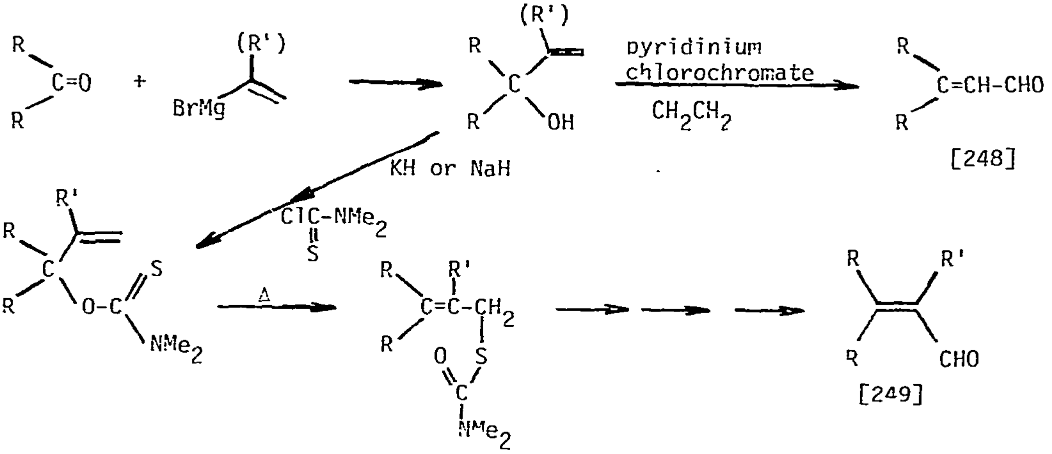
Carbonyl addition also takes precedence over α-halogen displacement in $ArC(O)CH_2Cl$ [246].

D. Other additions to aldehydes and ketones

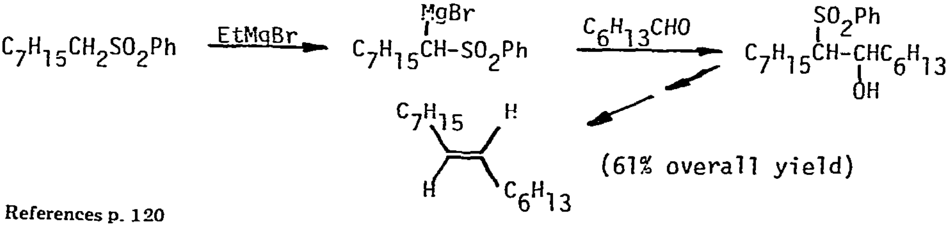
A modified Grignard reaction procedure has been presented in which the carbonyl compound in methylene chloride or ethylene chloride is added to the ethereal Grignard reagent solution. It is reported that yields in a typical student preparation are improved from 60 to 80% by the modification [247].

The Grignard reaction is a critical step in some recently-reported general synthetic sequences.

Two routes utilize a vinyl Grignard reagent addition in a sequence which produces the same over-all result as an aldol addition:

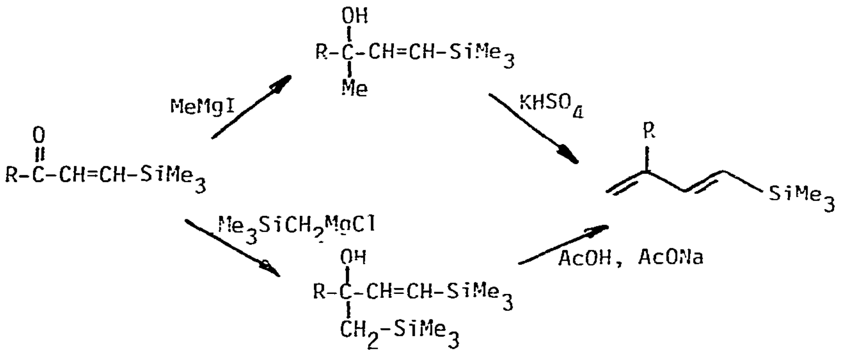


A synthetic sequence for pure trans alkenes utilizes an α-sulfonyl Grignard reagent [250]:



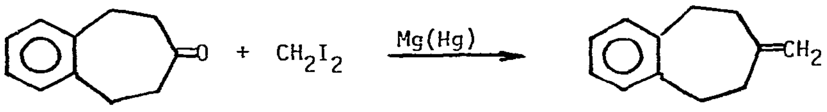
(61% overall yield)

Silylated dienes, which are potentially useful synthetic intermediates, may be prepared by two alternative Grignard syntheses [251].



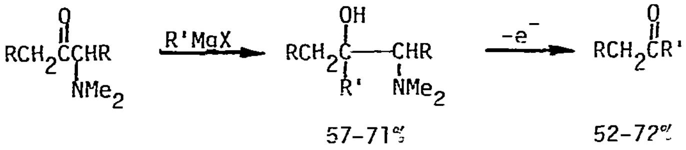
A series of di-acetylenic alcohols was synthesized by the Grignard reaction between propargaldehyde and acetylenic Grignard reagents [252].

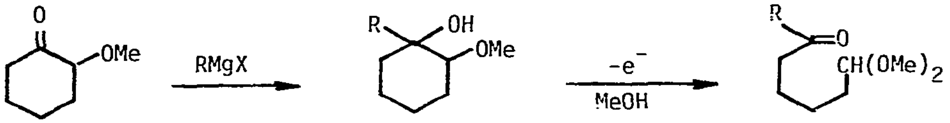
The use of methylene iodide as a Wittig reagent substitute is illustrated by the synthesis of a number of deuterated analogs of 134 [30].



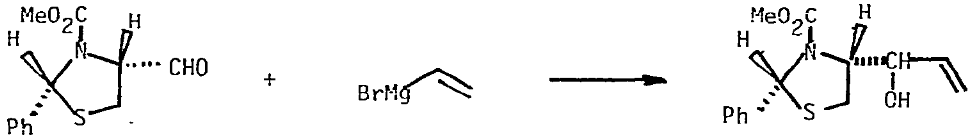
134

Electrochemical oxidation of the addition product from α-amino or α-methoxy ketones provides an unsymmetrical ketone synthesis [253].

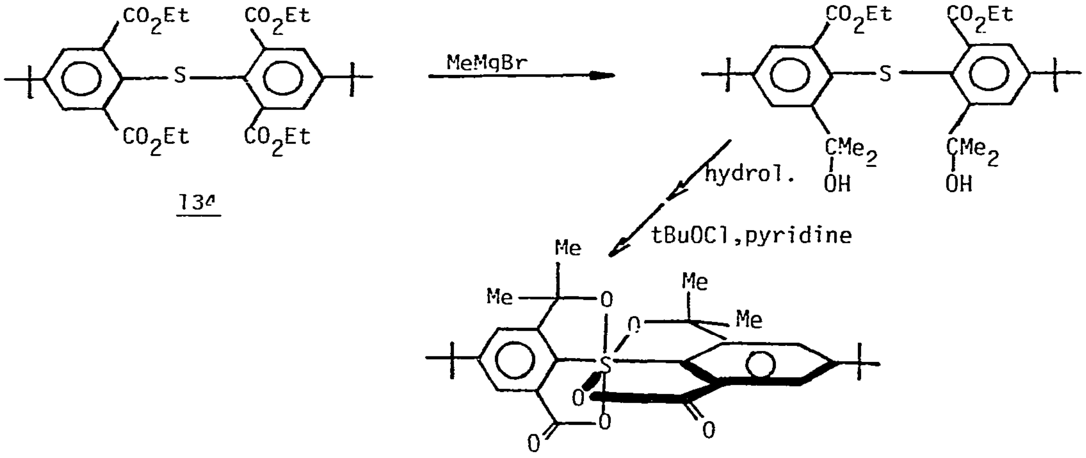




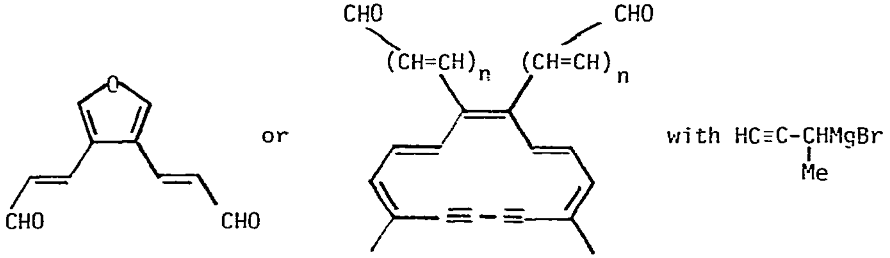
A stereospecific total synthesis of biotin from L(+)cysteine utilizes the step [254]:



Reaction of the tetra-ester 134 with an excess of Grignard reagent leads to an intermediate which undergoes oxidative cyclization to the first persulfurane lacking fluorine ligands [255]:



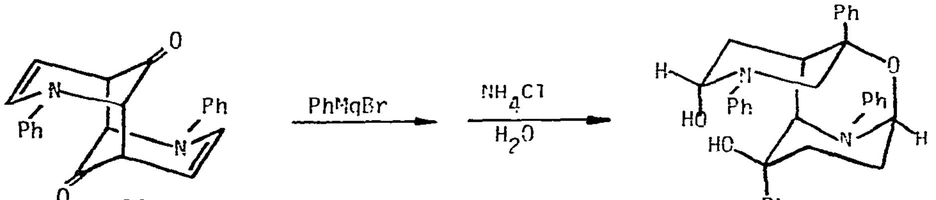
Grignard addition reactions play an important role in routes to macrocyclic aromatic compounds [159,160]: e.g.



n = 1 or 2

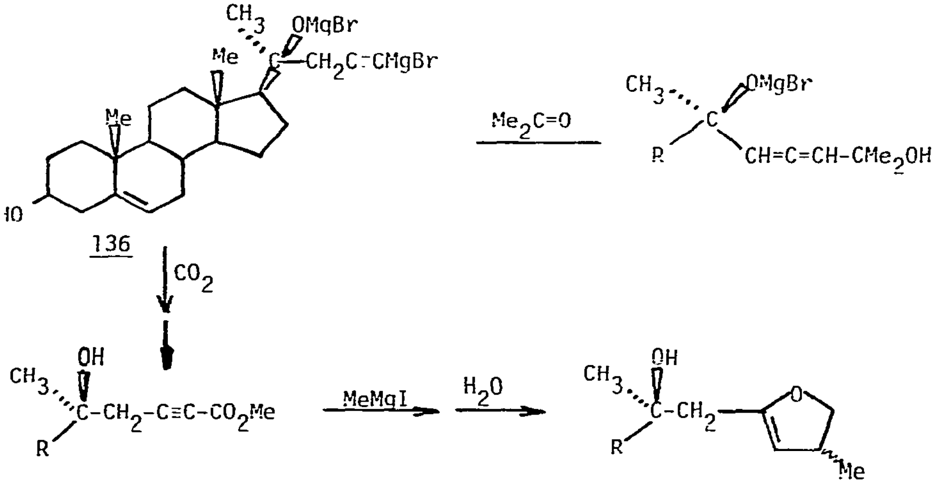
Cyclopentadienylmagnesium bromide reacts with fluorenone or tetraphenylcyclopentadienone to yield mixtures of alcohols which are dehydrated to fulvalenes [256].

Hydration and cyclization of the adduct from 135 with two moles of Grignard reagent leads to a product with a cage structure [257].



135

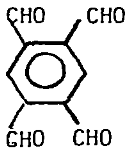
The acetylenic Grignard reagent 136 is claimed to yield an abnormal product on reaction with acetone, and an unexpected cyclization is reported on subsequent conversions of the carbonation product [258].



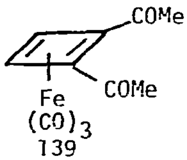
The metallocarborane aldehyde 137 reacts with non-reducing Grignard reagents (methyl, phenyl, vinyl) to yield addition products (as a mixture of diastereomers in some cases). Ethylmagnesium bromide give 70% reduction and only 30% addition, while propylmagnesium bromide gives all reduction [259].

$cpCoB_9H_9C_2HCHO$

137



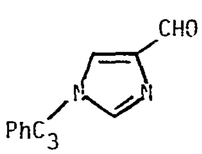
138



139

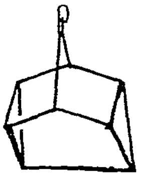
Reactions of 138 with excess PhC≡CMgBr [260] and 139 with excess methylmagnesium iodide or phenylmagnesium bromide [261] gave the alcohol products of multiple additions.

The following additions to aldehydes and ketones occur in the normal fashion:



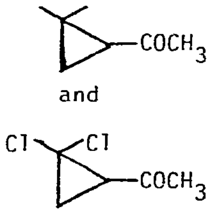
+ RMgX

[262]



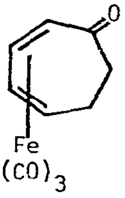
+ ArMgX

[263]



+ ArMgX

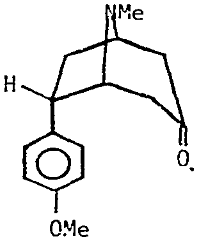
[264]



+ ArMgX

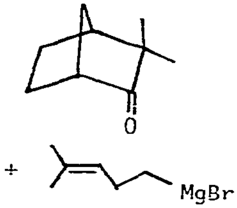
[265]

In the cases noted below no addition product (or a very low conversion to product) was observed:

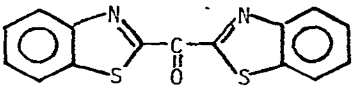


+ MeMgCl

[266]



[267]



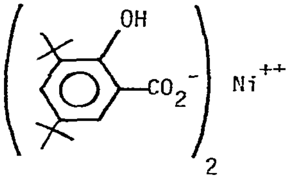
+ p-Tol-MgBr

[268]

E. Reactions with carboxylic acids and derivatives

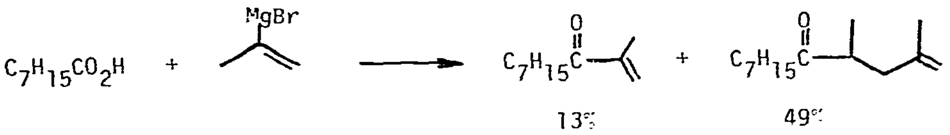
1. Open-chain derivatives

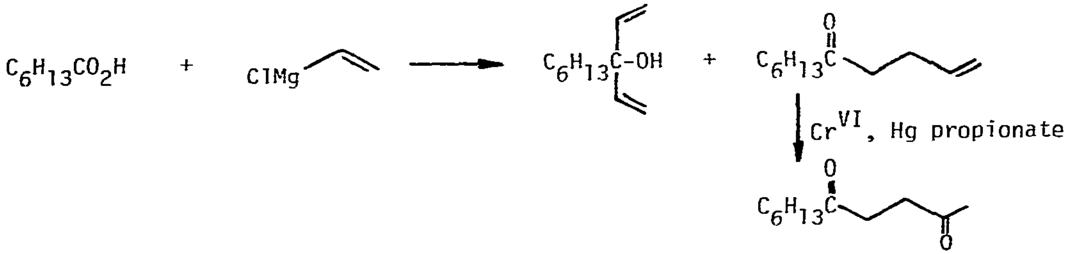
Sodium trifluoroacetate reacted with aryl Grignard reagents to yield trifluoromethyl ketones [269]. Reaction of the nickel salt 140 with ethyl magnesium bromide produced epr signals corresponding to the radical anion of the corresponding ethyl ketone [177].



140

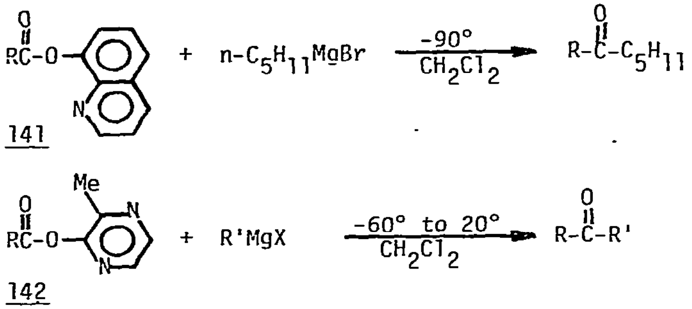
A number of publications reported reactions of vinylic Grignard reagents with carboxylic acids. The use of cuprous chloride increases the conjugate addition of the second mole of Grignard reagent. Typical results are [270-273]:





In the latter example, oxidation provides a 1,4-diketone synthesis [272,273].

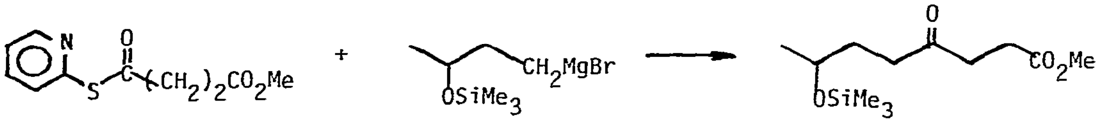
In a number of reports, reaction of a Grignard reagent with an ester activated for nucleophilic attack furnished a synthesis of ketones [274-276]:



141

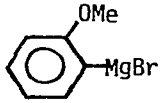
142

R = Me, Ph R' = alkyl, Ph

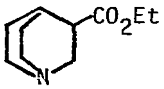


With 142, yields generally in the range of 80 to 97% were obtained; competition experiments showed that 142 is more reactive than 141 [275].

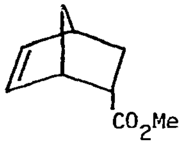
The ketone is also the product in the following reactions:



+ $EtO_2C\text{-}CO_2Et$
(to keto-ester)
[277]

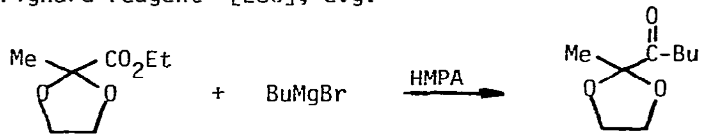


+ RMgBr
(R=n-hexyl, 2-thienyl)
[278]

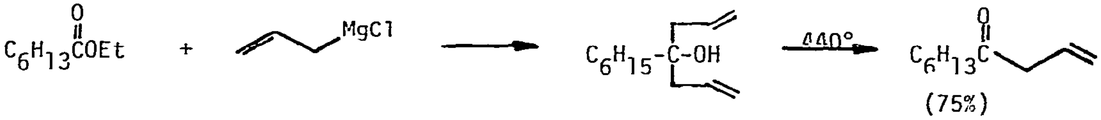


+ $Me_2N(CH_2)_3MgCl$
[279]

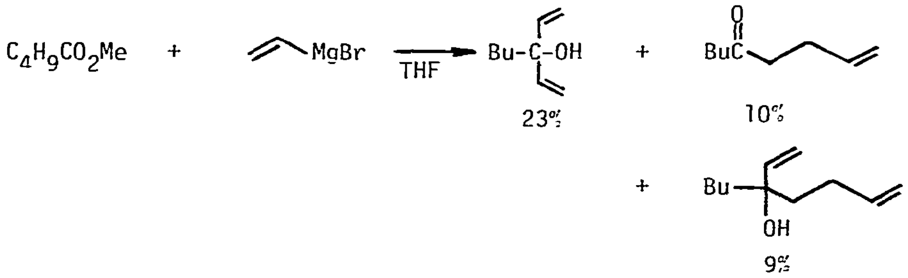
Reaction of ketals of α-keto esters with Grignard reagents in HMPA stops at the ketone stage because the ketone is selectively enolized by excess Grignard reagent [280]; e.g.



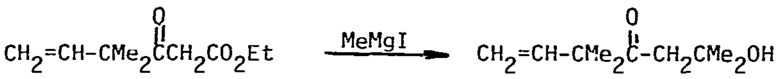
Allyl ketones may be synthesized in good yield from esters by pyrolysis of the normal product of addition of two molecules of Grignard reagent [281]:



Vinylic Grignard reagents react with esters to produce a mixture of products. A major product frequently results from conjugate addition of a second mole of Grignard reagent to the initially-formed vinyl ketone [270,271, 282]; e.g.

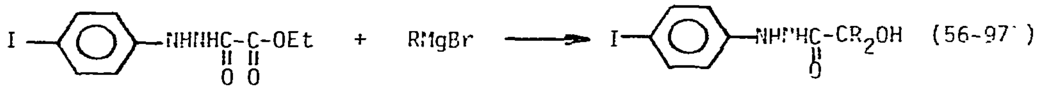


Unusual selectivity, with the ester function more reactive than a hindered ketone, was found in the following example [283].



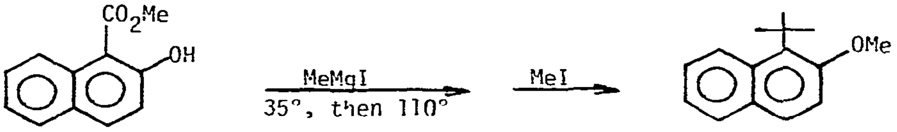
$$CH_2{=}CH\text{-}CMe_2\overset{O}{\overset{\|}{C}}CH_2CO_2Et \xrightarrow{MeMgI} CH_2{=}CH\text{-}CMe_2\overset{O}{\overset{\|}{C}}\text{-}CH_2CMe_2OH$$

Preferential reaction with the ester group also occurs with <u>143</u> [234].

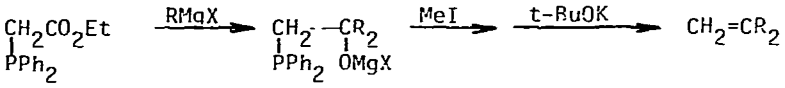


143

A novel conversion of an ester to a tert-butyl group involves dehydration of the tertiary alkoxide intermediate, followed by conjugate addition of a third mole of Grignard reagent [284]:



A combined Grignard-Wittig reaction for olefin synthesis starts with eithe an ester or a ketone having α-diphenylphosphino substitution. Best yields were obtained with benzyl and allyl groups [285]:

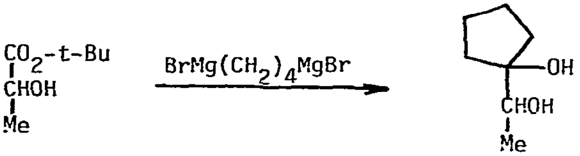


$$\underset{\mathrm{PPh_2}}{\mathrm{CH_2}}\mathrm{CO_2Et} \xrightarrow{\mathrm{RMgX}} \underset{\mathrm{PPh_2}}{\mathrm{CH_2}}-\underset{\mathrm{OMgX}}{\mathrm{CR_2}} \xrightarrow{\mathrm{MeI}} \xrightarrow{t\text{-}\mathrm{BuOK}} \mathrm{CH_2{=}CR_2}$$

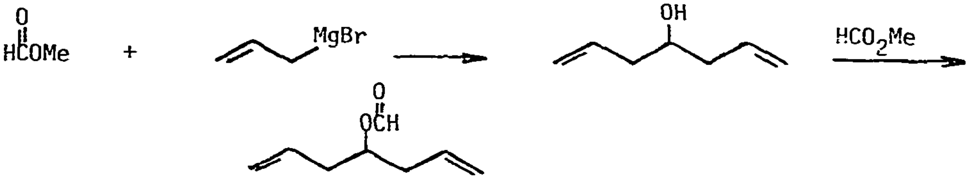
A synthetic sequence for symmetrical ketones starts with Grignard reagent addition to a methoxy ester [253]:

$$\mathrm{MeOCH_2CO_2Me} \quad + \quad 2\ \mathrm{RMgX} \qquad \underset{48\text{-}85\%}{\mathrm{MeOCH_2CR_2OH}} \xrightarrow[\text{carbon rod electrode}]{-e^-} \underset{80\text{-}88\%}{\mathrm{R_2C{=}O}}$$

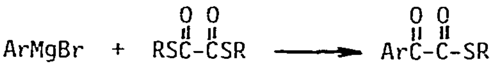
Reaction of a di-Grignard reagent with an ester was used to synthesize a cycloalkanol [286]:



A side reaction noted in the reaction of allylmagnesium bromide with methyl formate was transesterification by the product alcohol [287].



Reaction of thiooxalates with one mole of Grignard reagent led to α-keto-thioesters. Pyrolysis of the adduct before hydrolysis gave a low yield of α-hydroxy-thioester [288,289]:

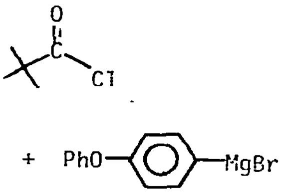


$$\mathrm{ArMgBr} + \mathrm{RS}\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}\mathrm{SR} \longrightarrow \mathrm{Ar}\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-\mathrm{SR}$$

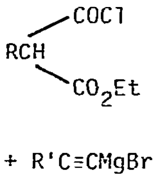
The reaction of acid chlorides with Grignard reagents to yield ketones in the presence of cuprous salts is reported in several studies [290]. Yields of hindered ketones from a variety of aliphatic acid chlorides and Grignard reagents ranged between 50 and 89%; however, a yield of only 20% was obtained from Me_3CCH_2MgCl and $Me_2(iPr)CCOCl$ [291]. In a mechanistic study, it was concluded that the organometallic reagent forms an intermediate with the acid chloride. This intermediate is converted to ketone on hydrolysis or by thermal reaction, but is destroyed without ketone formation by oxygenation [292]

The use of manganous iodide with Grignard reagents, presumably involving an alkylmanganese iodide, also gives good yields of ketones [293]. The formatio of esters from ethyl chloroformate and ketones from phosgene is also reported [294].

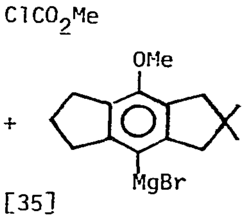
The formation of ketones from acid chlorides, and an ester from methyl chloroformate without transition metal intervention is also reported in the following instances:



[295]



[59]



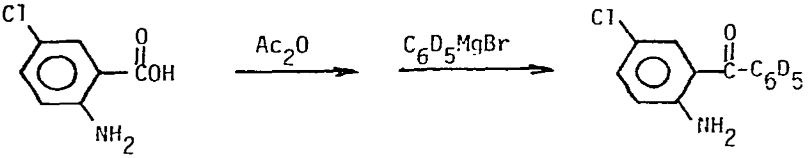
[35]

A CIDNP study of the reaction of o-bromobenzoyl chloride with tert-butylmagnesium chloride has been noted previously (section IV.A) [178].

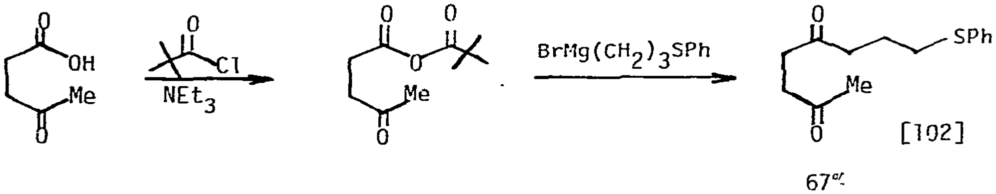
The reaction of Grignard reagents with anhydrides can also be used to prepare ketones. Acetic anhydride was reported to react with the following reagents to yield the corresponding methyl ketones, the former in 70% yield:

$MeCH{=}CH{-}C{\equiv}CMgBr$ [296] $MeCH{=}CH{-}CH_2CH_2MgBr$ [297]
($-78°$, Et_2O)

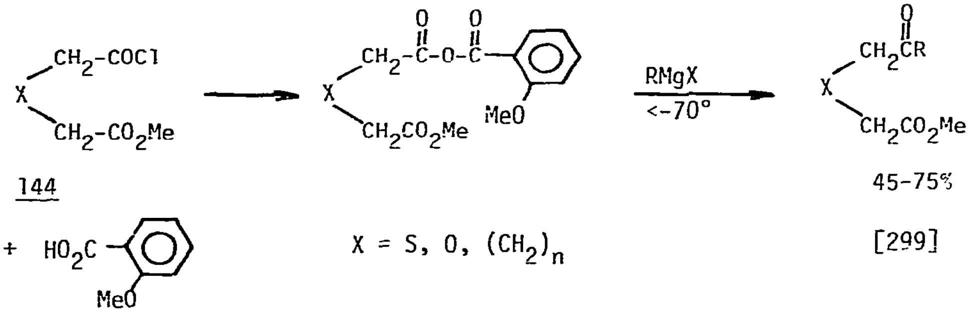
Mixed anhydrides, formed from an acid, may be used to activate the carboxy group for ketone formation:



[298]



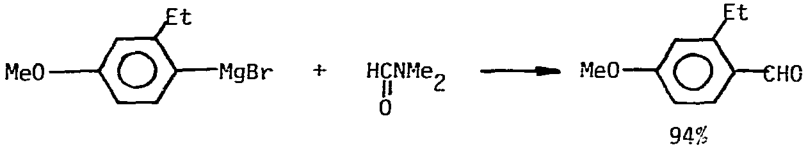
[102]



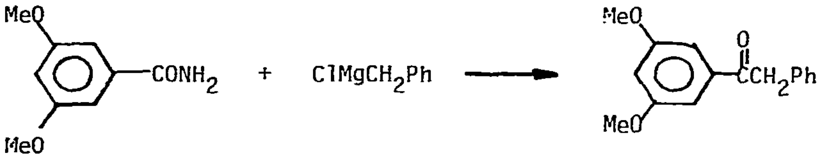
[299]

The selectivity toward the anhydride function may be noted in the last two cases. With 144, a rather extensive study was made. Poor yields were obtained for X=O and other α-alkoxy anhydrides.

Aldehyde and ketone syntheses are also reported from amides:

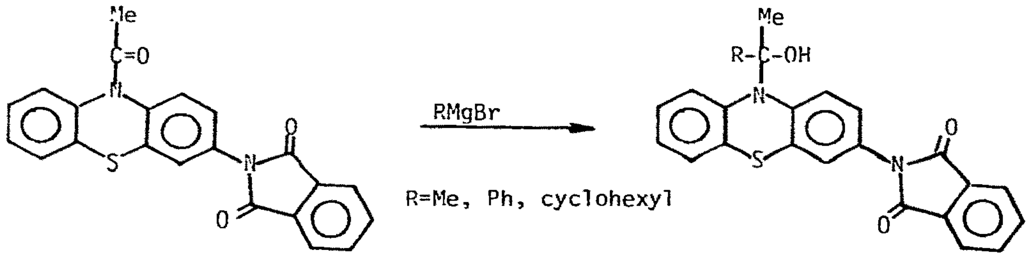


[300]

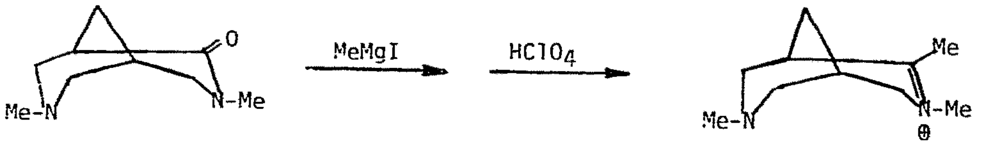


[301]

Stable carbinolamines or immonium ions are obtained in other instances:



[302]

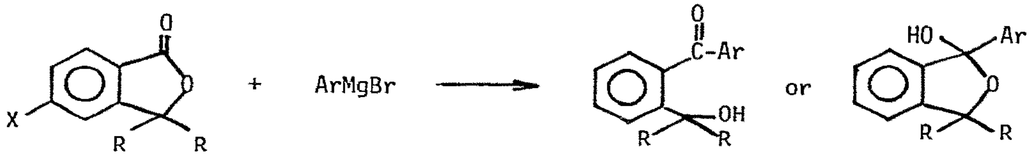


[303]

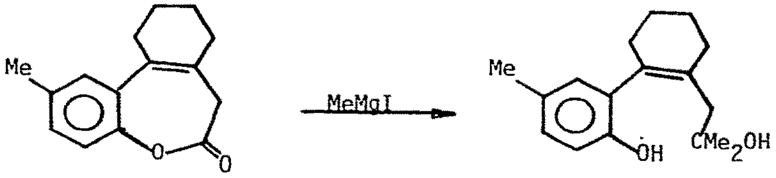
Acylation of pyrrolyl and indolyl Grignard reagents has been noted earlier in section III.C.

