# MAGNESIUM

## ANNUAL SURVEY COVERING THE YEAR 1976

E. ALEXANDER HILL

*Department of Chemistry, University of Wisconsin-Milwaukee,*
*Milwaukee, Wisconsin 53201*

---

Magnesium, Annual Survey covering the year 1975 see J. Organometal. Chem., Vol.138(1977)p.1-124.

## I. Introduction

The year 1976 marked the seventy-fifth anniversary of the publication of Victor Grignard's thesis. The occasion was noted with brief historical reviews by Bruylants, Urbanski, and Recarey [1-3].

A variety of review articles published during 1976 have contained significant segements of organomagnesium chemistry:

* Riecke and Hashimoto have both reviewed recent advances in the preparation of active metals and their use in the synthesis of various organometallic compounds [4,5].

* A review by Davidson, Lappert, and Pearce on "Metal σ-Hydrocarbyls" includes discussion of dialkylmagnesium compounds [6].

* In a review of intramolecular coordination of basic groups to the metal of organometallic compounds, Prokof'ev covers the cyclization of Grignard compounds by interaction with a carbon-carbon double bond, in addition to discussion of coordination with oxygen and nitrogen groups [7].

* Okubo and Maruyama published three reviews which concentrate upon the importance of single electron transfer processes in the formation and reaction of Grignard reagents [8].

* Three reviews, by Tamao and Kumada [9], by Schlosser [10], and by Beletskaya, Artamkina, and Reutov [11] are concerned with coupling reactions of organometallic compounds with alkyl halides.

- Boireau, Abenhaim, Namy, and Henry-Basch have reviewed the reactions of epoxides with organometallic compounds [12].
- Reviews by Tillett, on nucleophilic substitution at tricoordinated sulfur [13], by Fokin and Kolomiets on reactions of epi-thiocompounds [14], and by Volpin and Kolomnikov on reactions of organometallic compounds with carbon dioxide [15] include sections on organomagnesium reagents.

A convenient Grignard reaction experiment for undergraduate students has been described [16].

Several theses in organomagnesium chemistry were published. In addition to literature reviews which they include, research results from many of them have been published, and results are cited in appropriate locations elsewhere in this survey, or in surveys from previous years. They include:

- T. Holm (Danmarks Tekniske Højskole), "Thermochemical and Reaction Kinetic Studies on Grignard and Alkyllithium Reagents" [17].
- L. M. M. Thiessen (Univ. Antwerpen), "Reactions of 4-Substituted Pyridines and Salts with Grignard Reagents" [18].
- G. R. Buske (University of Illinois at Urbana-Champaign), "Additions of Cyclopentadienyl Metal Compounds to Benzyne and the Stereochemistry of 7-Benzonorbornadienyl Grignard Reagents" [19].
- C. E. Cannon (University of Wisconsin-Milwaukee), "Some Rearrangements of Tricyclic and Bicyclic Organomagnesium Compounds" [20].
- P. D. Livant (Brown University), "Applications of Chemically Induced Dynamic Nuclear Polarization: Radical Aspects of Certain Organometallic Reactions" [21].
- R. B. Banks (Florida State University), "The Stereochemistry of Organometallic Reactions at the Vinyl Carbon-Halogen Bond" [22].
- W. A. Nugent (Indiana University), "Mechanistic Studies in Organometallic Chemistry;" sections on electron transfer in reactions with peroxides and on Kharasch reaction catalysis [23].
- C. W. Wilkins, Jr. (Pennsylvania State University), "The Stereochemistry of Addition of Grignard and Lithium Reagents to Norbornenols" [24].
- D. A. Hutchinson (Purdue University), "The Structure of Substituted Allylic Grignard Reagents as Shown by Nmr; Solvolytic Studies of Substituted Allylic Grignard Reagents" [25].

## II. Preparation of Organomagnesium Compounds

### A. Reaction of Magnesium with Organic Halogen Compounds

Lawler and Livant have observed CIDNP (chemically induced dynamic nuclear polarization) enhancement in the spectrum of the Grignard reagent formed in iron-catalyzed functional exchange between i-propylmagnesium bromide and butyl bromide [21,26]. The spin polarization closely resembles that reported earlier in the formation of butylmagnesium bromide from butyl bromide and magnesium metal. For this reason, they suggested that the polarization in the latter process may result from a concurrent exchange side-reaction, and not from the Grignard-formation itself.

The preceding paper was answered by Schaart, Bodewitz, Blomberg, and Bickelhaupt [27]. They pointed out that preformed Grignard reagent does not react significantly with alkyl halides under most conditions of Grignard reagent formation which they had previously studied; exchange of magnesium with alkyl iodide in THF did not generate polarization in the reagent which formed in that exchange. Reaction of isobutyl iodide with magnesium in the presence of ethylmagnesium bromide produced enhancement only in the forming isobutylmagnesium iodide, and the extent of polarization did not depend upon the concentration of preformed Grignard. Further, they found that ethyl radicals generated by photolysis of tetraethyllead in the presence of ethylmagnesium bromide did not produce a polarized Grignard reagent spectrum.

In a study of the reduction of alkyl halides with aromatic radical anions, Bank and Juckett have discussed the possible existence and stability of $RX^{\overline{\cdot}}$ species as intermediates in Grignard reagent formation [28]. They concluded that their results were consistent with proposed rate-determining electron transfer, but that in some cases, cleavage to a radical may occur simultaneously with the transfer.

Ashby and coworkers [29,30] found that the reaction of aromatic ketones with a large excess of methylmagnesium bromide produces alcohol *by reduction*, besides the normal products of of methyl addition and single electron transfer (see section IV A). The reduction product was traced to small amounts of a magnesium hydride species, formed in about 0.2% yield as a side-product during Grignard formation. Selectivity in the reduction byproduct was similar to that found for authentic magnesium hydride in the presence of Grignard reagent. The hydride is destroyed by rapid reaction with excess methyl bromide, and the amount of hydride which survives the Grignard formation stage depends upon the size of the magnesium turnings and rate of bromide addition. The source of reducing hydride was shown to be methylene hydrogens of ether used in the preparation; a radical mechanism was proposed:

$$ROCH_2CH_3 + \cdot MgBr \longrightarrow RO\dot{C}HCH_3 + HMgBr$$

Grignard reagents were prepared from the $^{14}C$-labeled halides *1* [31]; no rearrangement of the label was found.

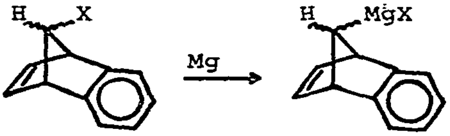
$$Ar_2\overset{*}{C}{=}CArBr \qquad Ar = \text{phenyl, p-anisyl}$$

*1*

A Grignard reagent made from optically active *2* had 61% retention of configuration. Unreacted bromide was not racemized, and once formed, the Grignard reagent was configurationally stable [22].

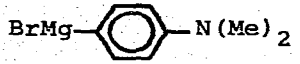
*2*

Buske and Ford reported a detailed study of Grignard reagent formation from *syn-* and *anti-3* [19,32]. Reagents were formed from ordinary "Grignard grade" turnings, from "Riecke" magnesium ($MgX_2$ + K) [4] and with Na naphthalene and $MgCl_2$. The Grignard reagent formed from *anti-3* and magnesium with nearly complete retention, and maintained configuration despite reflux in THF. Formation of reagent using sodium naphthalene-$MgCl_2$ gave little stereoselectivity, and the *syn*-halides were also less selective. Stereoselectivity was attributed to kinetic control from surface-bound radicals. Yields of Grignard reagent were variable and only fair; hydrolysis with $D_2O$ led to considerable undeuterated hydrocarbon, but little dimer. The protium was not derived from solvent, and the authors discounted adventitious moisture as its source.



*3*

In other instances, active magnesium from reduction with potassium has been used for difficult-to-prepare Grignard reagents. These include the amino-substituted reagents *4* and *5* [33].



*4*

$ClMgCH_2CH_2CH_2N(Et)_2$

*5*

$(Me)_2C=CHCH_2MgBr$

*6*

The prenyl Grignard *6* was prepared and reacted *in situ* using this active magnesium [34]. The *in situ* Barbier-Grignard technique was also used for ethoxymethylmagnesium chloride, with amalgamated magnesium [35].

Failure to form a Grignard reagent has been reported for *7*, even using active magnesium ($MgX_2$ + K), although the corresponding bromide does react [36]. Attempted Grignard formation from *8* and *9* was also unsuccessful [37].

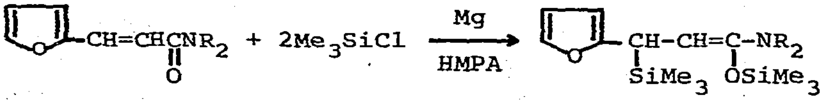
$CH_2=C=CH(CH_2)_3Cl$ *7*

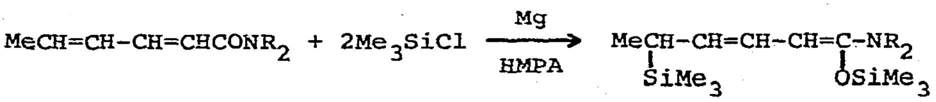
$ClCH=CHCH_2Cl$ *8*

$CH_2=CCl-CH_2Cl$ *9*

The *in situ* technique--reaction of an organic halide with magnesium in the presence of another reactant--has been quite frequently employed. Further examples are noted elsewhere in this review: amino-substituted organomagnesium compounds (section II, C, 3); di-magnesium derivatives (section II, C, 7); coupling reactions with metal or metalloid halides (section VI, D).

Chlorotrimethylsilane and magnesium metal react with a variety of organic compounds, particularly in HMPA solution. A new example reported is reaction with unsaturated amides [38].



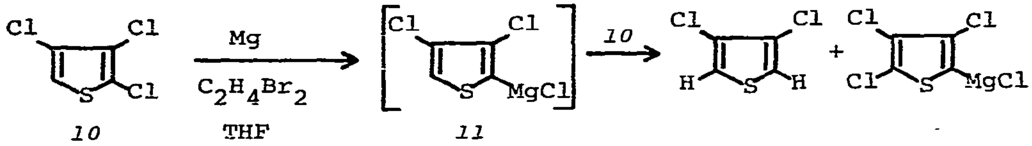


$$MeCH=CH-CH=CHCONR_2 + 2Me_3SiCl \xrightarrow[HMPA]{Mg} \underset{SiMe_3}{MeCH}-CH=CH-CH=\underset{OSiMe_3}{C}-NR_2$$

Some controversy has been generated over the possibility of silylmagnesium intermediates (see 1973-75 surveys). Rösch, Erb, and Müller have presented some supporting evidence [39]. Reaction of the chlorosilane with active (Riecke) magnesium in

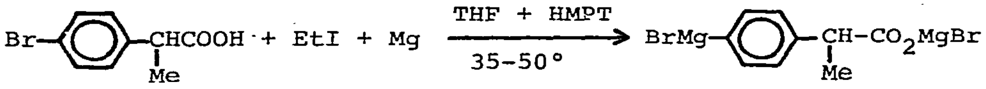
THF at -10° generated new nmr signals--most predominantly that from $Me_3SiSiMe_3$. Hydrolysis produced trimethylsilane, although attempts to isolate a silylmagnesium precursor were unsuccessful. Other experiments, in which products were derived from attack on HMPA or 1,3-diethoxypropane solvent, were explained on the basis of the same intermediate.

In an attempt to prepare a Grignard reagent from 2,3,4-trichlorothiophene, Rahman and Gilman found metallation occurring concurrently with the reaction between magnesium and starting material [40]:



Addition of $Me_3SiCl$ before completion of reaction allowed trapping of some of the intermediate *11*.

An interesting variant used for preparation of hydroxy-containing Grignard reagents has been patented [41]. A Grignard reagent was prepared in THF from a mixture of 3-chloro-1-propanol and ethyl bromide, which serves to deprotonate the OH group. A similar technique has been used for preparation of a carboxy-substituted Grignard reagent [42]:

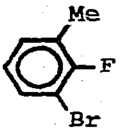


A patent was also issued on a process for preparing Grignard reagent complexes in non-ether solvents [43]. The halide (alkyl chloride or chlorobenzene) reacts with powdered magnesium in a toluene solution of $Mg(OR)(OCH_2CH_2OR')$, to which catalytic amounts of ethyl ether and $NaAlH_2(OCH_2CH_2OMe)_2$ have been added. Solutions obtained were stable for at least two weeks, and reacted normally with carbonyl compounds.

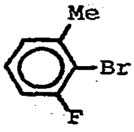
A potentially useful technique for preparation of vinylmagnesium bromide in THF [44], and a high-yield (>95%) preparation of butylmagnesium chloride in isopropyl ether [45] have been published.

An apparatus and method for a continuous manufacturing process for Grignard reagents has been published [46]. Yields of 96-98% of cyclohexylmagnesium chloride are reported; the halide is vaporized into the bottom of a column, and magnesium is replenished and Grignard solution removed at the top. A patent was also issued for a method of ether recovery in processes involving Grignard reagents from amino-substituted alkyl halides [47]. A mathematical model has been developed for control of "potentially dangerous" production processes of high reaction rate, and applied to Grignard reagent production [48].

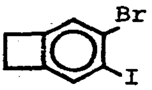
Two papers concerned with benzyne-formation from aryl dihalides and magnesium may be noted. Halides *12* and *13* led to the same mixture of trapping products as from a diazocarboxylate, indicating a free benzyne intermediate [49]. A benzyne has also been generated from *14* [50].



*12*



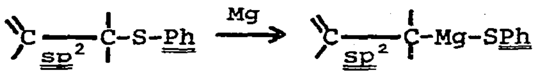
*13*



*14*

B. Other Methods of Formation

Maercker has continued his study of the formation of allylic organomagnesium compounds from nonhalogen reactants. An earlier procedure in which allylic phenyl ethers react with magnesium is substantially improved by changing to β-naphthyl ethers [51]. Addition of ethylene bromide reduces the induction period for reaction. The phenyl ether technique has been applied by Ford for formation of 2-phenylallylmagnesium phenoxide [52]. Maercker and Jaroschek have also studied the reaction of thio-ethers with magnesium [53]. The normal structural requirement for successful organometallic formation was apparently:

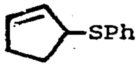


$$>C\underset{sp^2}{\text{---}}\overset{|}{\underset{|}{C}}\text{-S-}Ph \xrightarrow{Mg} >C\underset{sp^2}{\text{---}}\overset{|}{\underset{|}{C}}\text{-Mg-S}Ph$$

Three cases are of further note. From sulfide *15*, only a 12% yield of carbonation product was formed, along with 81% of coupling. The organometallic failed to give a positive Gilman test. Reaction of sulfide *16* appeared to stop at about 50% completion. An unreactive complex between reactant and the

$Me_2C=CH-CMe_2SPh$

*15*



*16*

$MeCH=CHSPh$

*17*

organometallic was proposed. Carbonation product was produced in 23% yield from *17*, although the intermediate organometallic is neither allylic nor benzylic.

During 1976, there were additional published studies of diene--magnesium compounds, reporting experimental details of their formation. The 1,3-butadiene complex was prepared by reaction with metallic magnesium in THF or tetrahydropyran, in the presence of about 1% of $I_2$ or various organic bromides or iodides [54]. No reaction was observed in ether, dioxan, or 1,2-dimethoxyethane at 80° over periods up to one week. Products containing one, two, and three butadienes per magnesium were isolated. The products formed depended upon the ratio of reactants, and their production was shown to be a sequential process of addition of butadiene units.

The reaction of myrcene (*18*) with magnesium was also studied. Formation of adduct was catalyzed in THF by ethyl bromide and transition metal halides ($FeCl_3$, $CuCl_2$, $NiBr_2$, $PdCl_2$) [55] or Lewis acids ($BF_3OEt_2$, $Al(OiPr)_3$ $ZnCl_2$) [56]. In addition to the 1:1 complex, a 2:1 complex was formed with excess alkene and the transition metal catalysts. A 1:1 adduct was also observed with *19* and magnesium [55].

*18*

*19*

Spectroscopic and chemical characterization of the diene-magnesium adducts is described in section III, D.

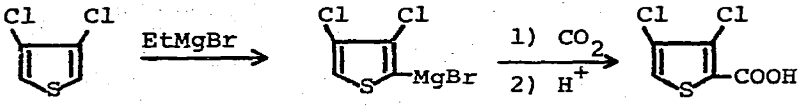
Some other reports of reaction of magnesium with organic compounds are more peripheral. Reaction of magnesium with biphenyl in liquid ammonia led to 1-, 3-, and 4-phenylcyclohexenes [57]. The reaction most probably involves the radical anion of biphenyl. Reaction of nitrosamines with magnesium (or lithium) produced the metal dialkylamide [58]:

$$2R_2NNO + 2Mg \longrightarrow 2R_2N^- + Mg^{++} + MgO + N_2O$$

Magnesium atoms, codeposited at 77°K with cycloalkanones, give products which may be attributed to a carbene [59]. Most significantly, reaction with cycloheptanone produced a small amount of norcarane (intramolecular insertion) and cycloheptane (possibly from H-abstraction by triplet carbene) along with larger amounts of cycloheptene, a pinacol, and aldol condensation products. Finely divided bulk magnesium does not lead to these products. Catalysts from magnesium or magnesium amalgam and $TiCl_3$ or $TiCl_4$ were found useful in coupling aliphatic aldehydes and ketones to pinacols [60].

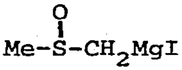
Replacement of acidic hydrogen by metallation with an organomagnesium compound has been reported in several cases noted here; other reactions in which the organomagnesium compound functions as a base are included in section VI, F.

Metallation of 3,4-dichlorothiophene by ethylmagnesium bromide has been reported [61]:



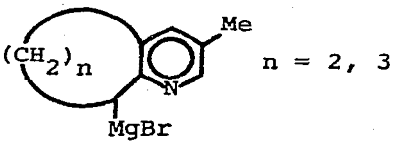
A similar metallation of 2,3,4-trichlorothiophene during its reaction with magnesium was noted above (section II, A).

Grignard reagents *20* [62] and *21* [63] were formed by



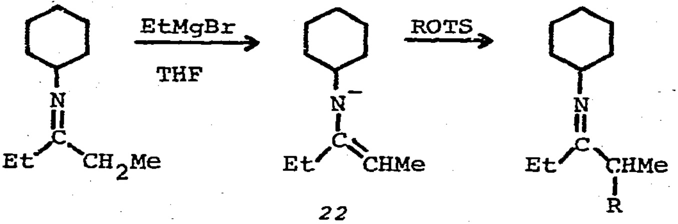
$Me-\overset{O}{S}-CH_2MgI$

*20*



*21*

magnesium-hydrogen exchange and characterized by carbonation or reaction with benzaldehyde respectively. The anion *22* has also been prepared and alkylated [64].



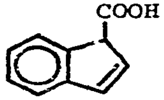
*22*

Although the formation of acetylenic organomagnesium compounds by reaction of terminal alkynes with alkylmagnesium derivatives is commonplace, the following example is included because of the unusual combination of metallation and displacement by the Grignard reagent [65]:

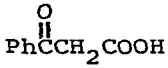
$$HC\equiv CCH_2Cl + MeMgX \xrightarrow[THF]{CuCl} XMgC\equiv C\text{-}CH_2Me$$

Kinetic studies of the metallation of acetylene are covered in section VI, F, and magnesium enolates are in II, C, 4.

Metallation of "active methylene compounds" with tertiary amines and $MgCl_2$ has been reported [66]. In this fashion, good yields of carbonation products *23* and *24* were obtained.



*23*

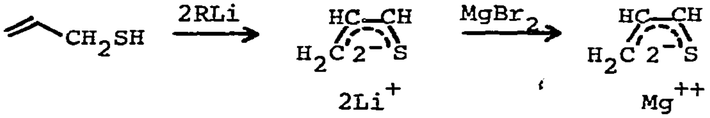


$PhC(=O)CH_2COOH$

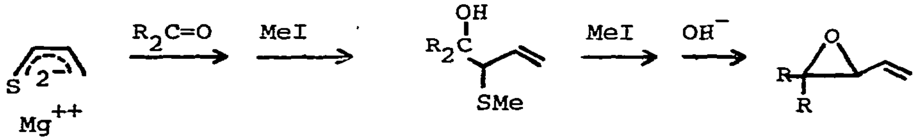
*24*

The isomerization of butenes over magnesium oxide is proposed to involve allylic anions [67]. In effect, this corresponds to metallation, producing a surface organomagnesium intermediate.

Magnesium-lithium exchange has been used by Seebach to prepare the magnesium derivative of the thioacrolein dianion [68]:

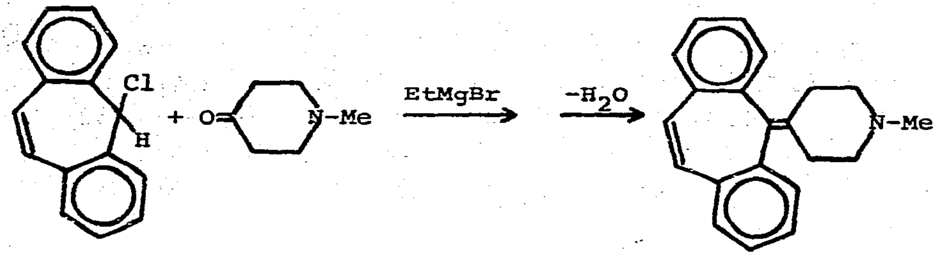


Unlike the lithium derivative, which reacts with electrophiles in the γ-position, the magnesium compound undergoes reaction with aldehydes and ketones α to the sulfur. The sequence shown leads to synthetically useful vinyl oxirane intermediates:

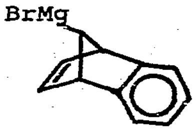


Di(cyclopentadienyl)tin undergoes exchange with cyclohexylmagnesium bromide to yield di(cyclopentadienyl)magnesium and a Sn(IV) compound of undetermined structure [69].

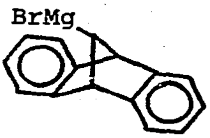
Metal-halogen exchange may also result in formation of organomagnesium compounds. As noted earlier, CIDNP polarization has been observed in the butylmagnesium bromide formed by iron-catalyzed exchange between isopropylmagnesium bromide and butyl bromide [21,26]. Some uncatalyzed exchange occurs between phenylmagnesium iodide and 1,8-diiodonaphthalene [70]. A patent abstract gives the following reaction, which may require a metal-halogen exchange [70a]:



Cycloaddition of benzyne to cyclopentadienylmagnesium bromide produced *25* [71]. The product had mostly the anti-

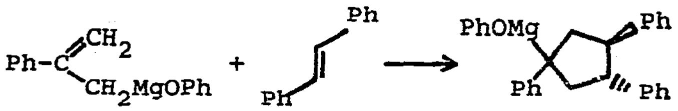


*25*



*26*

configuration shown. Reaction *via* a small fraction of $\sigma$-cyclopentadienylmagnesium compound was proposed, since alkali metal cyclopentadienides give instead phenylcyclopentadiene, while cycloaddition is observed with trimethylsilyl- and trimethylstannylcyclopentadienes. Indolylmagnesium bromide reacts similarly, forming *26*. Another cycloaddition, catalyzed by HMPA or a cryptate or aza-crown ether, has been studied [52]:



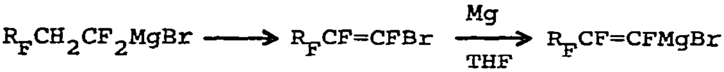
Complexes of organomagnesium with other organometallic compounds appear frequently in the patent literature as polymerization catalysts (see section VII, B). In addition to these, we may note at this point complexes formed between dialkylmagnesium compounds and either zinc or boron alkyls [72]. A hydrocarbon-soluble complex formed by preparation of alkyllithium or -sodium compounds in the presence of magnesium alkoxides may be carbonated, and is active in metallation of aromatic or heteroaromatic compounds [73].