2. Lactones, lactams, and cyclic anhydrides

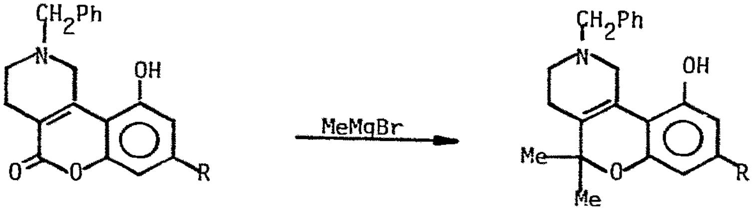
Reactions of lactones with Grignard reagents may stop with one mole of reagent, producing a ketone or cyclic hemiketal [304-306].



A second mole of Grignard reagent gives a tertiary alcohol, which may cyclize to an ether. Only two of numerous examples will be noted.

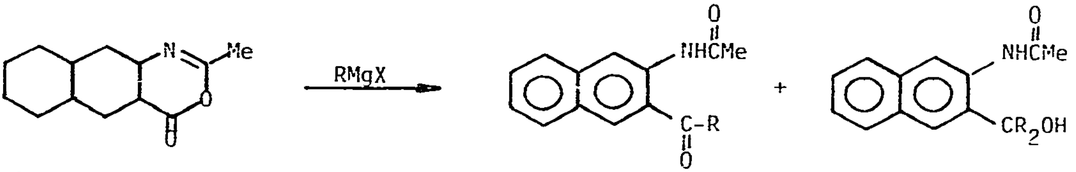


[307]



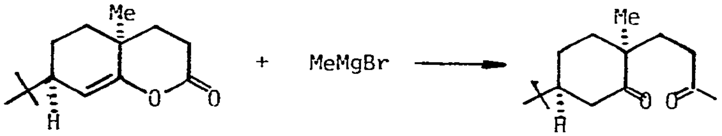
[308]

Ring-opening with formation of a ketone and unmasking of an amide or ketone group is observed in the following:

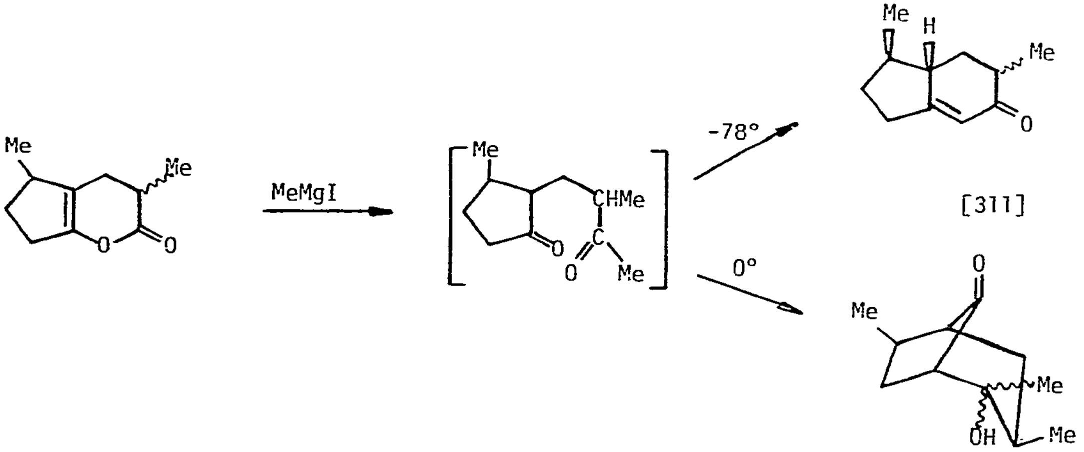


(and related structures) (44%) (37%)

[309,310]

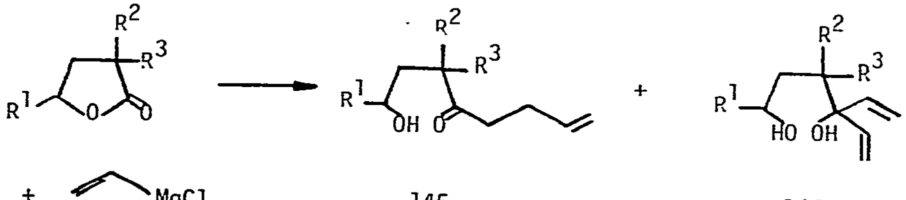


[44]



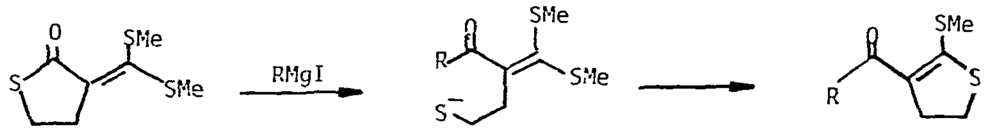
[311]

Reactions of various substituted γ-lactones with vinyl Grignard reagents yield the ketone 145 or alcohol 146. In the presence of CuCl, only ketone is reported [312].



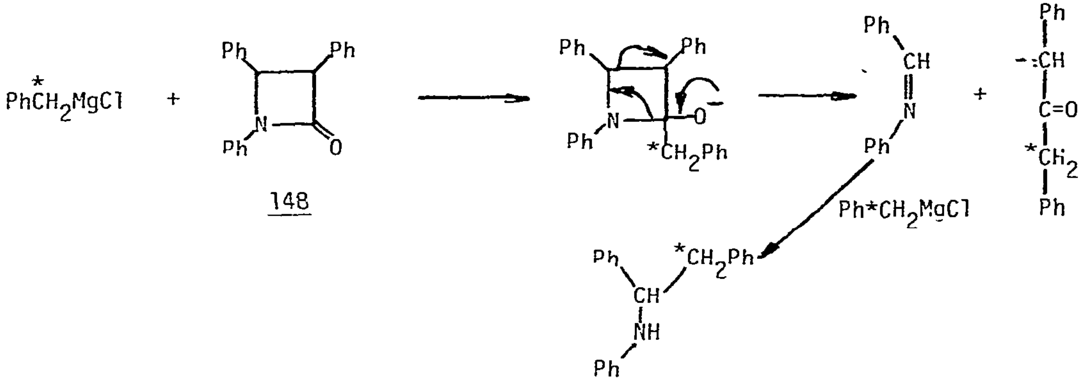
145 146

The intermediate produced from thiolactone 147 cyclized by a conjugate addition [313].



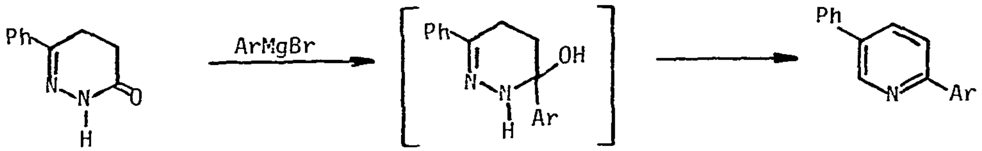
147

A carbon labelling experiment was performed to confirm the following mechanism for cleavage of β-lactam 148 [314].



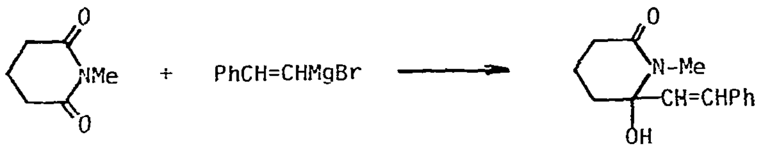
148

Dehydration and air oxidation follow addition to the amide group of 149 [315].

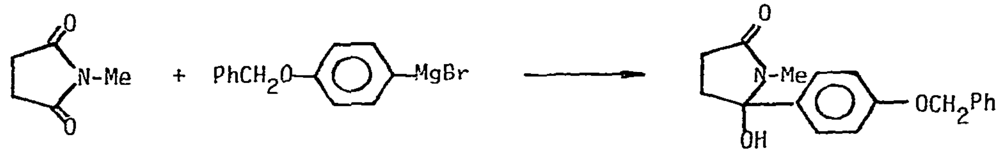


149

Carbinolamine products are isolated from the following reactions of imides



[316]

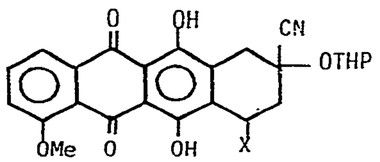


[317]

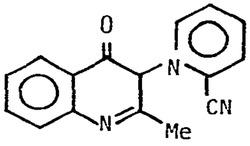
V. ADDITION OF ORGANOMAGNESIUM COMPOUNDS TO OTHER UNSATURATED FUNCTIONS

A. Reactions with carbon-nitrogen unsaturation

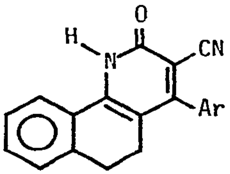
Straightforward addition to the cyano group in the presence of other potentially reactive functional groups produced the expected ketone from the following substrates:



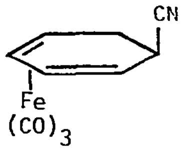
(X = H or glycoside function)
+ MeMgI
[317a,b]



+ PhMgBr (33%)
[318]

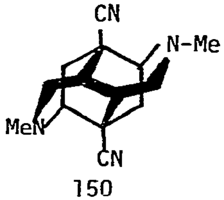


+ MeMgI or PhMgBr
[319]

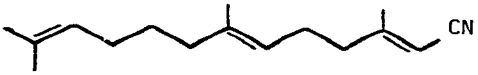


+ MeMgX
[320]

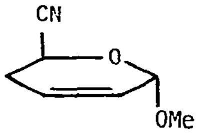
The cyano groups of a styrene-acrylonitrile copolymer reacted with $Me_2NCH_2CH_2CH_2MgCl$ to introduce amino-ketone functions [321]. Compound 150 reacts at either one or both cyano groups [322]. Only 1,2-addition was reported with 151 [323].



150

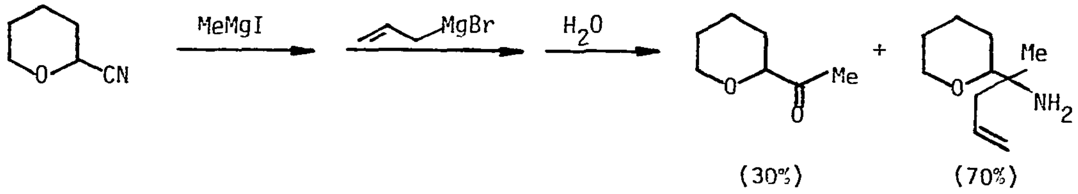


151

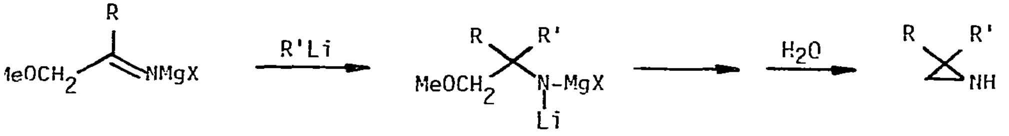


152

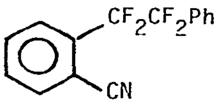
Several α-alkoxy or α-acetal-substituted nitriles reacted normally [324-326]; however, 152 failed to react with vinyl, phenyl, allyl, or cyclohexyl reagents, while undergoing reaction with others [327]. The imine salt from addition of one mole of Grignard reagent to some α-alkoxynitriles will react further with allylic Grignard reagent (or RLi) to produce a useful yield of amine [328,329]; e.g.,



Side reactions in the synthesis above include elimination of alkyllithium, aldol-type condensation, and cyclization to an aziridine:



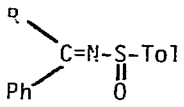
With careful work-up, the imines were isolated from reactions of 153 and 154. The intermediate imine salt from reaction of benzonitrile with various



153
+ MeMgBr
[82]

CF_3CN

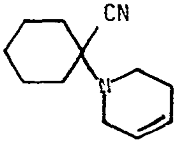
154
+ ArMgBr
[330]



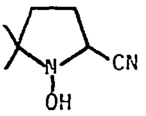
155

Grignard reagents was trapped with menthyl p-toluenesulfinate to yield sulfinimides 155 with high stereospecificity [331].

Displacement of cyanide rather than addition occurs with the α-aminonitriles 156 and 157, while removal of α-hydrogen and reversal of cyanoethylation occurs with 158.



156
+ PhMgBr
[332]

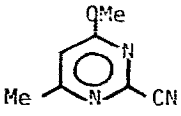


157
+ PhMgBr
[333]

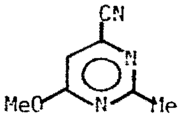
$Et_3SiCH_2CH_2CH_2NHCH_2CH_2CN$

158
+ EtMgBr
[334]

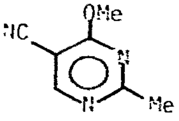
With a variety of cyano-substituted pyrimidines [335,336], phthalazines, cinnolines and quinoxalines [337], addition to the cyano group competes with addition to the ring and displacement of cyanide. Compounds 159 and 160 give the ketone, but addition to the ring occurs with 161 and 162. Products



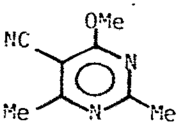
159



160

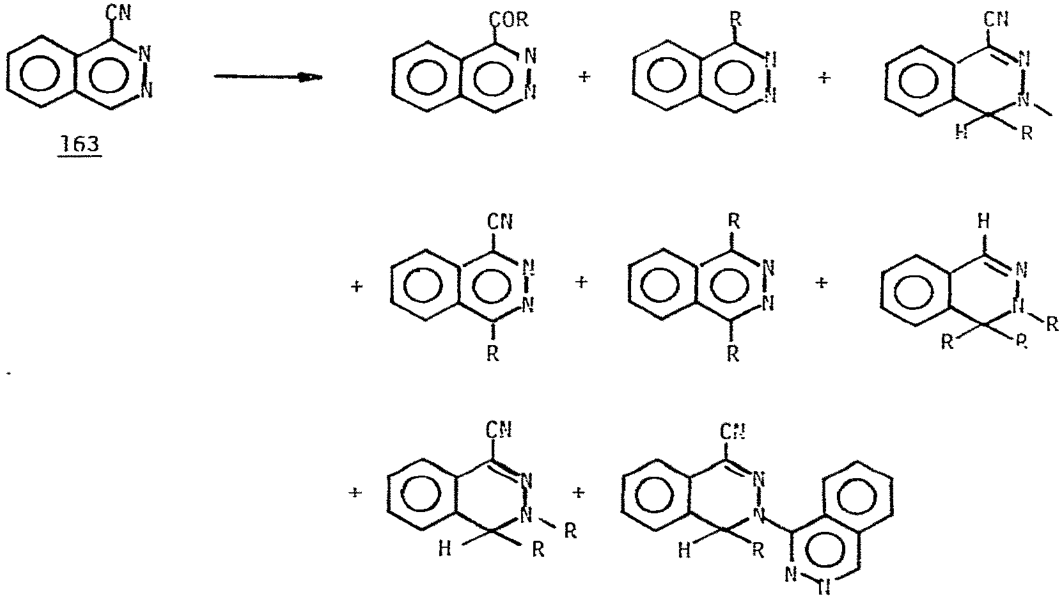


161



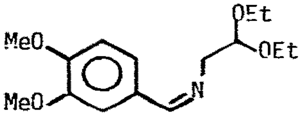
162

obtained from the phthalazine 163 are shown to indicate the variety of reaction paths followed.



163

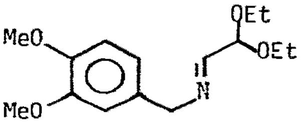
Addition to the carbon-nitrogen double bond in analogous fashion to the carbonyl group is reported for the following:



+ RMgX

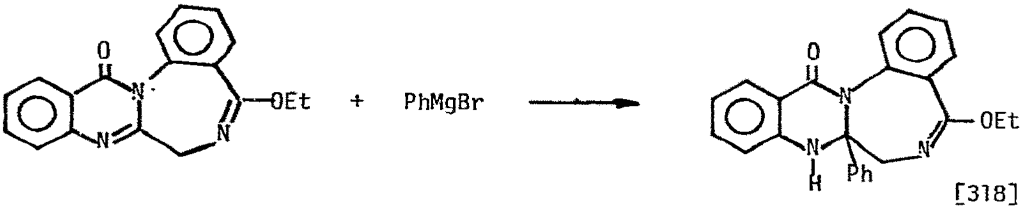
(R = allyl, benzyl)

[338,339]

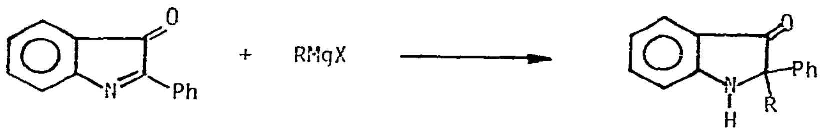


+ RMgX

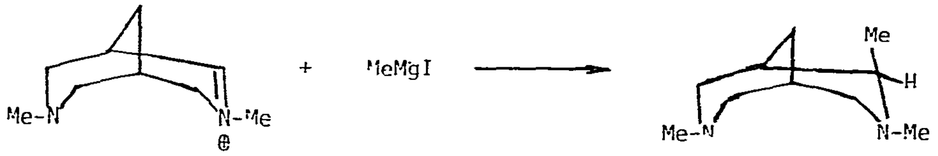
[338]



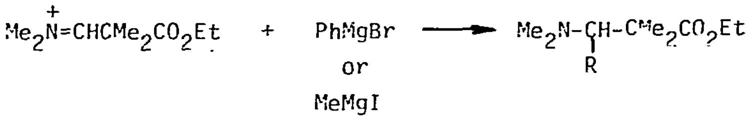
[318]



[179]

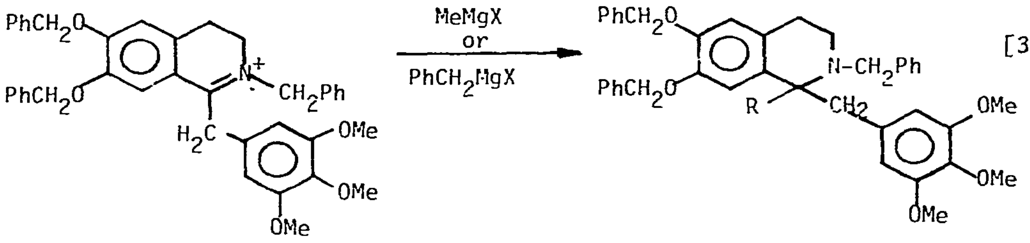


[303]



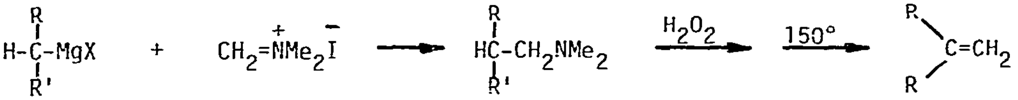
$$\mathrm{Me_2\overset{+}{N}{=}CHCMe_2CO_2Et} + \mathrm{PhMgBr}\ \text{or}\ \mathrm{MeMgI} \longrightarrow \mathrm{Me_2N{-}\underset{R}{C}H{-}CMe_2CO_2Et}$$

[340]



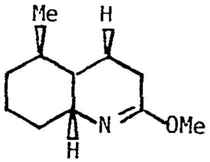
[341]

A synthesis of tertiary amines utilizes an addition to "Eschenmoser's salt"; subsequent conversion to an alkene provides an alternative to the Wittig reaction in yields up to 84% [342].

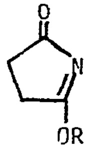


$$\mathrm{H{-}\underset{R'}{\overset{R}{C}}{-}MgX} + \mathrm{CH_2{=}\overset{+}{N}Me_2\overset{-}{I}} \longrightarrow \mathrm{H\underset{R'}{\overset{R}{C}}{-}CH_2NMe_2} \xrightarrow{H_2O_2} \xrightarrow{150°} \mathrm{\begin{matrix}R\\R\end{matrix}{>}C{=}CH_2}$$

A net replacement of the alkoxy group occurs with the following:

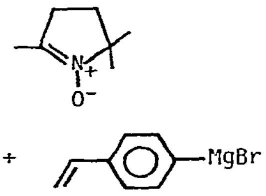


+ PrMgBr
[110]

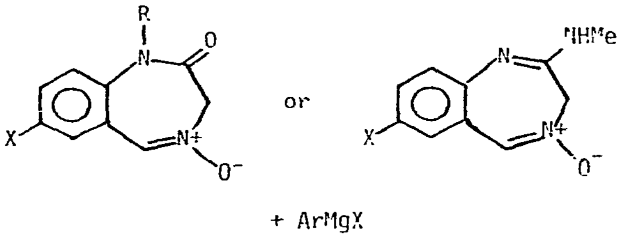


+ RMgX
[343]

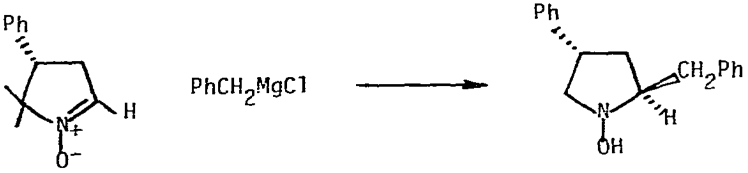
Additions to the carbon-nitrogen bond of nitrones, yielding hydroxylamines, have been important in syntheses of nitroxyl spin labels (see also ref. 21):



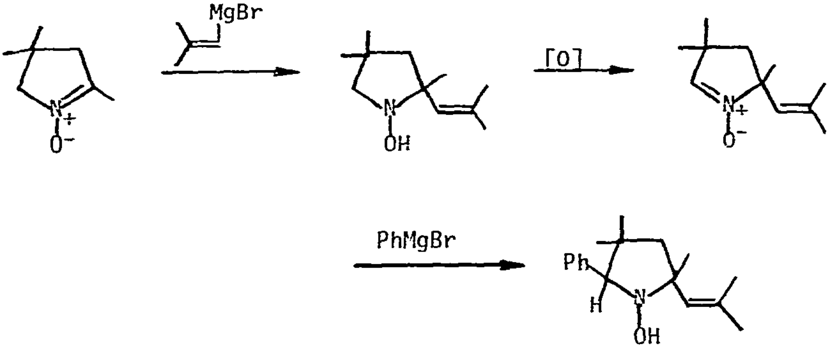
[343]



[344,345]



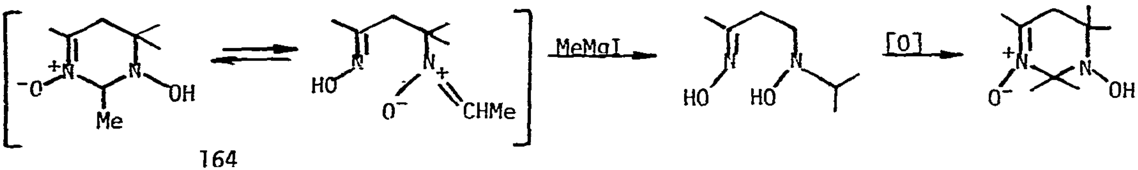
[346]



(mixture of diastereomers)

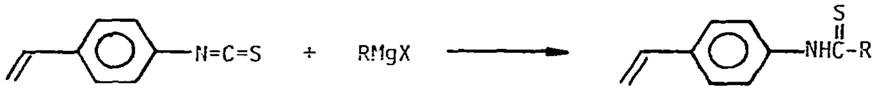
[347]

With 164 [348] and a number of five-membered ring analogs [349], addition to the open-chain tantomer occurs:



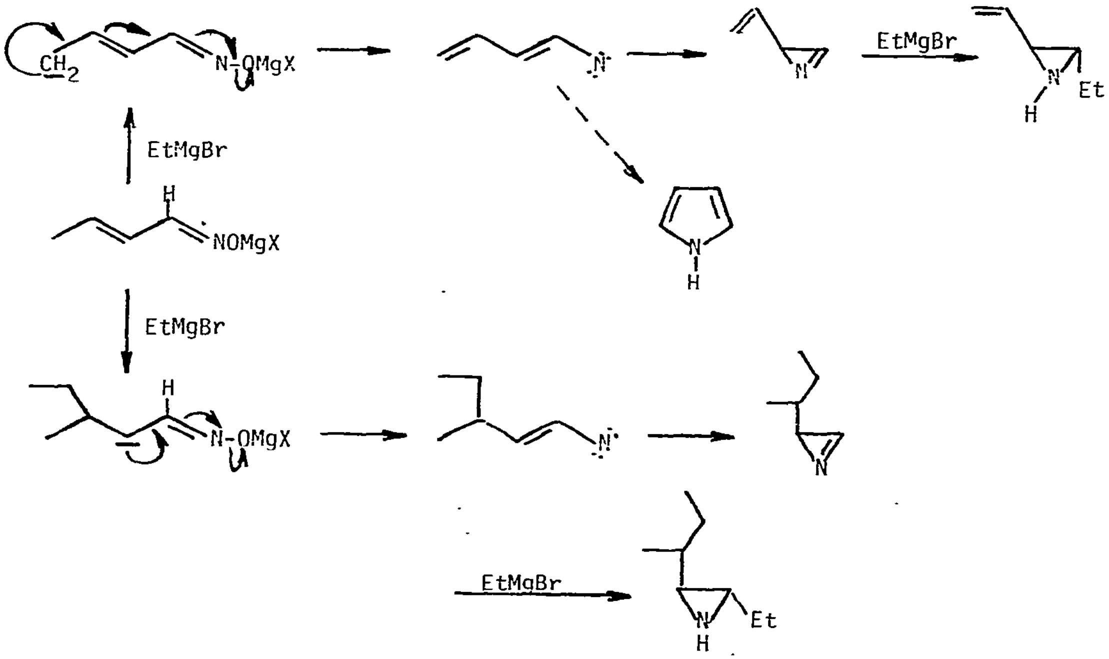
164

Addition of Grignard reagents to isothiocyanates is reported to form low to moderate yields of thioamides [350,351]; e.g.

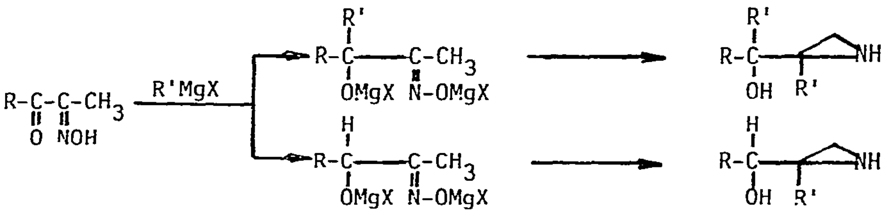


(30-75%) [350]

Aziridine formation in the reaction of ethylmagnesium bromide with crotonaldehyde oxime probably occurs via nitrene intermediates. Grignard reagent adds stereospecifically to the azirine formed by cyclization of the nitrene. A trace of pyrrole was also detected [352,353]:



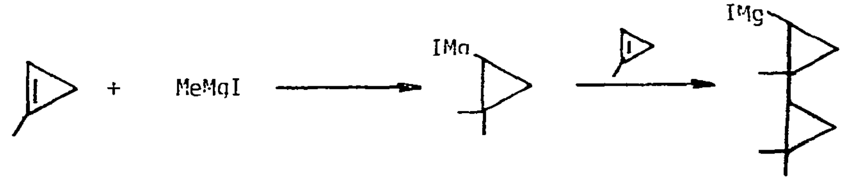
Keto- or hydroxy-oximes were also converted to aziridines [354,355]:



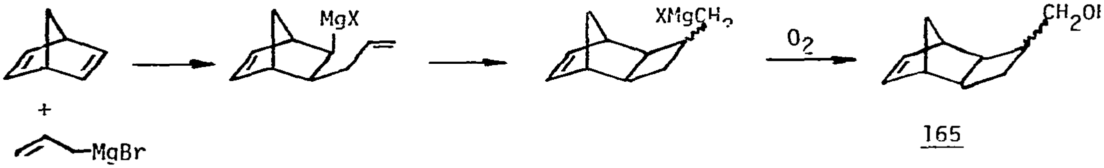
Reduction competed with addition of the first mole of Grignard reagent. Stereoselectivity between diastereomers in the final product was rationalized as a steric effect on addition to the azirine intermediate.

B. Reaction with carbon-carbon unsaturation

Addition of methylmagnesium iodide to 1-methylcyclopropene produced a mixture of monomeric and dimeric products on hydrolysis or carbonation [356]:

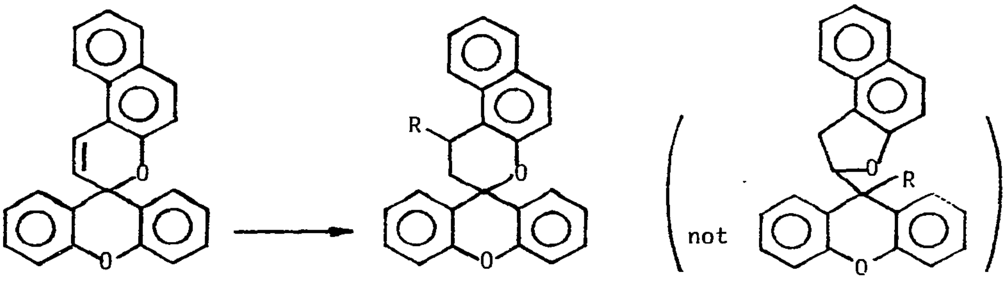


The addition of allylmagnesium bromide to norbornadiene, followed by cyclization and oxygenation, yields 165 [357].



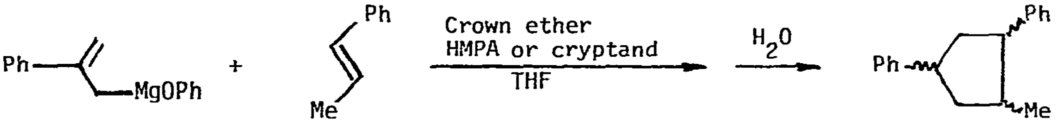
165

Reaction of Grignard reagents with 166, which had previously been reported to yield product 168, is now claimed to occur by addition to the double bond to form 167 [358].



166 167 168

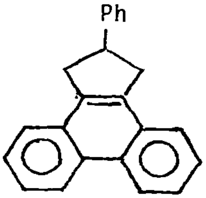
Reaction of the allylic organomagnesium compound 169 with a variety of alkenes has been studied [359]. Cycloaddition to *cis*- and *trans*-1-phenylpropene,



169

(mixture of diastereomers)

2-phenylpropene (see eq'n), and 1,1-diphenylethylene was observed. With phenanthrene, hydrogen transfer from the immediate cycloaddition product to another phenanthrene occurred, producing 170.



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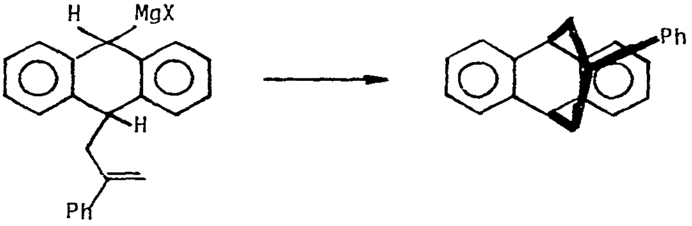
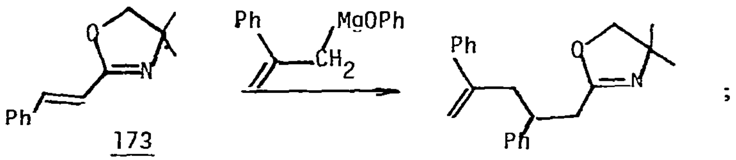


171 172

With anthracene, the initial product 171 was slowly converted to the cyclic 172. There was no addition to norbornene or cyclooctene, and only oligomerization of perfluoro-2-butene. Addition occurs with 173, and replacement of fluorine with 174 and 175. In the latter two, stereochemistry at the double bond is lost. Also, 169 catalyzes rapid isomerization of *cis*-stilbene, without any H-D exchange. The mechanism favored for these reactions was a stepwise addition-cyclization mechanism; the cyclization step is an intramolecular addition to a phenyl-substituted double bond.



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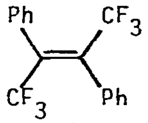

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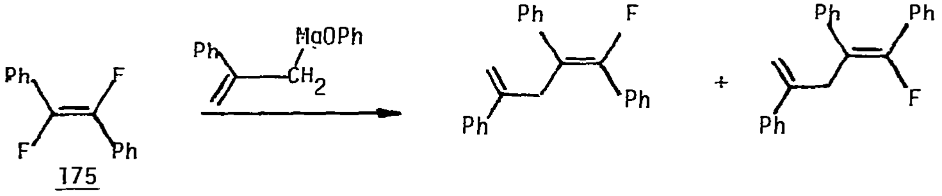


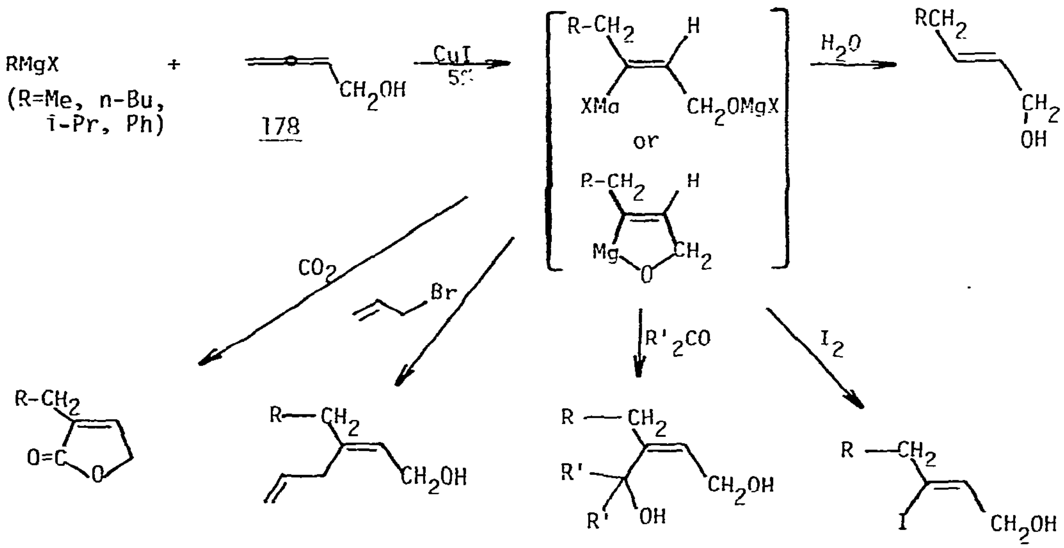
175

A cycloaddition reaction of allylic Grignard reagents has also been found with benzyne [360]:

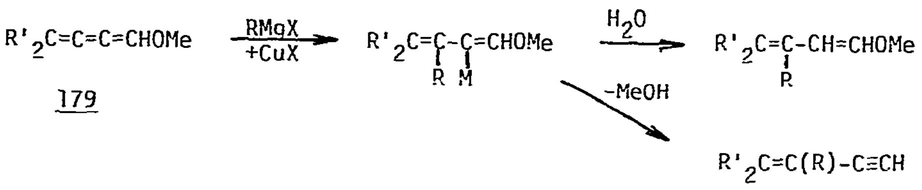
176 177

The organomagnesium compounds generated were characterized by hydrolysis with D_2O. Corresponding products are formed with crotylmagnesium bromide. Since 176 and 177 are not interconverted, it was concluded that they result from concurrent [2+2] and [4+2] additions.

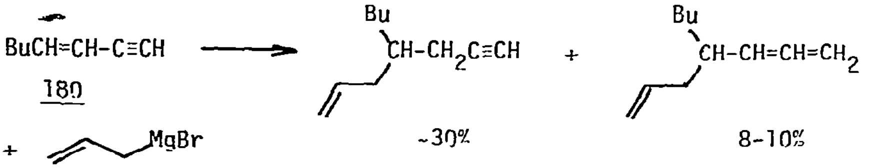
Grignard reagents added with copper catalysis to the hydroxy-substituted allene 178; the organomagnesium intermediate is synthetically useful in a variety of further reactions. Product is formed stereospecifically [361].



Addition of the reagent prepared from a Grignard reagent and a cuprous halide to the cumulene 179 gave an intermediate which could be hydrolyzed to an 80-90% yield of addition product. With catalytic amounts of CuBr, elimination occurs in good yield [362].



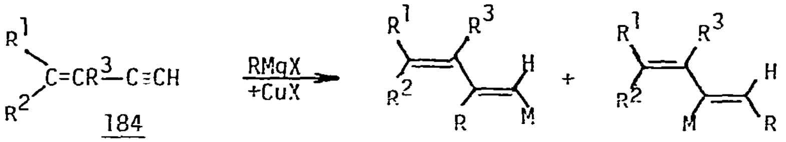
The addition of allylic Grignard reagents to the double bond of enyne 180 has been studied:



With 3-substituted allylic Grignard reagents, the "branched" product is obtained. Only a low yield of 1,2-addition to the internal multiple bonds of 181 and 182 is observed, and 183 does not react [363].

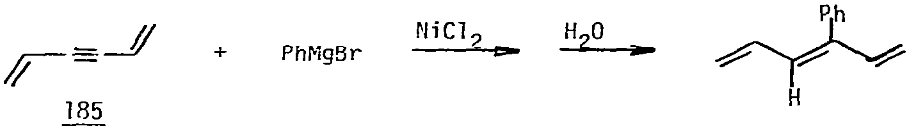
$BuCH{\equiv}C{-}C{\equiv}CH$ 181 $\qquad$ $BuCH{=}CHC{\equiv}CMe$ 182 $\qquad$ $BuC{\equiv}C{-}C{\equiv}CMe$ 183

Magnesium organocuprates, on the other hand, add preferentially and stereospecifically syn to the triple bond of 184 [364]. The first product, with the



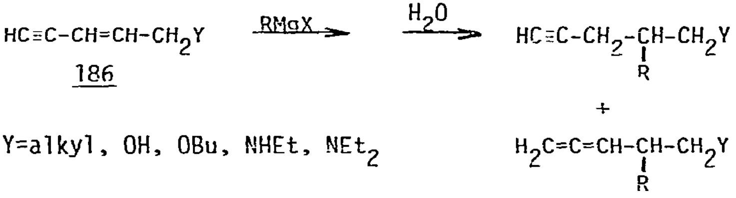
184

metal on the terminal carbon, is formed almost exclusively with primary Grignard reagents, but comparable amounts of the two are formed with secondary and tertiary. Phenylmagnesium bromide adds with $NiCl_2$ catalysis to 185 [365]:



185

Saturated and benzyl Grignard reagents add without catalyst to the double bond of enynes 186 [366]. The alkyne and allene products are produced in similar amounts when Y=OH or OR, but the alkyne predominates to an increasing degree with Y=amino and alkyl. Hydrolysis by D_2O introduced two deuterium atoms in the product, indicating that Grignard reagent had reacted first with the acetylenic hydrogen.

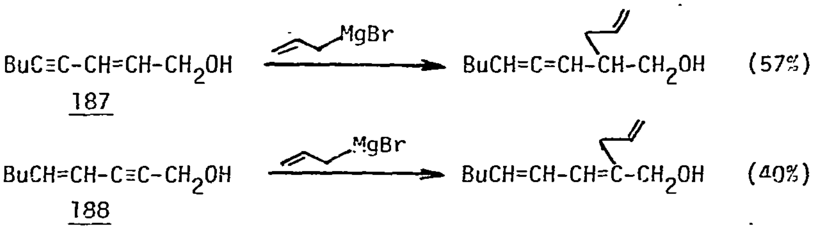


$$HC{\equiv}C{-}CH{=}CH{-}CH_2Y \xrightarrow{RMgX} \xrightarrow{H_2O} HC{\equiv}C{-}CH_2{-}\underset{R}{\underset{|}{C}}H{-}CH_2Y + H_2C{=}C{=}CH{-}\underset{R}{\underset{|}{C}}H{-}CH_2Y$$

186

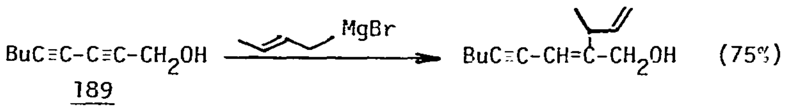
Y=alkyl, OH, OBu, NHEt, NEt_2

An OH function also directs uncatalyzed addition to the closer unsaturated group in 187-189 [367].

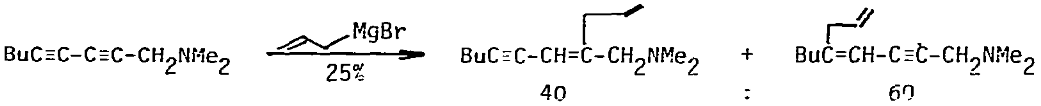


187

188



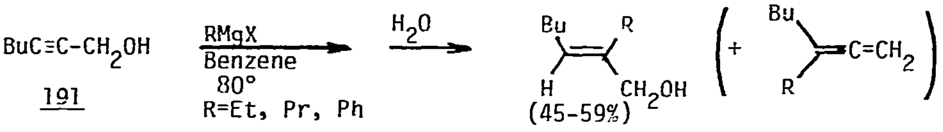
The corresponding amines give similar products (but in lower yields) except for

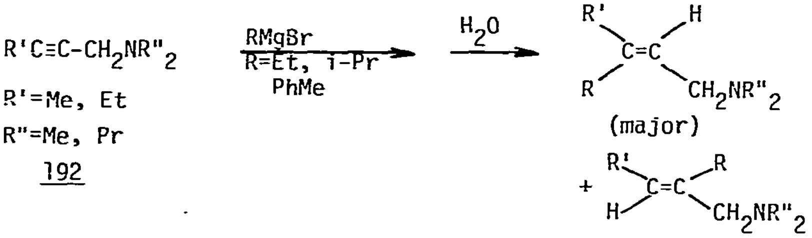


Catalyzed addition to the triple bond of 190 also occurs [368].

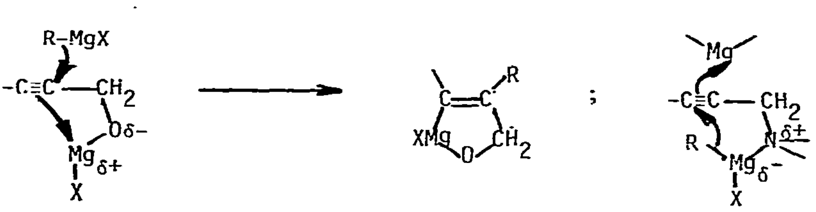
$$CH_2{=}CH{-}C{\equiv}C{-}SiMe_3 \xrightarrow[\text{Ni, Co or Pd salts}]{RMgX} \xrightarrow{H_2O} RCH_2CH_2C{\equiv}C{-}SiMe_3$$

The propargylic alcohol 191 reacts with a number of Grignard reagents as indicated, but shows little tendency to react with methyl, *t*-butyl, and benzyl reagents under these conditions [369]. Addition to amines 192 occurs mainly

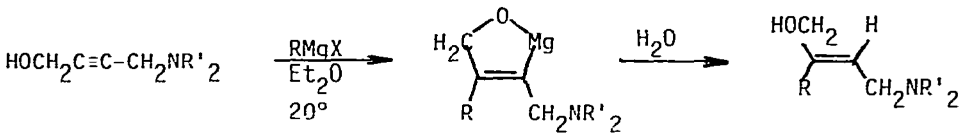




with the opposite orientation. The stereochemistry of both additions is anti. It is proposed that the opposite effects of OH and NR_2 are partly electronic in origin, and are also related to different mechanisms of assistance by the two groups:



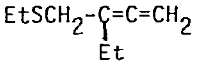
With both hydroxy and amino groups present, the addition occurs readily with a variety of Grignard reagents [369-371].



Addition also is reported for the corresponding methoxy-amine and diamine [371].

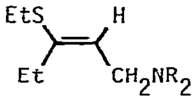
The thioethers 192 do not react as readily [372]. There was no isolable product when Y=SEt, and low yields of the allene 193 were formed by elimination from the intermediate adduct when Y=OH or OR. The amines (Y=NR_2) gave a low yield, with 194 predominating. However, in the presence of 5% of copper salts, the yield was improved (to 61%) and 195 was the major product.

$EtSCH_2C{\equiv}CCH_2Y$
Y=OH, OR, NR_2,SEt
192

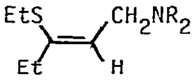


$EtSCH_2\text{-}C(Et){=}C{=}CH_2$

193

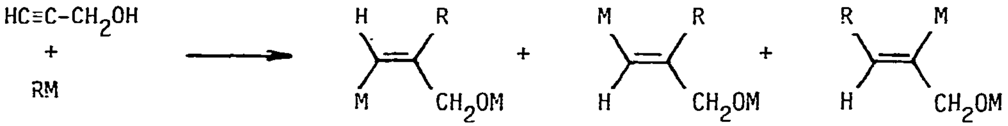


194



195

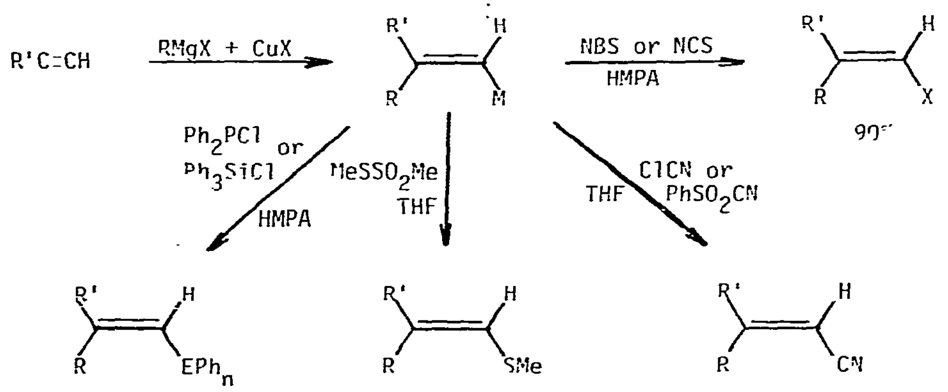
The copper-catalyzed addition of Grignard reagents to propargyl alcohol was compared with additions of stoichiometric magnesium cuprate reagents [373].



196 197 198

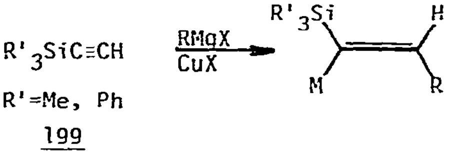
In ether solution, both led largely to 196; in THF, 197 was the major product in the catalyzed reaction, but the cuprates produced more similar amounts of the two. Only minor amounts of 198 formed.

Magnesium organocuprates add regiospecifically and stereospecifically (syn) to terminal alkynes. A number of papers report on subsequent synthetic conversions of the intermediate adduct with electrophiles [374-377]:

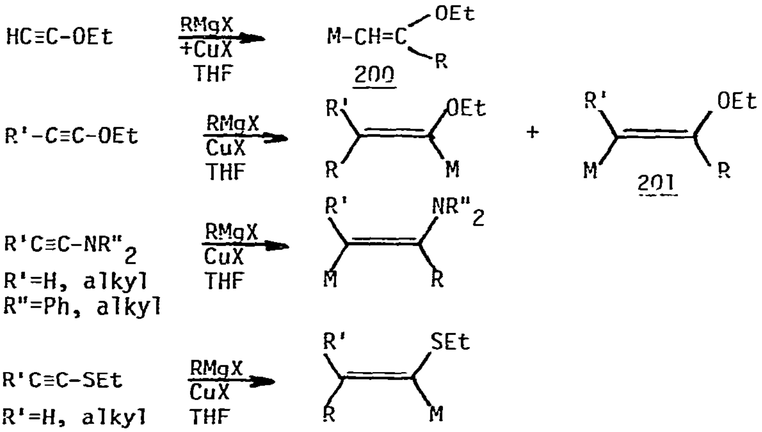


The adduct prepared using CuBr·SMe_2 is particularly useful for conjugate additions to unsaturated ketones [378]. The presence of dimethyl sulfide or HMPA also helps to prevent symmetrical coupling reactions [374].

Additions to the silyl alkynes 199 are also reported. The intermediate adduct was halogenated and alkylated [379,380].

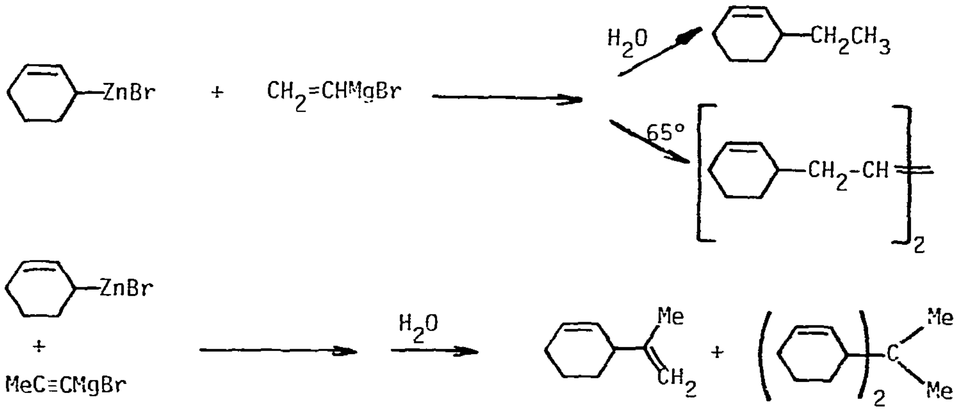


Additions of magnesium organocuprates to heterosubstituted alkynes occur with the following regiospecificity [381]:



The alkoxy groups of 200 and 201 are eliminated above -20°, but the other products are stable. Subsequent synthetic reactions include protonation, halogenation, alkylation, carbonation, coupling (with O_2), conjugate addition, and hydrogenolysis of the thioethoxy compounds (Li/NH_3).

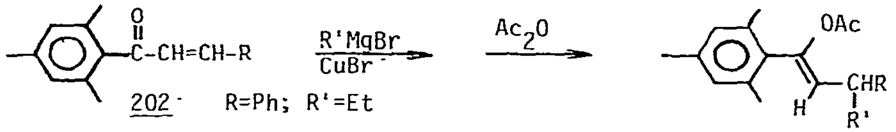
In a reversal of roles from reactions described above, it has been shown that allylic zinc compounds add to the double and triple bonds of alkenyl and alkynyl Grignard reagents [382,383]; e.g.



Additions of Grignard reagents to conjugated carbonyl derivatives are discussed in the next section. A number of other reactions in which allylic halogens or other leaving groups are displaced with allylic rearrangement (S_N2') may involve preliminary addition to the double bond (see sections VI.A., B.).

C. Reaction with conjugated carbonyl and carboxy derivatives

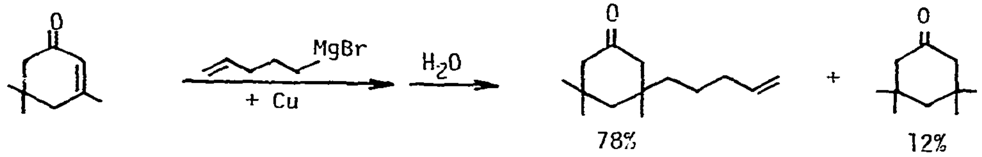
A study of the conjugate addition of ethylmagnesium bromide to 202 in the presence of one half mole of cuprous bromide concludes that three reagents of differing selectivity and reactivity are present, in amounts depending upon



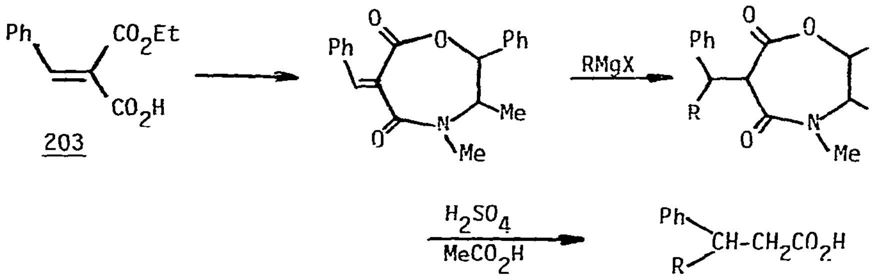
202 R=Ph; R'=Et

aging of the reagent. The yield and E:Z ratio in the acylated product vary with treatment of the reagent [384]. Variations in stereochemistry are also reported on interchanging R and R' groups (e.g., R=Me; R'=Ph vs. R=Ph; R'=Me) [385].

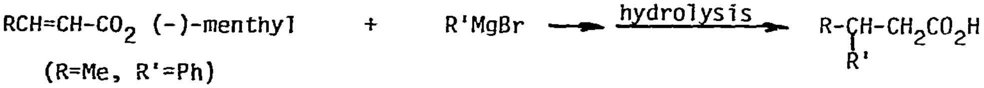
It is reported that the reagent prepared from a Grignard reagent and methylcopper has advantages over lithium cuprates in conjugate additions to highly substituted substrates. Except for the allyl reagent, transfer of the group from the Grignard reagent occurs in preference to methyl transfer [386]; e.g.



Reaction of 203 with ℓ-ephedrine hydrochloride, followed by Grignard reaction and hydrolysis produced carboxylic acid products in 65-92% yield, and with optical purities (depending upon the reagent, solvent, and whether a transition metal catalyst was used) as high as 99% [387].



The stereochemistry of the conjugate addition of phenylmagnesium bromide to (-)-menthyl crotonate (R=Me, R'=Ph) was studied. The acid produced had a

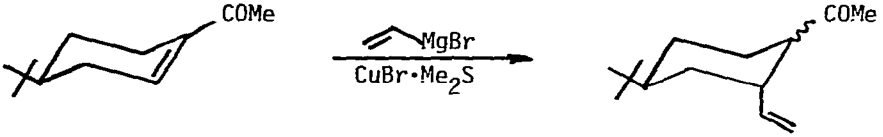


$$\mathrm{RCH{=}CH{-}CO_2\ (-)\text{-}menthyl} \quad + \quad \mathrm{R'MgBr} \longrightarrow \xrightarrow{\text{hydrolysis}} \mathrm{R{-}\underset{R'}{C}H{-}CH_2CO_2H}$$

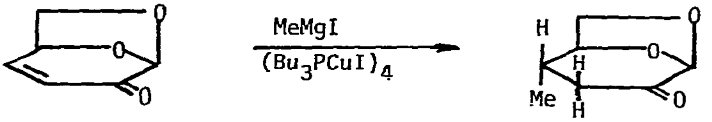
(R=Me, R'=Ph)
or (R=Ph, R'=Me)

positive rotation (up to 15.5% optical yield) in the absence of catalyst, but a negative rotation with catalysis by salts of iron, copper, and a variety of other transition and main-group metal salts (up to 21% optical yield with iron salts). Product of negative rotation was formed with R=Ph, R'=Me. It was proposed that the uncatalyzed reaction occurs by a "linear Michael addition" mechanism in the s-trans configuration, while the catalyzed reactions involve a cyclic metal complex in the s-cis form [388].

In the following copper-catalyzed conjugate addition, the vinyl group approaches mainly from the axial direction [389]:

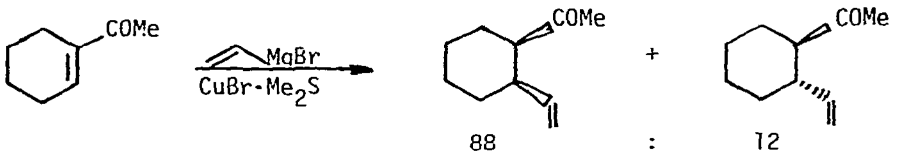


Other additions in which stereochemistry may be noted are:

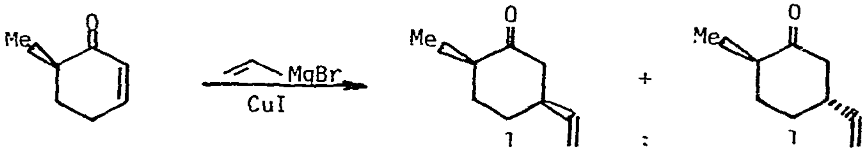


\+ 1,2-products [216]

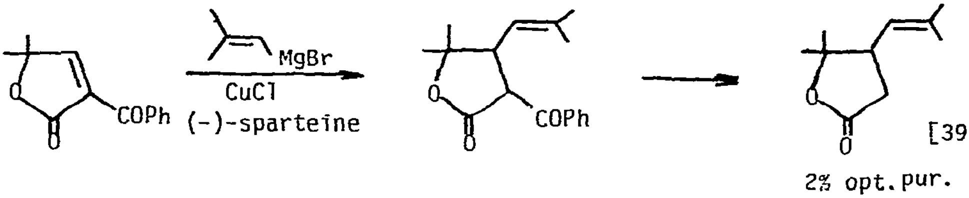
(64%) (18%)



[389]

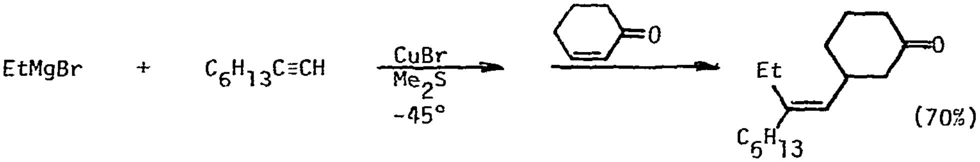


[390]

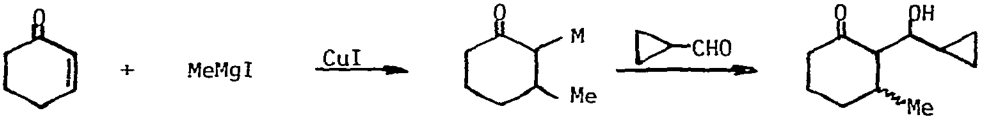


[391]

The magnesium organocuprate generated by addition to an alkyne may subsequently be added to an enone [378]; e.g.

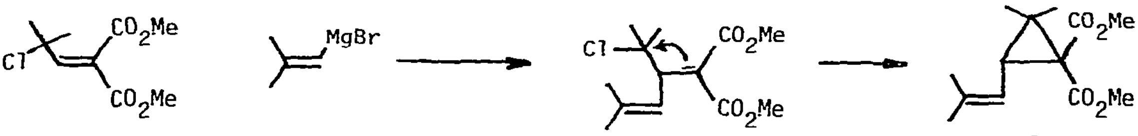


The enolate formed from the enone may itself react as a nucleophile:



[392]

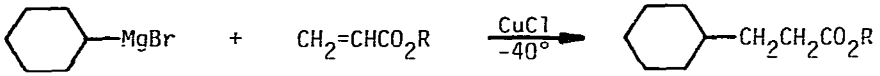
[393]



[394]

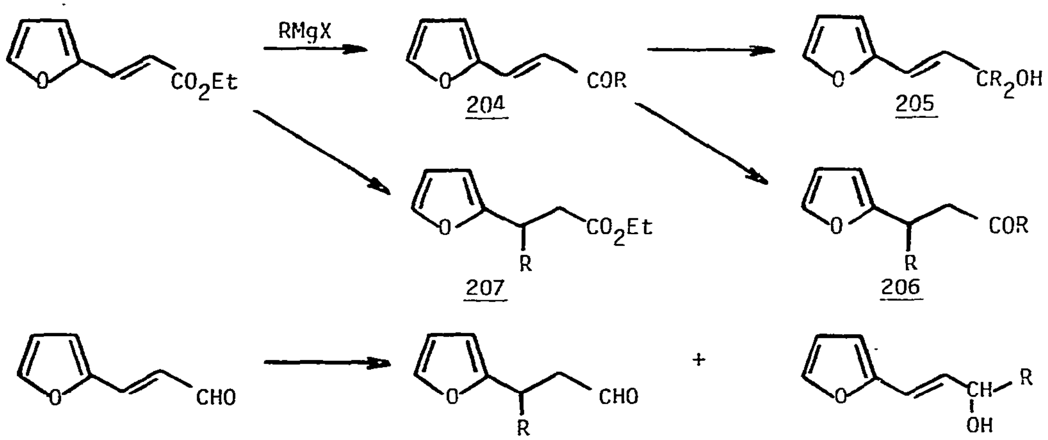
The last example occurs more rapidly and in better yield with CuCl catalysis.

The conjugate addition of Grignard reagents to acrylate esters, catalyzed by cuprous chloride, provides a useful three-carbon chain extension. The temperature must be kept low to avoid polymerization [395]; e.g.