## C. Some Organomagnesium Compounds Prepared or Studied

The major portion of the literature of organomagnesium chemistry consists of the formation and reaction of simple alkyl- or arylmagnesium halides. In this section, we survey some of the variety of less routine organomagnesium compounds which have been prepared and studied or used during the past year.

### 1. Halogen-substituted compounds

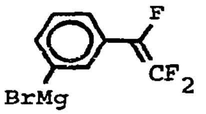
Perfluoroalkylmagnesium halides are prepared by metal-halogen exchange between perfluoroalkyl iodides and Grignard reagents or from a halide plus magnesium metal. Their preparation and reaction with N-sulfinylimines has been studied [74]. Thermal decomposition of perfluoroalkylmagnesium bromides produced perfluorovinyl bromides which were in turn, converted to Grignard reagents. The latter did not occur in ether or by exchange with an alkyl Grignard reagent [75]:

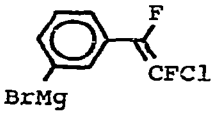


$$R_FCH_2CF_2MgBr \longrightarrow R_FCF{=}CFBr \xrightarrow[THF]{Mg} R_FCF{=}CFMgBr$$

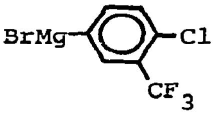
Carbonation and protolysis products had the *trans*-configuration.

The following halogenated aryl Grignard reagents have been prepared:





[76]

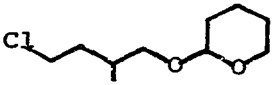


[77]

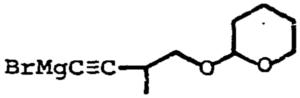
These react normally, but the first two will also undergo oligomerization. Chloro-substituted thienyl Grignard reagents and benzyne reactions from o-dihaloaromatic compounds have been mentioned in sections II, A and II, B.

### 2. Alkoxy, acetal, and hydroxy-substituted compounds

Grignard reagents with a hydroxy or carbonyl function protected as silyl ether [78] or acetal [79-82] are quite regularly encountered. Reagents with these groups in the δ-position or further removed from the metal appear to be formed and used quite routinely. However, it has been reported that chloride *27* failed to react with magnesium under normal conditions

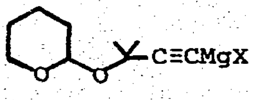


*27*

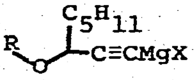


*28*

[83]. It was necessary to utilize the acetylenic organomagnesium *28* and hydrogenate in a subsequent synthetic step. A γ-alkoxy group is likewise frequently encountered [84-88], and the Grignard reagent from 1-bromo-3-phenylthiopropane has been used [89]. γ-substituted acetylenic Grignard reagents *29* and *30* are also reported [90,91].



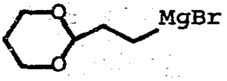
*29*



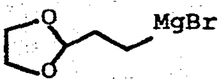
(R = THP or MgBr)

*30*

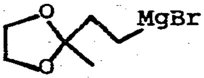
With an acetal function in the γ-position, the properties of the organometallic are modified. Stowell finds that *31* reacts cleanly with an acid chloride at -95° to produce an excellent yield of the ketone product [92]. While *31* may be prepared in refluxing THF, the dioxolan *32* decomposes above 30°. The reaction of *32* with an α,β-unsaturated aldehyde is also reported in a patent [93]. Ponaras reports that the similar dioxolan *33* may be prepared in THF below 25° by entrainment with a small amount of ethylene bromide [94]. Internal solvation by the ketal function markedly reduces its reactivity; it reacts sluggishly with ketones, selectively forms ketones by reaction with acid chlorides, and forms an ester with methyl chloroformate.



*31*

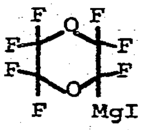


*32*

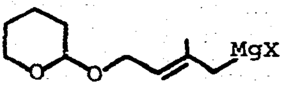


*33*

A fluorinated β-alkoxy Grignard reagent *34* has been prepared by reaction of the bromide with magnesium [95]. However, attempts to prepare Grignard reagents from hydroxy-protected 6-iodoglycosides led to coupling [96]. Compound *35*, which is the vinylog of a β-alkoxyorganomagnesium compound, has been reported in a patent [97].



*34*

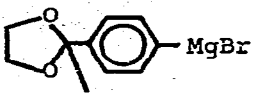


*35*

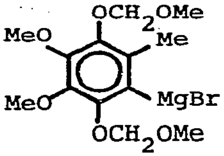
Ethoxymethyl magnesium chloride has also been used synthetically [35,98]. The reagent was prepared and used in a

Barbier-Grignard *in situ* reaction with amalgamated magnesium.

Two examples of acetal-substituted aromatic Grignard reagents are [99-101]



and



Preparation of a hydroxy-substituted Grignard reagent was noted in section II, A [41]. Another example [102] is:

$BrMgOCR_2{-}C{\equiv}CMgBr$, R = H, Me

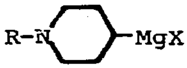
3. Amino-substituted compounds

γ-Dialkylamino Grignard reagents have appeared in a substantial number of reports. An Organic Syntheses preparation using *36* provides full experimental details [103]. Use

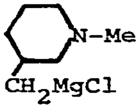
*36*

*37*

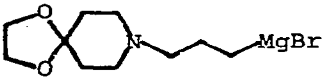
of active magnesium for the diethylamino analog was noted previously [33]. Other examples, many from the patent literature, include *37* [104], *38* [105], *39* [106], and *40* [77]. The unsaturated analog *41* also forms and reacts normally [107].



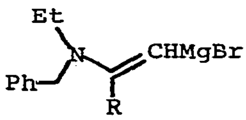
*38*



*39*

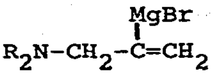


*40*



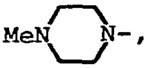
*41*

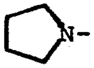
Unsaturated β-dialkylamino Grignard reagents *42* are



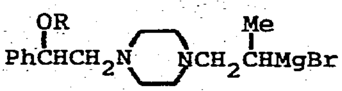
$$R_2N{-}CH_2{-}\overset{MgBr}{\overset{|}{C}}{=}CH_2$$

*42*

$R_2N$ = $Me_2N$–, $Et_2N$–, 

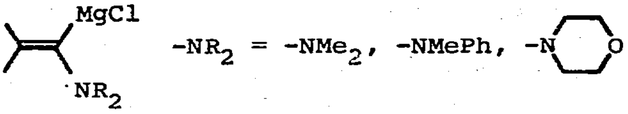
or 

reported in patent literature [108]; reaction *in situ* was used in one report [109]. The abstract of a patent appears to indicate a saturated β-dialkylamino reagent *43* [110].



*43*

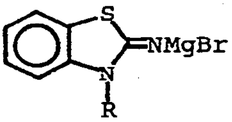
The unsaturated α-amino organomagnesium compounds *44* are acyl anion equivalents with synthetic potential [111]. Their preparation from the chloride and magnesium is accompanied by



*44*

dimer formation and "hydrolysis" product. The reagents react normally with $CO_2$, acetaldehyde, and acetic anhydride, and couple with similarly constituted aminovinyl halides. They did not react with ethyl acetate or acetonitrile.

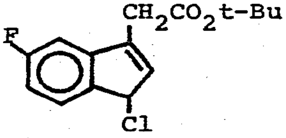
While it is not accurately an organomagnesium compound, some interesting coupling and dimerization reactions of *45* appear to involve ring cleavage and single electron transfer processes [112].



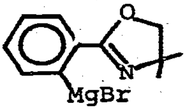
*45*

### 4. Carbonyl and carboxy-substituted compounds; enolates

In section II, A, preparation of a carboxylate-substituted Grignard reagent is described [42]. A "Grignard reaction" of the halo-ester *46* with an aldehyde is described in



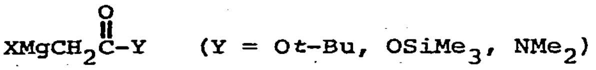
*46*

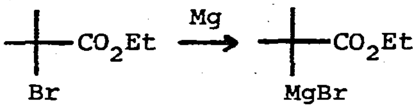


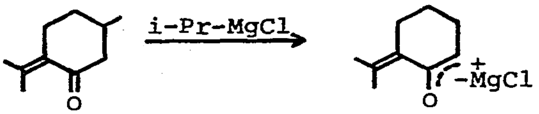
*47*

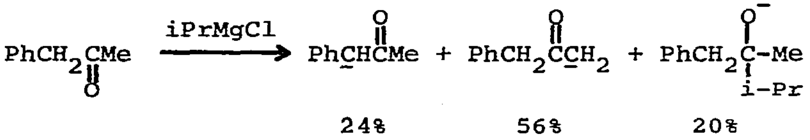
a patent [113]. In *47*, a carboxy group is protected as an oxazoline [114].

Magnesium enolates which have been prepared and studied include the following:


$XMgCH_2C(=O)\text{-}Y \quad (Y = Ot\text{-}Bu,\ OSiMe_3,\ NMe_2)$ [115]

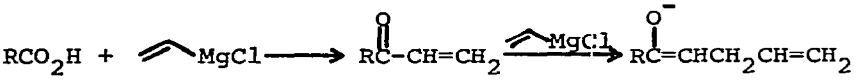

[116]


[117]


$PhCH_2C(=O)Me \xrightarrow{iPrMgCl} Ph\underline{C}HC(=O)Me + PhCH_2C(=O)\underline{C}H_2 + PhCH_2C(O^-)(i\text{-}Pr)\text{-}Me$ [118]

24% 56% 20%

$CH_2(CO_2Et)_2 \xrightarrow{EtMgBr} {}^{-}CH(CO_2Et)_2$ [119]

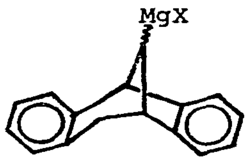

$RCO_2H + CH_2{=}CHMgCl \longrightarrow RC(=O)\text{-}CH{=}CH_2 \xrightarrow{CH_2=CHCH_2MgCl} RC(O^-){=}CHCH_2CH{=}CH_2$ [120, 121]

References [117] and [118] discuss subsequent aldol condensations. The enolate generated in references [120] and [121] is acylated on carbon and oxygen by acid chlorides, anhydrides, and esters.

### 5. Unsaturated and polycyclic compounds

A detailed preparation of diindenylmagnesium has been published [122]. Grignard reagents from p-chlorostyrene have been used to prepare unusual monomers [123-125].

Reaction of the Grignard reagent *48* with acetaldehyde and with amino ethers has been reported in patents [126,127].



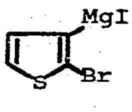
*48*

Benzonorbornadienyl Grignard reagents have been discussed in sections II, A and II, B [32,71].

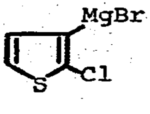
With allylic, propargyl, or allenic organometallic compounds, "allylic isomerism" of both the organometallic itself and its reaction products may be significant. Contributions to this area will be discussed in section III, D.

### 6. Heteroaromatic compounds

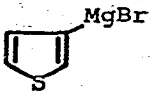
Previous mention has been made of the generation of chlorinated thienyl Grignard reagents by metallation [40, 61]. Procedures have also been published for formation of synthetically useful Grignard reagents *49* and *50* [128] and *51* [129] from the corresponding halides and magnesium. Thenyl Grignard reagent *52* has also been used [130]. The tribromoselenophene *53* undergoes halogen-metal exchange with ethylmagnesium bromide in the 2- (70-80%) and 5-positions (~10%) [131].



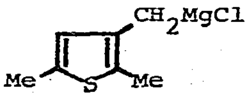
*49*



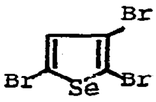
*50*



*51*

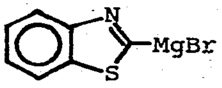


*52*



*53*

The benzothiazole Grignard reagent *54* has been prepared [132].



*54*

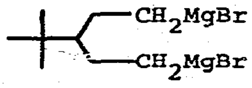
### 7. Di-magnesium derivatives and other metal-substituted or metallo-organomagnesium compounds

Di-Grignard reagents *55* (X = Br) have been prepared

$XMg(CH_2)_nMgX$

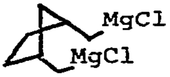
*55*

*56*

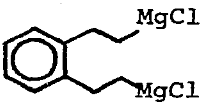


*57*

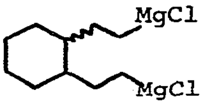
and converted into tin (n = 4) [133,134], platinum (n = 4, 6) [135], and arsenic (n = 5) [136] metallocycles. Magnesiacyclopentane was also studied [133]. Grignard reagent *57* [137], and the primary-secondary and secondary-secondary di-Grignard reagents corresponding to *55* (n = 4) were prepared [135]. Whitesides and Gutowski studied Grignard reagents *55*, n = 4-12, in coupling to cycloalkanes [138]. They found the best yields from the chlorides in refluxing THF; poorest results were obtained with n = 8 or 9, and the highest with n = 4-6. They also reported the interesting reagents *58-61*. The



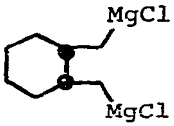
*58*



*59*



*60*



*61*

unsaturated allylic di-Grignard reagent *62* was silylated *in situ* [139].

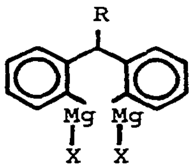
$BrMgCH_2CH{=}CHCH_2MgBr$ *62*

$BrMgCH_2MgBr$ *63*

Methylenebis(magnesium bromide) *63* has been studied as an alternative to the Wittig reagent in carbohydrate chemistry (see section IV, D). The reagent was prepared from $CH_2Br_2$ with a catalytic amount of $I_2$ and $HgCl_2$. Best results were obtained when the Grignard was used *in situ* [140].

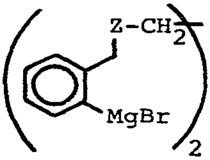
Diene-magnesium adducts, discussed in sections II, B and III, D, are also organo-bis-magnesium derivatives.

Aromatic di-Grignard reagents *64* [141] and *65* [142] have been reported.



R = H, X = Cl
R = Ph, X = Br

*64*



Z = NMe
or O

*65*

Trialkylmetal-substituted Grignard reagents *66-71* have been prepared and studied:

$R_3Sn(CH_2)_nMgBr$ R = Me, Bu, Ph; n = 3-5 [143]

*66*

$RSiMe_2CH_2MgCl$ *67*, R = Me [144]; *68*, R = $Me_3Si$, $Me_3SiO$- [145]

$Me\{SiMe_2C\equiv C\}_nMgBr$ *69* [146]

$R_3GeC\equiv CMgBr$ R = Et, Ph *70* [147]

$R_2Ge(C\equiv CMgBr)_2$ *71* [147]

The reaction of carborane Grignard reagents $RCB_{10}H_{10}CMgBr$ and $RCB_{10}H_{10}CCH_2MgBr$ with phenyl isocyanate was reported [148].

Synthetic procedures for preparation of transition metal-magnesium derivatives have been presented. These complexes are thermally stable but pyrophoric, and couple with alkyl halides to produce alkyl transition metal compounds [149].

$$[cpFe(CO)_2]_2 \xrightarrow[THF]{Mg\ (Hg)} (THF)_2Mg[Fe(CO)_2cp]_2$$

$$Co_2(CO)_8 \xrightarrow[pyridine]{Mg\ (Hg)} (py)_4Mg[Co(CO)_4]_2$$

$$cpMo(CO)_2PBu_3I \xrightarrow[THF]{Mg\ (Hg)} (THF)_4Mg[Mo(CO)_2cpPBu_3]_2$$

$Mo(cp)_2H_2$ and $W(cp)_2H_2$ react with a variety of Grignard reagents to form complexes containing magnesium and molybdenum or tungsten [150]. The molybdenum complex with cyclohexylmagnesium bromide was determined by X-ray crystallography to be a bridged dimer with Mo-Mg bonds. Local disorder prevented a complete X-ray structure of the isopropyl analog. These complexes are highly reactive, giving products of substitution or addition on the molybdenum or tungsten with $CO_2$, CO organic halides, and butadiene.

Other organometallic complexes with likely metal-magnesium bonds are reported:

$$NbCl_4\cdot 3(pyridine) + (PhCH_2)_2Mg \xrightarrow[0°]{C_6H_6}$$

$$NbCl\cdot 1.5(PhCH_2)_2Mg\cdot 1.5(pyridine) \xrightarrow{I_2}$$

$$3PhCH_2I + NbClI_3 + 3/2MgI_2 \qquad [151]$$

$$cpRe(CO)_2I_2 + RMgX \longrightarrow cpRe(CO)_2IMgX \qquad [152]$$

Reaction of the latter with acid chlorides acylated the rhenium.

Complex materials have also been obtained from titanium compounds. A substance represented as $Ti(MgCl)_2 \cdot TiCl_2$ was formed from $TiCl_3 \cdot 3THF$ and magnesium. The influence of oxidizing agents ($C_3H_7Cl$) and reducing agents ($C_3H_7MgCl$ and Na) on the nitrogen-fixing properties of this complex were studied [153]. Another nitrogen-fixing system from $[(\eta_5\text{-cp})_2TiR]_2N_2$ and $i\text{-}C_3H_7MgCl$ has been studied [154]. A complex represented as $MMg_2Cl_2(THF)N$ (with M = Ti or V) is formed from $MCl_4$ and Mg; it reacts with $CO_2$ to give isocyanate complexes [155].

Triphenylsilyl- and triphenylgermylmagnesium derivatives have been synthesized by a metal exchange:

$$Ar_3M\text{-}Co(CO)_4 \xrightarrow{RMgBr} Ar_3M\text{-}MgBr \qquad (M = Si,\ Ge)$$

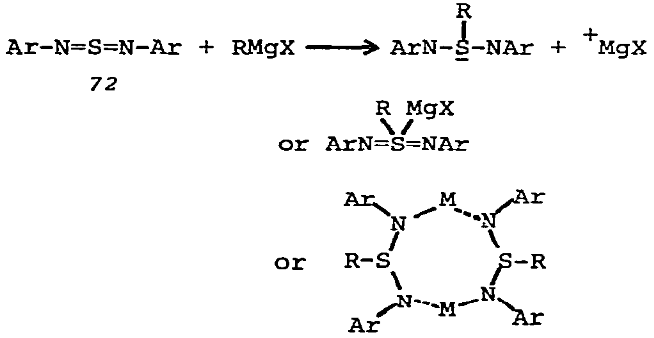
The products were characterized by hydrolysis ($H_2O$ and $D_2O$), alkylation with benzyl chloride or allyl bromide, or reaction with $Me_3SiCl$. Retention of configuration was found [156]. Evidence for a trimethylsilylmagnesium compound has been cited in section II, A [39].

Reaction of $tert\text{-}C_4H_9PCl_2$ with Mg in THF [157] gave the cyclic trimer $(tert\text{-}C_4H_9P)_3$.

"Ate"-complexes from methylcopper and primary, secondary, tertiary, or aryl Grignard reagents in THF are formed in high yield [158]. These complexes are soluble at 25°, but form a suspension at −78°. They have substantially greater thermal stability than $LiR_2Cu$ compounds. The complexes form ketones with acid chlorides at −78°, selectively transferring the other organic function in preference to methyl. They are also usefully reactive toward alkyl halides and $\alpha,\beta$-unsaturated ketones.

### D. Analysis of Organomagnesium Compounds

Addition of organomagnesium or -lithium compounds to intensely colored sulfurdiimines *72* produces a colorless adduct.



$$Ar\text{-}N{=}S{=}N\text{-}Ar + RMgX \longrightarrow ArN\text{-}\overset{R}{\underline{S}}\text{-}NAr + {}^{+}MgX$$

*72*

pronounced loss of color at the equivalence point, which does not occur with alkoxide or oxide, makes the reagent useful for titrimetric analysis of Grignard reagents [159,160].

## III. Spectra, Properties, and Structures of Organomagnesium Compounds

### A. Spectroscopic Studies

Infrared and Raman spectra of diethylmagnesium and its $MeCD_2$- and $CD_3CH_2$- isotopic analogs have been obtained by Kress and Novak at 90 and 300°K [161]. Fundamental modes of the ethyl groups and the carbon-magnesium chains were assigned. The spectrum at 300°K was consistent with an infinite chain structure, but at 90°K there appear to be differences in chain configuration. The C-Mg force constant is 1.05 mdyne/A°.

Kress has also determined Raman spectra of diethylmagnesium in ether between 160 and 300°K [162]. Bands in the low-frequency region were assigned to the C-O-C deformation of free ether (440 $cm^{-1}$), to the ring-stretching frequency of the dimer (360 $cm^{-1}$) and the symmetrical CMgC stretch of the monomer (410 $cm^{-1}$). From these, a concentration-dependent equilibrium constant and thermodynamic parameters were derived:

$$(Et_2Mg\cdot ether)_2 + 2\ ether \rightleftharpoons 2(EtMgBr\cdot 2\ ether)$$

$$d \quad + 2\ s \quad \rightleftharpoons \quad 2\ m$$

$$K_c = \frac{m^2}{ds^2c} = 0.05 \text{ at } 296°K \qquad \Delta H° = -2300 \text{ cal/mol}$$

(c = total diethylmagnesium concentration)

The effects of concentration, temperature and the R/Cl ratio on the proton nmr spectrum of *tert*-BuMgCl in THF were studied [163]. Separate resonances were observed for RMgCl and $R_2Mg$ up to at least 60°. Results were interpreted in terms of the equilibrium:

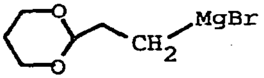
$$2\,t\text{-}BuMgCl \rightleftharpoons (t\text{-}Bu)_2Mg + MgCl_2$$

Precipitation of $MgCl_2$ occurred below 10°. Variations in the equilibrium constant and thermodynamic parameters with temperature, concentration, and the R/Cl ratio were attributed to differences in the solvation number.

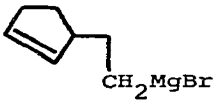
Infrared, Raman, and nmr spectra of γ-picoline complexes of ethyl- and phenylmagnesium bromide have been reported [164].