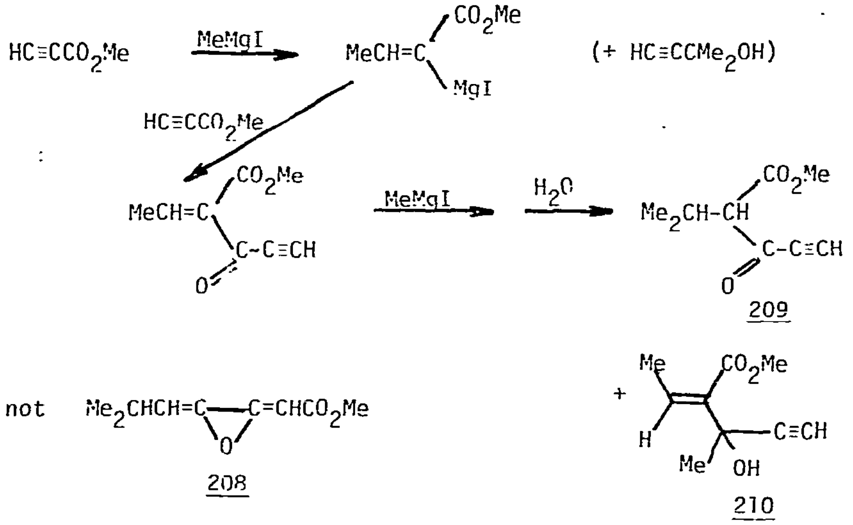
In an earlier section of this survey, conjugate addition (with and without transition metal salt catalysis) has been noted in the reactions of vinyl Grignard reagents with carboxylic acids and esters (see section IV.E).

The reactions of furylacrylic acid and furylacrolein with Grignard reagents have been studied:

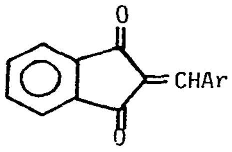


With the former, methylmagnesium iodide reacts initially at the ester group, followed by competing 1,2 and 1,4-addition to yield 205 and 206 in a 7:3 ratio. Isobutyl, isopropyl, and *tert*-butyl Grignard reagents give increasingly larger amounts of conjugate addition to form 206 and 207. The *tert*-butyl reagent also forms small amounts of 1,6 and 1,8-addition products, with alkylation of the furan ring [396]. Competition between 1,2 and 1,4-addition is also seen in reaction of the aldehyde with isopropyl, *tert*-butyl, or benzyl Grignard reagents [397]. The extent of 1,4-addition increased at low concentrations, and was also dependent on the halogen in the reagent. It appeared that an insoluble complex was formed, which reacted with additional Grignard reagent; the selectivity may be related to the heterogeneity. Methylmagnesium iodide gave only 1,2-addition in the absence of copper catalysis.

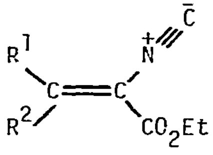
An earlier paper had reported that addition of Grignard reagents to propiolate esters led to the unusual product 208. In a reinvestigation, it was shown that the major products (other than the tertiary alcohol) are 209 and 210, most probably formed via the route [398]:



With two conjugating, electron-withdrawing substituents, conjugate addition becomes more important, as observed in the following cases:

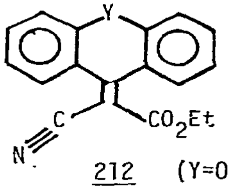


+ Ar'MgBr
[399]



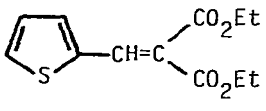
211

+ R^3MgX
[400]

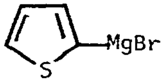


212 (Y=O, S, or direct bond)

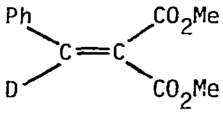
+ RMgX
[401]



+



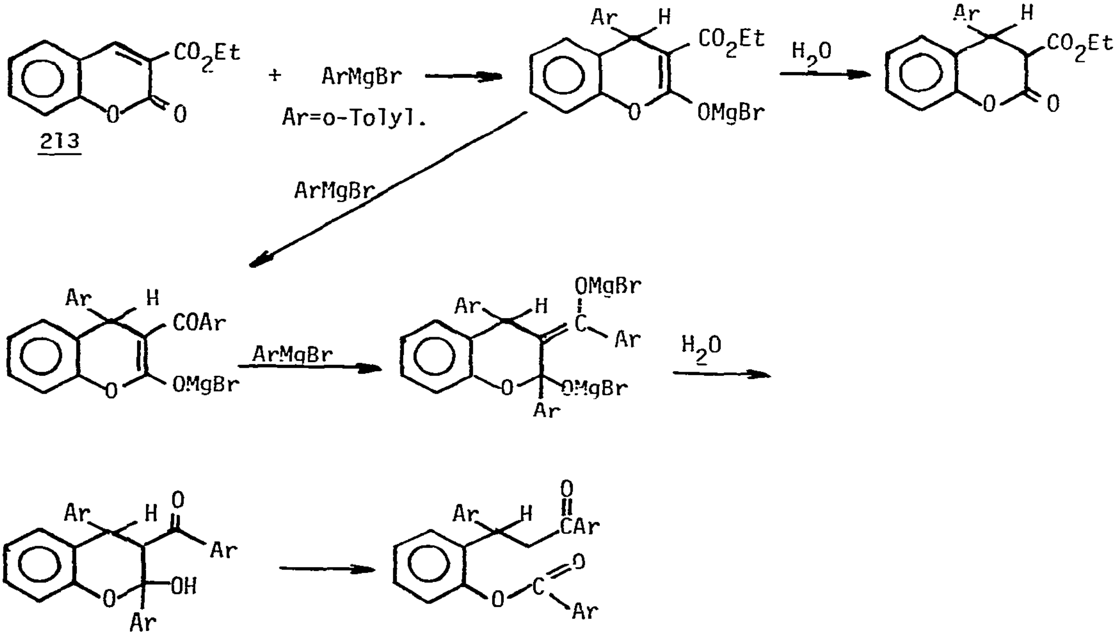
[402]



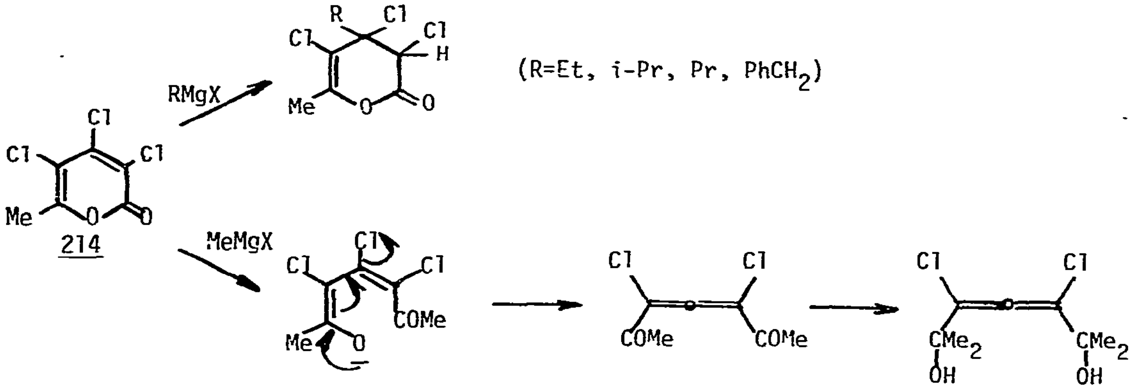
+ MeMgI

[403]

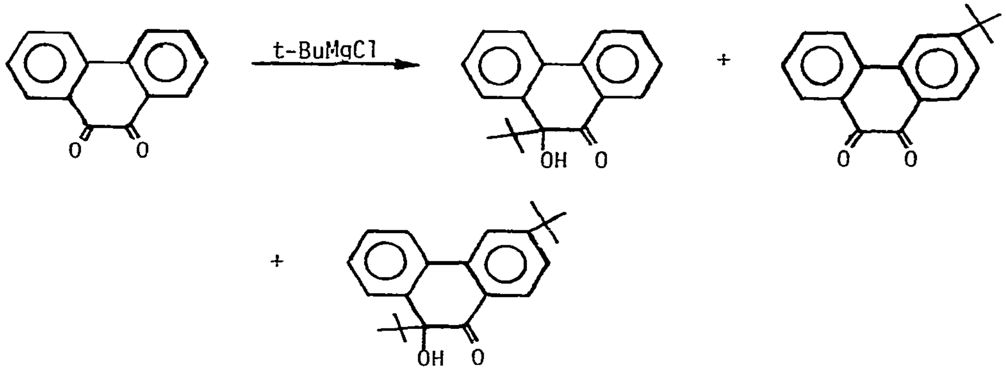
With the isonitrile 211, the reaction stops after one mole of reagent has been added, because the magnesium salt formed is insoluble; lower yields are obtained in THF. In the reaction of isobutyl Grignard reagent with 212 (Y=O), reduction by hydride transfer to the β-carbon occurs. A more complex sequence, including two conjugate additions and a reverse alcohol reaction is followed by 213 with excess reagent [404].



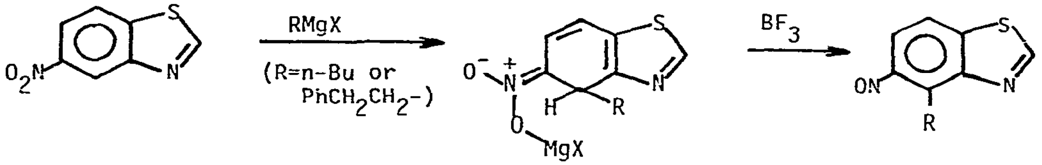
In the reactions of 214, the methyl Grignard reagent adds to the carbonyl group , leading eventually to an allene; other Grignard reagents react by conjugate addition [405].



Conjugate addition to the benzene rings of phenanthrenequinones was studied [406]:

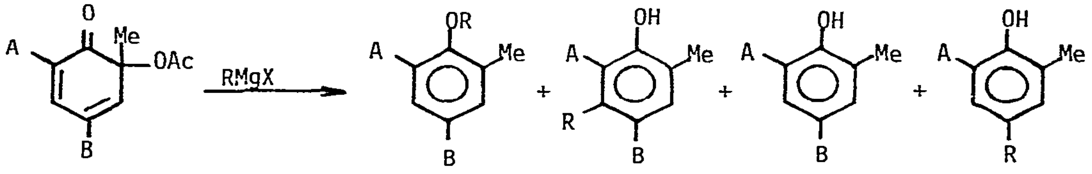


In another reaction, involving addition to a nitro-activated aromatic ring, oxidative aromatization by the nitro group occurs [407]: e.g.



Conjugate additions to the benzene ring of benzophenones in mechanistic EPR studies of the Grignard reaction have been noted previously [173,176] (section IV.A.).

An extensive study of the addition of Grignard reagents to o-quinol acetate 215 has been made [408-410]. This reaction is unusual in that a major product is the phenyl ether 216 formed by addition to the oxygen:

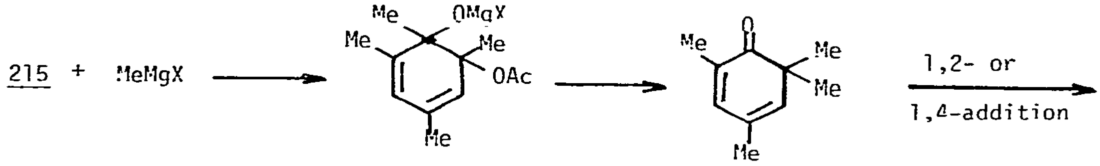


215 216 217 218 219

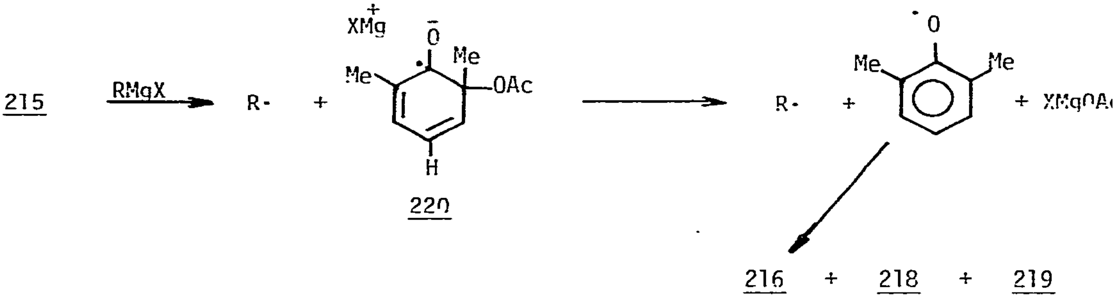
A=B=Me
A=Me; B=H
A=t-Bu; B=H

(when B=H)

Other minor products appear to arise from rearrangement following 1,2-addition:

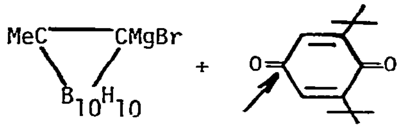


The addition to oxygen is most important for benzyl, tertiary, and secondary reagents, is favored by electron-donating substituents in the benzyl group, and is of increased importance for dialkylmagnesium reactants. Transition metal salts increase the proportion of reduction product 218, but have little effect on the ratio of 216 to 217. An electron transfer mechanism was proposed for some of the products:

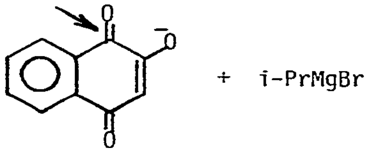


The 1,2- and 1,4-additions may follow independent pathways or arise from radical pair 220 before loss of acetate ion.

With substituted benzoquinones, 1,2-addition to a carbonyl group is observed typically; e.g.

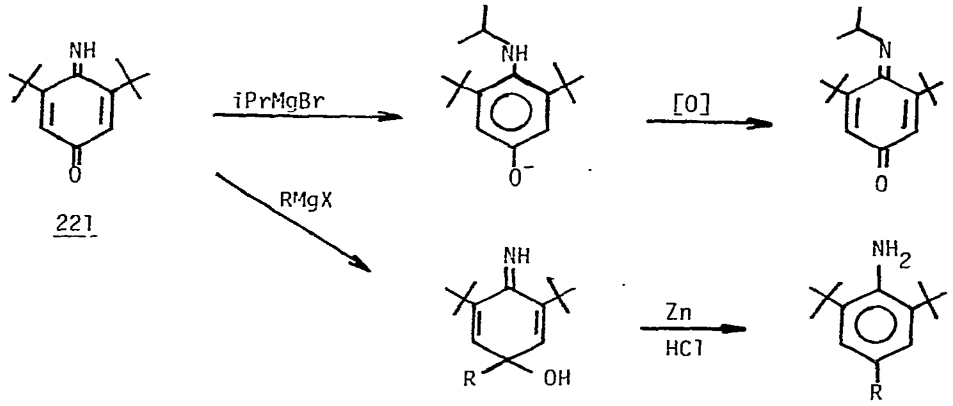


[129]



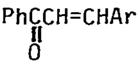
[411]

Most Grignard reagents add normally to the carbonyl group of 221, but *tert*-butylmagnesium chloride gives reduction to the corresponding aminophenol, and the isopropyl Grignard reagent adds to nitrogen [412]:



221

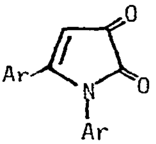
Some other instances of conjugate addition, in which transition metal catalysis does not appear to be cited, include:



$\mathrm{Ph}\underset{\underset{\textstyle O}{\|}}{\mathrm{C}}\mathrm{CH{=}CHAr}$

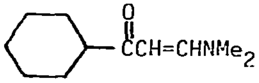
+ MeMgI

[413]



+ RMgX

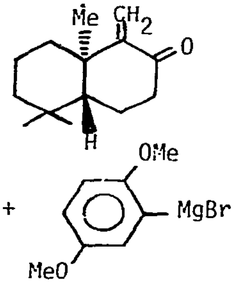
[414]



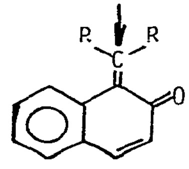
+ RMgX

(displaces NMe_2)

[415]



[416]

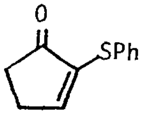


(R=Me, Ph)

+ PhMgBr

or MeMgBr

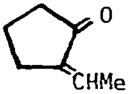
[417,284]



+ RMgBr

(45%)

[418]

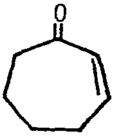


74% 1,2

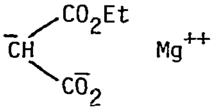
14% 1,4

+

[419]



+

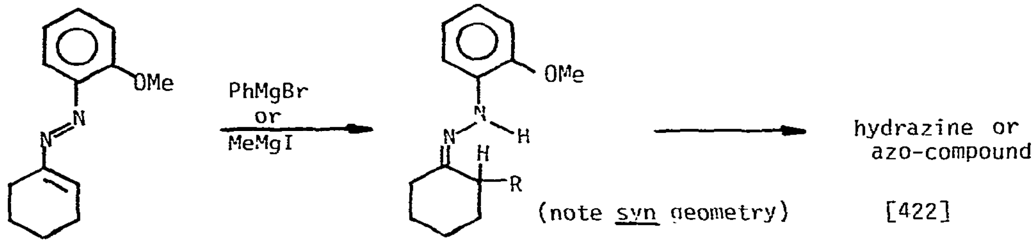


(64%)

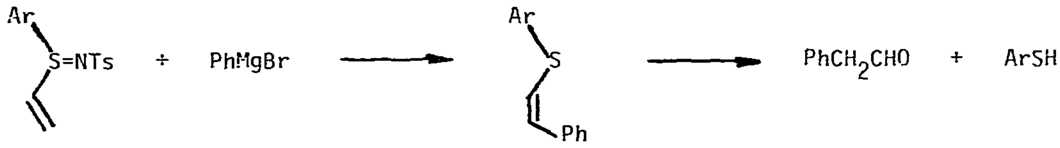
[420]

Although mesityl oxide normally undergoes 1,2-addition, its imines yield only 1,4-addition product in yields of 30-50% [421]. In an earlier section of this survey, conjugate addition to an unsaturated oxime was noted as a step in its conversion to an aziridine [352,353] (section V.A.).

Some other conjugated unsaturated functions gives conjugate addition to the carbon-carbon double bond.



[422]

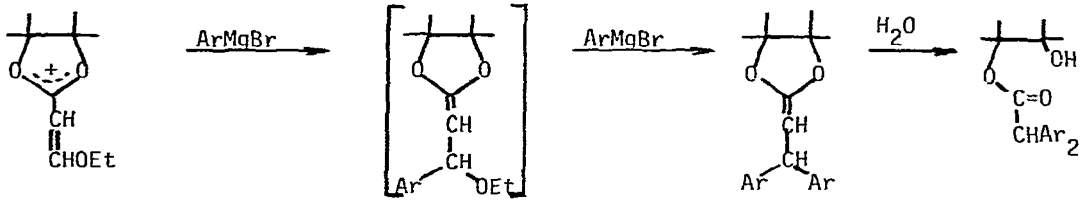


222

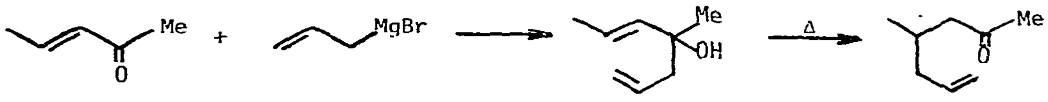
[423]

The reactant 222 serves as a synthon of the acetaldehyde enol cation.

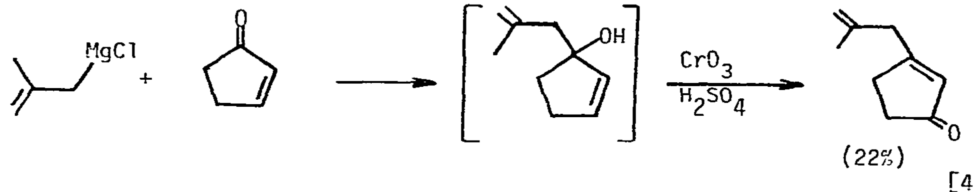
The double bond of 223 is conjugated with a cation which is the electronic equivalent of a protonated carboxy group. Conjugate addition is followed by displacement of the ethoxy group [424].



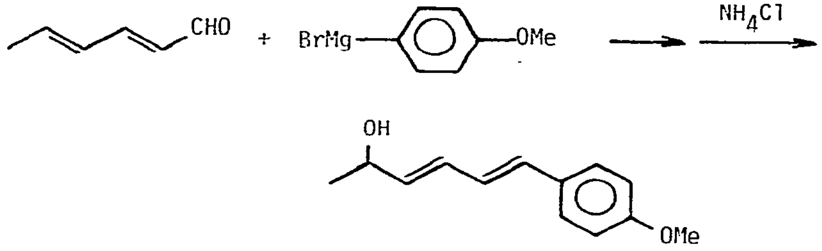
In the following cases, normal 1,2-addition occurs, but subsequent reaction produces isomeric products:



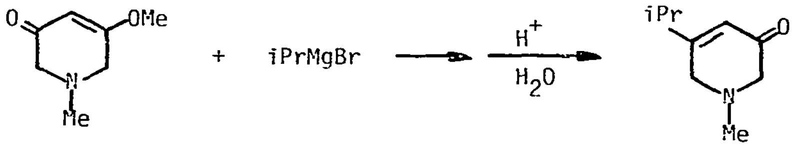
[389]



[425]

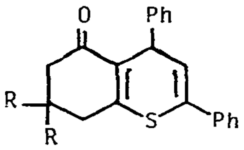


[426]

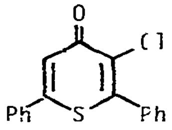


[427]

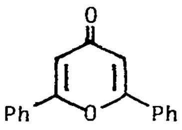
In the following instances, 1,2-addition was observed, despite possibilities for conjugate addition:



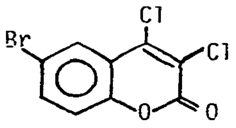
+ $PhCH_2MgCl$
[428]



+ MeMgBr
[429]



+ RMgBr
[430]

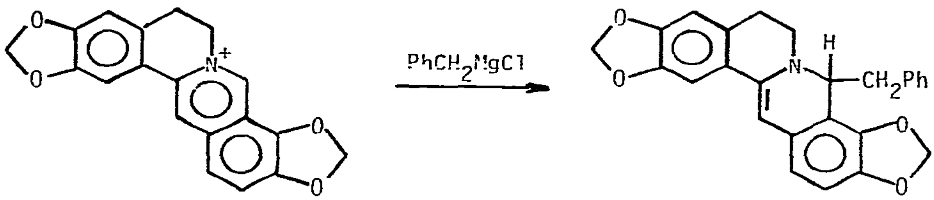


+ PhMgBr
[431]

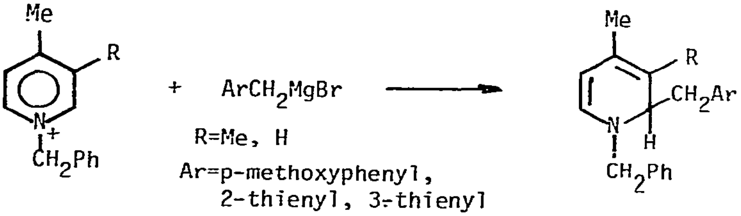
D. Addition to heteroaromatic compounds

A number of reactions described earlier as additions to cyclic carboxylic acid derivatives (section IV.E.2.), to carbon-nitrogen unsaturation (section V.A.) and as conjugate additions (section V.C.) can equally well be described as additions to heterocyclic rings.

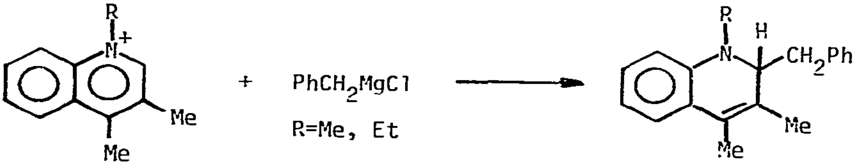
Other additions to nitrogen heterocyclic compounds include:



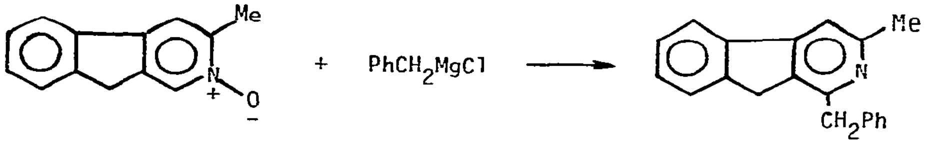
[432]



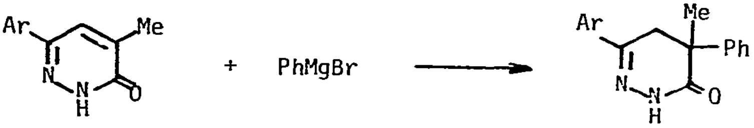
[115,116,433]



[434]

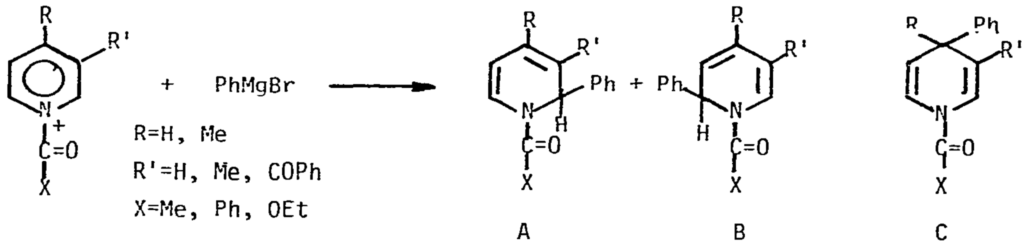


[435]



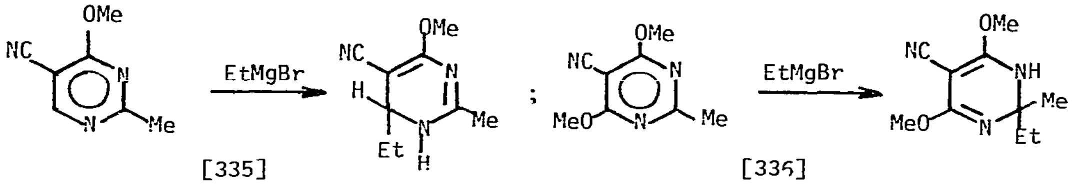
[315]

Reactions of a variety of N-acylpyridimium salts with phenylmagnesium bromide were studied [436]. Reaction occurs primarily at the α-positions, the

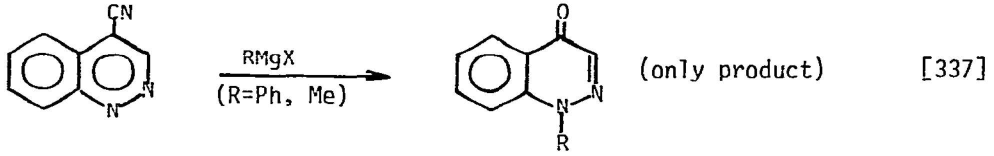


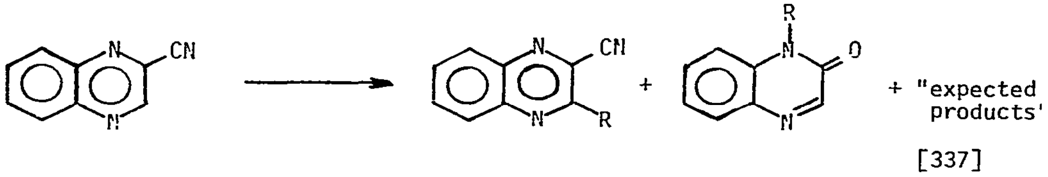
amounts of A and B depending upon steric effects. C was a minor product when R'=COPh. Reaction of pyridine with the acid chloride is very fast; the acid chloride may be added to a mixture of pyridine and Grignard reagent without serious competition from reaction between the acid chloride and the Grignard reagent.