Infrared and nmr spectra of complexes between magnesium halides and 4-substituted pyridines have been determined [18]. Frequency shifts and the variations of ir intensity of Mg-N frequencies indicated strong bonding and the lack of back-donation.

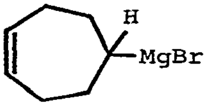
The nmr spectra of some organomagnesium compounds have been determined in conjunction with other studies. These include *73* (t, $\delta$ -0.7 ppm) [92]; *74* (t, $\delta$ -0.5 ppm, $J$ = 8.5 Hz) [165]; *75* (apparent pentuplet, $\delta$ +0.5 ppm, $J$ = 5.5 Hz) [165].



*73*



*74*



*75*

In a photochemical rearrangement study (see section VII, A), ultraviolet absorption bands of allylic Grignard reagents have been reported [166]. Allylmagnesium bromide and methallylmagnesium chloride have absorption at 246 nm ($\varepsilon$ 4300) and 251 nm ($\varepsilon$ 4100) respectively.

Spectra of allylic organomagnesium compounds and diene—magnesium adducts are discussed in III, D. A number of CIDNP studies of organomagnesium reactions have been reported. These are summarized elsewhere in this survey with the appropriate reactions: sections II, A (formation), IV, E (reaction with acyl halides), VI, A (with alkyl halides), VI, E (with peroxides), and VII, D (thermal decomposition).

## B. Other Physical Measurements

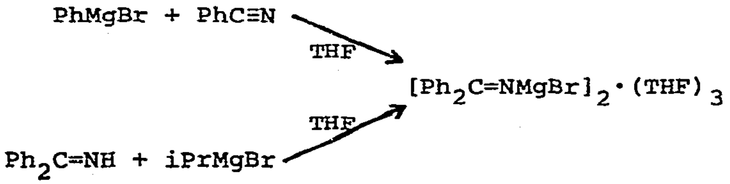
The heat of formation of butylmagnesium chloride has been determined as -107.6 ± 0.5 kcal/mol [167].

Oxidation potentials of a variety of organometallic compounds were determined [168]. The electron-transfer reaction with polynuclear aromatic hydrocarbons was used as a probe, and electrochemical techniques were used to monitor formation of the aromatic radical anion. In some cases, a second wave indicated reduction to the arene dianion. Results found were: i-PrMgCl and EtMgCl ~ -2.6 v; $C_2H_3MgCl$ < -2.5; EtMgBr < -2.45; BuMgCl ~ -2.45; MeMgCl < -2; PhMgCl and MeMgBr > -2. Basicities of alkylmagnesium halides and dialkylmagnesium compounds were also studied electrochemically [169]. Halide ion decreased the basicity of the solutions by displacement of the Schlenk equilibrium. The titration curve of $R_2Mg$ with alcohol or aniline had two breaks, indicating sequential protolysis of the alkyl groups with different basicity.

Molecular association studies showed the 2:1 butadiene—magnesium complex (see section III, D) to have a molecular weight of about 3000, corresponding to an i-value of about 11 [54].

A phase diagram was reported for the system diethylmagnesium-diethyl ether in the range from 0 to 50 mol percent diethylmagnesium [162]. A triple point occurs at about -70° and a mol fraction of about 24% diethylmagnesium. At higher temperature and concentration, the solution is in equilibrium with crystals of the dimer; below the triple point, the monomer crystallizes.

X-Ray crystallography has been used to determine the structure of the adduct between phenylmagnesium bromide and benzonitrile [170]. The magnesium atoms were bridged by two $Ph_2CN$ groups and by one of the THF molecules with long bonds. The magnesiums are thus pentacoordinated; the Mg-Mg distance is 2.89 Å. A dimeric adduct with only two THF molecules crystallized from benzene, but its structure was not yet determined.



The structure of a complex from cyclohexylmagnesium bromide and $Mo(cp_2)H_2$ has also been determined (see section II, C, 7) [150].

## C. Theoretical Studies

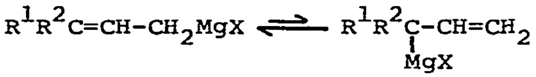
*A priori* calculations of the structure of unsolvated monomeric MeMgF and MeBeF have been reported [171]. Linear MeMgF is predicted to have a dipole moment of 2.38 D, and C-Mg and MgF bond lengths of 2.08 and 1.78 Å; the latter is very close to that observed for $MgF_2$ (1.77 Å). The highest occupied molecular orbital has its largest contribution from $C_{2p}$. Population analysis places net charges of -0.55 and -0.78 on methyl and fluorine, and +1.33 on magnesium.

A new non-empirical electronegativity scale is based on floating spherical Gaussian orbital calculations [172]. Electronegativities of magnesium, carbon, bromine, and chlorine on this scale are 1.24, 2.35, 2.52, and 2.84; for comparison the Pauling scale gives 1.31, 2.55, 2.96, and 3.16, and the Allred-Rochow scale gives 1.23, 2.50, 2.74, and 2.83, respectively.

*Ab initio* calculations for α-oxa and α-thia carbanions led to the conclusions: adjacent sulfur does not utilize d-p π-bonding; polarization of the electron-distribution by the anionic charge is important; relative anion-stabilizing effects should be in the order OH < OMe < SH < SMe; stereo configuration is important, with conformations having a lone pair *anti* to the carbanionic electron pair less stable; and similar results apply to lithium (and presumably also magnesium) derivatives [173].

### D. "Allylic Isomerism" in Allylic and Related Organomagnesium Compounds

Nmr spectra of allylic Grignard reagents, mono- or di-substituted in the 3-position, indicate the presence of only the primary isomer *76* within the limits of detection [252.



$$R^1R^2C{=}CH{-}CH_2MgX \rightleftharpoons R^1R^2\underset{\displaystyle MgX}{C}{-}CH{=}CH_2$$

*76* *77*

Rapid *cis-trans* equilibration *via 77* occurs even at low temperatures. The Z(*cis*)-configuration of *76* is preferred in the absence of large steric effects.

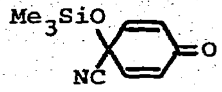
Reaction of crotyl Grignard reagents (*76*, $R^1$ = Me, $R^2$ = H) with $R_3MX$ (where R = Me, Ph and M = Si, Ge, Sn, Pb) gave a mixture of crotyl and methallyl products [174,175]. The crotyl isomer was favored for Si and formed exclusively for Pb; for Ge and Sn the methallyl predominated. There was a slight *trans* preference with Si (~3:2) and Ge, *cis* with Pb. In reaction with $Me_3SiCl$, the product was independent of starting material, solvent (ether *vs* THF) and order of addition; *in situ* reaction produced the same mixture.

Grignard reaction of *78* with silanes led to products from reaction at the primary carbons [139].

$$BrCH_2CH{=}CHCH_2Br + R_3SiCl \xrightarrow[THF]{Mg} R_3SiCH_2CH{=}CHCH_2SiR_3$$

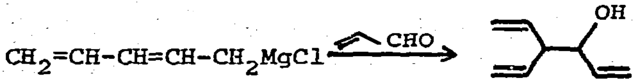
*78*

With the prenyl Grignard reagent (*76*, $R^1$ = $R^2$ = Me), the only product isolated from reaction with $Me_3SiCl$ was the "unrearranged" prenylsilane [176]. Reaction at the primary carbon was also observed in addition of the prenyl Grignard reagent to bicyclic ketones (see section IV, B) [177]; however, an *in situ* reaction of prenyl bromide with *79* and related ketones occurred at the tertiary position [34].



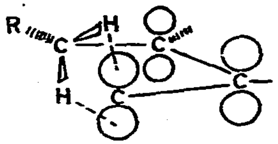
*79*

Reaction of a variety of substituted allylic Grignard reagents with a C=N function produced a mixture of "linear" (unrearranged) and "branched" (rearranged) products, depending upon the degree of steric hindrance at the γ-carbon [178]. Addition of the pentadienyl Grignard reagent produced the secondary product [178a]:

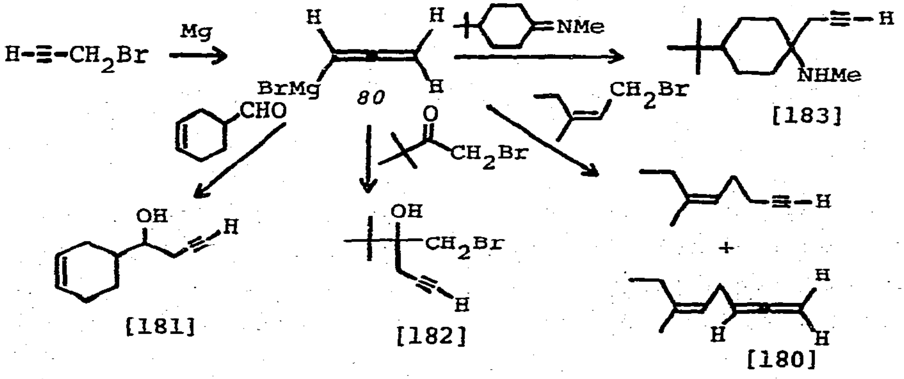


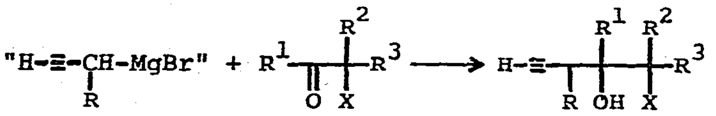
Protolysis of allylic Grignard reagents with strong acids, water, alcohol, or hindered amines led to protonation at $C_3$ (allylic rearrangement), while unhindered amines gave mostly the product of protonation at $C_1$ [25].

A study of allylic derivatives of several metals has shown that the slight equilibrium preference for the Z(*cis*)-isomer in the Grignard reagent is much stronger with the more electropositive alkali metals [179]. Stabilization of a Z-carbanion in an initmate ion pair by hydrogen bonding from the *cis*-alkyl group was proposed:



The Grignard reagent from propargyl bromide is represented [180] as the allenic structure *80*. Reaction products obtained were:

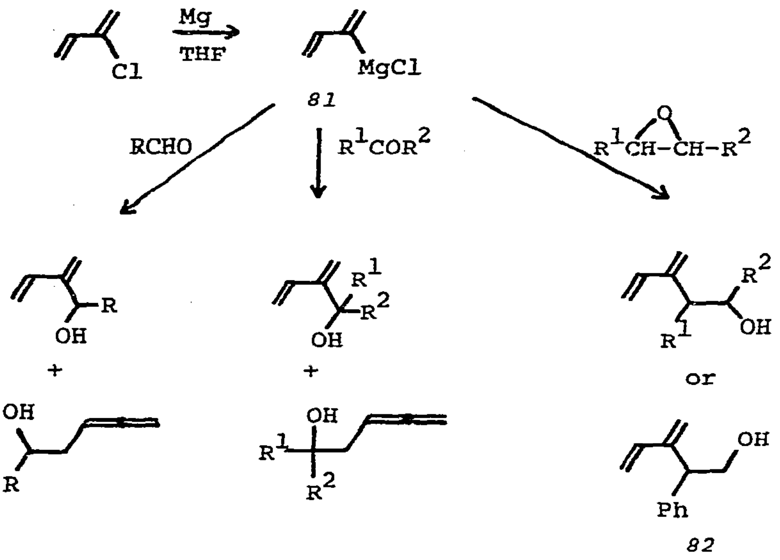




$$\text{"}H\text{-}\equiv\text{-}CH(R)\text{-}MgBr\text{"} + R^1\text{-}C(=O)\text{-}C(R^2)(X)\text{-}R^3 \longrightarrow H\text{-}\equiv\text{-}CH(R)\text{-}C(R^1)(OH)\text{-}C(R^2)(X)\text{-}R^3$$

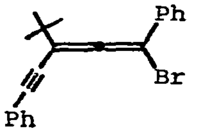
[184]

The Grignard reagent from chloroprene, which appears spectroscopically to have structure *81*, leads to a mixture of products, depending on the reactant [185,186]. Allene products are formed in larger amount with benzaldehyde, acetophenone, benzophenone, or pinacolone. It was concluded that softer and



less hindered electrophiles prefer reaction at the 2-position. Styrene oxide forms *82*, along with minor allenic products.

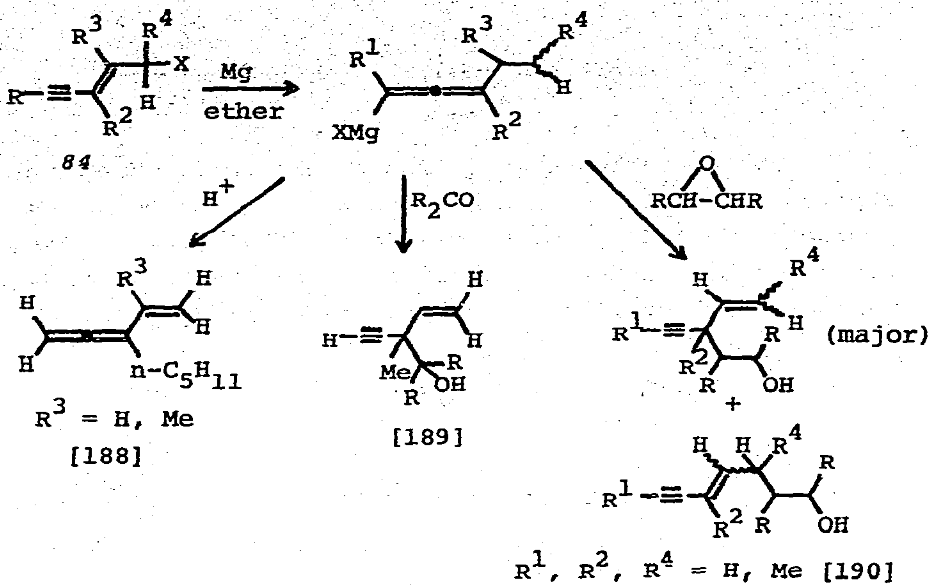
The Grignard reagent from *83* gives an allenic carbonation product [187].



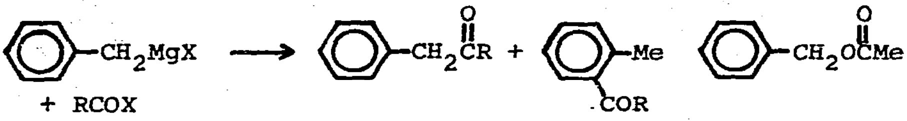
*83*

Several Grignard reagents from halides of the type *84* have been prepared. Some results of reactions are shown below.

Two reports have appeared on the formation of isomeric products from acylation of benzyl Grignard reagents. With a variety of acyl halides [191], yields of the "abnormal" product *85* increased with (a) decreasing basicity of the solvent, (b) with decreasing ionic character of the benzyl-metal bond (Li < Mg < Al), and (c) with increasing reactivity of the

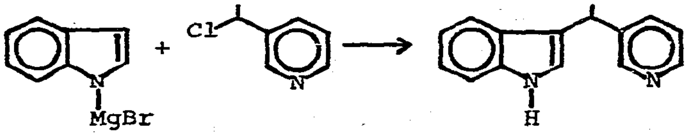


acyl halide. Benzylmagnesium chloride with acetic anhydride also gave *86*, produced in a radical chain mechanism requiring $O_2$ [192]. In HMPA, no *85* was formed. Excess magnesium had no effect.

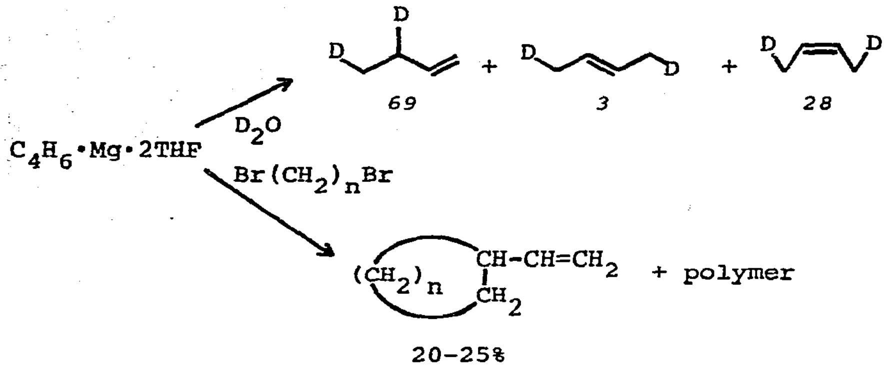


*85* *86*

A coupling reaction of indolylmagnesium bromide [193] and its reaction with oxalate esters [194] have been studied.

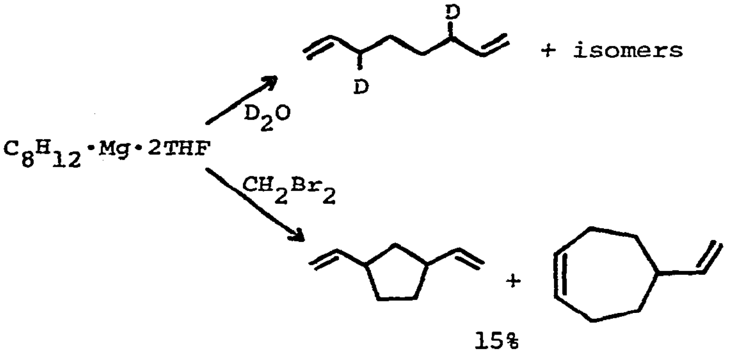


The characterization of butadiene-magnesium adducts has utilized chemical and spectroscopic techniques (see section II, B for preparation) [54,195]. The 1:1 adduct was insoluble in THF, and had C-C stretching bands at 1575 (*cis*) and 1604 cm$^{-1}$ (*trans*). Deutrolysis and alkylation with dihalides gave the following:



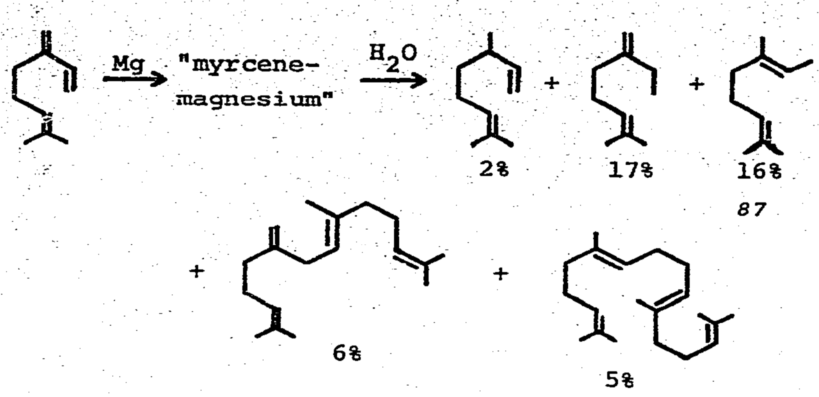
A polymeric chain structure Mg$\leftarrow$CH$_2$-CH=CH-CH$_2$-Mg$\rightarrow_n$ with THF coordinated to magnesium was proposed.

The 2:1 adduct also had ir bands indicating double bonds (1593 and 1619 cm$^{-1}$), a degree of association of about 11 in THF, and an nmr spectrum resembling that of crotylmagnesium compounds (1° C-Mg, predominantly *cis* double bond, and no change in appearance between -80 and +50°). Deuterolysis and alkylation produced the products illustrated:

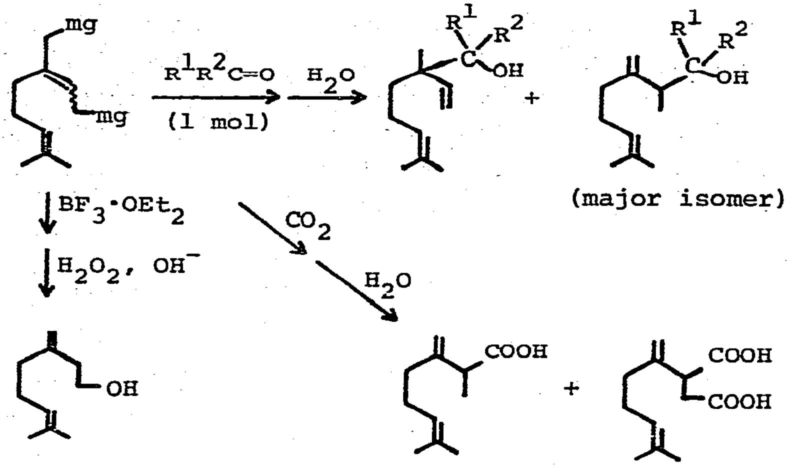


The 3:1 adduct had similar spectral properties. However, it was hydrolyzed to dideutrated products containing a ring, indicating cyclization by intramolecular addition of an allylic organomagnesium function to the double bond. It was unreactive to addition of further butadiene units at 80°, but did form a 4:1 adduct at 120°. The cyclization rearrangements are discussed further in section VII, A.

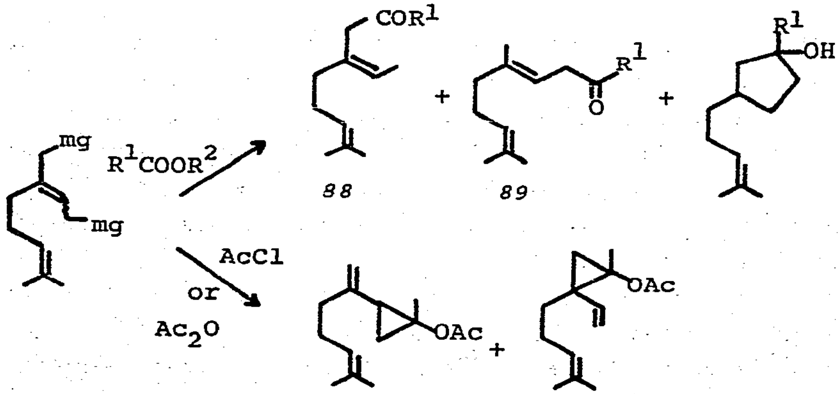
The adduct of myrcene with magnesium [55,56,196] was hydrolyzed to a mixture of monomeric and dimeric hydrocarbons; product *87* and the dimers were reported only when transition metal catalysts were used in the preparation [55]. A cyclic structure was proposed for the "adduct." The 1:1 compound was



characterized chemically:

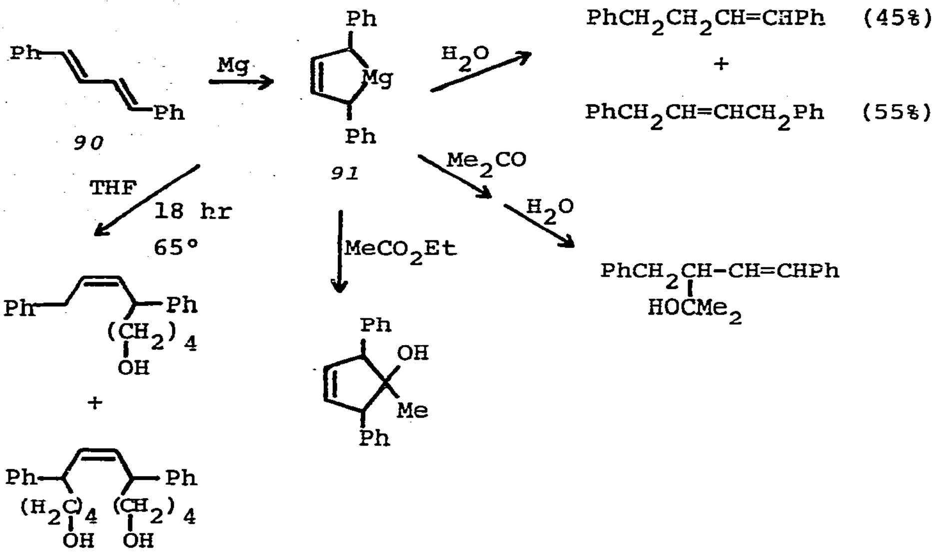


With acetonitrile and ethylene or propylene oxide, products similar to the aldehyde and ketone products were formed. Esters and acetyl chloride or acetic anhydride reacted as follows:



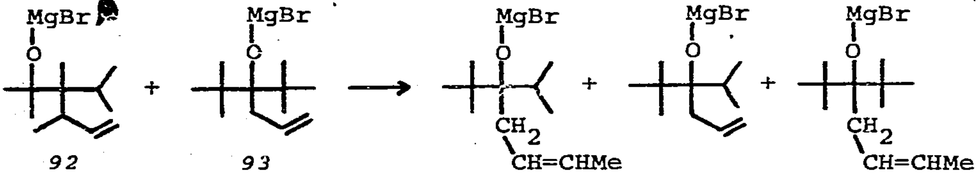
Products *88* and *89* were found with lower temperatures and shorter reaction times.

Infrared spectra of the 1:1 adduct between *90* and magnesium indicated a *cis*-double bond; the cyclic structure *91* was proposed [55,196]:

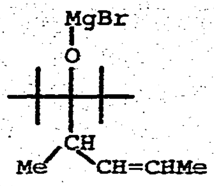


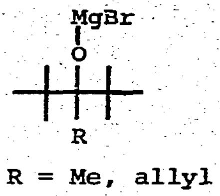
## E. Reversibility in Reactions of Allylic Organomagnesium Compounds

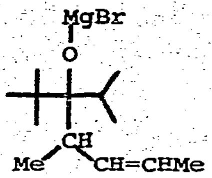
Two publications appeared during 1976 giving additional documentation about the reversibility of addition of allylic Grignard reagents to ketones. Benkeser and Siklosi showed that addition of the unsubstituted allyl Grignard reagent is reversible by observation of allyl-crotyl exchange between *92* and *93* [197]. Also, when *93* was heated in the presence of the corresponding alcohol, di-*tert*-butyl ketone was isolated.



Holm studied the alkoxide *94* [198]. Loss of α,γ-dimethylallylmagnesium bromide was followed by heating in the presence of methyl- or allylmagnesium bromide, which produced *95*, or in the presence of t-butyl isopropyl ketone, which gave *96*. Also, a 1:1 *cis:trans* mixture of *94* formed a 1:3 equilibrium mixture at the same rate. The addition of allyl or α,γ-dimethylallylmagnesium


*94*

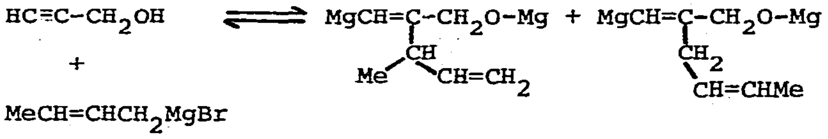

*95*


*96*

bromide to di-*t*-butyl ketone is less exothermic than addition of methylmagnesium bromide to the same ketone (-108 and -106 *vs* -150 kJ/mol), or the addition to acetone (-178 kJ/mol).

ΔH for formation of *94* was also determined as the differe between $\Delta H^{\ddagger}$ for the addition (31 kJ/mol) and the "retro-addition (120-130 kJ/mol).

Reversibility has also been found in the addition of crotylmagnesium bromide to propargyl alcohol [199]. The


*97* *98*

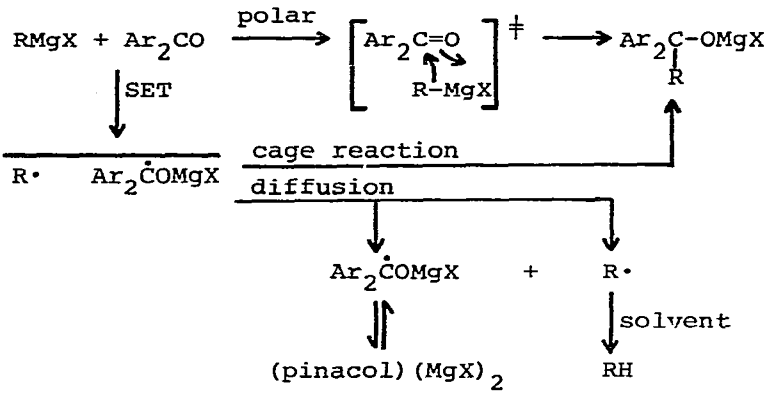
product mixture formed after 3 hr at 20° (*97:98* = 72:28) changed after 24 hr at 35° (*97:98* = 54:36).

## IV. Reactions of Organomagnesium Compounds with Carbonyl Functions

### A. Mechanism of the Grignard Addition

The dissertation of T. Holm, "Thermochemical and Reaction Kinetic Studies on Grignard and Alkyllithium Reagents" has been published [17]. Major portions of this work have appeared in earlier publications. The role of single electron transfer processes has been reviewed [8].

Ashby and coworkers have reported on the effect of transition metal catalysts on the formation of pinacols during the reaction of 2-methylbenzophenone with methylmagnesium bromide [30]. If the magnesium had greater than 20 ppm of iron or other first-row transition elements, substantial amounts of pinacol were formed in reactions run at high Grignard reagent concentration. There was a direct relationship between the concentration of transition metal and the amount of pinacol formed, or epr or uv observation of the ketyl. In a reaction at low temperature, addition and pinacol formation occurred in constant ratio throughout the course of the reaction. Pinacol formation was catalyzed by added salts of transition elements (only first row ones were effective). The effectiveness followed the trend V $\lll$ Fe $\ggg$ Ni. The oxidation state of the metal was unimportant. A variety of complexing agents were ineffective at inhibiting the transition metal effect. The iron catalyst also appeared to increase the rate of normal addition. The stereochemistry of pinacol formation was also investigated. The authors favored a mechanistic scheme similar to that proposed earlier by Blomberg and Mosher, in which a reduced iron species may be the agent which transfers an electron to ketone:

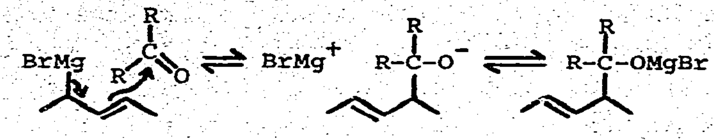


Another side product, 2-methylbenzhydrol, was formed by reduction of ketone by small amounts of a magnesium hydride species generated during Grignard reagent formation (see section II, A).

Holm [198] has reported rates and enthalpies of reaction of some allylic Grignard reagents with ketones [pseudo first order rate constant ($sec^{-1}$) with 0.05 M ketone in ethyl ether at 20°; ΔH(kJ) in parentheses]:

| | $Me_2CO$ | i-PrCO-t-Bu *(99)* | $t\text{-}Bu_2CO$ *(100)* | $Ph_2CO$ |
|---|---|---|---|---|
| $CH_2CHCH_2MgBr$ | $>10^4$(-178) | $>10^4$ | $>10^4$(-108) | (-157) |
| $MeCH{=}CHCH_2MgBr$ | $>10^4$ | 64(-105) | 19 | |
| $MeCH{=}CHCHMeMgBr$ | $>10^4$ | 100 | 2.3(-106) | |
| MeMgBr | -- (-204) | -- | -- (-130) | (-171) |

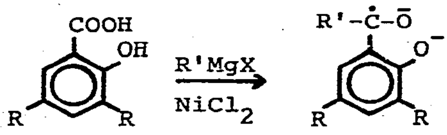
Reaction of crotylmagnesium bromide with *99* and α,γ-dimethylallylmagnesium bromide with *100* had $\Delta H^{\ddagger}$ of 27 and 31 kJ/mol respectively. The reverse of the latter had a positive $\Delta S^{\ddagger}$ of 25-42 J/mol °C; this was considered inconsistent with a cyclic $S_Ei'$ transition state, and more appropriate for the $S_E2'$ process:



A rate-limiting single electron transfer step, followed by radical combination, was felt to be most consistent with reactivities. An intense yellow color attributed to an ion radical was observed during reaction of the α,γ-dimethylallyl Grignard reagent with *100*.

Benzophenone ketyl forms a stable complex with $Mg^{++}$ at concentrations of $2.9 \times 10^{-5}$ to $2.4 \times 10^{-4}$ $\underline{M}$ in THF [200]. Using the epr spectrum as a quantitative standard, its absorption spectrum was shown to have ε 18,000 at 612 nm. With lower temperature or increased solvent polarity, a red shift was observed.

Reaction of *101* with Grignard reagents in the presence



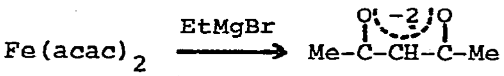
*101* *102*

R = i-Pr, t-Bu

R' = Et, $C_2D_5$, i-Bu, n-Pr

of $10^{-4}$ $\underline{M}$ $NiCl_2$ produced ketyls *102*, which were identified *via* their epr spectra [201].

Transition metal diketone complexes also reacted by electron transfer from Grignard reagents to generate radical dianions of the diketone [202]. For example:



$$Fe(acac)_2 \xrightarrow{EtMgBr} Me-\overset{O}{C}-CH-\overset{O}{C}-Me$$

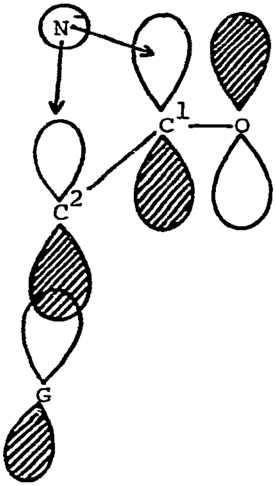
The dianion was identified by a septet of doublets in the epr spectrum. Methylmagnesium bromide reacted more slowly.

Several observations of potential mechanistic significance may be noted. Reaction of butylmagnesium bromide with $PhCO(CH_2)_4COOH$ gave a 22% yield of reduction product in addition to 70% of normal addition to the ketone [203]. The yield of addition product in reaction of 2-methylcyclohexanone with isopropyl Grignard reagents varied from 14% with the iodide to 41% with the chloride [204]. The rate of addition of a γ-ketal-substitute Grignard reagent to cyclopentanone was significantly accelerated in benzene-THF compared with THF alone [94].

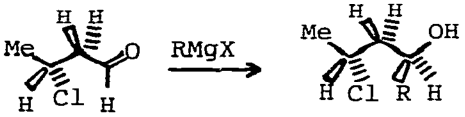
## B. Stereochemistry of Reaction with Aldehydes and Ketones

### 1. Stereochemistry with aldehydes and acyclic ketones

In a recent reconsideration of models for 1,2-asymmetric induction, Anh has calculated the energies of 24 different transition state conformations for reaction of MeCH(Cl)CHO or MeCHEtCHO with a nucleophile (represented as $H^-$) by an STO-3G *ab initio* method [205]. It was concluded that the conformations included in the approach by Felkin [Tetrahedron Lett., (1968) 2205 and 2201] correspond most closely to the lowest energy transition states. Results are influenced to only a minor degree by electrophilic assistance at the carbonyl oxygen, variation of the angle of attack, or solvation of the nucleophile. The most important factor appears to be interaction with the σ* orbital of an anti-periplanar group on the α-carbon:

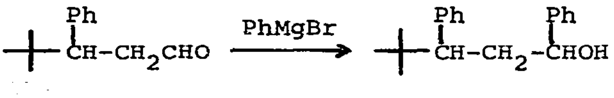


Up to 70% stereoselectivity observed in the reaction:



was explained by the model shown [206,207].

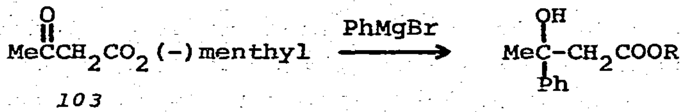
The addition reaction:



$$+\overset{Ph}{C}H-CH_2CHO \xrightarrow{PhMgBr} +\overset{Ph}{C}H-CH_2-\overset{Ph}{C}HOH$$

produced a mixture which is 24% erythro:76% threo. Two models were discussed: attack of a dimeric Grignard species, and attack of monomeric organomagnesium on aldehyde complexed second organomagnesium monomer [208]. On the basis of ste interactions evaluated for attack on a variety of conforme the former was preferred.

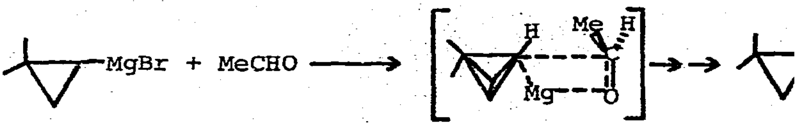
Addition to the keto ester *103*, with and without ca by CuCl, $FeCl_3$, $CoCl_2$, or NaH, produced an excess of 2.5 t of the (S)-configuration. Attack by the Grignard reagent o 6-membered cyclic inolate was proposed [209].



$$\mathrm{Me}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CH_2CO_2(-)menthyl} \xrightarrow{\mathrm{PhMgBr}} \mathrm{Me}\underset{\underset{\mathrm{Ph}}{|}}{\overset{\overset{\mathrm{OH}}{|}}{\mathrm{C}}}\mathrm{-CH_2COOR}$$

*103*

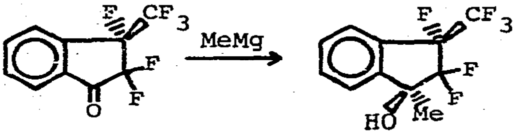
In the addition reaction below, *104* was formed in a



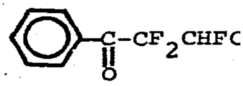
*10*

65:35 ratio over its diastereomer [210].

Addition to ketone *105* produced only one diastereom in 78% yield, while a 35:65 mixture of diastereomers resul with *106* [211]. Only a slight preference was observed in

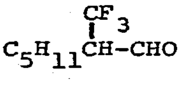


*105*



*106*

addition of methylmagnesium iodide to *107*, with the RS-SR

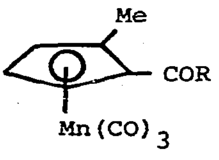


$$\mathrm{C_5H_{11}}\overset{\overset{\mathrm{CF_3}}{|}}{\mathrm{C}}\mathrm{H-CHO}$$

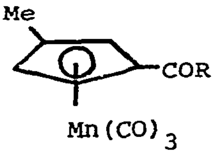
*107*

diastereomer favored 55:45 [212].

Reaction of cymantrene derivatives *108* and *109* with various Grignard reagents occurred with substantial asymme induction [213]. Curiously, the same diastereomer was pre from reaction of *109* (R = Me) with PhMgBr as from *109*, (R = with MeMgI. Results were interpreted on the basis of "pre conformations."



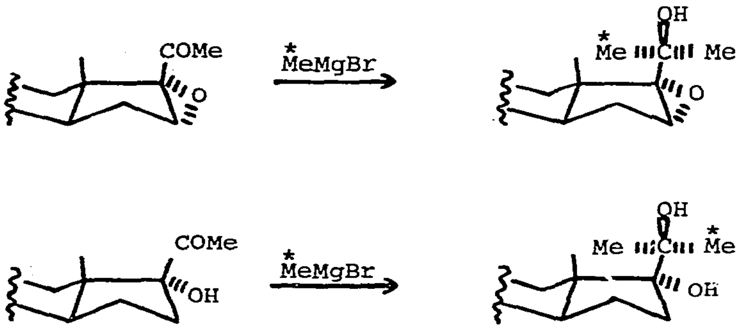
*108*



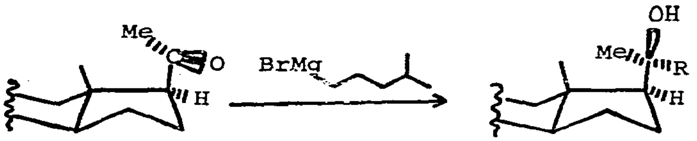
*109*

R = Me, Et, Ph, 2-thienyl

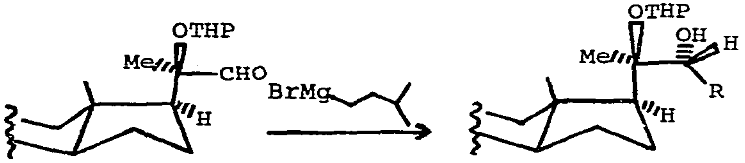
Addition to a 17-acetyl group on the steroid skeleton has been reported to occur stereoselectively. The two additions:



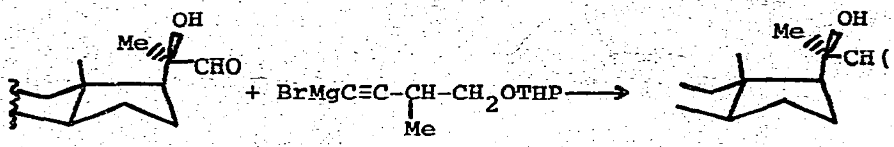
occur with high and opposite selectivity (93 and 99%). This is related to different conformations in the solid state and probably in solution [214]. In addition to pregnenolone, a mixture of epimers is formed, contrary to an earlier report. The preference shown is interpreted on the basis of addition from the back side to the dominant conformations of the acetyl group [215]:



Also in a steroidal system, the addition:

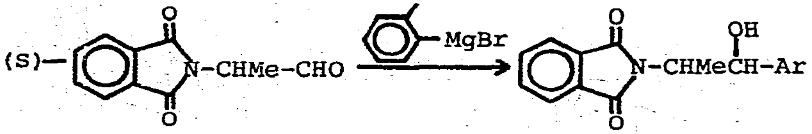


is reported to occur with "total stereoselectivity" [216]. However, in a similar instance, reaction of the hydroxyaldehyde *110* occurs with little stereoselectivity, although only one diastereomer of the Grignard reagent appears to react [83].



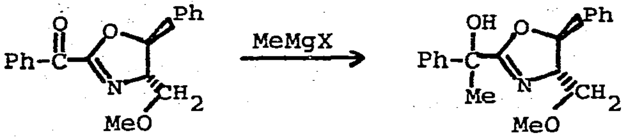
*110*

A variety of optically active β-aminoalcohols are synthesized with high preference for one diastereomer *via* a phthalimide derivative [217]; *e.g.*



erythro:threo = 4.3:1

Grignard addition to the chiral benzoyloxazoline derivative *111* occurred non-stereoselectively. However, by separation

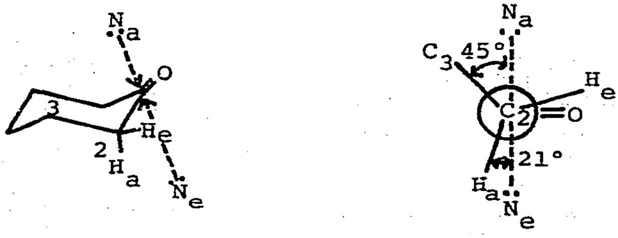


*111*

of diastereomers and hydrolysis, both enanteomers of atrolactic acid were obtained in high optical purity [218].

### 2. Stereochemistry with cyclohexanones and other cyclic ketones

A theoretical study of carbonyl addition reactions led to the conclusion that a major factor controlling the stereochemistry of addition is attack of the nucleophile in a geometry antiperiplanar to a bond on the α-carbon, maximizing overlap with the σ* orbital of that bond:



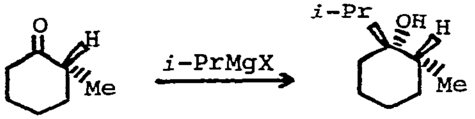
Attack from the axial side is more nearly anti-periplanar than from the equatorial side, and a slight flattening of the ring further improves the geometry [219]. Softness of the nucleophile favors addition anti-periplanar to a C-C bond (equatorial) rather than a CH bond (axial) because the σ* orbital of a C-C bond is lower in energy than that of a CH bond.

These factors have helped to rationalize the stereochemistry of addition of magnesium and other enolates of acetic acid derivatives to 4-*tert*-butylcyclohexanone [115,219]. The magnesium enolate of AcO-*t*-Bu gives predominantly equatorial attack, while that from $AcOSiMe_3$ gives more axial (72%),

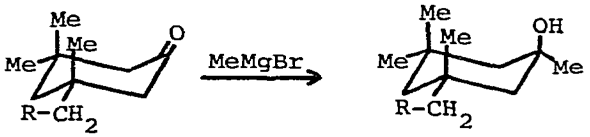
Similar principles were applied to interpreting the addition of allylmetal compounds to 4-*tert*-butylcyclohexanone [220] and to its methylimine [183]. The small magnitude of steric hindrance in an $S_E2'$ mechanism was expected to allow electronic effects to dominate. For the ketone, the fraction of axial addition increases from 15% for the soft allylzinc bromide to 51-55% for allylmagnesium bromide to ~65% for the alkali derivatives. Allylmagnesium bromide gave 88% axial addition to the imine, and the propargyl Grignard gave similar results.

In a different approach, a steric factor dependent upon the size of the attacking nucleophile was calculated for different conformations [221]. This was combined with a torsional factor to predict stereochemistry of addition of hydride and Grignard reagents to cyclic and bicyclic ketones.

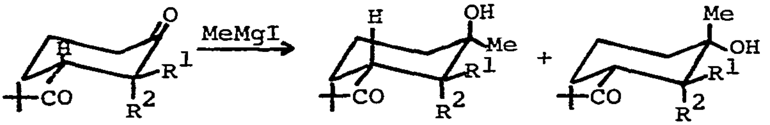
The following additional stereochemical results have also been reported:



("mostly") [204]

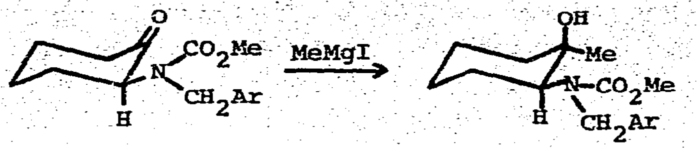


$R = p\text{-}ClC_6H_4$
>90% [222]
$R = Me_3Si$
85% [223]

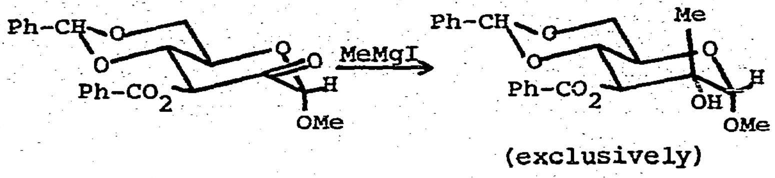


[224]

| | | | |
|---|---|---|---|
| $R^1 = R^2 = H$ | 40 | : | 45 |
| same, equilibrium | 2.7 | : | 1 |
| $R^1 = Me;\ R^2 = H$ | 4.5 | : | 1 |
| $R^1 = H;\ R^2 = Me$ | -- | | 80% |

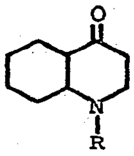


[225]



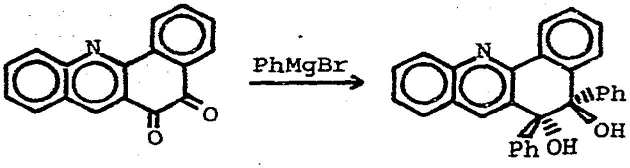
[226]

Addition of ethynyl-, vinyl-, and ethylmagnesium bromides gave a mixture of isomers from *trans-112*, but only one product from *cis-112* [227].