Addition of ethylmagnesium bromide to the pyrimidine ring in preference to the cyano group occurs with the following [335,336]:

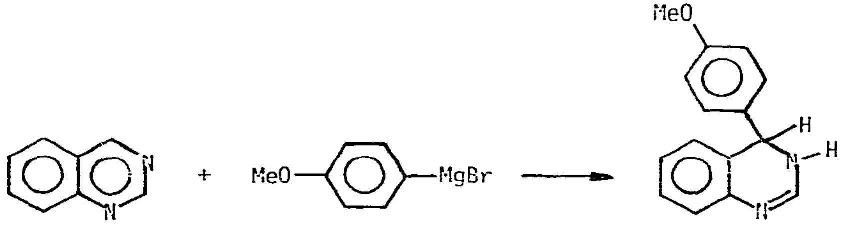


Other examples of addition to the heterocyclic ring, in competition with addition to or displacement of the cyano group are noted in section V.A. [337]. Additional "unexpected" products found include:

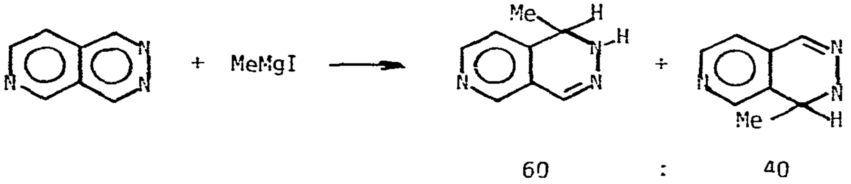




Additions to two neutral parent heterocycles are:

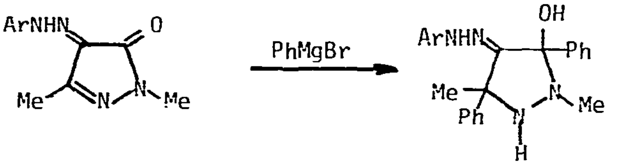


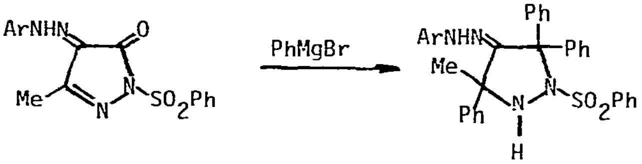
[437]



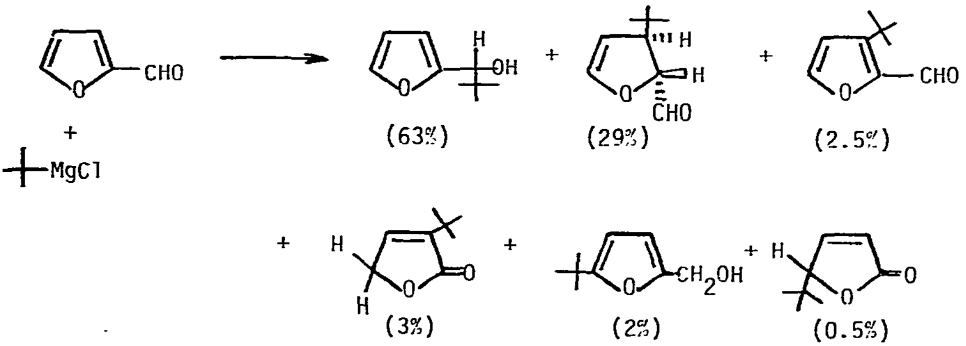
[438]

Additions to the carbonyl group as well as the carbon-nitrogen bond in the ring occurred in the following with excess Grignard reagent [439]:

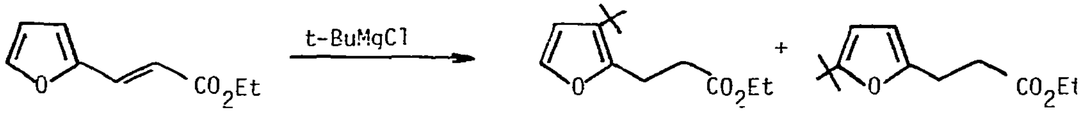




Although furfural reacts with most Grignard reagents only at the aldehyde group, a variety of products are obtained with *tert*-butylmagnesium chloride [440



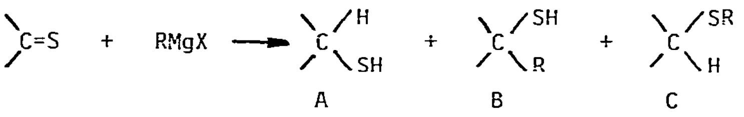
Conjugate addition to the furan ring was also found in [396]:



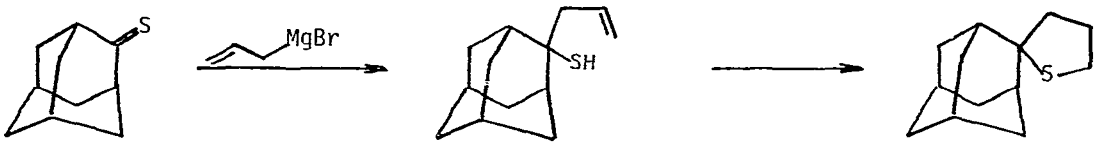
in addition to "normal" products

E. Addition to C=S groups

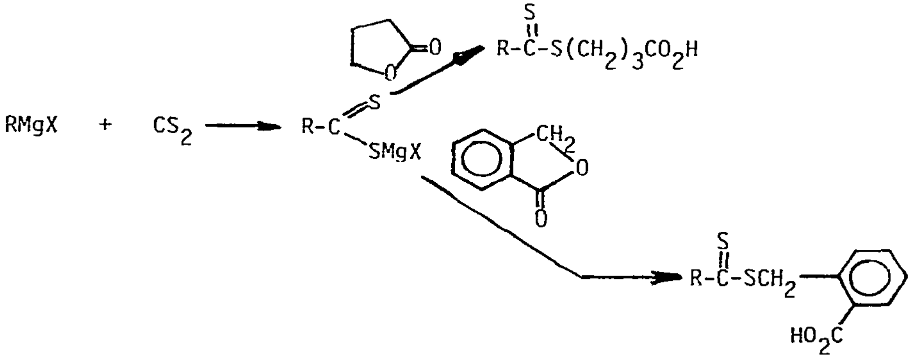
The reactions of di-*tert*-butyl thioketone 224 and thioadamantanone 225 with Grignard reagents were studied in detail [441]. Three kinds of product are formed:



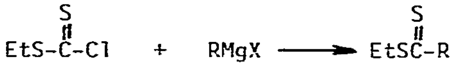
Saturated Grignard reagents other than methyl tend to give mostly reduction (product A) with a preference for thiophilic addition (product C) when addition occurs. Methylmagnesium bromide gives thiophilic addition in THF, and the iodide in ether gives carbophilic addition (product B). Vinylmagnesium chloride adds to sulfur with 224 and carbon with 225, and allylmagnesium bromide or propargylmagnesium bromide give only carbophilic addition product, which partially cyclizes under reaction conditions, e.g.



Addition of a wide variety of Grignard reagents to carbon disulfide, followed by reaction of the adduct with γ-lactones, provided an interesting synthesis of dithioesters [442]:



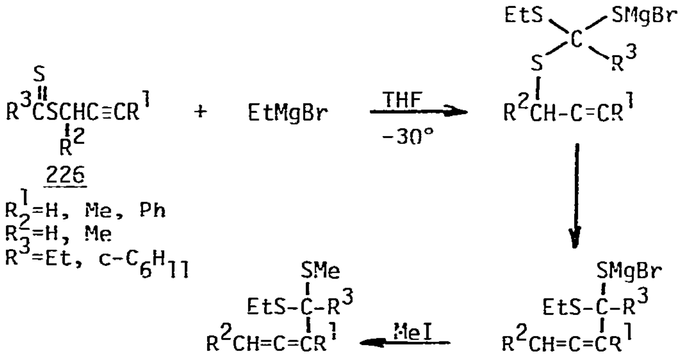
Dithioesters are also formed from [443]:



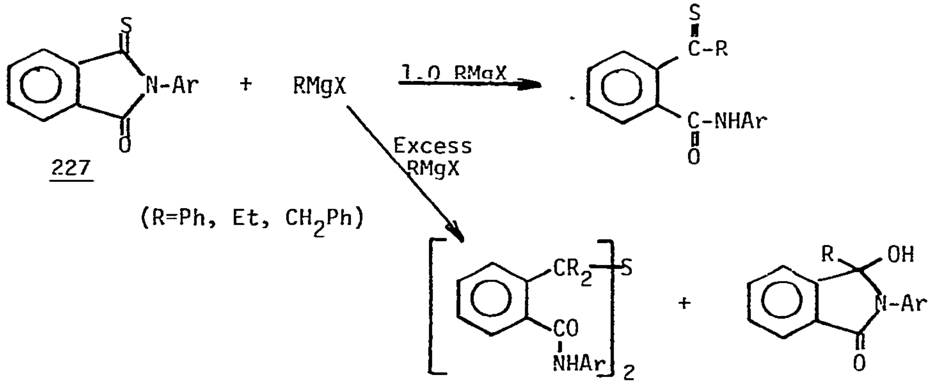
$$EtS{-}\overset{S}{\overset{\|}{C}}{-}Cl \quad + \quad RMgX \longrightarrow EtS\overset{S}{\overset{\|}{C}}{-}R$$

(R=Me, 40%; R=Et, 30%)

Thiophilic addition to the thioesters 226, followed by a spontaneous sigmatropic rearrangement, provided a route to allenic thioketals. Hydrolys without alkylation led to a variety of products, but the thioketone was not among them [444].

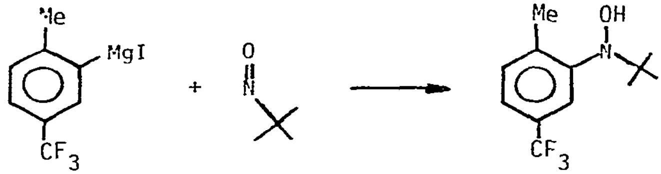


Preferential attack at the thiocarbonyl group of 227 gave simple ring opening with one mole of Grignard reagent, but more complex products when an excess was used [445]:

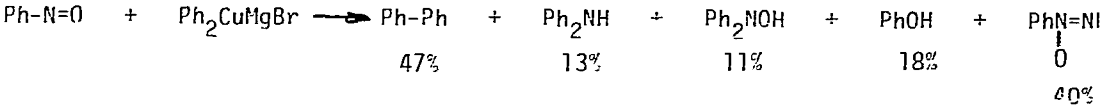


F. Additions to other unsaturated compounds

Reaction with the nitroso group is reported in two papers:



[446]



$$\text{Ph-N=O} + Ph_2CuMgBr \longrightarrow \underset{47\%}{\text{Ph-Ph}} + \underset{13\%}{Ph_2NH} + \underset{11\%}{Ph_2NOH} + \underset{18\%}{\text{PhOH}} + \underset{40\%}{\overset{}{\text{PhN=N}}\underset{\text{O}}{}}$$

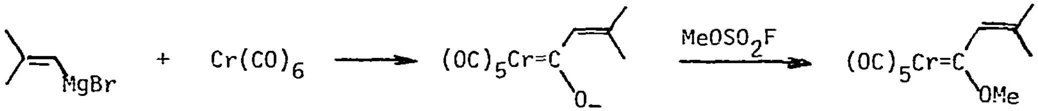
[447]

In the latter reaction an electron-transfer pathway was proposed.

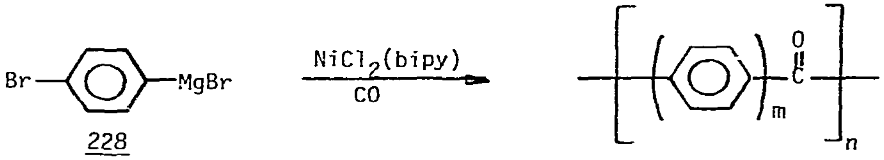
Sulfonyl chlorides were made in a one-pot sequence from Grignard reagents and sulfur dioxide [448]:

$$R_3SiCH_2MgCl \xrightarrow{SO_2,\ Cl_2} R_3SiCH_2SO_2Cl \qquad (\text{R=Me: }60\%;\ \text{R=Et: }40\%)$$

Preparation of a vinylcarbene complex utilized Grignard reagent addition to a coordinated carbon monoxide [449]:



When the polymerization of 228 was carried out under an atmosphere of carbon monoxide, the carbon monoxide was incorporated into a copolymer in a ratio of about one CO per two aromatic rings [78]:

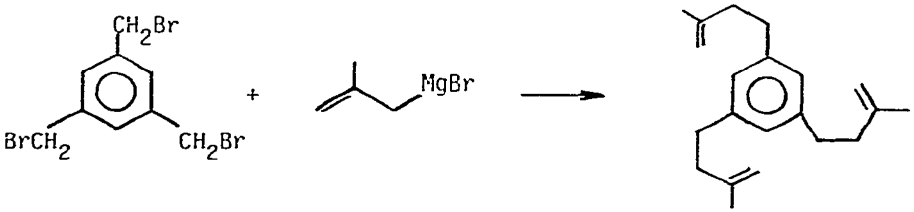


^{14}C-Labelled primary alcohols were prepared by direct reduction [$LiAlH_4$] of the magnesium salt produced by Grignard reagent carbonation [450].

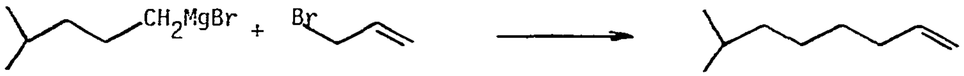
VI. DISPLACEMENT REACTIONS BY ORGANOMAGNESIUM COMPOUNDS

A. Coupling or displacement reactions with organic halides or sulfonates

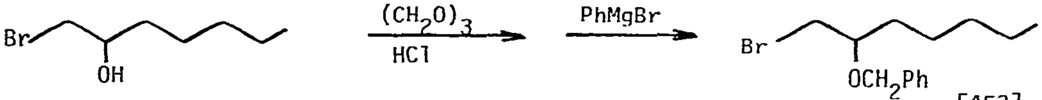
A halogen that is allylic, benzylic, propargyl, or α to an ether is readily displaced by a Grignard reagent. Some examples reported in 1977 are:



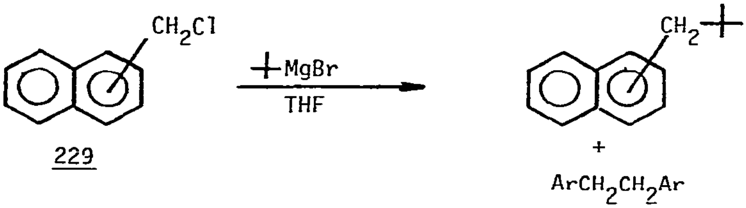
[451]



(70%) [452]



[453]

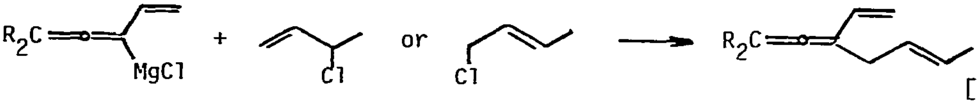


229

[454]

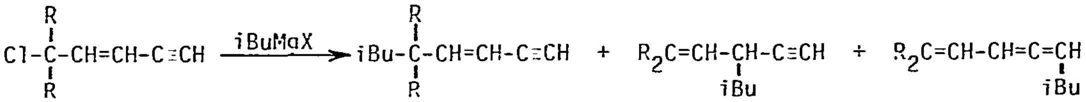
With 229 the yield was increased from -40% to 90% when Li_2CuCl_4 was used as catalyst.

A 1,4-polybutadiene, brominated with NBS, was then benzylated by treatment with benzylmagnesium bromide [455,456]. Allylic or propargyl halides may underg displacement with allylic rearrangement:



[163]

$C_6H_{13}MgBr \quad + \quad HC\equiv C-CH_2Br \longrightarrow C_6H_{13}CH=C=CH_2$ [457]

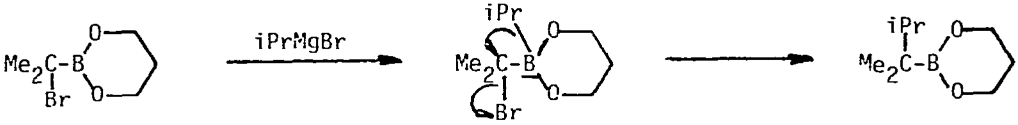


$$\mathrm{Cl{-}\overset{R}{\underset{R}{C}}{-}CH{=}CH{-}C{\equiv}CH \xrightarrow{iBuMgX} iBu{-}\overset{R}{\underset{R}{C}}{-}CH{=}CH{-}C{\equiv}CH + R_2C{=}CH{-}\underset{iBu}{CH}{-}C{\equiv}CH + R_2C{=}CH{-}CH{=}C{=}\underset{iBu}{CH}}$$

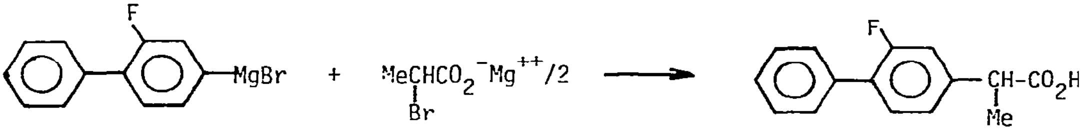
(R=H, Me)

[458]

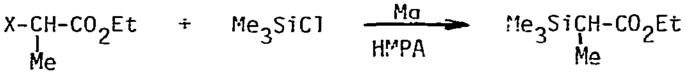
Displacements of α-brominated boranes also proceed readily and provide a useful general synthesis. Initial addition to the boron is a likely mechanism [459]; e.g.



Coupling reactions with α-halo acids or esters are also reported; e.g.



[460]



$$\mathrm{X{-}\underset{Me}{CH}{-}CO_2Et + Me_3SiCl \xrightarrow[HMPA]{Mg} Me_3Si\underset{Me}{CH}{-}CO_2Et}$$

(~70%)

[461]

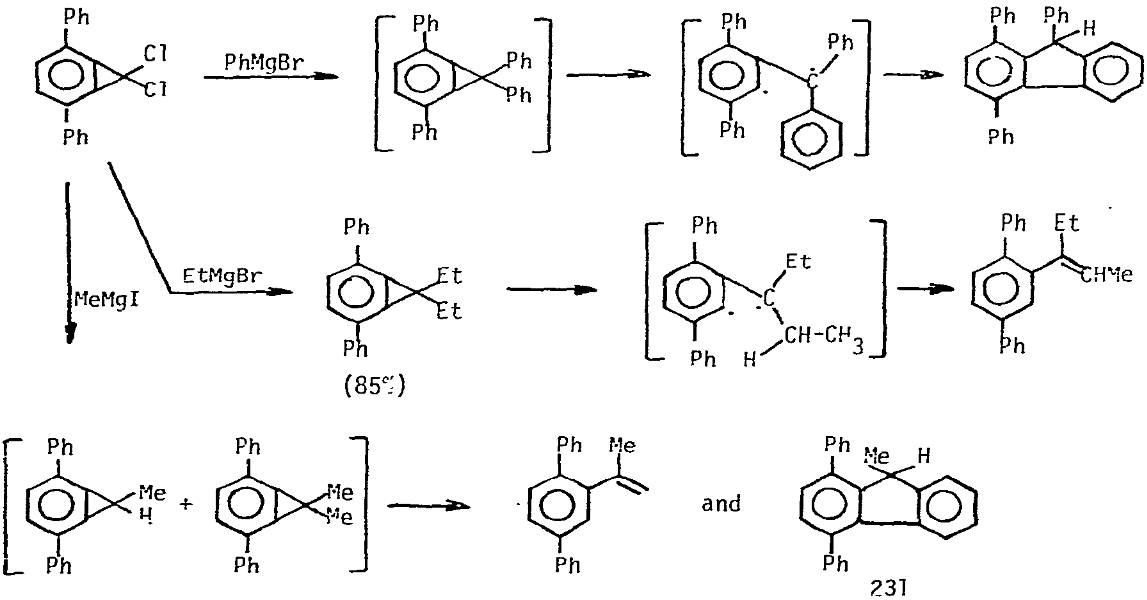
In the latter reaction, methyl β-bromopropionate also reacted (60%), but esters in which the halogen is further removed were inert.

Coupling of <u>230</u> occurs with a three-fold excess alkyl or aryl halides and magnesium [462]:

$$\mathrm{RX + ClC{\equiv}C{-}CMe_2OH \xrightarrow{Mg} RC{\equiv}CCMe_2OH}$$

<u>230</u>

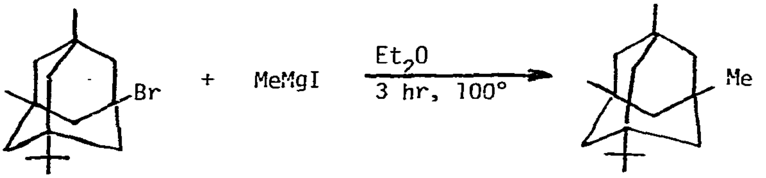
Halogen displacement also occurs with dihalobenzocyclopropenes. The immediate products are unstable, and in some cases only rearranged product is found [463]. An S_N1 mechanism for the displacement is proposed.



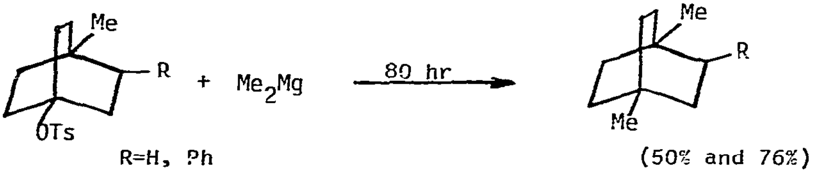
231

The origin of the reduction product 231 (one displacement and one reduction) with the methyl Grignard reagent is not clear. Isopropylmagnesium bromide gives only reduction [463]. Analogous products were formed from the naphtho- analog, except that the methyl Grignard reagent leads to no dimethylated product [464].

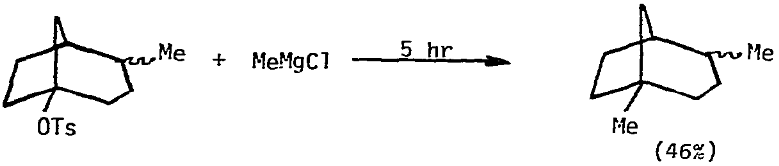
The replacement of bridgehead bromide and tosylate groups by methyl occurs slowly. Reactions with the Grignard reagents are more rapid than with



[465]



[466]

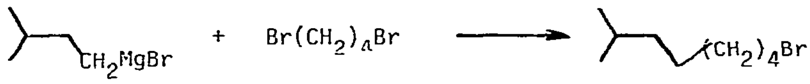


[466]

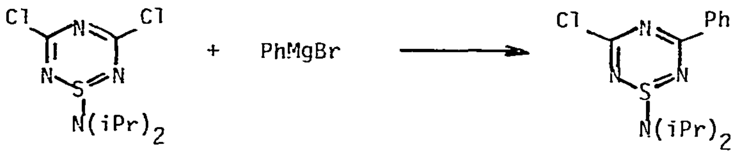
dimethylmagnesium, but lead also to halogen exchange, and in some cases to the corresponding alcohol or ethyl ether [466]. Hexamethylbiadamantyl has been made by bromination and then methylation of tetramethylbiadamantyl [465].

A trideuteromethyl group was introduced by reaction of a Grignard reagent with excess $(CD_3)_2SO_4$ [467].

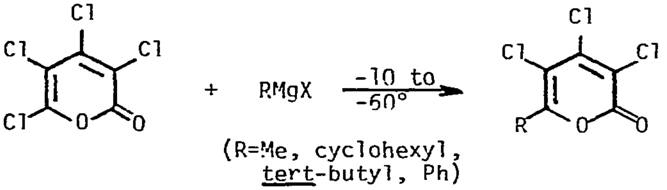
Selective reaction of one halogen of a dibromide may provide a useful chain extension [452]; e.g.



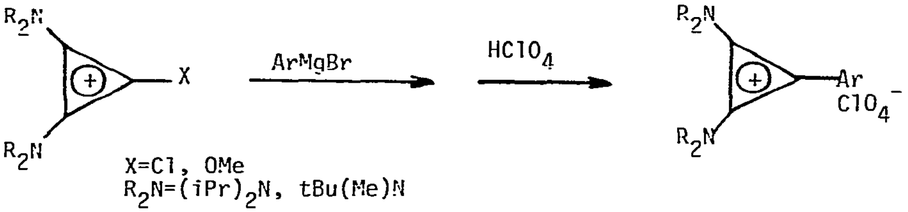
Halogen displacement is also the net result in some reactions which probably proceed via an addition intermediate:



[468]

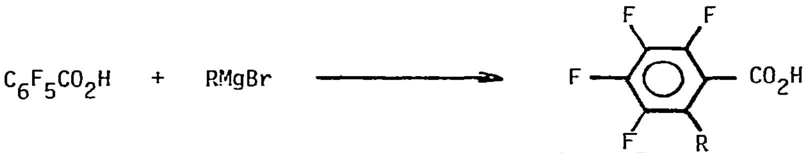


[405]

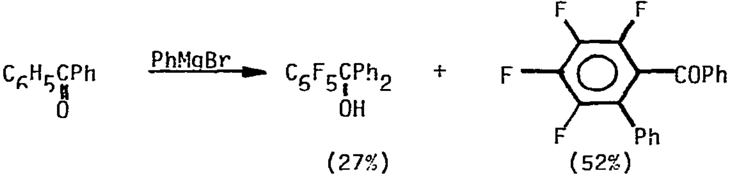


[63]

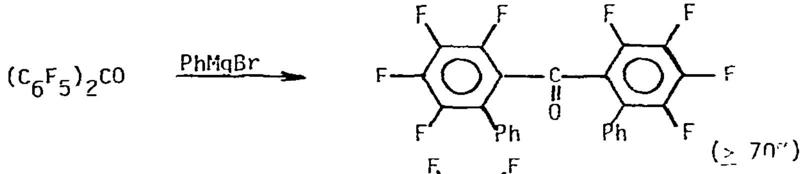
Replacement of an aryl fluorine has been reported in the reaction of several pentafluorophenyl derivatives with Grignard reagents:



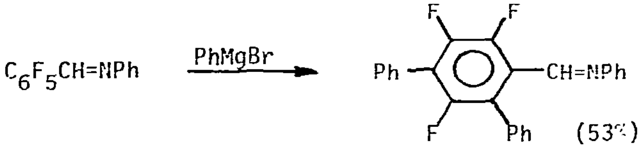
[469]



[470]

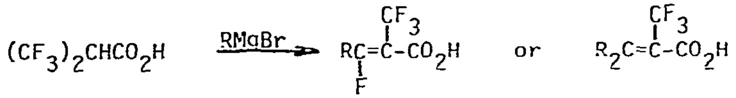


[470]



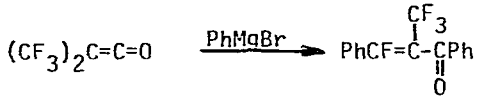
[471]

Addition occurred with C_6F_5COMe and PhMgBr; CH_3MgI gave only normal addition and enolization reactions [470]. In the reaction of C_6F_5MgBr with chlorosilanes, various side products isolated were formed via elimination to a benzyne and nucleophilic displacement of fluorine [472]. Fluorine displacement is also found in the following reactions, most probably via a conjugate addition-elimination sequence [473]:



$$(CF_3)_2CHCO_2H \xrightarrow{RMgBr} RC(F)=C(CF_3)-CO_2H \quad \text{or} \quad R_2C=C(CF_3)-CO_2H$$

(R=Pr, Bu, Ph)



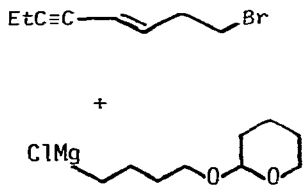
$$(CF_3)_2C=C=O \xrightarrow{PhMgBr} PhCF=C(CF_3)-C(=O)Ph$$

(38%; *cis*:*trans*=1:3)

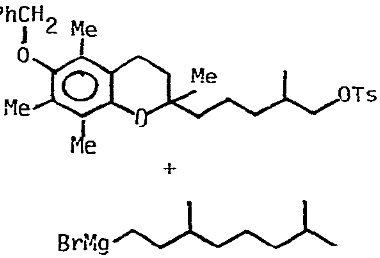
Another example was noted previously in section V.B. [359].

Other uncatalyzed displacements have been mentioned earlier in sections II.C.2. [101] and III.C. [154,165].

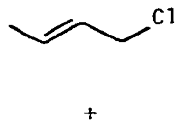
A variety of coupling reactions catalyzed by copper salts may be noted:



and similar combinations
with Li_2CuCl_4
[474]

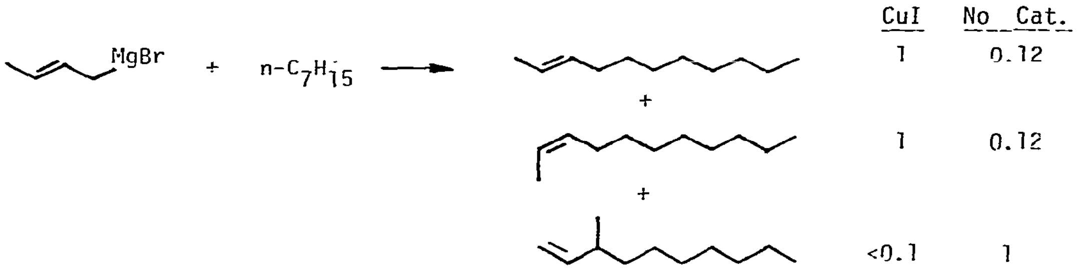


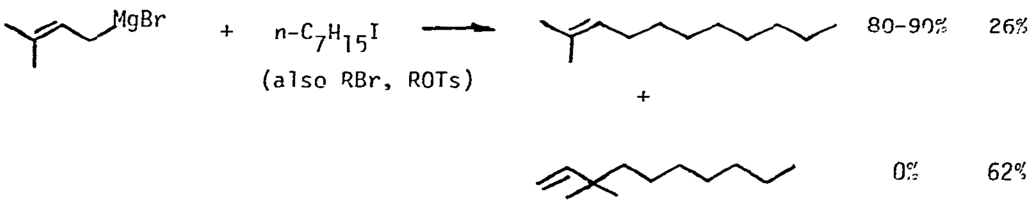
with Li_2CuCl_4
[475]



$BrMgC\equiv C(CH_2)_2CO_2MgBr$
with CuCl
[105]

Allylmagnesium bromide reacts with 1-iodooctane to yield 80% of pure undecene in the presence of 0.13 eq. of cuprous iodide (0°, 1.5 hr in ether). Without catalyst, only 28% of product is found after 28 hr at 0°. The product formed from substituted allylic Grignard reagents also depends upon the presence or absence of catalyst [476]:





The copper-catalyzed coupling reaction occurs in the presence of a variety of other functional groups. The reaction of ethylene bromohydrin or its acetate or ethyl ether with a variety of Grignard reagents (in the presence of 5% cuprous iodide or a cuprous bromide-triethyl phosphite complex) has been studied [477].

$$RMgCl \quad + \quad BrCH_2CH_2OY \xrightarrow{5\%\ CuI} RCH_2CH_2OY$$

(Y=H, Ac, Et)

The bromohydrin itself gives good yields, generally better than ethylene oxide (e.g., 85% with n-heptyl, 56% with tert-butyl, and 88% with phenyl). The reaction also occurs without catalysis on heating in benzene. The acetate gives excellent yields with n-alkyl Grignard reagents (75-80%), but no product with *tert*-butyl or phenyl; the ether produces similar results. The corresponding chlorides do not react, and the iodides form ethylene via metal-halogen exchange.

Displacement of bromide occurs in the presence of a chlorine, and an allylic halide is preferentially replaced [478].

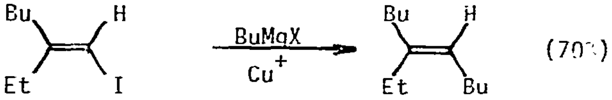
ω-Bromo esters undergo smooth displacement [20]; e.g.

$$Br(CH_2)_4CO_2Et \quad + \quad C_5H_{11}MgBr \xrightarrow{Li_2CuCl_2} CH_3(CH_2)_8CO_2Et$$

(79%)

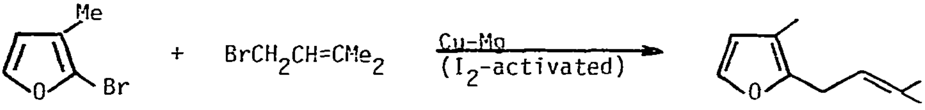
Ketones give a complex product mixture , and addition to aldehydes predominates.

The coupling of several vinyl iodides with a variety of Grignard reagents has been studied [479]; e.g.



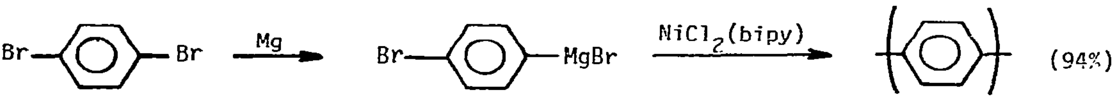
Yields with a variety of other Grignard reagents (1°-3°, allyl, benzyl) are comparable. The product is accompanied by ~25% of reduction and 5% of dimerization; a mediocre yield was obtained with bromides, and none with chlorides.

The following coupling reaction may involve a copper-catalyzed Grignard reagent displacement [480].