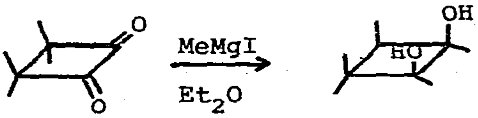


*112*

Di-addition to 1,2-diones occurred with variable stereochemistry:

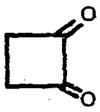


[228]

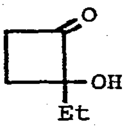


[229]

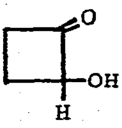
Addition of a variety of Grignard reagents to *113* gave largely



*113*

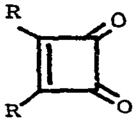


*114*

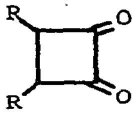


*115*

or entirely *cis* isomer in ether; in THF a mixture was formed, but only the *trans* isomer was found with vinylmagnesium bromide. The vinyl Grignard reagent in THF produced a mixture of the isomers from *114*, but reaction of MeMgI, EtMgBr, or PhMgBr in ether or $C_2H_3MgCl$ in THF with *115* produced the *cis* isomer [229]. The *cis* isomer was formed on addition of PhC≡CMgBr to *116* or *117*.



*116*

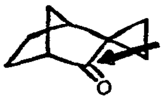


*117*

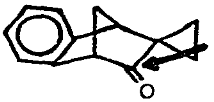
R = H, Me, Et

The stereochemistry of the aldol condensation of the magnesium enolate pulegone (see section II, C, 4) with itself or with two molecules of benzaldehyde was studied [117].

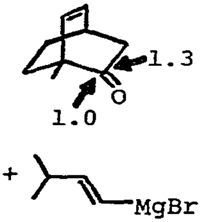
Addition of Grignard reagents to bicyclic ketones occurred with stereochemistry as follows:



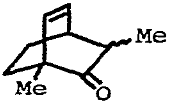
+ MeMgI
[231]



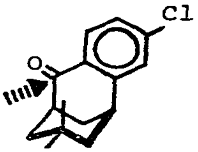
+ MeMgI
[231]



[177]



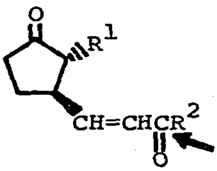
stereospecifically
*trans* to Me
[177]



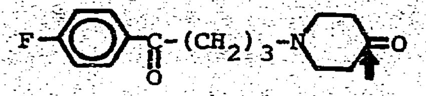
+ MeMgBr
[222]

## C. Selective Reactions with Aldehydes and Ketones

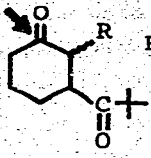
A number of examples illustrate the selectivity between carbonyl groups in various environments or selective reaction with carbonyl groups in the presence of other reactive functions. In the following instances reaction at the indicated carbonyl function was reported:



$R^1 = (CH_2)_6CO_2Me$ [232]
$R^2 = H$
$R^1 = CH_2CH{=}CH(CH_2)_3CO_2Me$ [233]
$R^2 = n\text{-}C_5H_{11}$

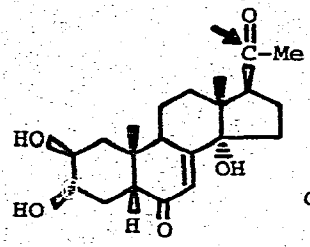


[234]

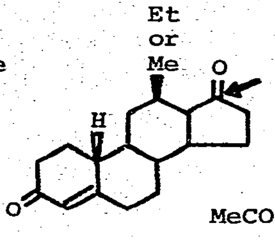


R = H, Me

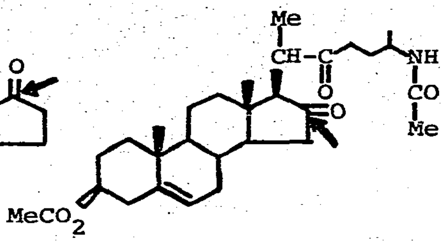
[224]



[235, 236]

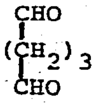


[237]



[238]

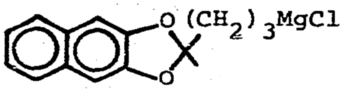
Reactions of *118* [82] and *119* [239] can be controlled to give reaction of one carbonyl group. In the case of *118*, subsequent reaction of the second aldehyde group with vinylmagnesium chloride was reported.

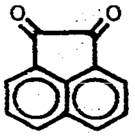


$OHC(CH_2)_3CHO$

*118*

+

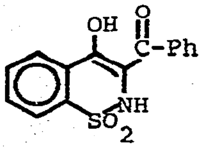




+ ArMgBr

*119*

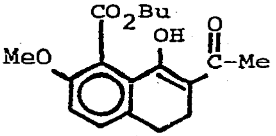
Enols *120* and *121* react at the ketone function shown:



+ PhMgBr

*120*

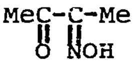
[240]



+ MeMgI

*121*

[241]



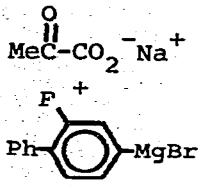
$MeC(=O)-C(=NOH)-Me$

*122*

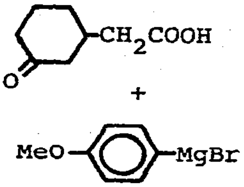
+ PhMgBr

Reaction at the ketone function occurs preferentially in *122*, but a second Grignard may then be added to react with the oxime [242].

Preferential reaction of the ketone group in the presence of acid, ester, amide, or nitrile function is illustrated by the following reactions reported in 1976:

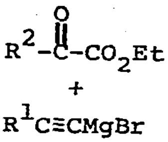


[243]



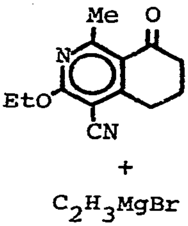
(in pyridine)

[244]

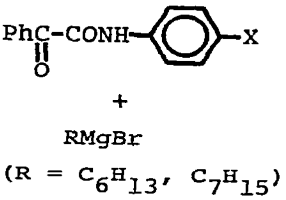


$R^2-\overset{O}{\overset{\|}{C}}-CO_2Et$ + $R^1C{\equiv}CMgBr$

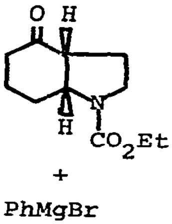
[245]



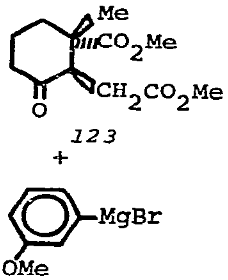
[246]



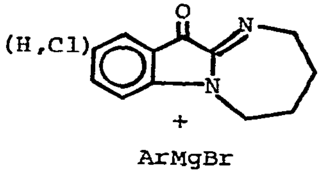
[247]



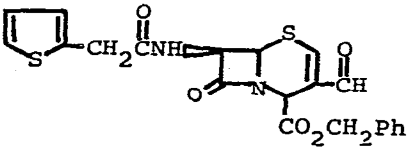
[248]



[249]



[250]

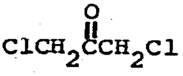


+ MeMgI, PhMgBr, $C_2H_3MgBr$

[251, 252]

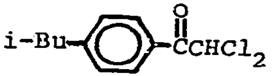
In the case of *123*, the addition product cyclizes to a lactone. Other examples are in references noted earlier [93,225].

Halo-ketones *124*, *125*, and *126* react normally at the carbonyl group to yield chloro-alcohols.



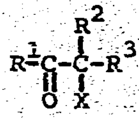
$ClCH_2\overset{O}{\overset{\|}{C}}CH_2Cl$ + $CD_3MgI$ [253]

*124*



+ MeMgI [254]

*125*



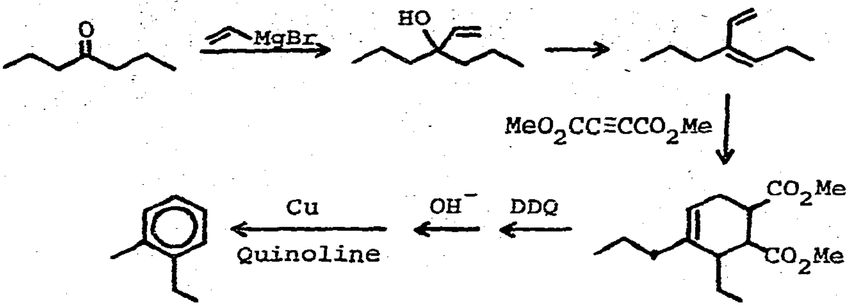
$R^1\text{-}C(=O)\text{-}C(R^2)(X)\text{-}R^3$ + propargylic Grignard reagents [182,184]

*126*

D. Other Reactions with Aldehydes and Ketones

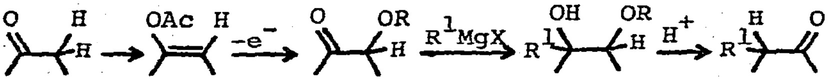
In several instances, a Grignard addition reaction is a step in a newly published general synthetic procedure.

A benzoannelation of ketones follows the sequence:



Several interesting applications are reported [255].

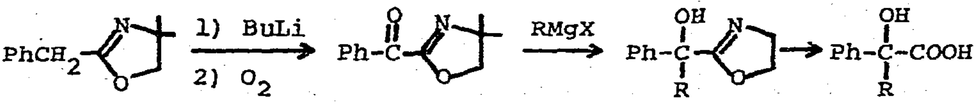
A 1,2-carbonyl transposition has been explored, and several examples given [256]:



A convenient synthesis of ketones from aldehydes proceeds in overall yields of 55-90% [257]:

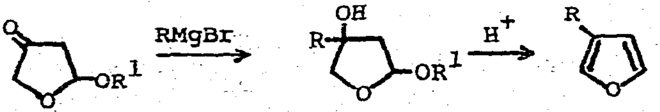
$$R^1CHO + R^2MgBr \longrightarrow [R^1R^2CHO^-\overset{+}{M}gBr] \xrightarrow[t\text{-}BuO^-Li^+]{\text{N-chlorosuccinimide}} {R^1 \atop R^2}\!\!>C{=}O$$

A variety of α-substituted mandelic acids were prepared in good yield by the route [258]:



R = Me, Et, *i*-Pr, Ph, PhC≡C

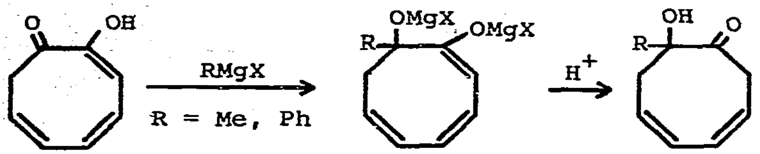
3-Substituted furans were prepared [259]:



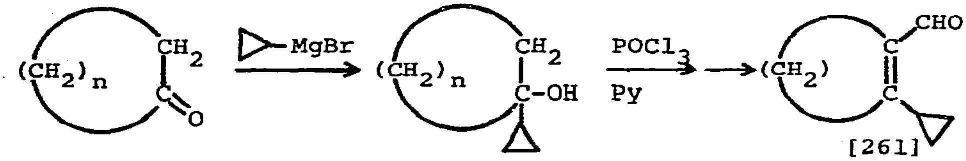
R = Ph or isopentenyl

Methylenebis(magnesium bromide) was studied as an alternative to the Wittig reaction in carbohydrate chemistry [140]. Yields were generally the same or better by this method.

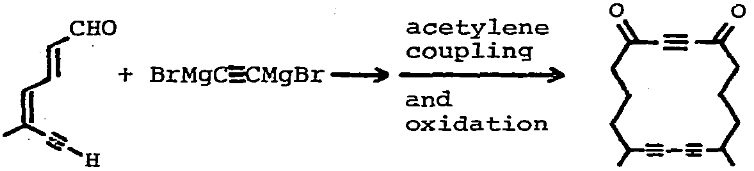
Some other interesting reactions or reaction sequences are:



[260]



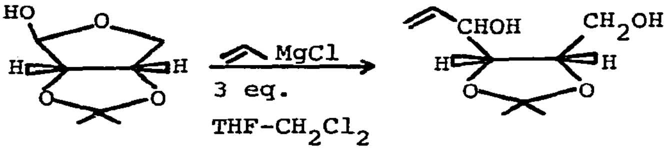
[261]



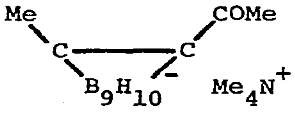
[262]

[263]

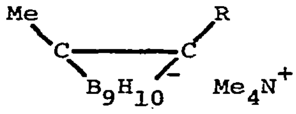
The first step in a chiral synthesis of prostaglandins from an L-erythrose derivative was [264]:



Grignard reagents with 1,2-dicarbaundecaborate derivatives gave varied results [265]. The methyl ketone *127* reacted only



*127*

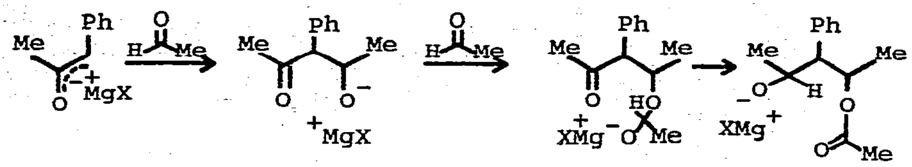


*128*, R = $CMe{=}CH_2$

*129*, R = $CHMe_2$

*via* enolization with ethyl or phenyl Grignard reagents; methylmagnesium iodide gave about 55% enolization, plus a 1:1 mixture of *128* and *129*. The corresponding phenyl ketone gave the tertiary carbinol with phenylmagnesium bromide and secondary carbinol by reduction with ethylmagnesium bromide. A variety of tertiary cymantrene alcohols were prepared by Grignard reactions of acylcymantrenes [266].

The primary magnesium enolate from benzyl methyl ketone with *i*-PrMgCl forms the ketol with another molecule of the ketone [118]. The secondary enolate is unreactive to self condensation, but slowly forms the ketol *via* interconversion with the primary enolate. It condenses in an interesting fashion with acetaldehyde:

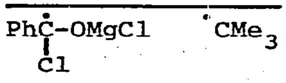


E. Reactions with Carboxylic Acids and Derivatives

1. Open-chain derivatives

Trifluoroacetic acid reacted with pentylmagnesium bromide to generate 1,1,1-trifluoro-2-heptanone in 51% yield [212]. Ketyls of the corresponding ketones were produced by $Ni^{++}$-catalyzed addition of Grignard reagents to substituted salicylic acids [201] (see section IV, A).

The reaction of benzoyl chloride with *tert*-butylmagnesium chloride in DME was studied using CIDNP [267]. Products which showed spin polarization included phenyl *tert*-butyl ketone (methyl hydrogens only), isobutane, 2,2,3,3-tetramethylbutane, isobutylene, and *tert*-butyl chloride. It was proposed that radical pairs *130* and *131*, formed by single electron transfer, both contributed to the polarization. Additional polarization



$\overline{Ph\dot{C}(Cl)\text{-}OMgCl\quad {}^{\bullet}CMe_3}$

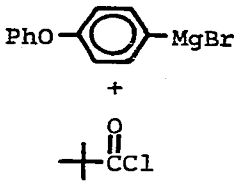
*130*

$\overline{Ph\dot{C}O\quad {}^{\bullet}CMe_3}$

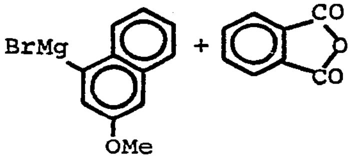
*131*

must result from encounter pairs, since experiments run in the presence of styrene to trap free radicals showed decreased polarization of some components.

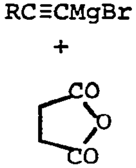
Formation of ketones in reaction of Grignard reagents with acid chloride or anhydrides is reported in a number of cases. As noted in section II, C, 2, Grignard reagents substituted with a 1,3-dioxan or 1,3-dioxolan group in the β-position react quite selectively with acid chlorides, stopping at the ketone stage [92,94]. Ketones were also produced in the reactions:



[268]

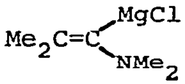


[269]



[91]

Manganous iodide, used with Grignard reagents in either a 1:1 or a 1:2 stoichiometry, yielded reagents which produce ketones in 60-90% yields from acid chlorides [269]. Organocuprates formed from Grignard reagents and methyl copper selectively transfer the group other than methyl in reaction with acid chlorides at -78° [158]. In this fashion, ketone yields of 75-100% are reported, starting with primary through tertiary or aryl Grignard reagents, and acetyl, pivaloyl or benzoyl chlorides. The acyl-equivalent organomagnesium compound *132* [111] and the rhenium-magnesium compound *133* [152] are also



$Me_2C{=}C(MgCl)(NMe_2)$

*132*

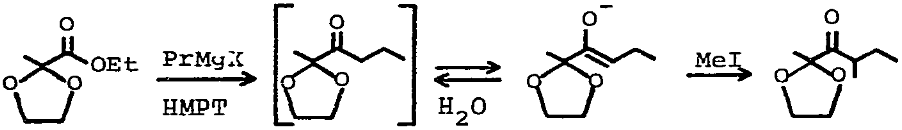
$(\eta\text{-}C_5H_5)Re(CO)_2I\text{-}MgI$

*133*

acylated with acetic anhydride and acyl halides, respectively.

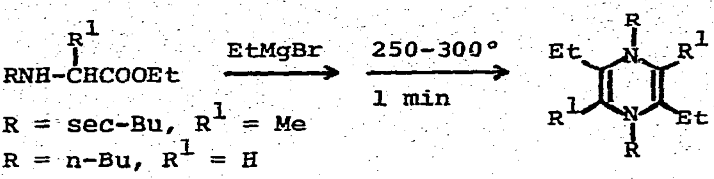
The reaction of myrcene-magnesium with acetyl chloride is cited in section II, D [196].

When ketals or thioketals of α-keto esters reacted with Grignard reagents in HMPT, the ketone formed in the first addition stage was enolized by excess organometallic [271]; *e.g.*



37%
(insol.)

The reaction of amino esters *134* followed by heating was reported to produce the heterocycle *135*. Formation of this product implies Grignard reaction to the ketone stage [273].

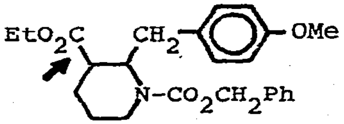


134 135

Reaction of esters or acids with vinylmagnesium chloride leads to a mixture of products [120,121,273,274]:

In a study with β-hydroxy esters, it was found that α-substituted esters reacted with excess reagent to give more of the unsaturated ketone, while esters unsubstituted in the α-position gave tertiary alcohol [273].

Selective reaction with the indicated ester function was found in *136* [275] and *137* [276], yielding the corresponding tertiary alcohols:

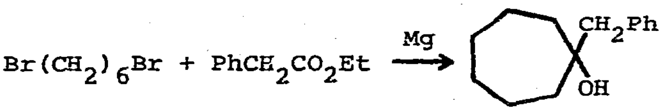


*136*

*137*

Selective reaction of a Grignard reagent with the acetate group of a steroidal epoxy-derivative was found to be more effective than hydrolysis for generating the hydroxy-epoxide [277]. Reaction of ethyl chloroacetate with 1-propynylmagnesium bromide produced the corresponding tertiary chloro-alcohol [184].

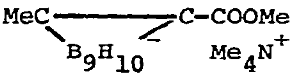
Di-organomagnesium compounds may react with esters to produce cyclic alcohols [278]:



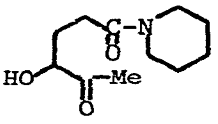
See also reactions of myrecene-magnesium with esters [196] in section III, D.

Reactions of several esters with a mixture of two different Grignard reagents has led to useful yields of the mixed tertiary alcohol addition product [279].

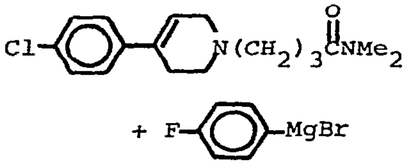
The carborane ester *138* reacted with phenylmagnesium bromide to produce the corresponding tertiary carbinol. Reaction with ethylmagnesium bromide gave a secondary alcohol by addition followed by reduction; its homolog reacts normally to give tertiary alcohol [265].


*138*

Two reports may also be noted in which ketones were formed in reaction between amides and Grignard reagents:


+ MeMgI

[280]

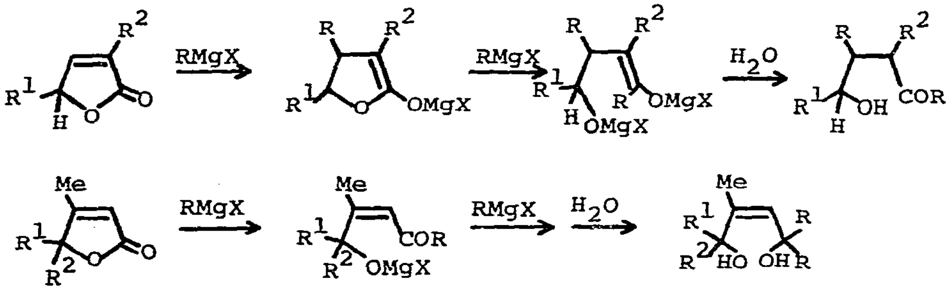

60% yield in benzene-THF

[281]

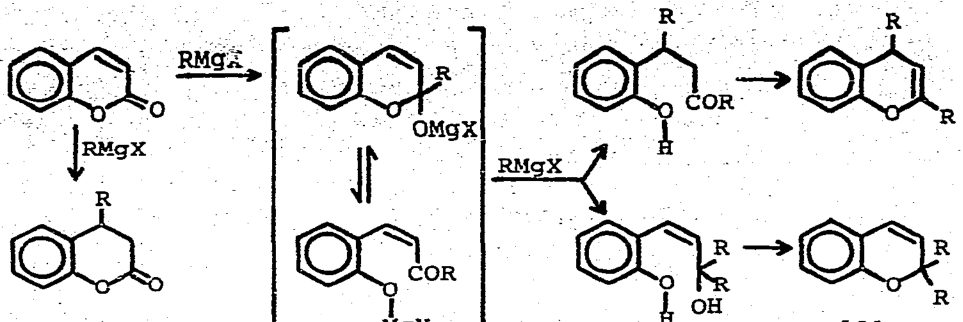
In the first case, reaction occurred both at the original keto group and the amide, producing a hydroxyketone. The 2-bromo-3-thienyl Grignard reagent gave a 60% yield of aldehyde with dimethylformamide [128].

### 2. Lactones, lactams, and cyclic anhydrides

The reaction course with α,β-unsaturated butenolides was found to depend upon the substitution pattern [282]:

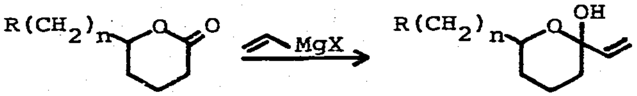


The reaction of coumarin with Grignard reagents was found to follow a variety of paths, depending upon the alkyl group and halogen of the reagent [283]. Results were interpreted on the basis of CNDO calculations of charge, bond order and frontier orbital coefficients, and the effects of complex formation with magnesium. Results were also reported for coumarins with methyl or phenyl substitution on the heterocyclic ring [284]. A number of examples in more complex systems leading to products of the type *139* have appeared in the patent

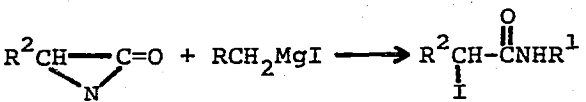


139

literature [*e.g.* 285,286]. Single addition of vinyl Grignard reagents to lactones has also appeared in patents [*e.g.* 287,288]:



Two papers report results of α-lactone reactions [289, 290]. A reaction path involving displacement by iodide was favored; other products were derived from *140*:

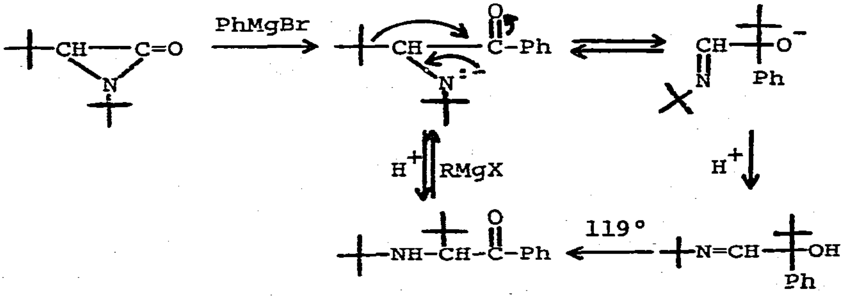


$$R^2\underset{\underset{R^1}{N}}{CH\text{—}C{=}O} + RCH_2MgI \longrightarrow R^2\underset{I}{CH}\text{-}\overset{O}{\overset{\|}{C}}NHR^1$$

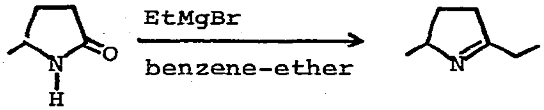
*140*

$R^1$ and $R^2$ = 3° alkyl; R = H, Me

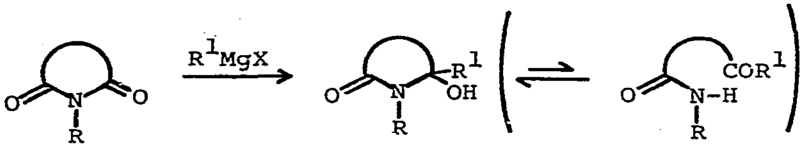
Reaction with phenylmagnesium bromide at the carbonyl carbon gave a product *via* an apparently reversible rearrangement:



Other additions to lactams or cyclic imides are:



[291]



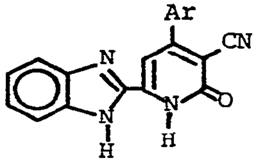
R = alkyl, aryl, H; $R^1$ = alkyl, aryl, styryl, $R^2C{\equiv}C-$
[91,292-294]

## V. Addition of Organomagnesium Compounds to Other Unsaturated Functions

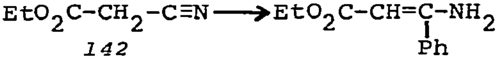
### A. Reaction with Carbon-Nitrogen Unsaturation

The yield of ketone in the reaction of Grignard reagents with nitriles is increased by addition of $LiClO_4$ or $(Bu)_4NClO_4$ [295]. The crystal structure of the adduct of benzonitrile and phenylmagnesium bromide was determined (see section III, B) [170].

Addition to the cyano group in preference to other functions was observed for *141* and *142*.



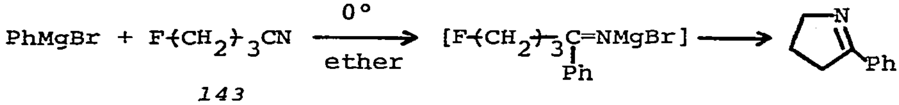
*141*
+ excess MeMgI
[296]



$$EtO_2C{-}CH_2{-}C{\equiv}N \longrightarrow EtO_2C{-}CH{=}\underset{Ph}{\underset{|}{C}}{-}NH_2$$

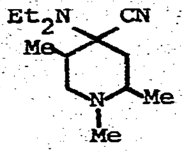
*142*
+ PhMgBr
[297]

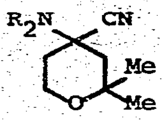
The initial adduct from fluoronitrile *143* cyclizes spontaneously, possibly due to $Mg^{++}$ catalysis; cyclization of the chloro and bromo analogs occurs only on heating [298].

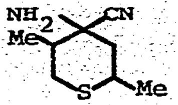


*143*

Although α-aminonitriles may react with displacement of the cyano group, the following are reported to undergo normal conversion to ketones:

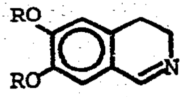

[299]

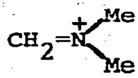

[299]

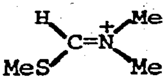

[299]


[300]

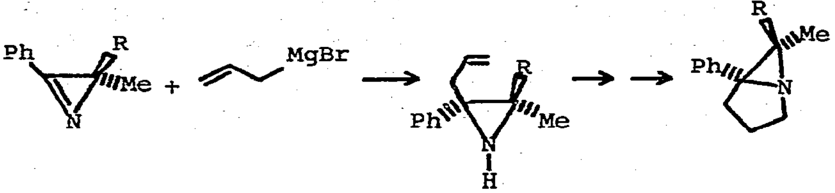
Addition to the carbon-nitrogen double bond, yielding an amine, is reported for the neutral and cationic substrates:


+ $ArCH_2MgBr$
[301]

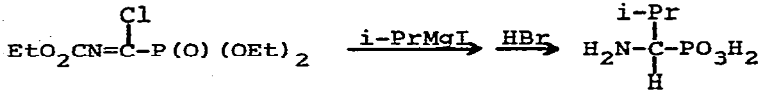

+ ArMgBr
[302]


+ PhMgBr
[303]

Addition of a Grignard reagent to 2-phenyl-3,3-dimethylazirine has been studied [36], and this addition forms part of a synthesis of fused aziridines [304]:

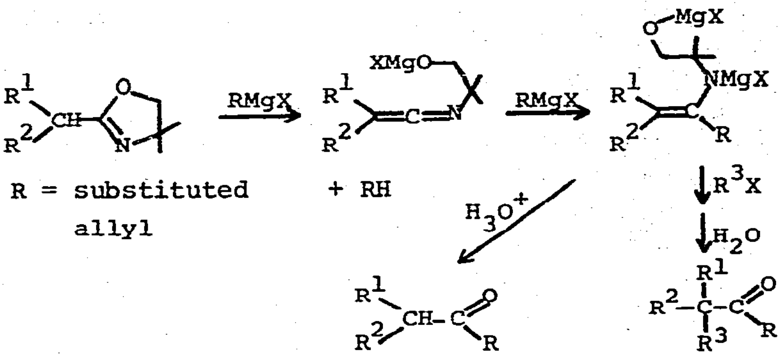


Aminoalkylphosphonic acids were prepared *via* C=N addition [305,306]; *e.g.*


$$\mathrm{EtO_2CN{=}\overset{Cl}{C}{-}P(O)(OEt)_2} \xrightarrow{\text{i-PrMgI}} \xrightarrow{\text{HBr}} \mathrm{H_2N{-}\underset{H}{\overset{i\text{-}Pr}{C}}{-}PO_3H_2}$$


$$\mathrm{EtO_2C{-}N{=}\overset{SEt}{C}{-}P(O)(OEt)_2} \xrightarrow{\text{MeMgI}} \mathrm{EtO_2C{-}NH{-}\overset{SEt}{C}{-}P(O)(OEt)_2}$$

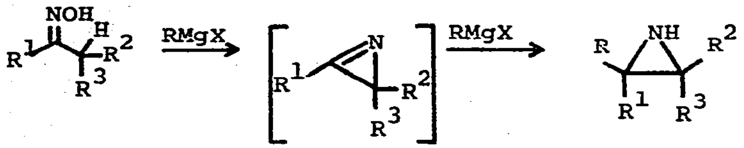
A ketone synthesis utilizing reaction of an allylic Grignard reagent with an oxazoline has been reported [178]:



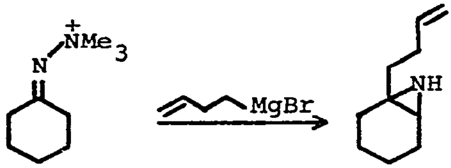
R = substituted allyl

+ RH

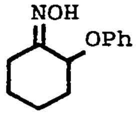
A variety of examples were reported of aziridine-formation by reaction of a Grignard reagent with oximes [242,307-309]:



A similar aziridine-formation occurred with hydrazonium salt *144* [304]. However, a different pathway was observed for *145* with PhMgBr, which gave mainly elimination of phenol and formation of aniline [308].

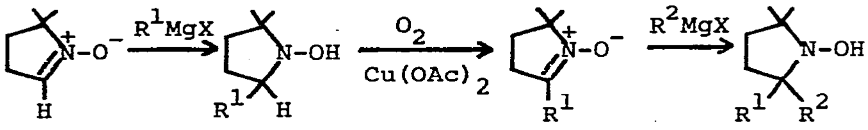


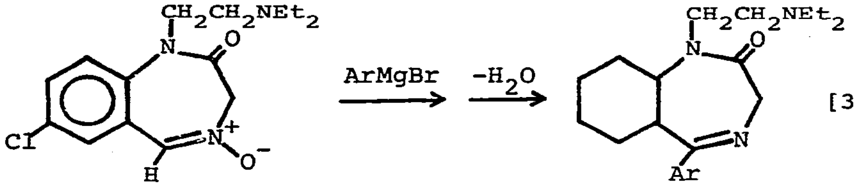
*144*



*145*

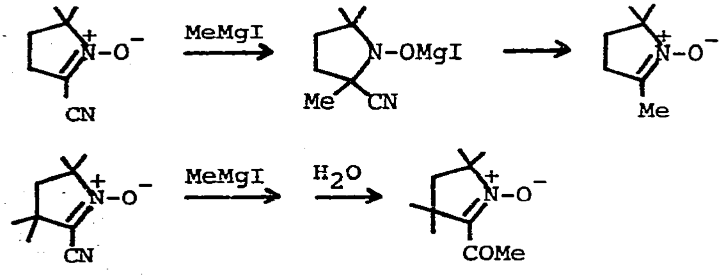
Hydroxylamine formation by Grignard addition to nitrones was studied [310-313]:

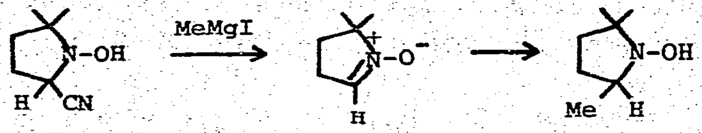




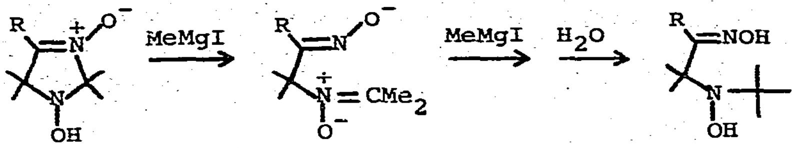
[314]

Cyano-substituted nitrones reacted as follows [315]:





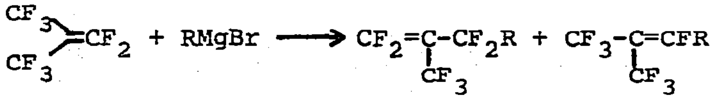
Another nitrone reaction proceeds *via* preliminary ring opening [316]:



B. Reaction with Carbon-Carbon Double Bonds

Additional studies have been reported on reactions of Grignard reagents with per-fluoro or fluoro-chloro alkenes:

$ArMgBr + F_2C{=}CFCl \longrightarrow ArCF{=}CFCl$ [317]



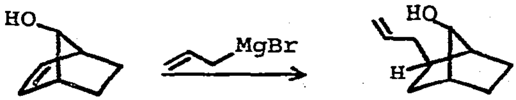
$$\begin{matrix}CF_3\\CF_3\end{matrix}\!\!>\!C{=}CF_2 + RMgBr \longrightarrow CF_2{=}\underset{CF_3}{\underset{|}{C}}{-}CF_2R + CF_3{-}\underset{CF_3}{\underset{|}{C}}{=}CFR$$ [318]

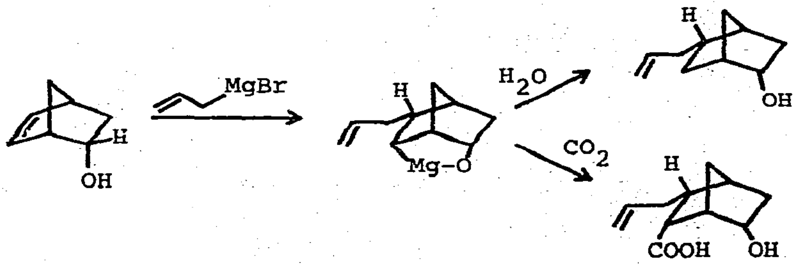
R = benzyl, n=butyl, i-propyl

$F_2C{=}CCl_2 + ArMgBr \longrightarrow ArCF{=}CCl_2$ [319]

In the last study, reactions with alkyl Grignard reagents were found to be more complex; some $RCF_2{-}CCl_2H$ product was isolated on hydrolysis.

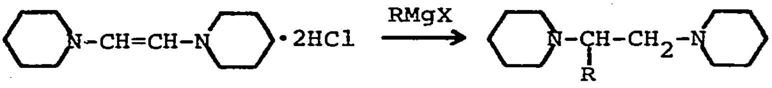
Richey has studied the stereochemistry of the hydroxyl-facilitated addition of allylmagnesium bromide to the double bond of two norbornenols [320]:





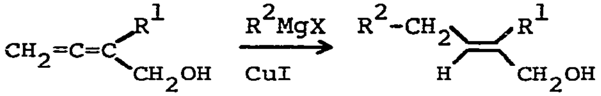
No reaction was observed under similar conditions for the epimeric alcohols. The configuration of product in the latter case demonstrates that the allyl group is delivered to the double bond from the same side as the OH group.

Addition of several Grignard reagents to the diamine dihydrochloride *146* was reported [321]:

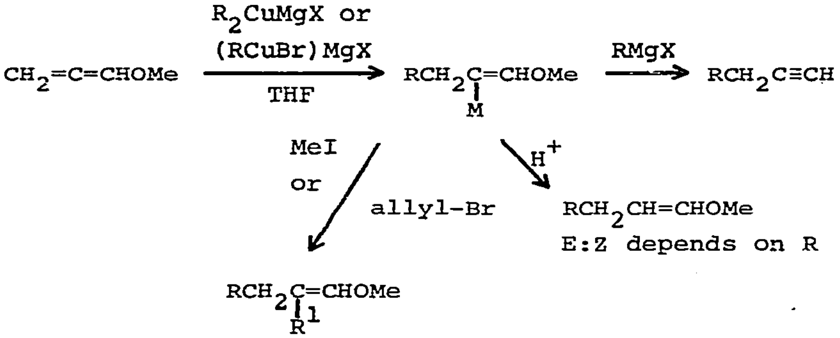


*146*

Copper-catalyzed additions of Grignard reagents to allenic alcohols and ethers have been reported:

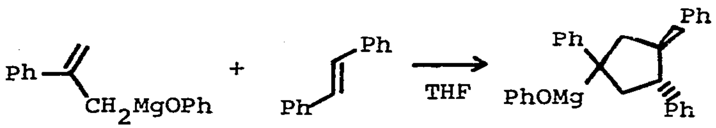


(stereospecific and regio-specific) [322]



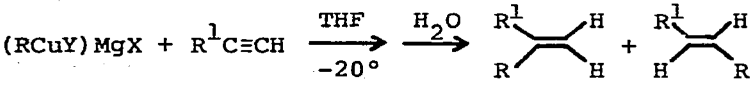
[323]

Cycloaddition of 2-phenylallylmagnesium phenoxide with *trans*-stilbene was catalyzed by HMPA, cryptates, crown ethers and aza-ethers [52].



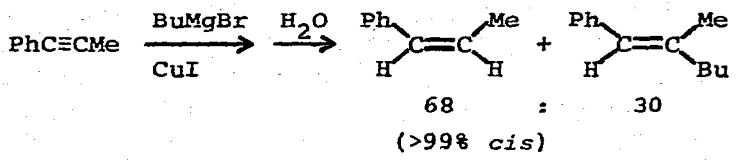
C. Reaction with Carbon-Carbon Triple Bonds

Magnesium organocuprates add smoothly to terminal alkynes at -20°C [324,325]. Primary, secondary, and tertiary

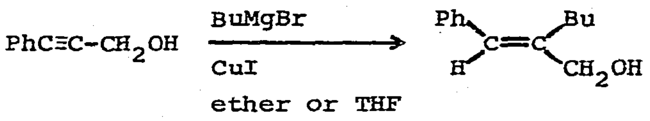


alkyl groups are all transferred in good yield. Little metallation of the alkyne occurred, and that could be suppressed by addition of LiBr.

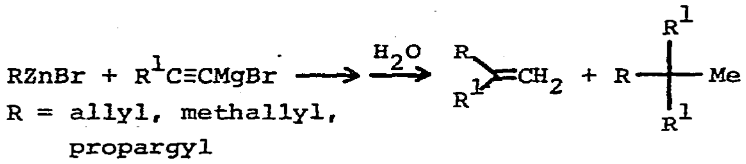
With several non-terminal alkynes, reduction was observed with a reagent derived from butyl- or ethylmagnesium bromide and CuI (2:1). Reaction occurred when the reagent, prepared at



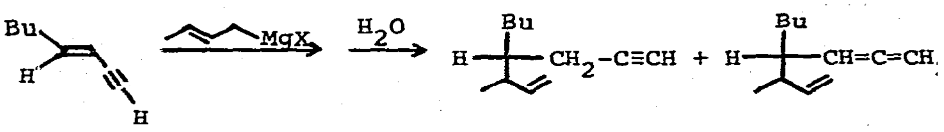
-35°C, decomposed on warming. Less (or no) reduction was found with *t*-butyl or i-propyl reagents or lithium cuprates. The product before hydrolysis could be alkylated with allyl bromide. However, addition occurred in high yield with:



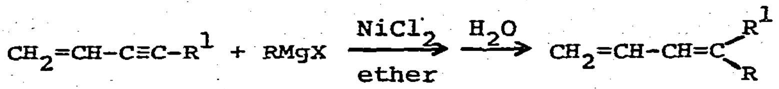
Allylic and propargylzinc bromides add to alkynylmagnesium halides [327,328]:



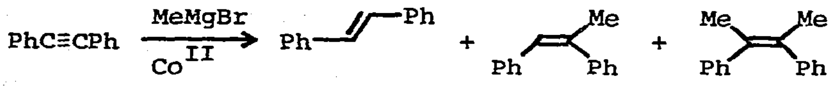
Addition reactions of a variety of enynes with allylic magnesium compounds were reported [329]; *e.g.*



With nickel catalysis, benzyl and aryl Grignard reagents were reported to add to the triple bond of enynes [330]:

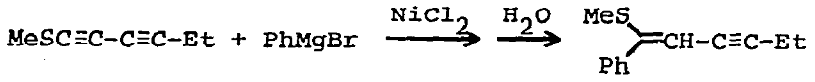


Diphenylacetylene is reported to react with MeMgBr in the presence of cobalt complexes; the reaction is influenced by the presence of oxygen [331]:



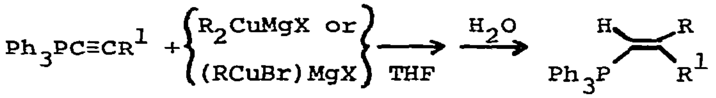
Addition has also been reported for some alkynyl heteroderivatives:

$$R_3SiC{\equiv}C\text{-}CH{=}CH_2 + PhMgBr \xrightarrow{NiCl_2} \xrightarrow{H_2O} R_3SiC{\equiv}C\text{-}CH_2CH_2Ph$$ [332]



[333]

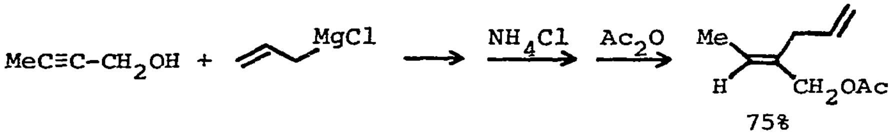
E:Z = 82:18

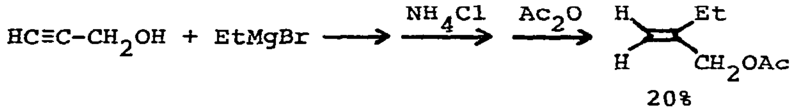


[334]

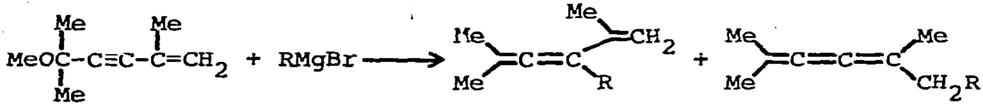
$R^1$ = H, Me; R = Me, 1°, 2°, 3°

Synthetic applications of the stereo- and regiospecific addition of Grignard reagents to alkynols have been described [335]:

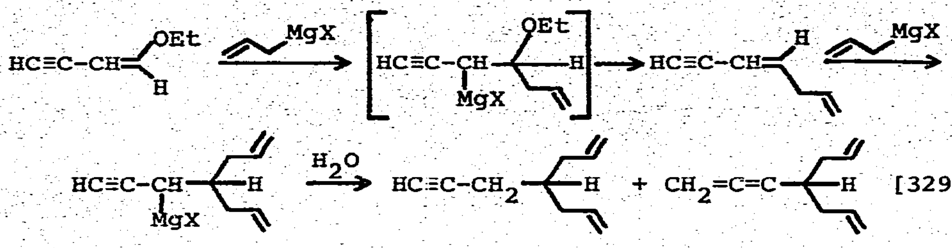




The reversibility of the addition to propargyl alcohol has been noted in section II, E [199]. Additions to enynes with alcohol, ether, and amino substituents have also been described [336]. In certain cases, the substituent in an allylic or vinylic position is displaced; *e.g.*

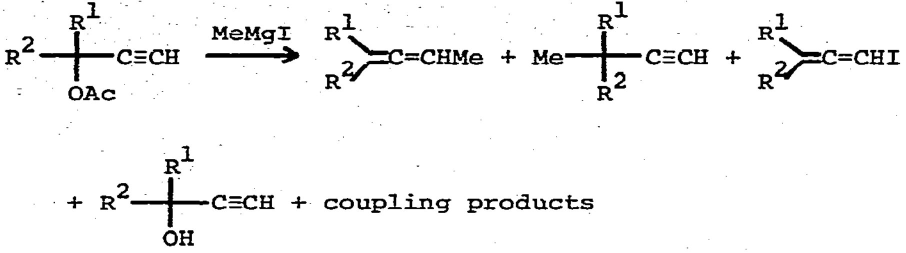


[337]



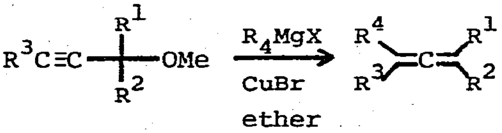
[329]

Propargylic acetates react with Grignard reagents to give products with replacement of the acetate group by the alkyl group or by iodide from the Grignard reagent [338-340]:

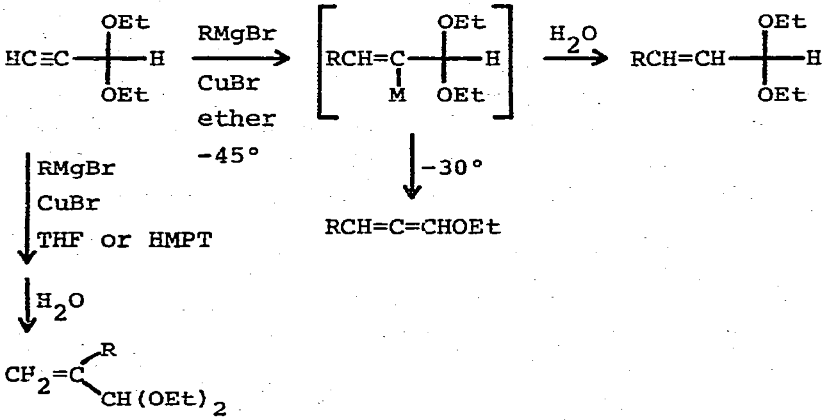


Mechanistic studies, including phenyl and cyclopropyl-substituted compounds, led to the conclusion that competing radical and ionic (carbonium ion) mechanisms are involved.