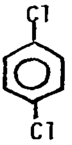


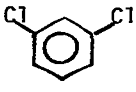
Nickel and palladium complexes catalyze the displacement reaction of aryl halide with Grignard reagents. Yields of 70% or more are reported for phenyl and benzyl Grignard reagents with p-iodoanisole and other aryl iodides or bromides. Biphenyl, from symmetrical coupling of the Grignard reagent, is the major side product [481]. Yields of 80-92% were obtained in the coupling of PhMgBr with p-IC_6H_4F or p-FC_6H_4MgBr with IPh, catalyzed by as little as 0.01 mol % of $PdCl_2$ [482]. Palladium metal has also been found useful as a catalyst, and comparable or better yields have been reported than with $PdCl_2$ [483]. Reactive palladium is formed in the reaction between $PdCl_2$ and phenylmagnesium bromide (forming also biphenyl). Other catalysts were studied, and among the most effective were $PdBr_2 \cdot (PPh_3)_2$ and $PhPdI \cdot (PPh_3)_2$. In a variety of reactions studied, symmetrical coupling was the major side product; iodides were more reactive than bromides or chlorides.

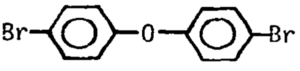
This coupling reaction has been used to produce a polymer from halo-substituted Grignard reagents [78]; for example:

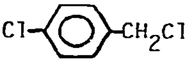


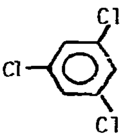
Degrees of polymerization from 12 to 46 were found. Other halides used to produce polymers in similar fashion were:

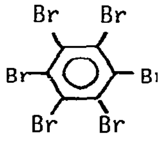






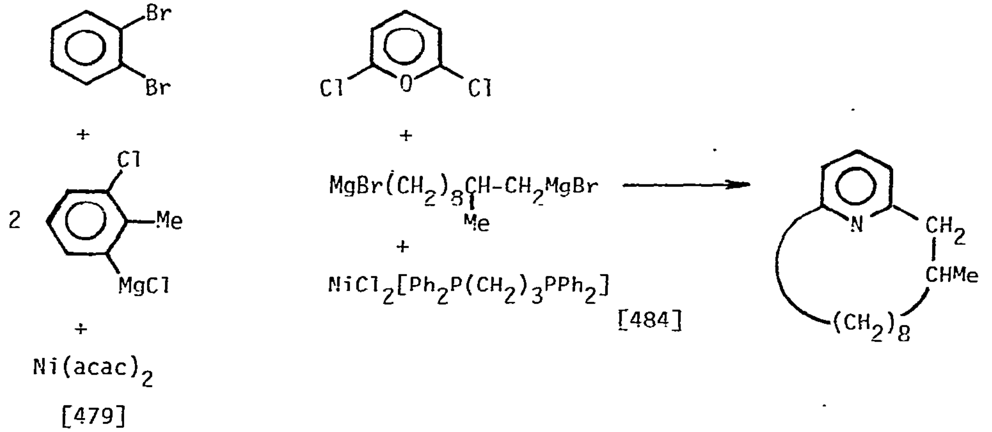




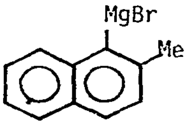


$NiBr_2(PPh_3)_2$, $FeEt_2(bipy)_2$ and $MeCrCl_2\cdot(THF)$ were also used as catalysts. Copolymerization with THF (ring opening) and CO was observed in some cases.

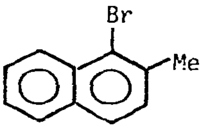
Reactions involving two displacements on a dihalide are:



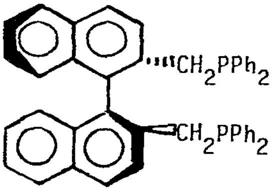
By the use of chiral nickel catalysts, it is possible to induce substantial optical activity in the products. A biphenyl derivative with a 12.5% enantiomeri excess was produced in the reaction of 231 with 232, catalyzed by the $NiCl_2$ complex of 233 [485].



231

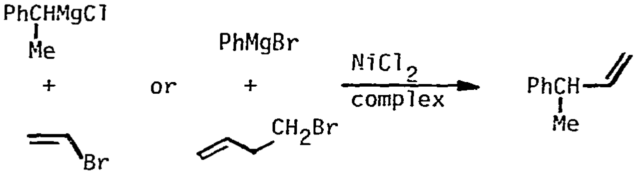


232

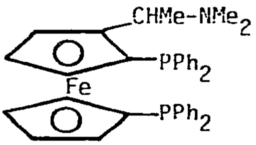


233

Either of the following coupling reactions produced the same product (note isomerization of the butenyl bromide):



In both cases, catalysis by complexes of the chiral ligands 234-236 led to optically active product. Using the complex of 234, up to 33.8% optical yield



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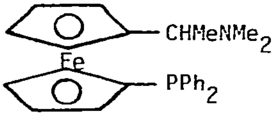

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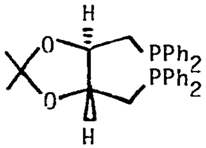


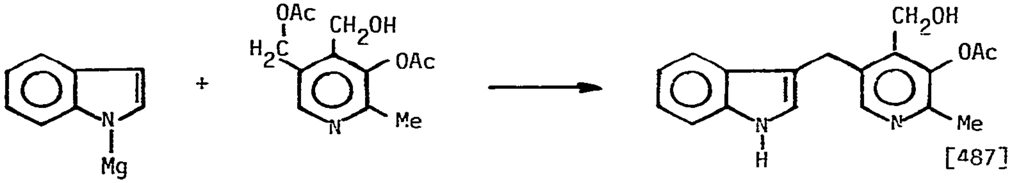
236

(R enantiomer) was obtained for the second combination of reagents; the first combination led to a higher optical yield, of the opposite configuration [486].

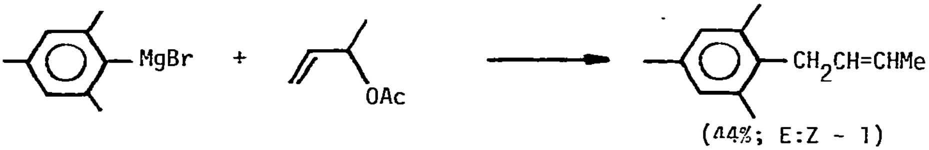
In the displacement reaction of organic halides with Grignard reagents, a side reaction may yield symmetrical coupling products from the Grignard reagent, the halide, or both. This may occur via halogen-magnesium exchange [479,481,483 which is found to occur readily in some cases even without catalysis. Exchange may also result in reduction of the aryl or vinyl halide [479] or other side reactions [477]. Symmetrical coupling of benzylic halide was noted in an uncatalyzed displacement [454].

B. Displacement reactions at C-O, C-S or C-N bonds

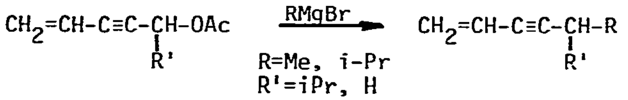
Some displacement reactions of sulfonate esters by Grignard reagents have been noted in the previous section. Displacements of allylic or benzylic acetates are illustrated in the following reactions. These displacements are competitive with normal reaction of the ester. Note that allylic rearrangement may occur in the displacement.



[487]



[488]



$$CH_2=CH-C\equiv C-\underset{R'}{C}H-OAc \xrightarrow[R=Me,\ i\text{-}Pr;\ R'=iPr,\ H]{RMgBr} CH_2=CH-C\equiv C-\underset{R'}{C}H-R$$

[458]

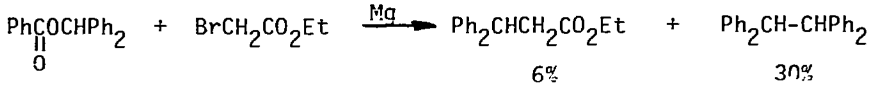
$CH_2=CH-C\equiv C-CMe_2OAc$ $\xrightarrow{RMgBr}$ $CH_2=CH-C\equiv C-CMe_2R$ [458]

(isobutyrate also studied) (R=Me, Et)

or $RCH_2CH=C=C=CMe_2$

(R=i-Bu, t-Bu)

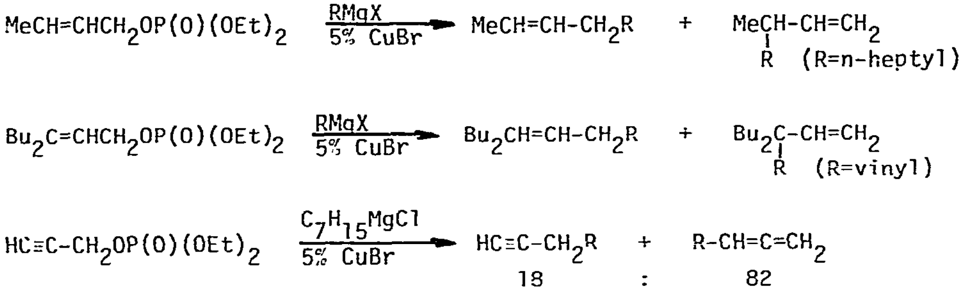
Displacement at the ester alkyl group also occurs to a small extent in the following [489]:



$$\underset{\overset{\|}{O}}{\mathrm{PhCOCHPh_2}} + \mathrm{BrCH_2CO_2Et} \xrightarrow{\mathrm{Mg}} \underset{6\%}{\mathrm{Ph_2CHCH_2CO_2Et}} + \underset{30\%}{\mathrm{Ph_2CH\text{-}CHPh_2}}$$

+ other alkylation and condensation products

Rearrangement was also observed with allylic phosphates. Total yields ranged from 70 to 92% [490].

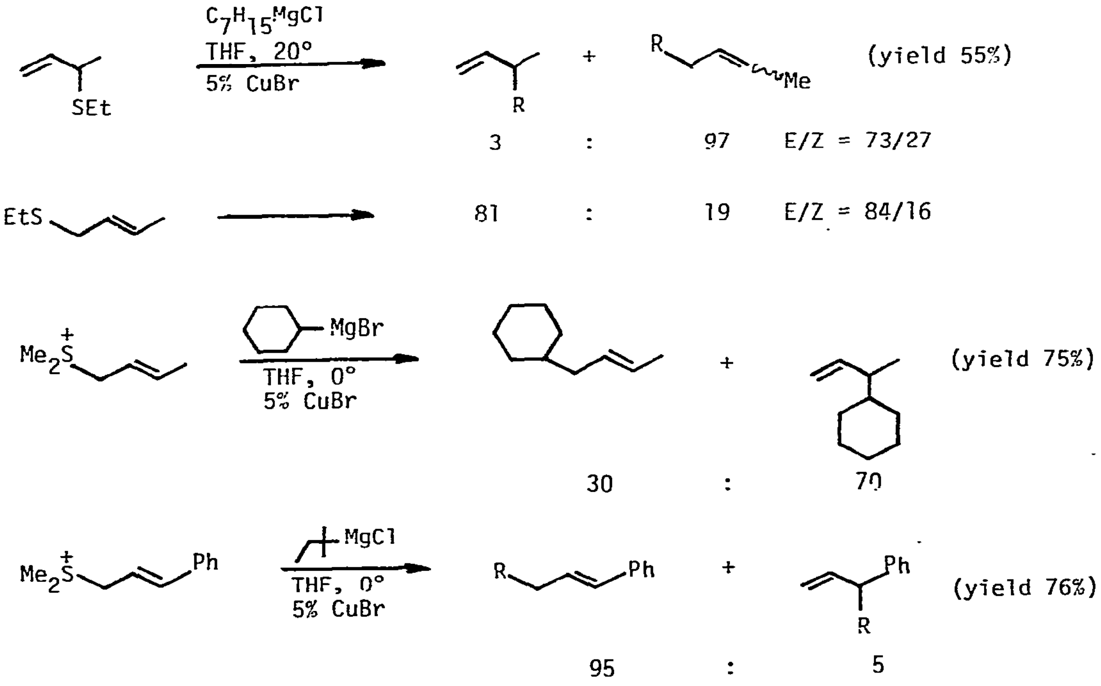


$$\mathrm{MeCH{=}CHCH_2OP(O)(OEt)_2} \xrightarrow[\text{5\% CuBr}]{\mathrm{RMgX}} \mathrm{MeCH{=}CH\text{-}CH_2R} + \underset{\mathrm{R}}{\mathrm{MeCH}}\mathrm{\text{-}CH{=}CH_2} \quad (\mathrm{R}=n\text{-heptyl})$$

$$\mathrm{Bu_2C{=}CHCH_2OP(O)(OEt)_2} \xrightarrow[\text{5\% CuBr}]{\mathrm{RMgX}} \mathrm{Bu_2CH{=}CH\text{-}CH_2R} + \underset{\mathrm{R}}{\mathrm{Bu_2C}}\mathrm{\text{-}CH{=}CH_2} \quad (\mathrm{R}=\text{vinyl})$$

$$\mathrm{HC{\equiv}C\text{-}CH_2OP(O)(OEt)_2} \xrightarrow[\text{5\% CuBr}]{\mathrm{C_7H_{15}MgCl}} \underset{18}{\mathrm{HC{\equiv}C\text{-}CH_2R}} \;\underset{:}{+}\; \underset{82}{\mathrm{R\text{-}CH{=}C{=}CH_2}}$$

Allylic thioethers and sulfonium salts react similarly with Grignard reagents [491]; e.g.



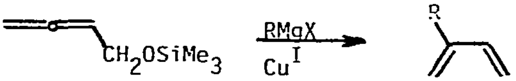
$$HC{\equiv}C\text{-}CH_2\overset{+}{S}Me_2 \xrightarrow[5\%\ CuBr]{C_7H_{15}MgCl} HC{\equiv}C\text{-}CH_2R + RCH{=}C{=}CH_2 \qquad \text{(yield 93\%)}$$

$$55 \quad : \quad 45$$

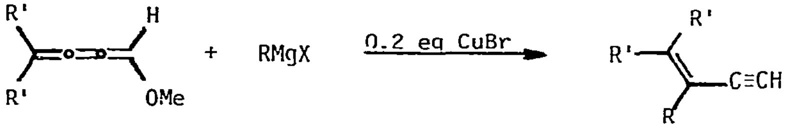
The thioethers are less reactive than allylic ethers or the sulfonium salts, and phenyl thioethers are more reactive than ethyl. Only primary Grignard reagents were successful with the thioethers, but a wide variety gave good yields with the sulfonium salts.

Allylic quaternary ammonium salts also undergo displacement reactions with a selection of varied Grignard reagents. Yields in examples investigated ranged to 97%, and consisted mainly of the unrearranged direct substitution product (85-100%). Catalysis by CuBr effected some improvement in yields, but was necessary only for the phenyl Grignard reagent [492].

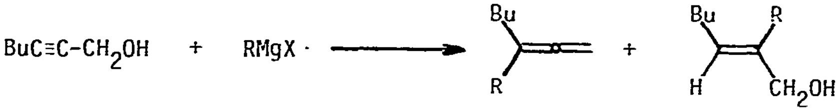
Some displacements, particularly those catalyzed by a copper salt, may reasonably proceed by an addition-elimination sequence:



[361]



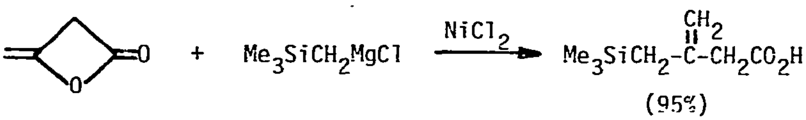
[362]



[369]

[372]

An unusual displacement reaction occurs with diketene [126,493].

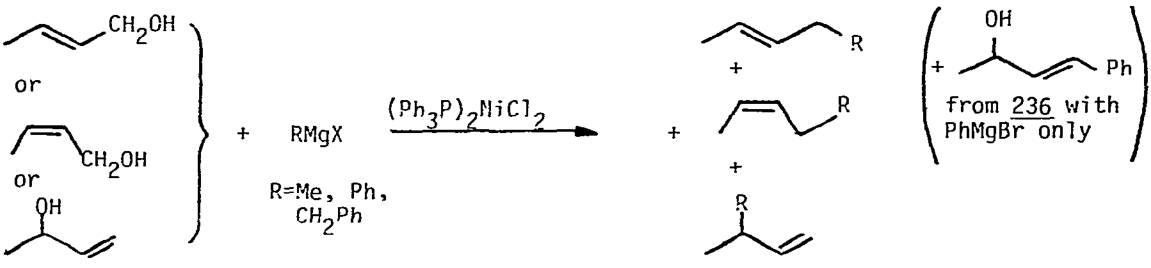


$$Me_3SiCH_2\text{-}\overset{\overset{\displaystyle CH_2}{\|}}{C}\text{-}CH_2CO_2H$$

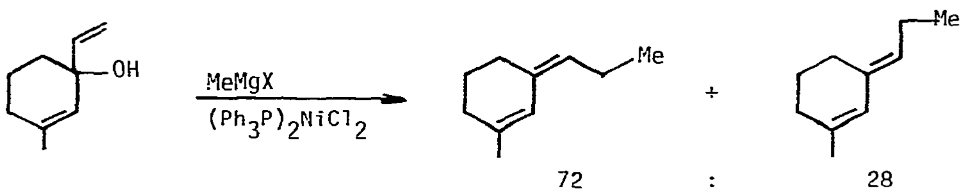
(95%)

The reaction is catalyzed in lower yield by CuI, $PdCl_2$ and $CoCl_3$, but does not follow this course with other Grignard reagents.

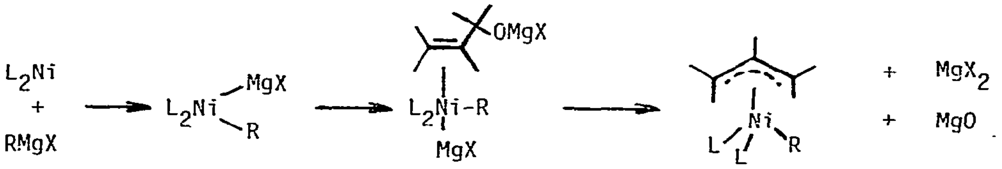
Allylic alcohols undergo displacement and reduction reactions with Grignard reagents in the presence of a nickel catalyst. With non-reducing Grignard reagents, substitution is observed [494]. Allylic isomers are obtained, but at least in some cases (such as the first example below) isomeric alcohols yield quantitatively different product mixtures:



236

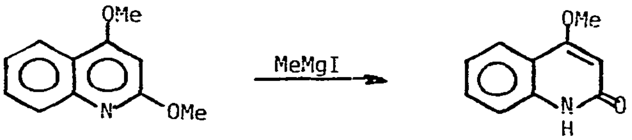


Reducing Grignard reagents (propylmagnesium bromide was used most frequently) produced analogous alkenes by β-hydrogen transfer from the Grignard reagent [495]. As in the substitution, a non-equilibrium mixture of allylic isomers is obtained, and there is an isomer "memory effect." Some catalysts give substantial yields of substitution, and the isomeric composition depends on the catalyst. In both reactions, a catalytic cycle is proposed in which the following steps are important:

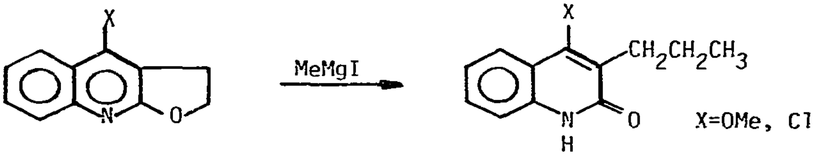


An alkyl group may then be transferred to the π-allyl ligand. With reducing Grignard reagents, a similar mechanism is proposed, except that the nickel-Grignard adduct eliminates alkene to form a nickel hydride (R=H). This pathway may be favored by loss of one phosphine molecule.

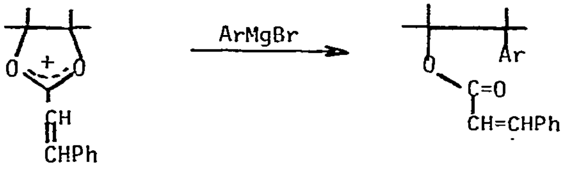
Ethers may also undergo displacement reactions with Grignard reagents. In examples reported, the ether is allylic, cyclic, or generates a particularly stable alkoxide leaving group:



[496]

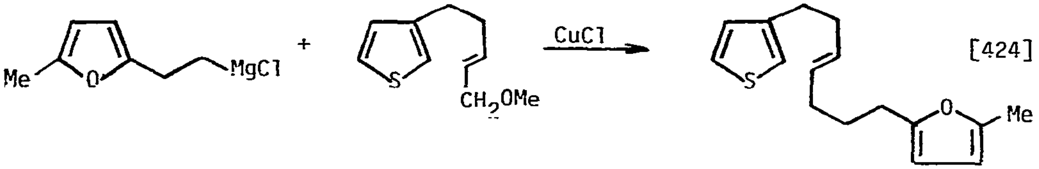


[496]



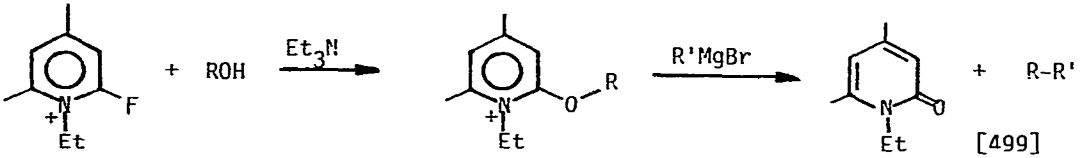
[497]

(another more typical displacement is in this reference)



[424]

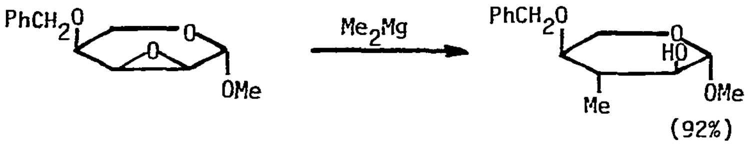
[498]



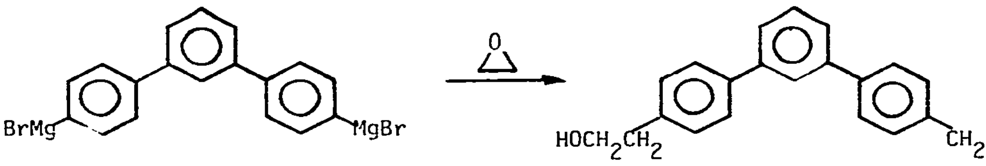
[499]

In the last case, a general high-yield one-pot crossed coupling of <u>allylic</u> alcohols with Grignard reagents is provided. Displacement appeared to occur without rearrangement for phenylmagnesium bromide, but the S_N2' product was formed with butyl, cyclohexyl and β-phenethyl Grignard reagents.

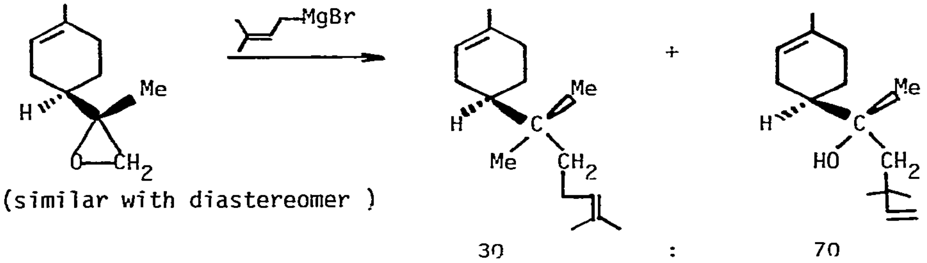
Some reported displacement reactions at an epoxide group are:



[500]

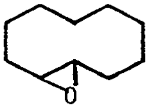


[501]



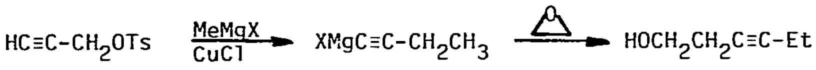
[155]

The trans-epoxide 237 gave no displacement with Grignard reagents; only transannular (probably cationic) rearrangement products were formed [502].



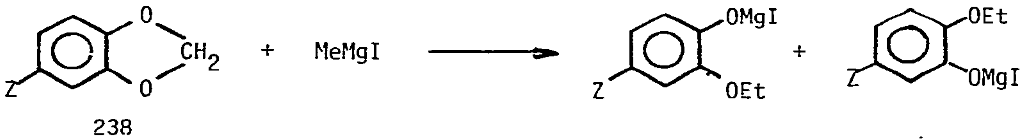
237

In the following reaction sequence, tosylate displacement and addition to an epoxide are combined [503]:



$$HC{\equiv}C\text{-}CH_2OTs \xrightarrow[CuCl]{MeMgX} XMgC{\equiv}C\text{-}CH_2CH_3 \longrightarrow HOCH_2CH_2C{\equiv}C\text{-}Et$$

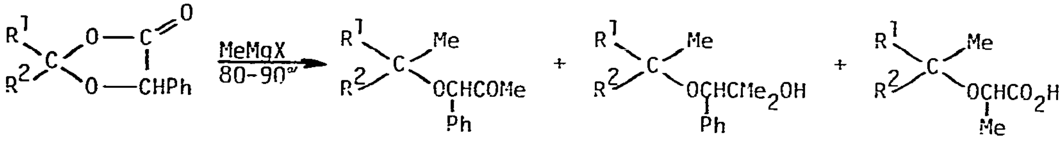
Displacements on the acetals 238 were studied under heterogeneous conditions with a suspension of the Grignard reagent in toluene [504].



238

Substituent effects were determined as p-Me:m-Me:unsubst:m-Cl:p-Cl = 1.43:1.04:1.00:0.78:0.26. The negative value of p, which contrasts with leaving group effects in other ArO$^-$ displacements, was explained by strong coordination of the magnesium.

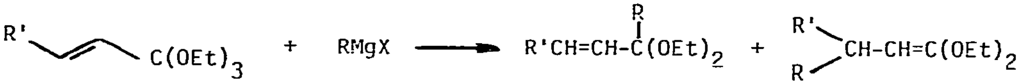
In reaction of the mandelic acid dioxolanones 239, initial attack of Grignard reagent at the ketal position was favored, although formation of product via addition to the carbonyl group was also discussed [505].



239

3 or 4 : 1 (~5%)

The allylic orthoesters 240 yield a mixture of isomers:

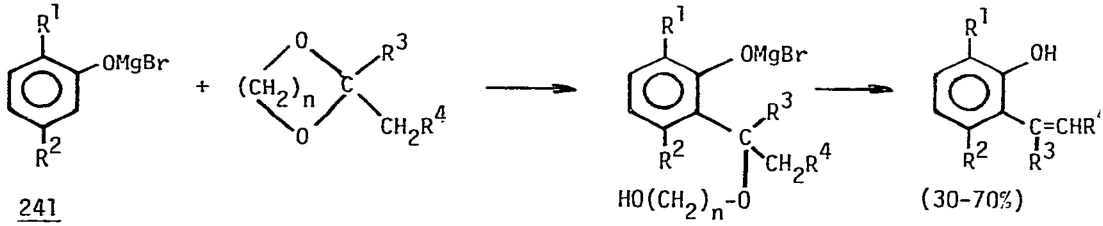


240

R'=H, Me, Ph R=Bu, i-Bu, Ph, allyl

The major product with Grignard reagents is generally unrearranged, but copper catalysis leads almost exclusively to the allylic isomer [506].

Carbon alkylation of phenoxide ions 241 with dioxans and dioxolans occurs in the ortho position, and is followed by elimination [507].

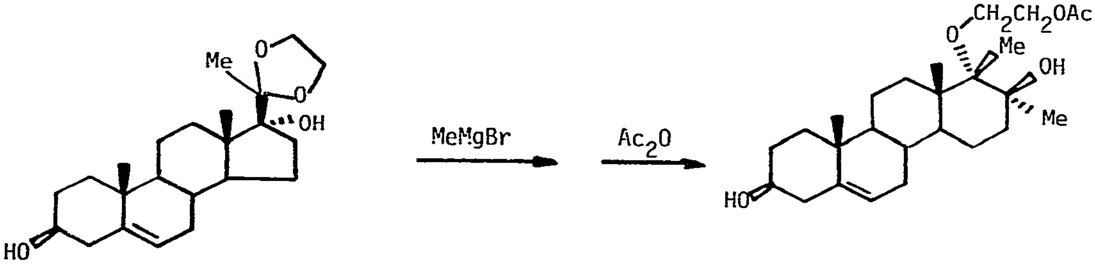


241

(30-70%)

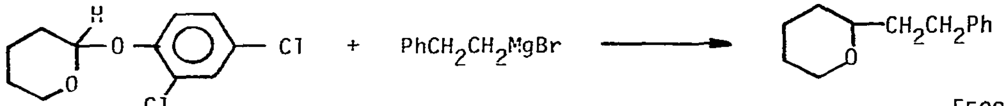
Reaction occurs in refluxing toluene, but fails in more basic solvents (THF, DME, (HMPA, etc.). Alkali phenoxides do not work.

Rearrangement in the reaction of 242 was shown by X-ray structure analysis of one of the products 243 [508]. It had been claimed earlier that separable rotamers of the expected simple ketal cleavage product were obtained.

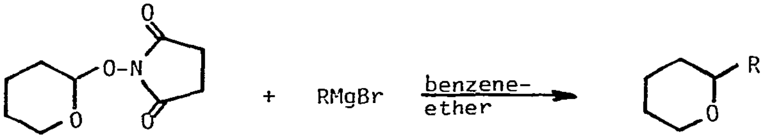


242 243

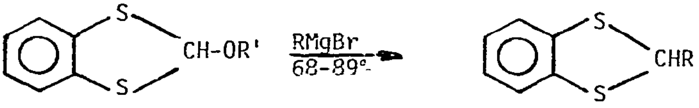
Other acetal, ketal, or orthoester reactions reported are:



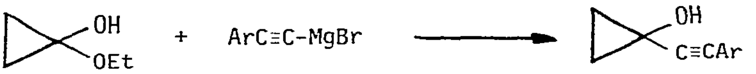
(one of many ether-forming reactions) [509]



[510]

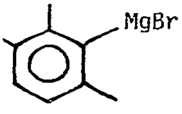


("acyl anion equivalent") [511]

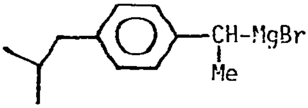


(75-86%) [512]

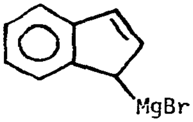
Reaction of ethyl orthoformate with Grignard reagents 244-246 was reported.



244
[513]

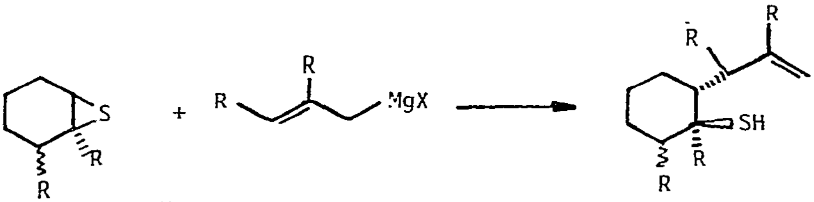


245
[527]

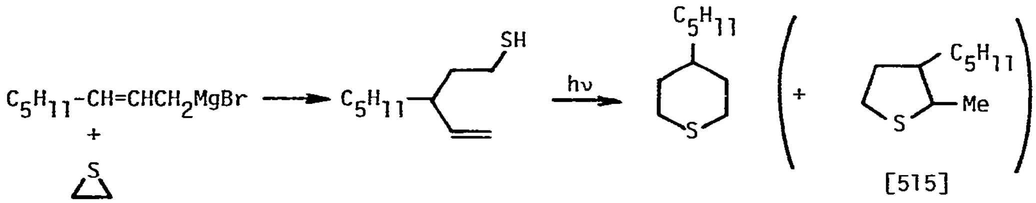


246
[203]

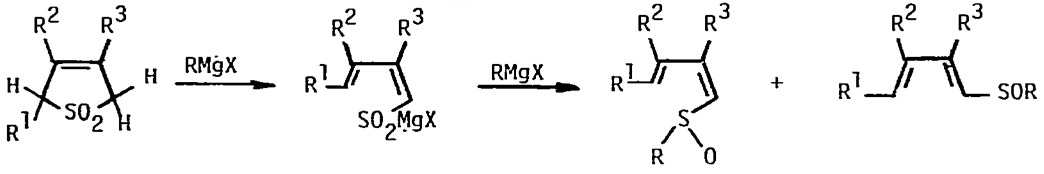
Ring opening of thioepoxides was reported in two cases.



R=Me, H [514]

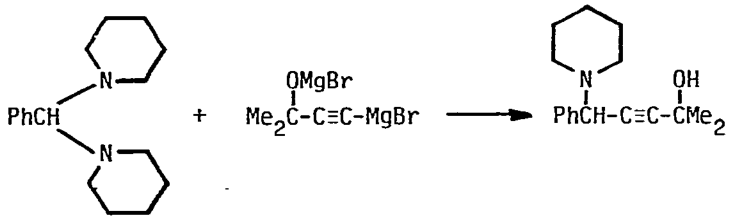

[515]

Sulfolenes lead to sulfoxides, apparently via a previously reported sulfinate.


Z/E ≥ 4; yield = 20-66%

An analogous reaction occurs when the starting material has a fused cyclopropane ring in place of the double bond [516].

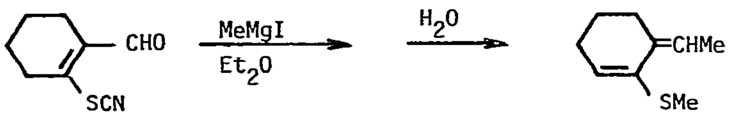
Displacement of a saturated C-N bond occurs with [87]:



Reactions of oxygen and nitrogen orthocarbonic acid derivatives, including reactions with Grignard reagents, have been reviewed [11].

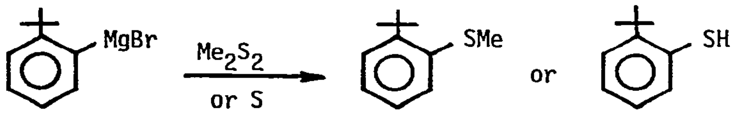
C. Displacement reactions at sulfur or phosphorous

Displacement at the thiocyanate sulfur, combined with carbonyl addition and dehydration, provides a synthesis of a functionalized diene [517, 518]. Acyclic cases are also reported.

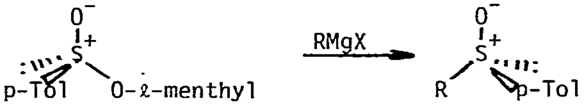

(75%)

Other displacements at divalent sulfur include:

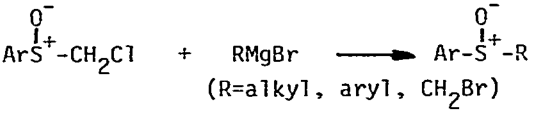
C_6F_5SSCl + PhMgBr $\longrightarrow$ C_6F_5SPh + Ph_2S + Ph-Ph [519]


50% 40% [520]

Inversion of configuration has been observed in the reaction of Grignard reagents with ℓ-menthyl-p-toluenesulfinate [521,522,83]:



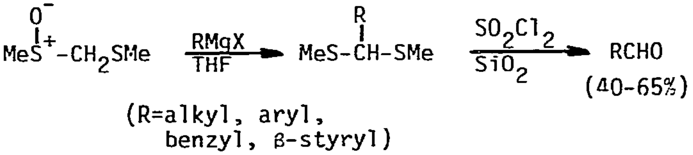
An unusual alkyl group displacement occurs with aryl α-chloroalkyl sulfoxides [523]:



$$\overset{O^-}{\underset{}{ArS^+}}-CH_2Cl \quad + \quad RMgBr \longrightarrow Ar-\overset{O^-}{S^+}-R$$

(R=alkyl, aryl, CH_2Br)

However, in contrast, α-thiomethyl sulfoxides are reductively alkylated at the α-position in a reaction which can serve as an aldehyde synthesis [524]:

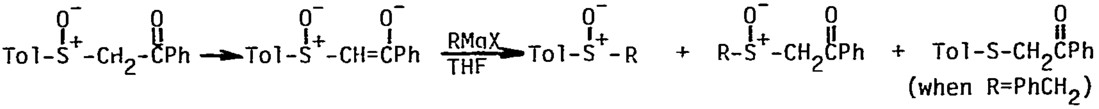


$$Me\overset{O^-}{S^+}-CH_2SMe \xrightarrow[THF]{RMgX} MeS-\overset{R}{C}H-SMe \xrightarrow[SiO_2]{SO_2Cl_2} RCHO$$

(R=alkyl, aryl, benzyl, β-styryl)

(40-65%)

β-Ketosulfoxides also undergo a displacement of alkyl or aryl [525]:

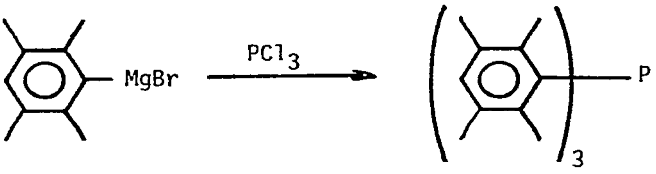


$$Tol-\overset{O^-}{S^+}-CH_2-\overset{O}{\overset{\|}{C}}Ph \longrightarrow Tol-\overset{O^-}{S^+}-CH=\overset{O^-}{C}Ph \xrightarrow[THF]{RMgX} Tol-\overset{O^-}{S^+}-R \quad + \quad R-\overset{O^-}{S^+}-CH_2\overset{O}{\overset{\|}{C}}Ph \quad + \quad Tol-S-CH_2\overset{O}{\overset{\|}{C}}Ph$$

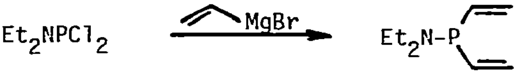
(when $R=PhCH_2$)

Optically active ketosulfoxide led to products of high optical purity.

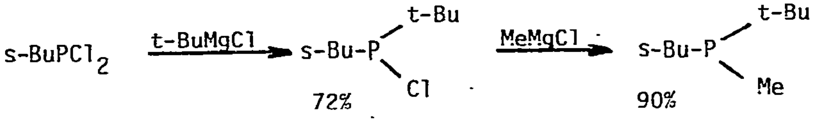
A number of papers report alkylation or arylation of chloro- or aminophosphines with Grignard reagents. Some selected examples are:



[526]



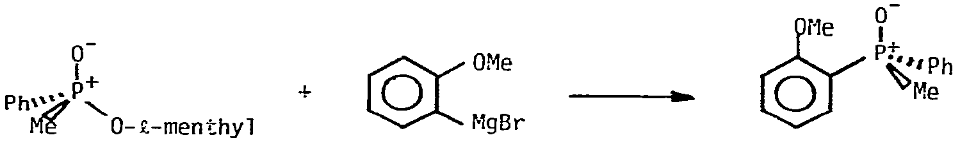
[527,528]



[529]

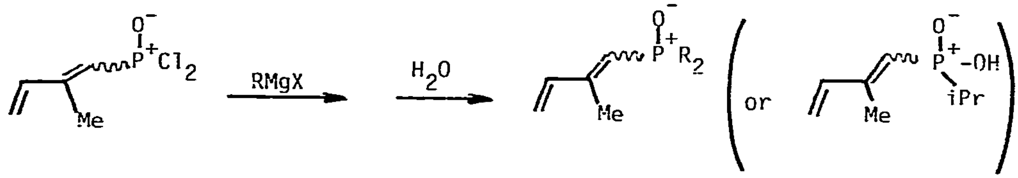
See also references 107 and 117.

Displacement of the ℓ-menthyloxy group from the phosphinate ester 247 occurs with inversion of configuration at phosphorous [530,531].

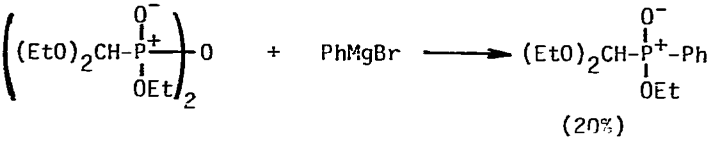


247

Some other displacement reactions of phosphinic or phosphonic acid derivatives were reported [see also references 113, 529]; e.g.



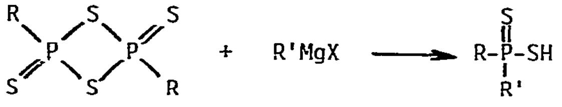
[532]



$$\left((EtO)_2CH-\overset{O^-}{\underset{OEt}{P^+}}\right)_2O + PhMgBr \longrightarrow (EtO)_2CH-\overset{O^-}{\underset{OEt}{P^+}}-Ph$$

(20%)

[533]

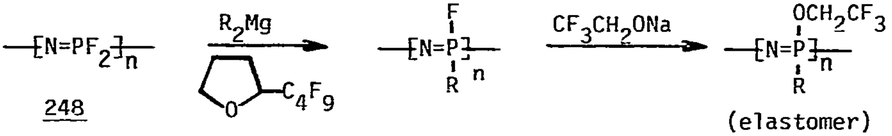


$$+ \; R'MgX \longrightarrow R-\overset{S}{\underset{R'}{\overset{\|}{P}}}-SH$$

[534]

R=Me, Ar R=Et, Ph, allyl, 1-naph.

Up to 80-90% of the fluorines in the inorganic polymer 248 may be replaced by ethyl or butyl groups, but an attempt to get complete alkylation led to chain shortening [535].



248

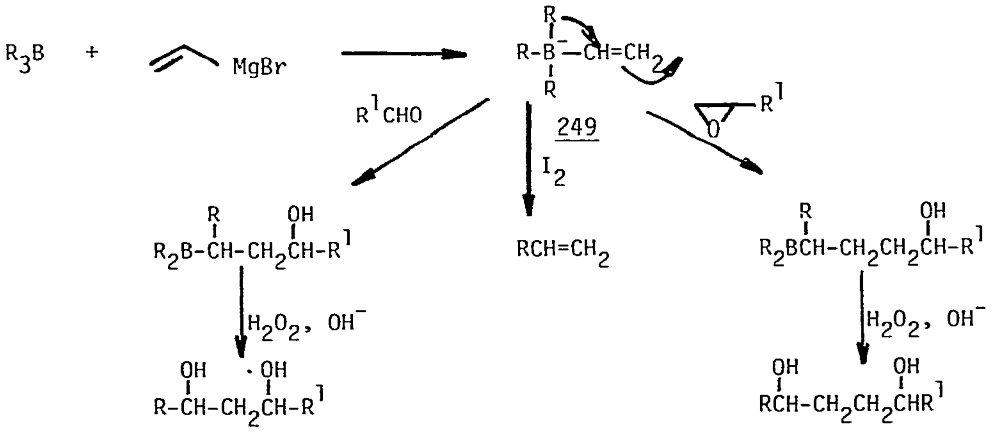
(elastomer)

D. Alkylation (displacement) at other elements

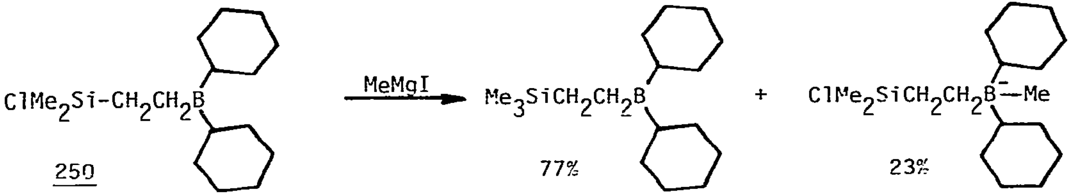
Because of the number of reactions reported, only some of the less routine examples will be included here, along with general synthetic and mechanistic studies.

Group II metals. Mixture of barium ethoxide with a variety of organomagnesium compounds appeared to form BaR_2 and RBaOEt species, which are capable of polymerizing butadiene and adding to 1,1-diphenylethylene [536]. Di-*tert*-butylzinc and *tert*-butylzinc chloride were prepared from zinc chloride and the *tert*-butyl Grignard reagent [537]; dialkylzincs containing $MeO(CH_2)_4$- or $EtS(CH_2)_3$-groups were prepared similarly [538].

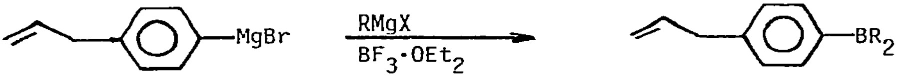
Group III. Interaction of trialkylboranes with vinylmagnesium bromide produced the novel and synthetically useful reagent 249 [539,540].



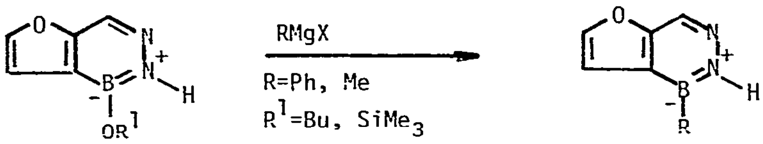
Competition between attack at silicon and boron was observed with 250 and a number of similar compounds [541].



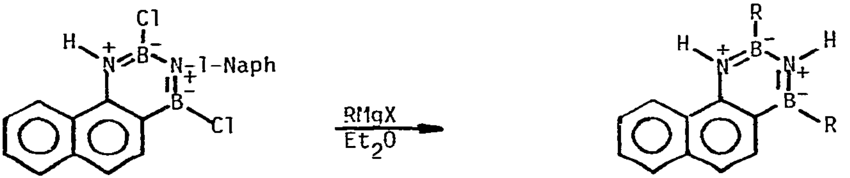
Othe alkylations at boron include:



[542]

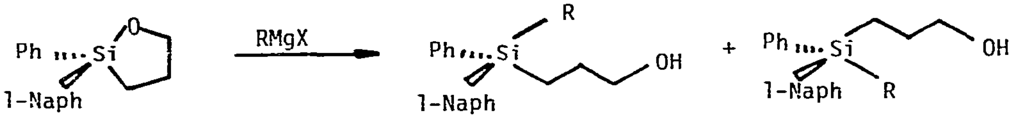


[543]



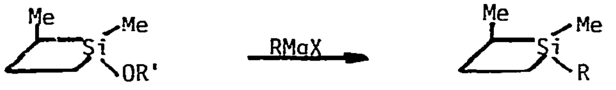
(R=Bu, Ph, allyl) [544]

Group IVa. The stereochemistry of substitution at silicon in 251 was found to depend upon the Grignard reagent used. The difference was rationalized in terms of apical attack by the softer allyl and benzyl vs. equatorial attack by the harder methyl- and butyl-magnesium bromides [545]:



251 (R=Me, Bu) (R=allyl, benzyl)

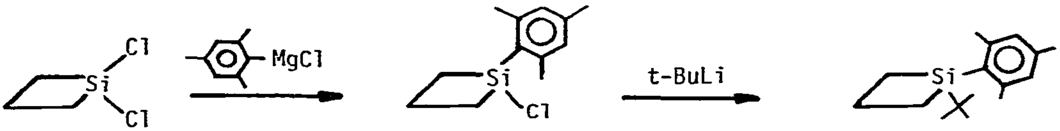
With 252, a variety of Grignard reagents displaced the alkoxy group with high stereospecificity for retention [546].



252

(R'=Me, t-Bu) (R=n-alkyl, i-Pr, Ph, allyl, benzyl)

Alkylation of dichlorosilane 253 could be done selectively with sequential introduction of different alkyl groups. The cyclic system itself is made by an internal Grignard alkylation [547,548].



253

$Cl_3SiCH_2CH_2CH(Br)$-R

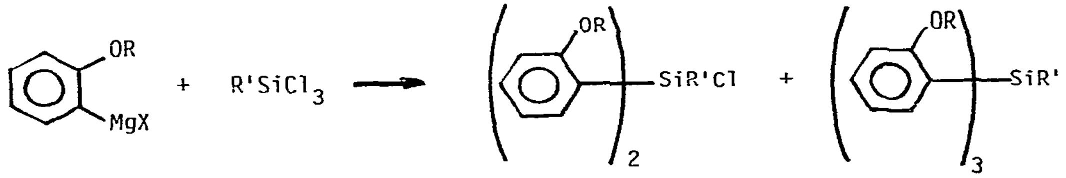
R=Me, Ph

Reaction of excess 254 with n-alkyl Grignard reagents gave mostly monoalkylation, along with 10-12% of dialkylation. Reactivity appeared to decrease

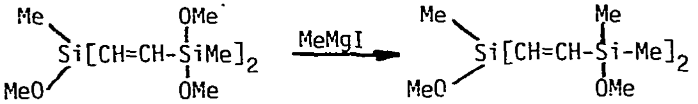
$$Me_2SiCl_2 \xrightarrow{RMgX} Me_2SiRCl + Me_2SiR_2$$

254

generally with chain length [549]. Steric hindrance appears to have a large effect in determining the necessary conditions and extent of reaction possible in the following arylation [550]:



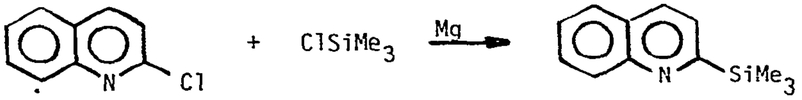
Some other examples of displacement at silicon follow.



$$\mathrm{Me(MeO)Si[CH{=}CH\text{-}SiMe(OMe)_2]_2} \xrightarrow{MeMgI} \mathrm{Me(MeO)Si[CH{=}CH\text{-}SiMe_2(OMe)]_2}$$

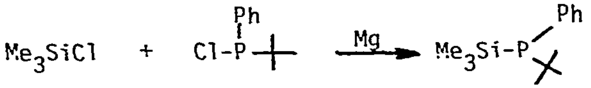
(61%) [551]

$$2,4\text{-}B_5H_5C_2[SiMe_2Cl]_2 \xrightarrow{(cp)MgCl} 2,4\text{-}B_5H_5C_2[SiMe_2(cp)]_2$$ [552]



[553]

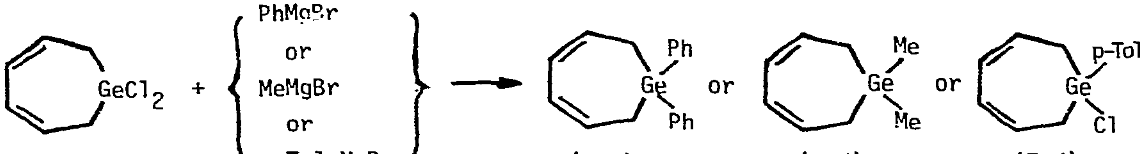
(34%) [554]



[555]

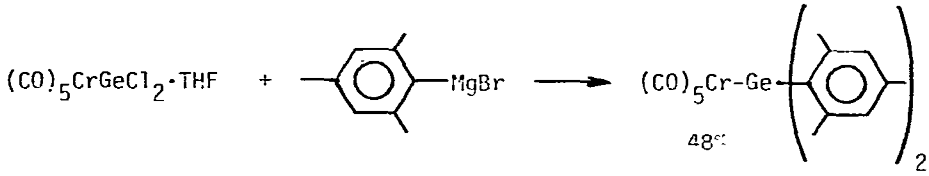
Similar reactions are reported in other references cited elsewhere in this survey [114,164].

Alkylation at germanium is illustrated by the following examples:

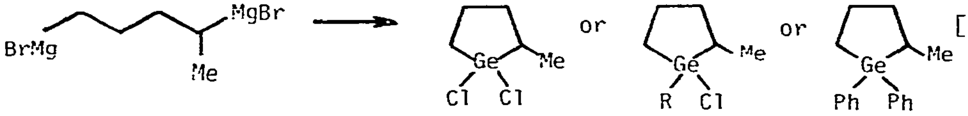


(80%) (83%) (75%)

[556]



[557]



[558]

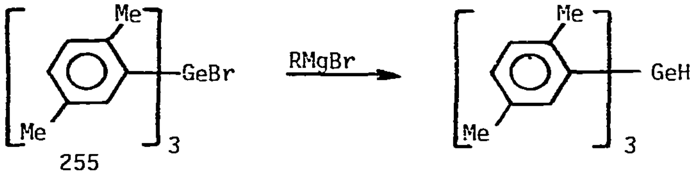
Germanium and tin tetraphenylporphyrins ($TPP \cdot MX_2$) were alkylated by Grignard reagents (to $TPP \cdot MR_2$), where R=ethyl, propyl, isopropyl, and CH_2SiMe_3 [559].

The reaction of trichlorogermane with excess methyl Grignard reagent led to oligomers [560]. Byproducts containing ethyl groups were formed.

$$HGeCl_3 \xrightarrow[Et_2O]{MeMgBr} Me[GeMe_2]_nMe \qquad n=1-7$$

α-Elimination to $GeCl_2$ or $GeMe_2$ was proposed in the polymerization mechanism. With ethyl or propyl Grignard reagents, increasingly large amounts of tetraalkylgermane were formed.

In another reaction which did not lead to simple alkylation, the bromide 255 was reduced by Grignard reagents [561].

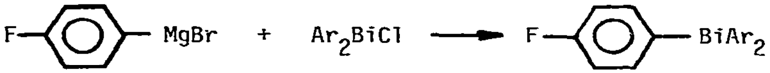


255

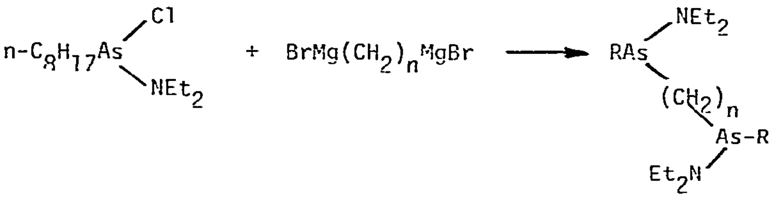
Alkylation of stannic chloride by *sec*-butylmagnesium bromide produced a statistically distributed diastereomeric mixture of tetra-*sec*-butyltins [562]. A chiral tetraalkyl tin was also made from optically active 2-methyl-1-butylmagnesium chloride [563]. A number of organotin derivatives were made by coupling tin halides with organic halides, using active magnesium produced by reduction of magnesium chloride [26].

p-Vinylbenzylmagnesium chloride was reacted with a series of Me_3MCl (M=Si, Ge, Sn, Pb) to produce styrene with $p\text{-}CH_2MMe_3$ substituent groups [111].

Group Va. A variety of p-fluorophenyl derivatives of antimony and bismuth were prepared by routes of the type:



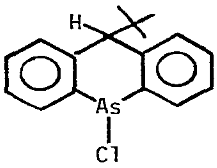
In reactions of p-F-$C_6H_4SbCl_2$ with arylmagnesium halides some displacement of the p-fluorophenyl group occurred [564]. Several other displacements at trivalent arsenic and bismuth were reported [see also reference 131]; e.g.



[564]

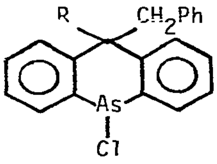
$$Me_3AsCH_2CH_2CH_2MgCl \quad + \quad BiCl_3 \longrightarrow (Me_2AsCH_2CH_2CH_2)_3Bi$$ [128]

Compound 256 failed to react, but 257 gave normal displacement [566].



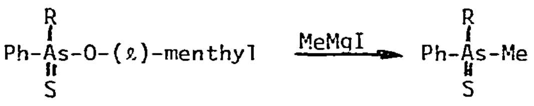
256

+ PhMgBr



257

The diastereomers of the ℓ-menthyl ester 258 (R=propyl) were separated and reacted with methyl Grignard reagent to produce enantiomers of the product in 90% optical purity [567]. The corresponding ethyl derivatives 258 (R=Et) reacted

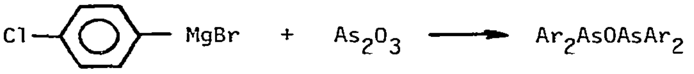


$$Ph\text{-}\overset{R}{\underset{S}{As}}\text{-O-}(\ell)\text{-menthyl} \xrightarrow{MeMgI} Ph\text{-}\overset{R}{\underset{S}{As}}\text{-Me}$$

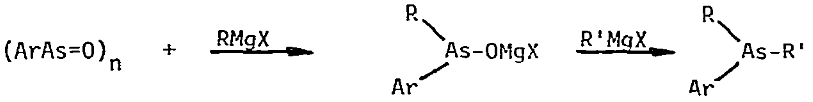
258

with propylmagnesium bromide with a high degree of inversion of configuration, although its oxygen analog gives racemic product [568,569].

Reaction of oxides with Grignard reagents led to organoarsenic derivatives:



[570,86]

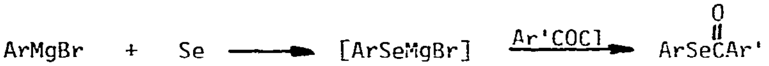


[571]

<u>Oxygen, peroxides and selenium</u>. Oxygenation of the butenyl Grignard reagent has been mentioned earlier (section III.C.). The peroxide initially

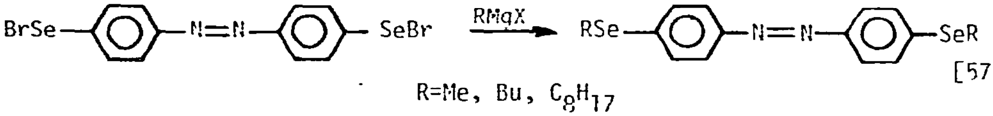
produced reacts quantitatively with the butyl Grignard reagent [153]. The reactions of a variety of peroxides with phenylmagnesium bromide were examined. Most peresters and diacylperoxides reacted smoothly, but peroxides with neighboring ether oxygen are slow, and some dialkyl peroxides did not react [572]

The following reactions at selenium have been reported:



$$ArMgBr + Se \longrightarrow [ArSeMgBr] \xrightarrow{Ar'COCl} ArSe\overset{O}{\overset{\|}{C}}Ar'$$

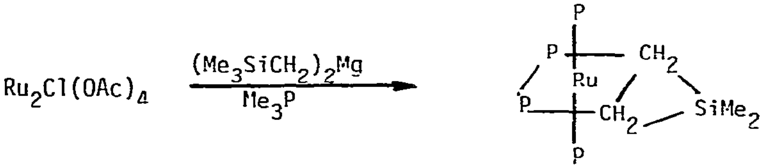
[573]

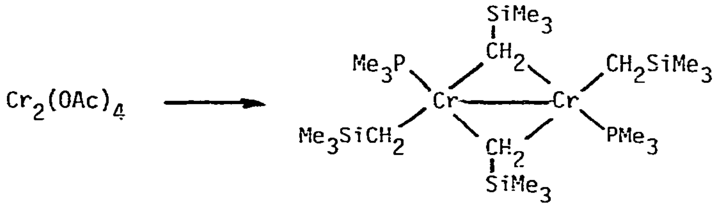


[574]

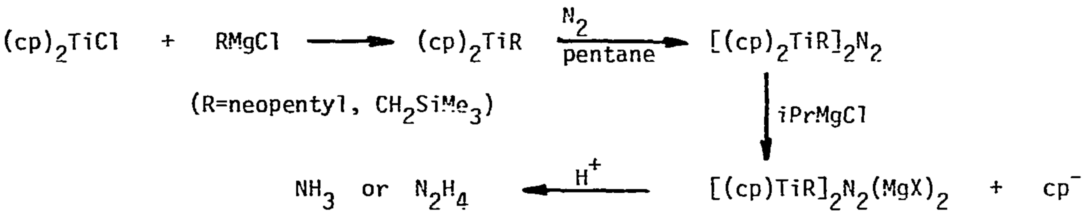
Transition elements. A summary has appeared of preparations of transition metal allyls and benzyls, largely via Grignard reagents [575].

Reactions of a number of binuclear transition metal acetate complexes with Grignard reagents were studied (Cr, Mo, Re, Rh, Ru). Among other interesting results, the following may be noted [576]:





Trivalent titanium complexes with nitrogen-fixing properties were prepared [577]:



However, similar attempts to prepare other alkyls failed. Titanium and the corresponding niobium hydride species, formed in the following reductive process, added to a double bond of cyclooctatetrane [578].

$$(cp)_2TiCl_2 \xrightarrow{iPrMgCl} (cp)_2TiCl \xrightarrow{iPrMgCl} [(cp)_2Ti\text{-}iPr] \longrightarrow (cp)_2TiH$$

+ 

Tetra(neophyl)zirconium (which catalyzes ethylene polymerization) [579] and mixed hafnium complexes $(cp)_2Hf(CH_2Ph)_2$ [580] and $(Rcp)(cp)Hf(CH_2Ph)Cl$ (the latter being chiral) [581] were prepared by Grignard reactions starting with the tetrachlorides.

Mixed tetravalent alkyl-alkoxyvanadium complexes were prepared by alkylation of $(tBuO)_4V$ and $(tBuO)_2VCl_2$ [582]. Organomagnesium compounds were also used to convert VCl_3 to mono- and triaryl complexes [583], and to prepare cyclopentadienyls $(cp)NbX_4$, $(cp)TaX_4$ and $(cp)_2VCl$ from the halides [584].

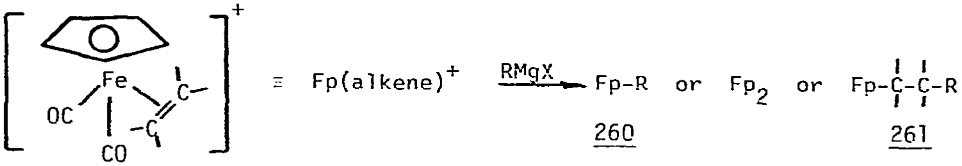
Nitrogen fixation by complexes formed from $CrCl_2$ and magnesium [585], and substitution in chromium [586] and molybdenum [587] complexes by aryl and allyl Grignard reagents were reported. Formation of a variety of polynuclear rhenium alkyls have also been reported [588]; e.g.

$$Re_3Cl_9 \longrightarrow Re_3Cl_3R_6 \quad ; \quad ReCl_4(THF)_2 \xrightarrow[Ar]{R_2Mg} Re_3R_{12}$$

$$(R=CH_2SiMe_3,\ \text{neopentyl},\ \text{neophyl})$$

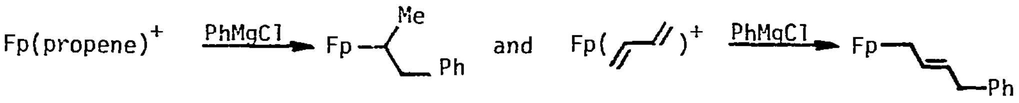
In the latter, reaction under nitrogen forms $[R_4Re]_2N_2$.