Other displacement reactions with propargylic derivatives, catalyzed by CuBr, have been reported:



[341]

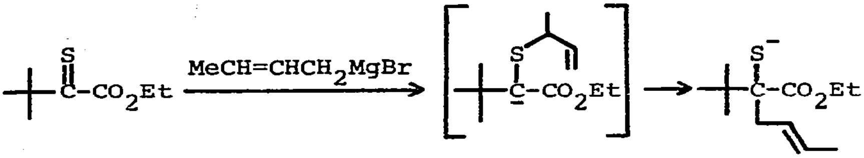


[342]

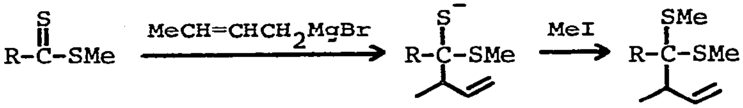
### D. Reaction at C=S Groups

Grignard reagents were shown to add to the sulfur of α-thiocarbonyl esters; with the crotyl Grignard reagent, the carbon-addition product is formed, probably *via* rearrangement [343]:

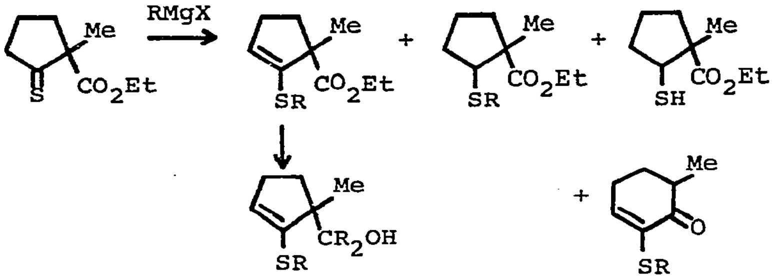
R = Me, Et, *t*-Bu



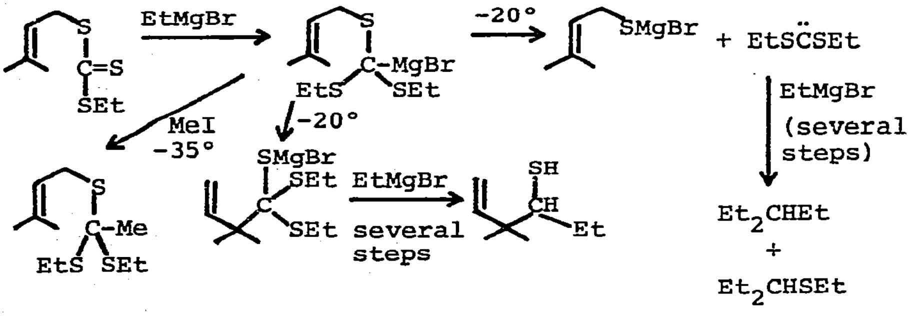
However, addition of the crotyl Grignard reagent to dithioesters apparently involves direct addition to carbon [344]:



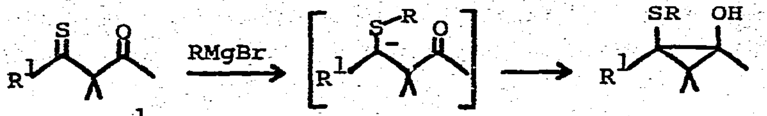
Thiophilic addition was also found in several cyclic examples [343]; *e.g.*



A variety of rearrangement and cleavage processes were found for a thiocarbonate [346]:

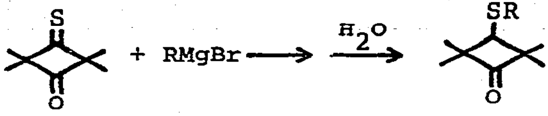


Thiophilic addition followed by cyclization occurred with β-keto thioketones and thioesters [347,348]:



$R^1$ = Me or S-alkyl

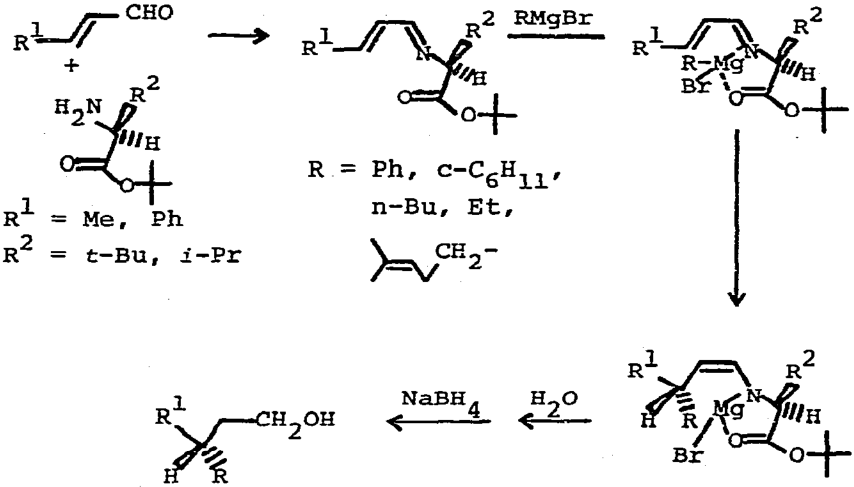
A concerted addition and cyclization was proposed. The thioketone *147* gave no cyclization and only addition to the thiocarbonyl group in the presence of excess Grignard reagent [347].



*147*

## E. Reaction with Conjugated Carbonyl and Carboxy Derivatives

A new asymmetric synthesis has been reported, whose critical step appears to be conjugate addition in a chelated Grignard reagent complex [349]:



$R^1$ = Me, Ph

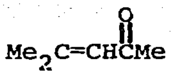
$R^2$ = t-Bu, *i*-Pr

R = Ph, c-$C_6H_{11}$, n-Bu, Et, $CH_2$-

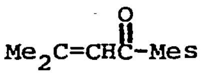
Optical yields of 91-98% ($R^2$ = *t*-butyl) and ~60% ($R^2$ = *i*-propyl) are reported, along with overall synthetic yields around 50%.

Copper-catalyzed conjugate additions of Grignard reagents to α-β-unsaturated carbonyl compounds are now quite commonplace. Use of the methylcopper-Grignard reagent complex for conjugate addition has been noted [158].

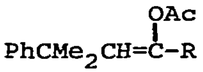
The effects of tetracyanoethylene and triphenylphosphine on the addition of magnesium diphenylcuprate to *147* and *148* have been reported [350]. The former decreased the rate of addition


$Me_2C{=}CH\overset{\overset{O}{\|}}{C}Me$

147


$Me_2C{=}CH\overset{\overset{O}{\|}}{C}{-}Mes$

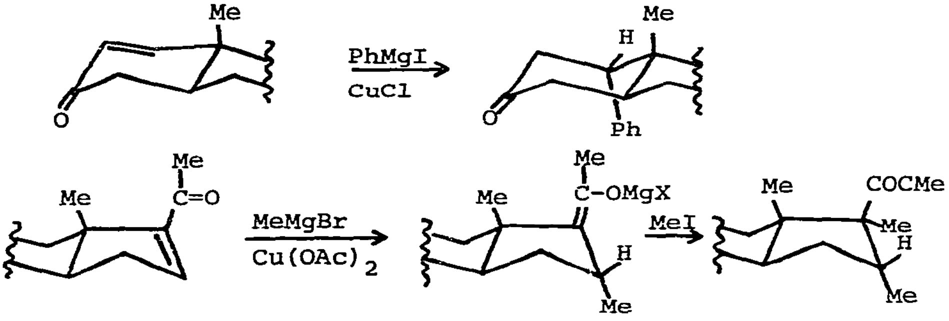
148


$PhCMe_2CH{=}\overset{\overset{OAc}{|}}{C}{-}R$

149

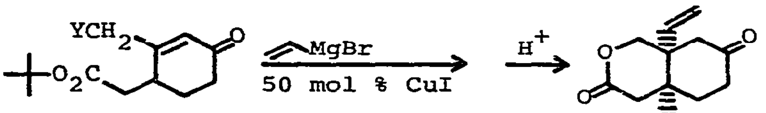
to *148*, presumably by competitive complexation with the cuprate, but had little effect on *147*. The latter led to a mixture of 1,2 and 1,4 addition with *147*, and influenced the E:Z ratio of the acyl derivative (*149*) of the product from *148*. Destruction of the cuprate, with formation of diphenylmagnesium and $Ph_3P$:CuI was proposed.

In two steroidal systems, the stereochemistry of the conjugate addition appeared to be controlled by steric considerations [351,352]:



In the latter reaction, a variety of other Grignard reagents gave conjugate addition with or without copper salt catalysis, but allyl magnesium bromide would give only 1,2-adduct. Minor byproducts included ethyl ketones, presumably formed *via* enolization in the acetyl group, followed by methylation.

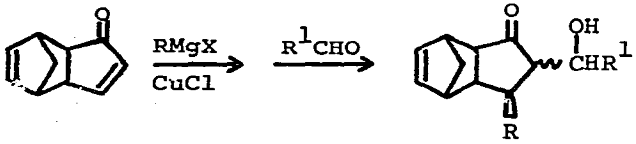
Reaction with vinylmagnesium bromide with *150* gave a 60-85% yield of *151* after acid-catalyzed hydrolysis and cyclization [353]. Lithium cuprates displaced an acetate group (*150*, Y = OAc).



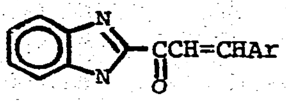
*150* (Y = OSiMe$_3$)

*151*

A critical step in a new prostanoid synthesis is [354]:

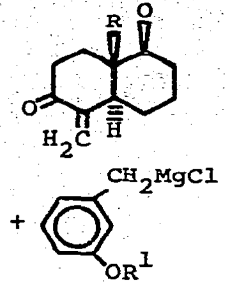


Several instances of conjugate addition may be noted in which copper catalysis was not cited:

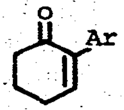


+ PhMgBr

[355]

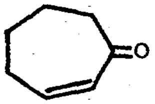


[356]



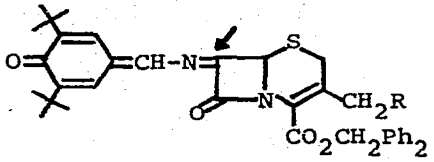
+ $Ar^1MgBr$
(*cis* product formed)

[357]



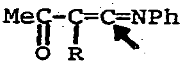
+ MeMgI
( ≥ 20% 1,4
addn)

[358]



+ MeMgBr

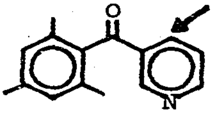
[359]



$\mathrm{Me\underset{\underset{O}{\|}}{C}-\underset{\underset{R}{|}}{C}=C=NPh}$

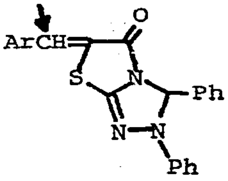
+ alkyl-MgBr

[360]



+
p-biphenyl-MgBr

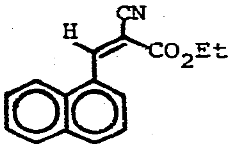
[361]



+ PhMgBr

[362]

Conjugate additions to methylenemalonic acid derivatives include:



+ RMgX

[363]

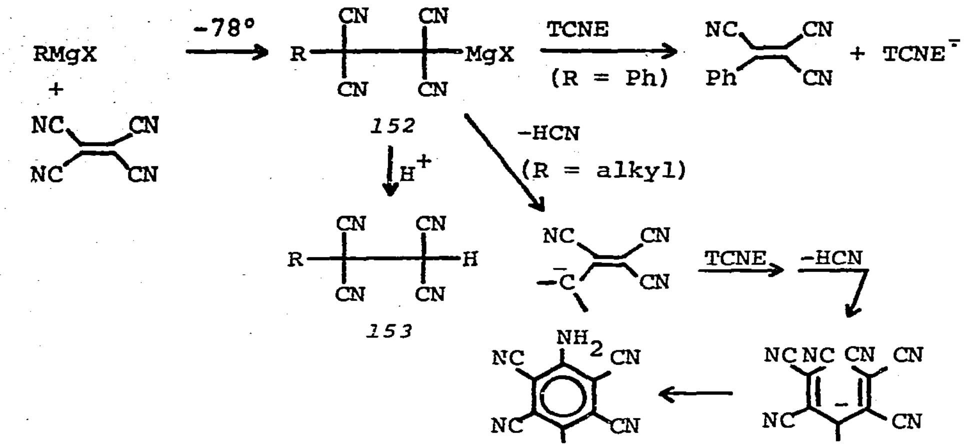
$MeO_2C\text{-}CH{=}C(CO_2Me)_2$

+ BuC≡CMgBr

[364]

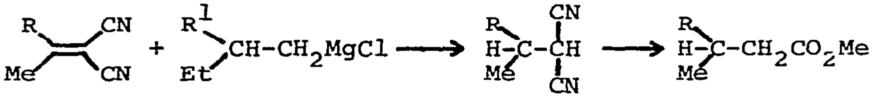
The reaction of esters with vinylmagnesium chloride has been cited earlier (section IV, E) [273,274].

Addition of one mole of Grignard reagent to tetracyanoethylene at -78° produces an adduct *152* [365]. With phenyl, the adduct is stable at room temperature, but alkyl derivatives decompose on warming, with slow evolution of HCN. Low temperature hydrolysis forms *153*. Products formed with additional TCNE are shown. Electron transfer and nucleophilic processes

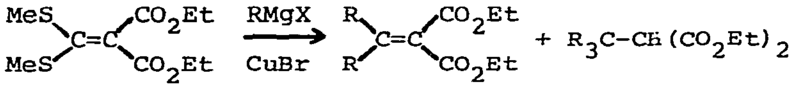


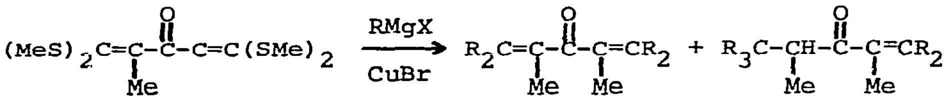
are discussed.

Reduction of substituted 1,1-dicyanoethylenes with chiral Grignard reagents produced chiral products [365a]. The configuration of the product depended on the number of aryl groups in the transition state.



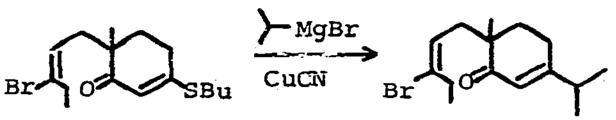
In several examples, conjugate addition of an α,β-unsaturated carbonyl derivative led to displacement of a leaving group on the β-carbon:

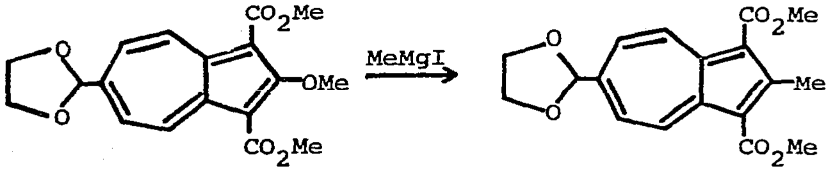

[366]

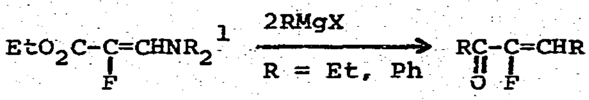


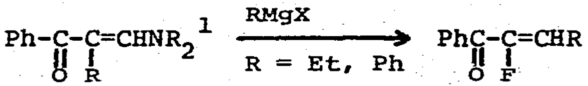
$$\mathrm{(MeS)_2C{=}\underset{Me}{C}-\overset{O}{\overset{\|}{C}}-C{=}C(SMe)_2 \xrightarrow[CuBr]{RMgX} R_2C{=}\underset{Me}{C}-\overset{O}{\overset{\|}{C}}-\underset{Me}{C}{=}CR_2 + R_3C-\underset{Me}{CH}-\overset{O}{\overset{\|}{C}}-\underset{Me}{C}{=}CR_2}$$

[366]


[367]

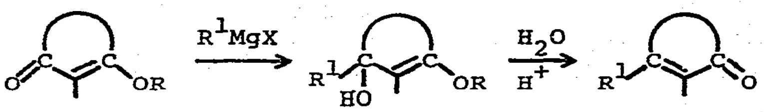

[368]


$$\mathrm{EtO_2C{-}\underset{F}{\underset{|}{C}}{=}CHNR_2{}^{1}} \xrightarrow[\mathrm{R\ =\ Et,\ Ph}]{\mathrm{2RMgX}} \mathrm{R\underset{O}{\underset{\|}{C}}{-}\underset{F}{\underset{|}{C}}{=}CHR}$$
[369]


$$\mathrm{Ph{-}\underset{O}{\underset{\|}{C}}{-}\underset{R}{\underset{|}{C}}{=}CHNR_2{}^{1}} \xrightarrow[\mathrm{R\ =\ Et,\ Ph}]{\mathrm{RMgX}} \mathrm{Ph\underset{O}{\underset{\|}{C}}{-}\underset{F}{\underset{|}{C}}{=}CHR}$$
[369]

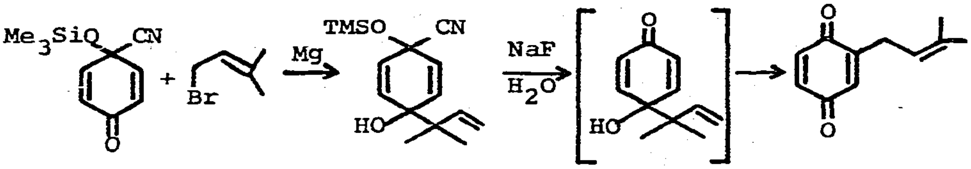
In the last instance, inverse addition gave the indicated product (*trans*) in 76-84% yield; normal addition of excess Grignard reagent gave subsequent 1,2-addition to the carbonyl group of the product.

A formally similar reaction of enol ethers of β-diketones [222,370-372] apparently follows a normal 1,2-addition course in most cases. In one case reported, reaction with $Me_3SiCH_2MgBr$

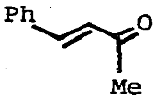


led to introduction of a methyl group and formation of $(Me_3Si)_2O$ by hydrolysis during the work-up [223].

1,2-Addition to a "masked quinone" followed by rearrangement also gave the equivalent of conjugate addition [34]:

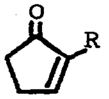


Normal 1,2-addition was noted for the following:



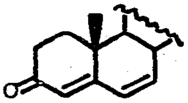
+ PhC≡CMgBr

[373]



+ $R^1MgX$

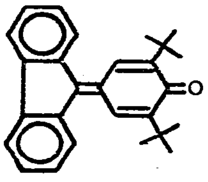
[374]



+ ArMgX

[375]

Although a variety of other nucleophiles gave conjugate addition, and phenyllithium added 1,2 to the carbonyl group, phenylmagnesium bromide reduced *154* to a dimer *via* single electron transfer [376].



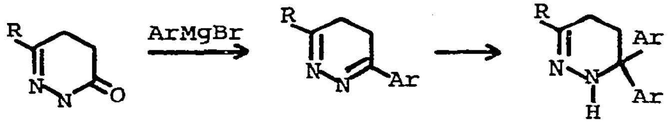
*154*

Some other reactions of unsaturated carbonyl compounds are included in sections IV, E, 2 and V, F.

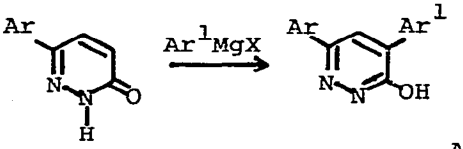
### F. Additions to Heterocyclic Compounds

In earlier portions of this review, reactions of heterocyclic compounds have been noted in connection with carboxylic acid derivatives (IV, E, 2), carbon-nitrogen unsaturation (V, A), and unsaturated carbonyl compounds (V, E).