Grignard reagents react by competing pathways with the iron-olefin complex 259 [589]. The ethylene complex reacts by displacement (260) with methyl or vinyl Grignard reagents, but allylmagnesium chloride and phenylmagnesium bromide give 14 and 66% of addition (261).



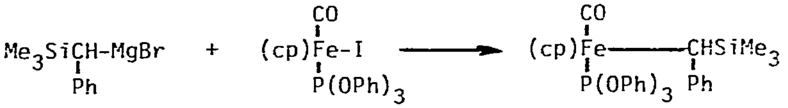
259

Other addition reactions are:



(43%) (55%)

Replacement of the alkene was proposed to occur via initial addition to a carbon monoxide ligand, or by single electron transfer. The complex 262 is formed as a mixture of diastereomers, one of which decomposes selectively [127].



$$Me_3Si\underset{Ph}{C}H\text{-}MgBr + (cp)\underset{P(OPh)_3}{\overset{CO}{Fe}}\text{-}I \longrightarrow (cp)\underset{P(OPh)_3}{\overset{CO}{Fe}}\text{—}\underset{Ph}{C}HSiMe_3$$

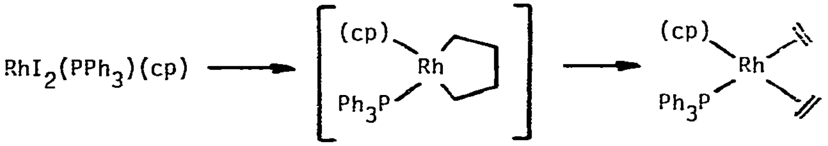
262

Cobalt and iridium metallocycles are formed by halide displacement from 263 and 264 with $(CH_2)_4Mg$ or $BrMg(CH_2)_4MgBr$ [590]. The analogous rhodium

$CoI_2(PPh_3)(cp)$ 263

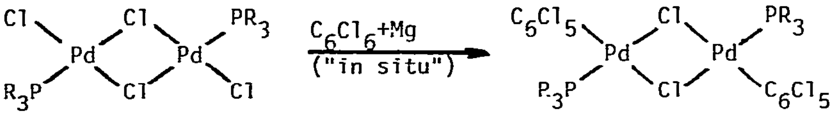
$IrCl_2(PPh_3)(cpMe_5)$ 264

complex forms metallocycles with longer-chain di-Grignard reagents, but the tetramethylene complex is apparently unstable [591]:

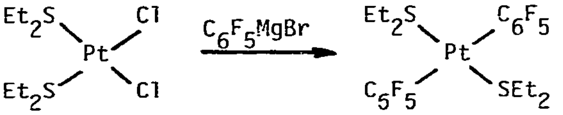


Substitution of bromine by C_6F_5MgBr in a cobalt complex is also reported [592]

Halide displacements in nickel, palladium and platinum complexes with halogenated aryl Grignard reagents are reported [see also references 50, 593]; e.g.

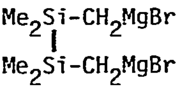


[594]

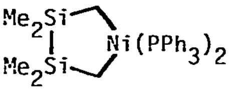


(<u>cis</u>-isomer with C_6F_5Li) [595]

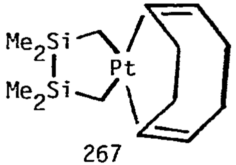
The interesting metallocycles 266 and 267 were prepared from the di-Grignard reagent 265 and the corresponding dichloride complexes [123]. Nickel and



265



266



267

palladium complexes are also implicated in catalyzed reactions of Grignard reagents with aryl or vinyl halides (see section VI.A.).

E. Reaction as a base; metallation

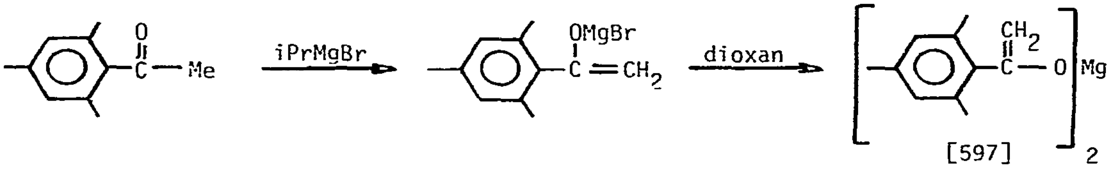
Preparation of a number of organomagnesium compounds by proton removal from an organic substrate has been discussed in section II.B. and II.C.

The kinetics of the reaction of acetylene with PhMgBr have been studied by a thermographic technique. Triethylamine increases the rate; magnesium bromide

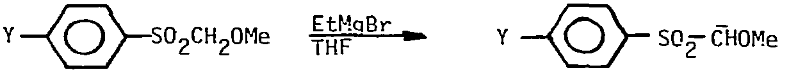
$$2HC{\equiv}CH \xrightarrow[\substack{Et_2O \\ Et_3N}]{PhMgBr} 2HC{\equiv}CMgBr \longrightarrow BrMgC{\equiv}CMgBr \quad + \quad C_2H_2$$

increases it with excess amine present, but slows the reaction otherwise. Different basicities of complexed PhMgBr and $PhMgBr{\cdot}MgBr_2$ compounds were postulated to rationalize the results [596].

Ketones react with Grignard reagents in HMPA by enolization in preference to addition [280]. Additional reactions involving magnesium enolates or similarly stabilized carbanion derivatives formed by deprotonation are:

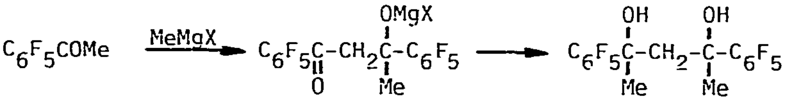


[597]



[598]

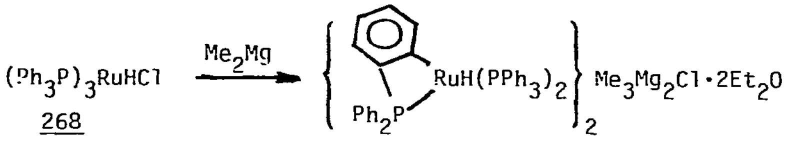
Y=H, Me, Cl



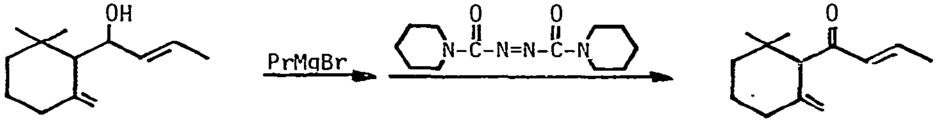
$$C_6F_5COMe \xrightarrow{MeMgX} C_6F_5\overset{}{\underset{\underset{O}{\|}}{C}}\text{-}CH_2\text{-}\overset{OMgX}{\underset{Me}{C}}\text{-}C_6F_5 \longrightarrow C_6F_5\overset{OH}{\underset{Me}{C}}\text{-}CH_2\text{-}\overset{OH}{\underset{Me}{C}}\text{-}C_6F_5$$

[470]

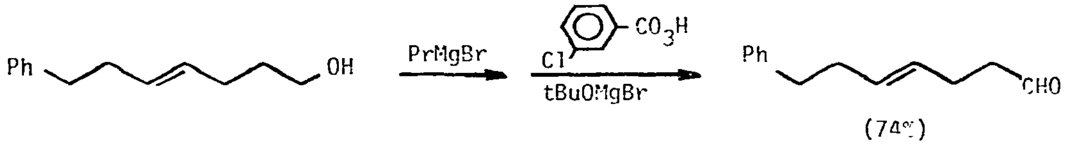
Removal of an ortho-proton in 268 generated a chelate [599].

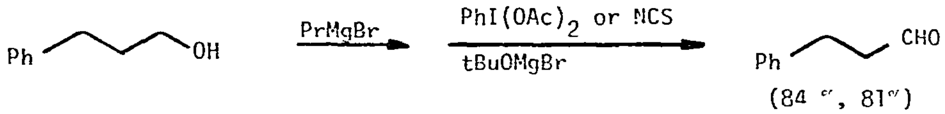


Procedures for alcohol oxidation have been reported in which the magnesium alkoxide is first generated by reaction with a Grignard reagent [600,601]. The



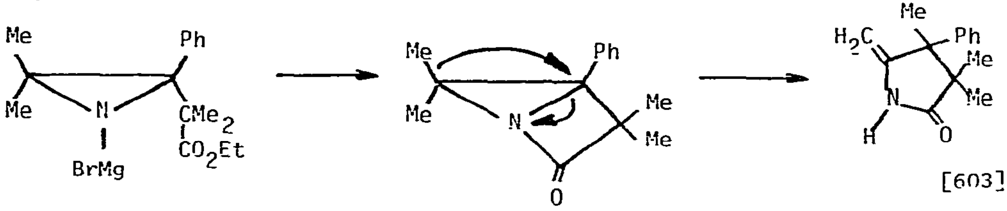
(75-87%)



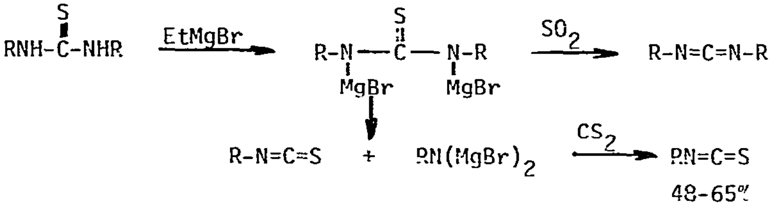


use of magnesium alkoxides generated in similar fashion for an asymmetric Meerwein-Pondorff-Verley-type reduction of ketones has also been studied. The stereochemistry may be significantly different from the aluminum alkoxide [602]

Other reactions consisting of, or initiated by, proton abstraction by a Grignard reagent include:

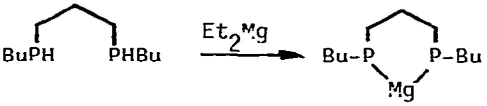


[603]

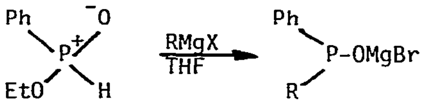


[604]

[605]



[606]



[607]

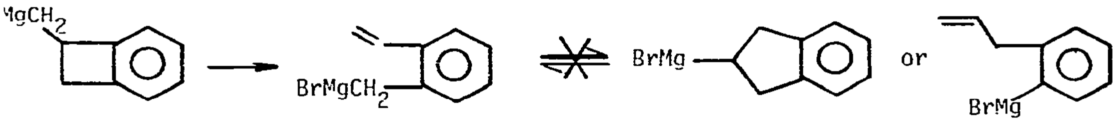
Previous instances in this review where the basicity of organomagnesium compounds has figured include aziridine-formation from oximes [352-355] and a de-cyanoethylation [334] (section V.A.), metallation during addition to an enyne [366] (section V.B.), and elimination of HF, to generate a reactive fluoroalkene [473] (section VI.A.).

VII. OTHER REACTIONS OF ORGANOMAGNESIUM COMPOUNDS

A. Rearrangements

Organomagnesium rearrangements have been reviewed [3].

The Grignard reagent 269 rearranged cleanly to 270, which incorporated 0.98 atoms of deuterium on hydrolysis with D_2O. Grignard reagents 271 and 272,

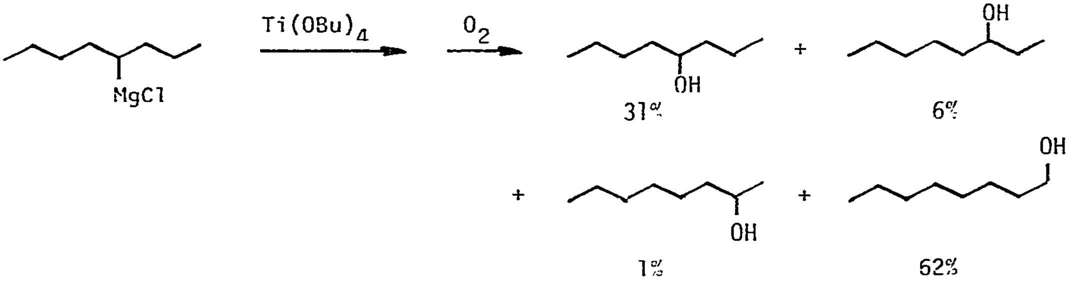


269 270 271 272

which were formed in the reaction of allylmagnesium bromide with benzyne (see section V.B.), were not interconverted with each other or with 270 [360]. Intramolecular addition to the double bond occurs in Grignard reagent 273 [357].

273

The titanium salt-catalyzed isomerization of Grignard reagents has been investigated in some detail. The 4-octyl Grignard reagent is converted to a mixture containing up to 62% of the 1-octyl reagent:



The alkoxides seem to be most effective, followed by $TiCl_4$; a Ti(III) species was considered to be the actual catalyst. In other isomerizations, tert-butyl was converted to up to 35% of isobutyl; 1-phenyl-2-butyl was converted to 38% 1-phenyl-1-butyl and 14% 1-phenyl-3-butyl; and little interconversion was noted between 1° and 2° neohexyl isomers [608].

The cyclization of a hexenyl group (presumably as the free radical) during a conjugate addition has been discussed earlier in connection with the mechanism of the Grignard addition reaction (section IV.A.) [173]. The intramolecular reaction between organomagnesium and acetal functions [100], and a rearrangement during the addition to a fused 2-chlorocyclobutanone (section IV.B.2.) [218] have been discussed previously.

B. Catalysis of polymerization and other reactions

The year continued to see great activity in the patent literature in catalysis of alkene polymerization by multicomponent formulations which include an organomagnesium compound. For the most part, these are solids formed by interaction of the organomagnesium compound with a titanium (or occasionally vanadium) halide. Commonly, aluminum chloride or an organoaluminum halide, a siloxane, or an alcohol, ester or other Lewis base is also a part of the catalyst combination. For polymerization of alkenes, the catalyst is combined with an aluminum alkyl [609]. Several patents were also issued which claim an organomagnesium complex useful as a catalyst component. These appear generally to be mixed aluminum-magnesium alkyl-alkoxides, sometimes hydrocarbon-soluble [610]. (Because of the numerous patents involved, the above references list only the appropriate chemical abstract numbers.)

Several papers report studies of ethylene or propylene polymerization with catalysts containing diphenylmagnesium. The activity of $TiCl_4$-Et_2AlCl-Ph_2Mg catalysts was increased by ultrasonic treatment [611], and the molecular weight, yield, and tensile strength of the polyethylene were influenced by amounts of $TiCl_3$ added [612]. Activities of propylene polymerization catalysts formulated from a complex $2(Ph_2Mg{\cdot}PhCl){\cdot}PhMgCl$ with $TiCl_3$ and Et_2AlCl varied with the Mg/Al ratio [613]. The molecular weight of polyethylene produced from similar catalysts varied with the sequence in which the components were combined [614]. Another study reports the stereoregular structure of polymers from organomagnesium catalysts [615]. Catalysts made from barium alkoxides and organomagnesium compounds, probably containing barium alkyls, polymerize butadiene [536].

A combination of $NiBr_2$ and mesitylmagnesium bromide polymerized 3-hexyne in THF at low temperature. Hexaethylbenzene and the tetraethylcyclobutadiene-$NiBr_2$ complex could also be isolated [616].

The kinetics of anionic polymerization of 2-vinylpyridine with di-sec-butyl- or dibenzylmagnesium were reported. Spectra indicated the presence of several different active species. A cyclic coordinated structure for the living polymer was proposed [617]. Polymerization by phenylmagnesium bromide in toluene gave a predominantly isotactic polymer, with stereospecificity increasing with high temperature or added TMEDA. In THF, the polymer was atactic, as was the polymer from 4-vinylpyridine [618].

In the anionic polymerization of α-substituted acrylates by organomagnesium compounds in toluene, small amounts of water, methanol or chloroform increased the isotacticity, apparently by selectively destroying syndiotactic active species [619]. In the butylmagnesium bromide polymerization of methyl methacrylate in THF-toluene, two distinct polymer fractions appear to be formed, which differ in triad content. Variation of the catalyst composition (Bu_2Mg to $BuMgBr + MgBr_2$) changed the efficiency of the process, but not the nature of the polymer. About 16% of the alkylmagnesium functions remained at the end of the polymerization, and only a small portion appear to actually initiate polymerization [620].

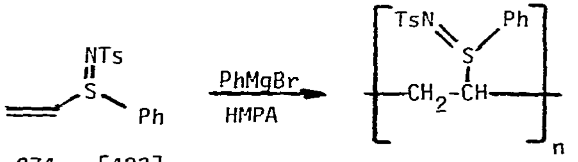
α,α-Dimethylbenzyl methacrylate was converted to an isotactic polymer by Grignard reagents, but to a predominately syndiotactic polymer by bromomagnesium piperidide [621].

Racemic α-phenylethyl methacrylate was polymerized using sparteine complexes of cyclohexyl or (-)-menthyl Grignard reagents. The polymer formed was highly isotactic, and up to 94% optically pure; recovered monomer was as much as 90% optically pure. Lower stereoselectivities were obtained with the 2-butyl ester [622].

A polymer was produced from ferrocenylmethyl methacrylate, initiated by Grignard reagents, and its properties described [623].

The influence of catalytic amounts of Lewis bases on the polymerizations of acrylonitrile, methyl methacrylate, and 2-vinylpyridine by organomagnesium compounds was studied. Effects on the orientation of monomer in a complex intermediate were considered important [624]. Catalysts useful for the anionic polymerization of styrene and acrylates were prepared using *tert*-butyl- or o-chlorobenzylmagnesium chloride with benzophenone; water and chlorosilanes were included [625].

Grignard reagents successfully polymerized the vinyl sulfinylimine 274, but not allylsilane 275. Fire-resistant polyamides were made by incorporation of hexachlorobutadiene and a trace of terephthaloyl chloride into poly(ε-caprolactam) made with ethylmagnesium bromide catalysts [626].

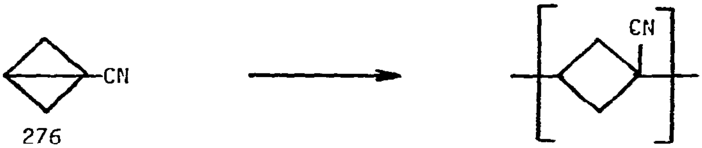


274 [423]

; $Ph_2Si(CH_2CH=CH_2)_2$

275 [554]

A ring-opening polymerization of the bicyclobutane derivative 276 is catalyzed by organomagnesium compounds.



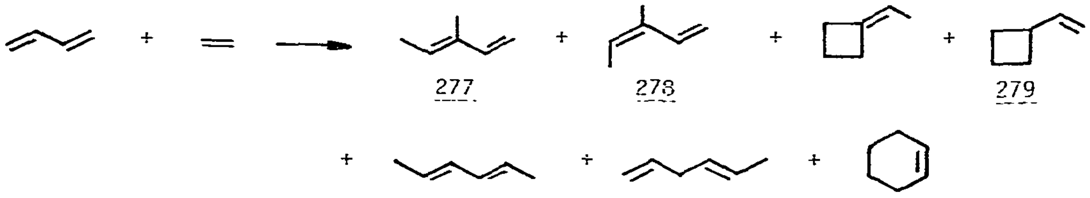
276

Chain termination is by addition to the cyano group [627].

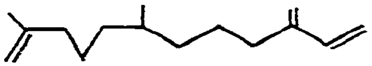
Olefin dismutation catalysts from Me_3SiCH_2MgCl or $(Me_3SiCH_2)_2Mg$ and WCl_6 [628,629] or MeMgBr and $MoCl_5$ or WCl_6 [630,631] were useful for polymerization of cycloolefins, including 5-carbomethoxynorbornene.

The polymerization of haloaryl Grignard reagents by nickel coupling catalysts has been discussed in section VI.A. [78].

Codimerization of ethylene with butadiene is catalyzed by combinations of titanium compounds and Grignard reagents.



A catalyst from $Ti(OR)_4$ and various Grignard reagents led to 279 as the major product [632], while $(cp)_2TiCl_2$ + EtMgBr gave a mixture of 277 and 278 in yields up to 90% [633]. *Isoprene was trimerized to* 280 *by a catalyst from* PhMgBr,



280

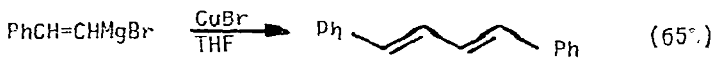
nickel naphthenate and $PhP(NEt_2)_2$ [634]. EPR studies of the hydrogenation of alkenes by $(cp)_2TiCl_2$ + BuMgBr indicate that bridged bimetallic hydrides are the active species [635].

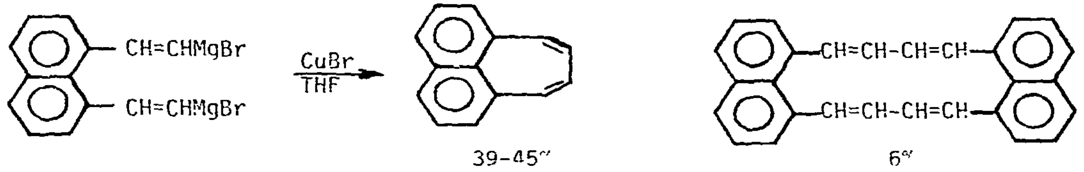
Propylene oxide and carbon dioxide react in the presence of a Grignard reagent and a nitrogen compound to produce propylene carbonate in 85% yield [636].

C. Other reactions

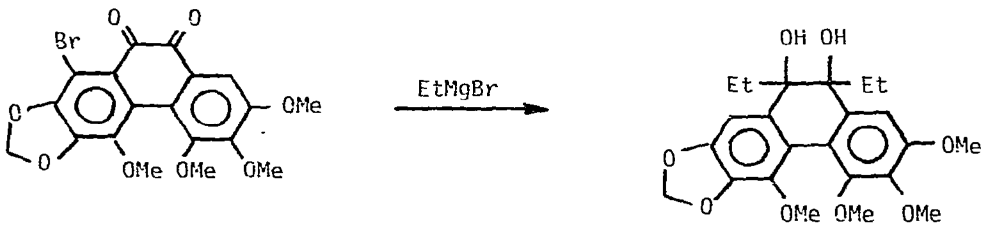
Displacements by the halide ion. In coupling reactions of chlorotrimethylsilane and ω-bromoesters $[Br(CH_2)_nCO_2Me]$ with magnesium, replacement of bromine by chlorine was important for n=2, and was the exclusive reaction when n=3 or 10 [461]. Replacement of chloride by bromide also occurs in the displacement reactions of dihalobenzocyclopropenes with Grignard reagents, but not with magnesium bromide alone [464].

Coupling reactions with metal salts. Thallium bromide was used to couple the 4-biphenylyl Grignard reagent to a 70% yield of p-quaterphenyl [637], and the Grignard reagent from 1-bromo-3,5-dimethyladamantane was coupled to a dimer with silver bromide [465]. The Grignard reagent from deuterated isopropyl iodide couples to the symmetrical dimer with cupric chloride [638]. β-Styryl-type Grignard reagents were coupled with cuprous bromide. The latter reaction was utilized for ring syntheses [639].



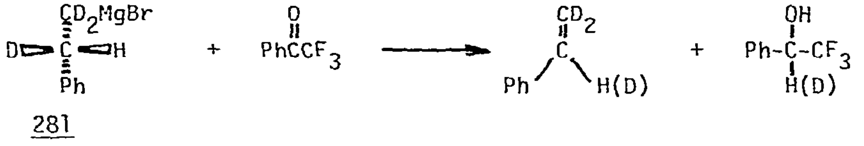


Halogen-metal exchange. Preparative examples have been noted in section II.B. In the attempted copper-catalyzed coupling of ethers I-CH_2CH_2OR, the major product was ethylene (55-60%) produced via Mg-I exchange and elimination [477]. Exchange of vinyl iodides with Grignard reagents is also a side reaction in their copper-catalyzed coupling reaction; on hydrolysis the alkene from "reduction" is isolated [479]. Metal halogen exchange during palladium complex-catalyzed reactions of aryl halides with aryl Grignard reagents is probably responsible for symmetrical coupling side-products formed. 3,5-Difluoroiodobenzene underwent ready exchange with phenylmagnesium bromide even in the absence of the palladium complex [483]. In the reaction:



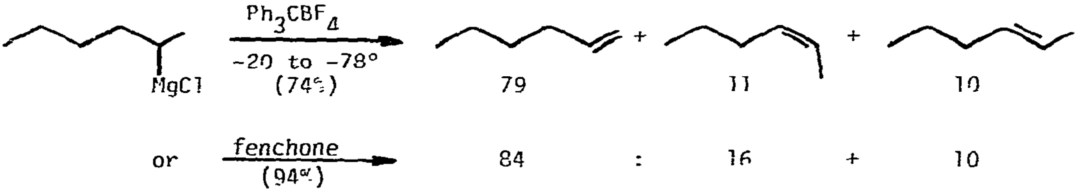
the loss of bromine was believed to occur via magnesium-bromine exchange, facilitated by the nearby alkoxide [640].

Hydride transfer. Asymmetric reduction by the chiral Grignard reagent 281

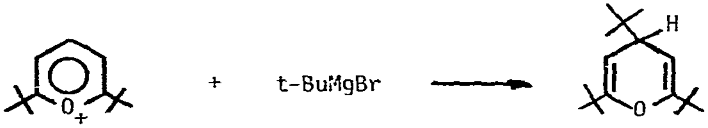


has been studied. Four alcohol products are formed: R and S enantiomers with H or D-transfer. The stereoselectivity and isotope effects were considered most consistent with a cyclic six-center transition state, non-linear hydrogen transfer, and tunnelling [641].

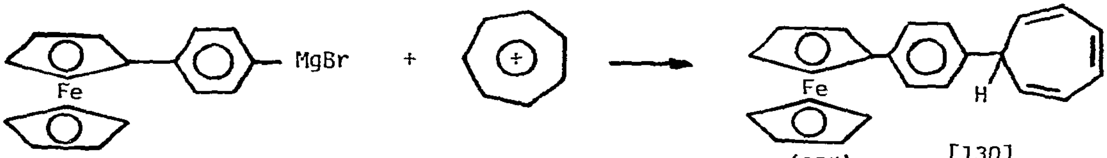
Hydride transfer from a Grignard reagent has also been considered as a synthetic equivalent to dehydrohalogenation, useful for primary alkyl halides, and favoring Hoffmann orientation. Hydride acceptors studied were fenchone [642] trityl fluoborate, and tri-sec-butyl- or tri-cyclohexylboranes [643]. For example:



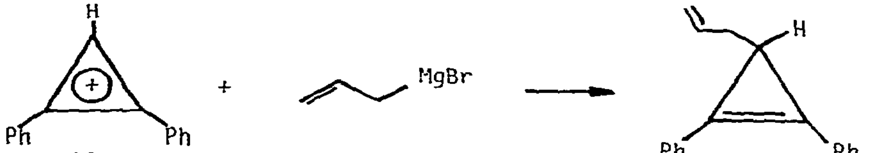
Reaction with oxidizing agents, organic cations, etc. Aryl Grignard reagents react with a MoO_5-pyridine-HMPA complex to yield the corresponding phenols in 67-89% yield [644]. Couplings of pyrylium, tropylium, and cyclopropenium cations 282-284 with Grignard reagents have been reported.



282 [645]



283 (25%) [130]



284 [646]

The cyclopropenium ions 285 undergo net displacement, while the iodo-derivative 285 (Y=I) exchanges magnesium for iodine [63].

285 (Y=Cl, OMe)

Miscellaneous reactions. Perfluoroalkyl Grignard reagents undergo thermal decomposition catalyzed by phenylmagnesium bromide to form a variety of products [647]:

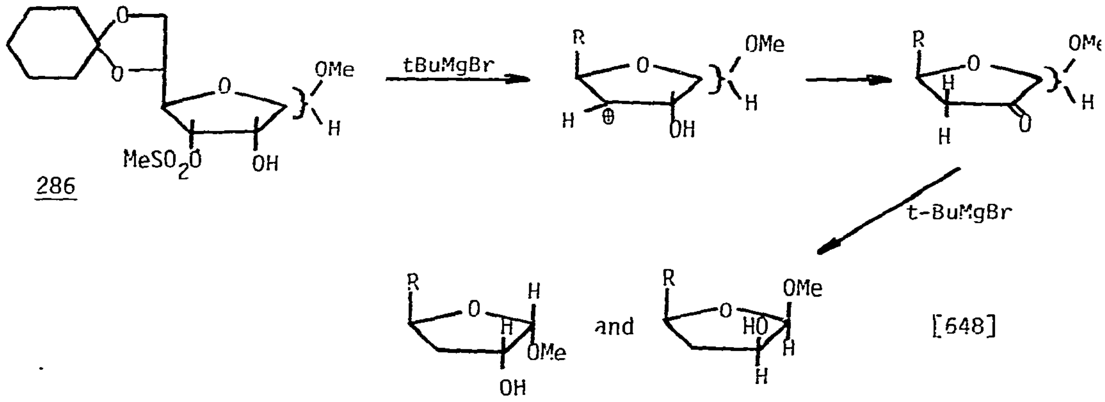
$$R_fCF_2CF_2MgBr \xrightarrow{PhMgBr} R_fCF{=}CHF + R_fCF_2CF_2H + R_fCF{=}CFBr$$

$$+ R_fCF{=}CFPh + R_fC{\equiv}CPh$$

$$R_fCF{=}CFMgBr \xrightarrow{PhMgBr} R_fC{\equiv}CPh$$

Formation of carbenes and arynes by decomposition of haloorganometallics was reviewed [13].

Lewis acidity of the Grignard reagent appears to induce ionization of the sulfonate group in 285. Hydride shift, followed by stereospecific reduction by excess Grignard reagent led to the unusual stereochemical result shown in which one product was formed from each diastereomer of the starting material. In a similar process, the mono-methanesulfonate of cyclododecane-1,2-diol yields cyclododecanone [648].



[648]

The dianions produced by reductive electron addition to o, m and p-dicarbadodecaboranes react with aryl Grignard reagents:

$$o\text{- or } m\text{-}[HCB_{10}H_{10}CH]^{-2} \xrightarrow{ArMgX} [HCB_{10}H_9ArCH] \xrightarrow{CuCl_2} o\text{-}[HCB_{10}H_9ArCH]$$

$$p\text{-}[HCB_{10}H_{10}CH]^{-2} \xrightarrow{ArMgX} [HCB_{10}H_9ArCH] \xrightarrow{CuCl_2} m\text{-}[HCB_{10}H_9ArCH]$$

In the former case, a mixture of positional isomers was obtained. Di- or triaryl derivatives were formed with excess reagent [649].

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