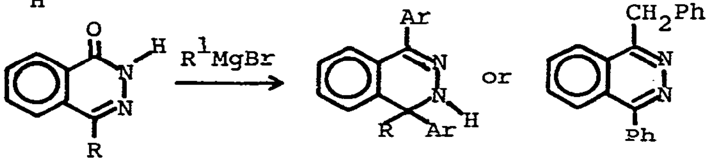
Other additions reported for heterocyclics with a formal amide function include:



[377]

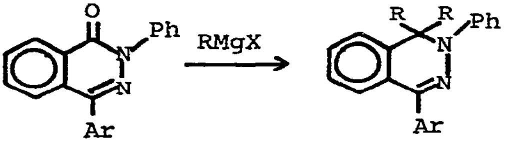


[378]



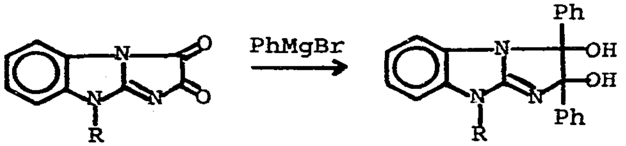
[379]

R = H, Ph; $R^1$ = Ar, benzyl



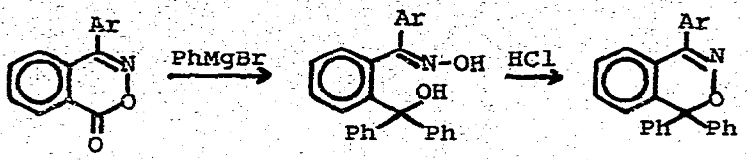
[379]

R = phenyl, benzyl

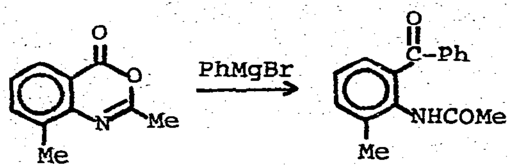


[380]

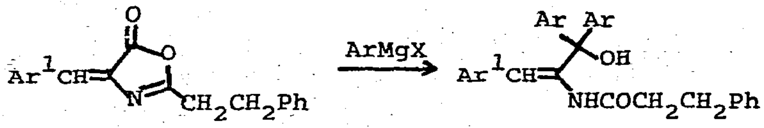
Ring-cleavage was observed in the following cases:



[381]

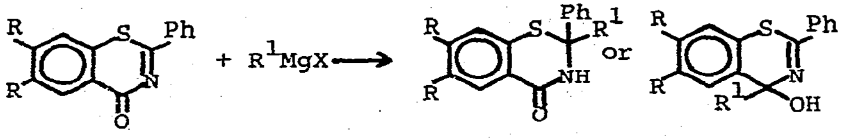


[382]



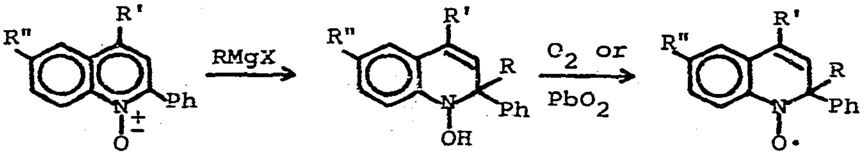
[383]

The principal pathway for the following reaction depends upon the Grignard reagent used [384]:

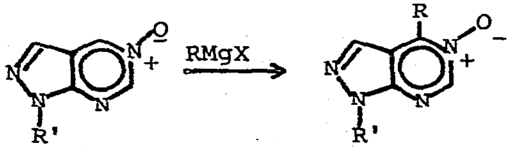


R = H, OMe $\qquad$ $R^1$ = alkyl $\qquad$ $R^1$ = Ph

Addition to azine oxides *155* [385] and *156* [386] has been reported:



*155*

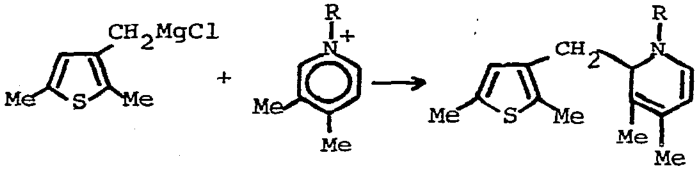


*156*

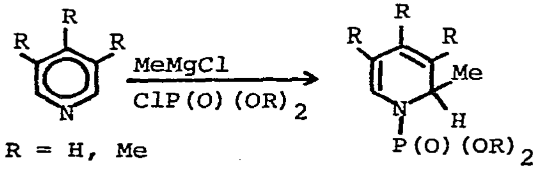
The reaction of pyridine with alkylmagnesium compounds has been studied under varied circumstances [387]. Ether-free butylmagnesium iodide in toluene gives exclusively 2-butylpyridine, but with excess magnesium some 4-butylpyridine is formed. Reaction of butyl halides with magnesium in refluxing pyridine gave higher yields, and only the 4-butyl isomer. Side-chain alkylation of methylpyridines was observed under similar conditions. For these and other results, a mechanism was

was proposed involving the pyridine radical anion. Allyl chloride produced allylpyridine, but heating to 118° before hydrolysis produced propylpyridines by an internal hydrogenation-dehydrogenation. In another study, orientation in addition to pyridines and 1-acylpyridinium salts was found to be influenced by steric effects [388].

The 1,2,4-trisubstituted dihydropyridines produced by addition of Grignard reagents to 1,4-disubstituted pyridinium salts were studied [18]. Other pyridine and pyridinium reactions include:

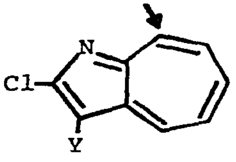


[130]

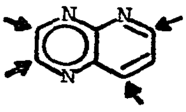


[389]

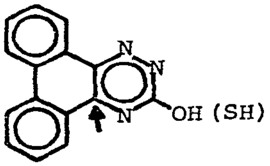
Addition of PhMgBr to *157* takes place preferentially at the 8-position, in contrast with MO calculations (which predict reaction at $C_4$) and 2-chloroazalene (in which chloride displacement occurs) [390]. Reaction of derivatives of *158* occurs at various positions depending upon aryl or bromine substitution on the rings [391]. The triazine derivative *159* reacts at the indicated position, in similar fashion to non-condensed 1,2,4-triazines [392].



*157*, Y = H, COOH

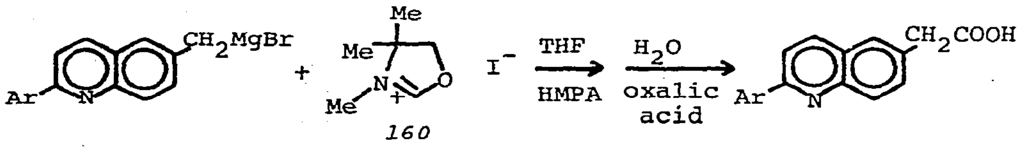


*158*

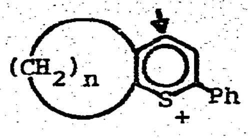


*159*

Reaction of the oxazolinium salt *160* with Grignard reagents led to the same net result as carbonation [393]:

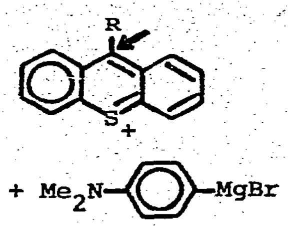


Addition of Grignard reagents to thiapyrilium ions was reported in two papers:



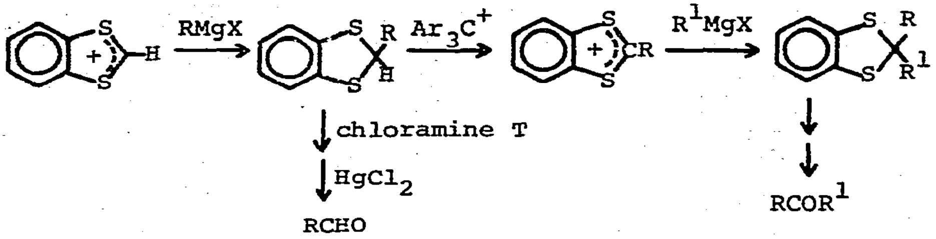
+ EtMgBr

[394]

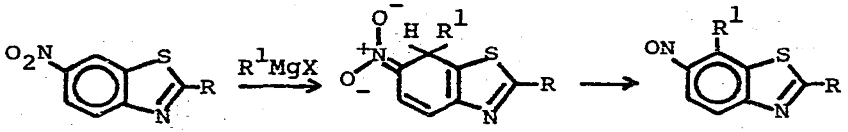


[395]

An aldehyde or ketone synthesis *via* Grignard coupling with a "masked acyl cation" has been published [396]:



An internal redox reaction aromatizes the intermediate *161* [397]:

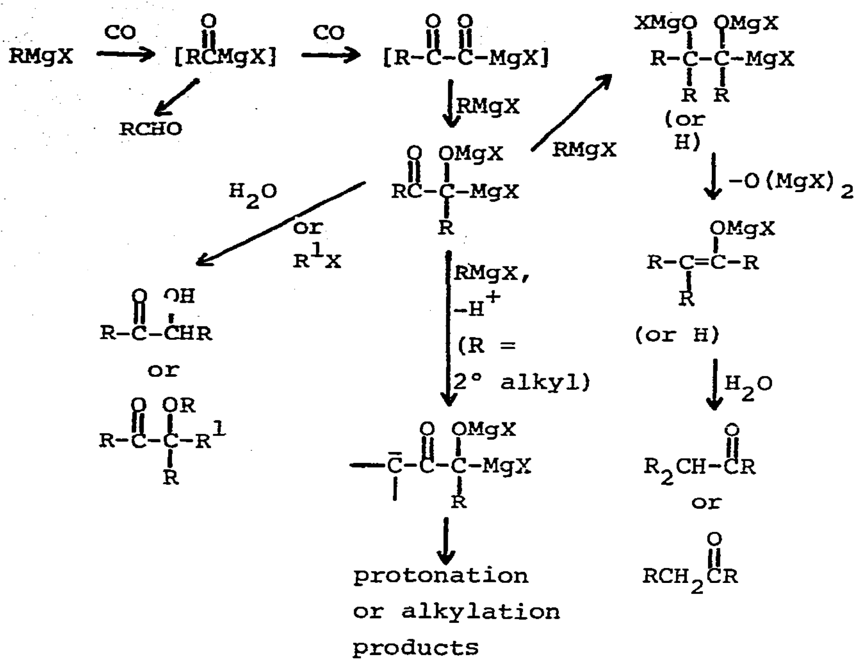


R = H, Me

*161*

G. Addition to Other Unsaturated Compounds

Carbonylation of Grignard reagents has been found to occur rapidly and in fair yield in the presence of HMPA [398, 399]. A variety of products was formed, depending upon the nature of the Grignard reagent (1°, 2°, 3°, or aryl) and condition The aldehyde from simple single addition was not normally present in large amount, but could be isolated in low yield (R = Ph, Bu). With tertiary or aryl Grignard reagents, an acyloin from two moles each of Grignard reagent and CO could be isolated in good yield. With primary Grignard reagents, addition or reduction by a third mole of Grignard reagent led to ketone as a major product. Mixtures were generally obtained from secondary Grignard reagents; enolization of the 2:2 intermediate adduct apparently occurs:

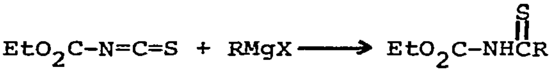


A catalytic carbonylation has also been reported [400]:

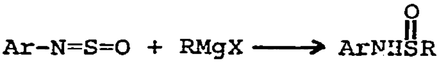
$$RMgX + R^1X + CO \xrightarrow{NiY_2L_2} RCOR^1 + R_2R^1COH$$

($Y$ = alkyl, halogen; $L$ = phosphine ligand; $R$, $R^1$ = alkyl, phenyl)

Other addition reactions reported include:



$$EtO_2C\text{-}N{=}C{=}S + RMgX \longrightarrow EtO_2C\text{-}NH\overset{\overset{S}{\|}}{C}R \qquad [401]$$



$$Ar\text{-}N{=}S{=}O + RMgX \longrightarrow ArNH\overset{\overset{O}{\|}}{S}R \qquad R = R^1C{\equiv}C\text{-} \ [402] \qquad R = \text{perfluoroalkyl} \ [74]$$

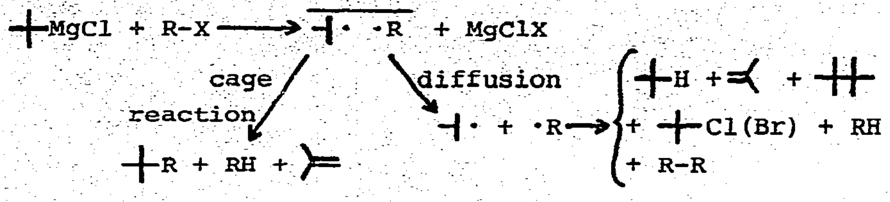
$$C_6Cl_5N{=}O + C_6Cl_5MgCl \longrightarrow (C_6Cl_5)_2NOH \qquad [403]$$

$$ArN{=}S{=}NAr + RMgX \longrightarrow (ArNS(R)NAr)MgX \qquad [159,160;\ \text{see section II, D}]$$

## VI. Displacement Reactions of Organomagnesium Compounds

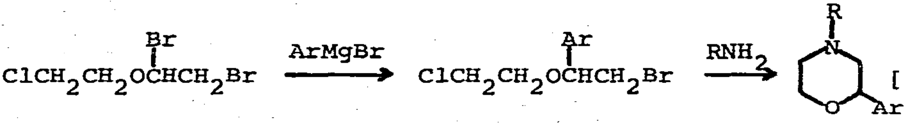
### A. Coupling or Displacement Reactions with Alkyl Halides or Sulfonates

CIDNP observations in the reaction of *t*-butylmagnesium chloride with $CHCl_3$, $CCl_4$, $CBrCl_3$, and $PhCHCl_2$ indicate an electron-transfer radical pair mechanism [404–406]:

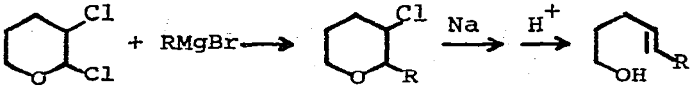


Styrene decreased polarization resulting from free radical encounter pairs [406]. Cage reaction of *t*-butyl and trichloromethyl radicals to produce *t*-butyl chloride and dichlorocarbene was also proposed to explain polarization of products derivable from $CCl_2$ [405]. Another CIDNP study of the iron-catalyzed Grignard reagent-alkyl halide reaction has been discussed in connection with the mechanism of Grignard reagent formation (section II, A).

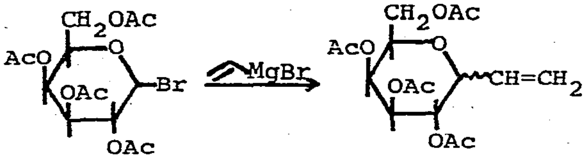
A number of examples of uncatalyzed coupling with organic halides may be noted. Important types include α-halo-ethers allylic or propargylic halides, and halogen α to carbonyl or other polar unsaturated groups.



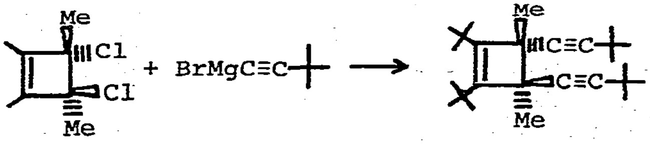
[40



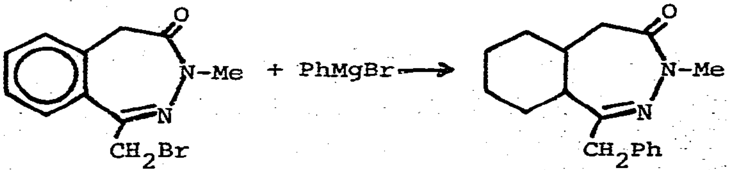
[408,409]



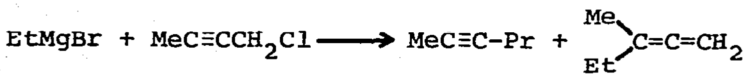
[410]



[411]

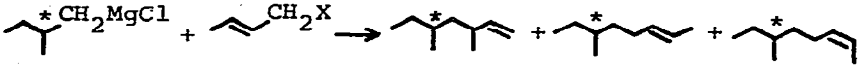


[412]

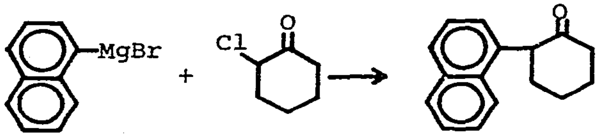


$EtMgBr + MeC\equiv CCH_2Cl \longrightarrow MeC\equiv C\text{-}Pr + (Me)(Et)C=C=CH_2$

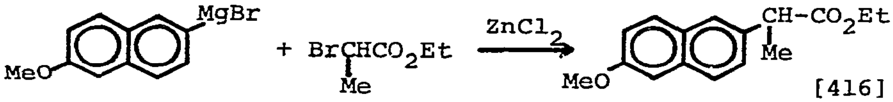
| | | | | |
|---|---|---|---|---|
| 0° | (ether) | 72 | 28 | [413] |
| 45° | (ether) | 39 | 61 | |
| 105° | (amyl$_2$O) | 2 | 90 | |



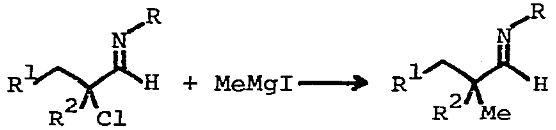
| | | | | | |
|---|---|---|---|---|---|
| (98% S) | X = Cl<br>(THF-HMPT) | 100 | 0 | 0 | [414] |
| | X = Br<br>(Et$_2$O, or Li$_2$CuCl$_4$ in THF) | ~50 | ~40 | ~10 | |



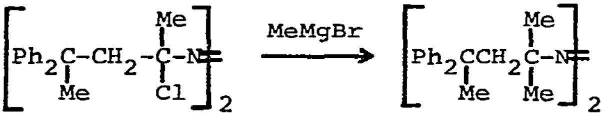
[415]



[416]



[417]

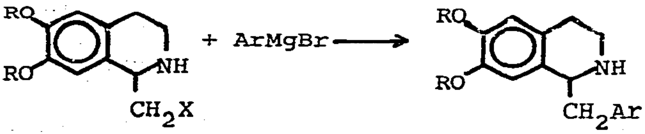


$$\left[Ph_2\underset{Me}{C}\text{-}CH_2\text{-}\overset{Me}{\underset{Cl}{C}}\text{-}N=\right]_2 \xrightarrow{MeMgBr} \left[Ph_2\underset{Me}{C}CH_2\overset{Me}{\underset{Me}{C}}\text{-}N=\right]_2$$

[418]

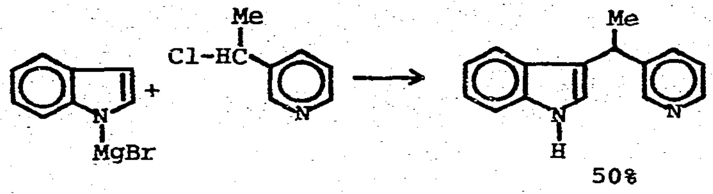
Several coupling reactions with allylic Grignard reagents have previously been noted in section III, D. The coupling reactions with α-halocarbonyl derivatives contrast with selective reaction at the carbonyl group for examples in sections III, C [182,184, 253,254] and III, E, [184]. Some additional uncatalyzed coupling reactions are:

$MeMgBr + ClC\equiv C\text{-}P(O)(OBu)_2 \longrightarrow MeC\equiv C\text{-}P(O)(OBu)_2$ [419]



[420]

$(\eta_5\text{-cp})_2\overset{CO}{\underset{PPh_2}{Fe}}\text{-}CH_2Cl \xrightarrow{RMgX} (\eta_5\text{-cp})_2\overset{CO}{\underset{PPh_2}{Fe}}\text{-}CH_2R$ [421]



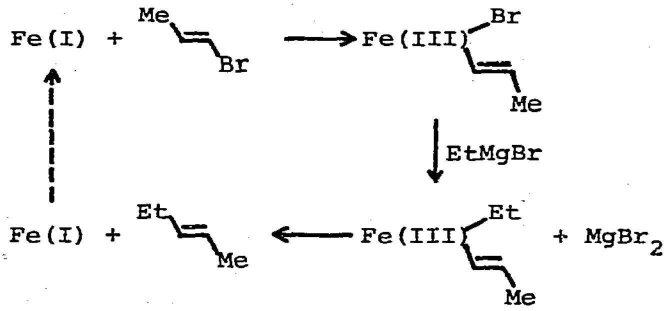
[193]

Reactions of Grignard reagents with fluoroalkenes are discussed in section V, B.

Catalysis of the coupling reactions of Grignard reagents with alkyl halides by transition metal salts or complexes have been studied by a number of groups. Several reviews have appeared [9-11].

In a careful study of the catalysis of coupling between vinyl halides and alkyl Grignard reagents by iron dibenzoylmethane, Smith and Kochi have proposed the mechanism [422]:

$$Fe(III) + EtMgBr \longrightarrow Fe(I) + C_2H_6 + C_2H_4$$



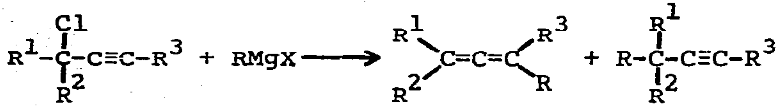
The rate was dependent upon vinyl bromide, but essentially independent of Grignard reagent concentration. The product was formed stereospecifically with retention. Side reactions included a few percent of metal-halogen exchange, and two processes with the stoichiometry:

$$2EtMgBr + MeCH{=}CHMgBr \longrightarrow C_2H_6 + C_2H_4 + MeCH{=}CH\text{-}CH{=}CHMe + 2MgBr_2$$

and

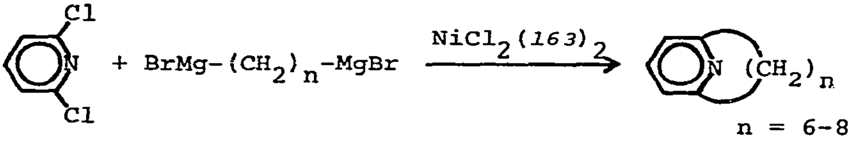
$$MeCH{=}CHBr + EtMgBr \longrightarrow MeCH{=}CH_2 + C_2H_4 + MgBr_2$$

A similar mechanism was proposed by Pasto for coupling of propargylic halides with Grignard reagents [423]:

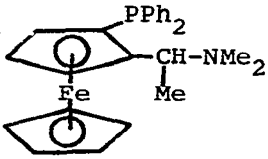


In the presence of $5 \times 10^{-5}$ M $FeCl_3$, allene is formed rapidly. Without catalysis, a mixture of allene and alkyne forms much more slowly. Discovery of the very efficient catalysis explains contrasting results in the literature, and provides a method of choice for allene synthesis.

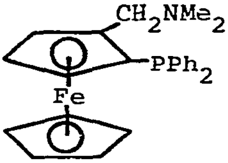
Several papers have been published by Kumada and coworkers on nickel catalysis of cross-coupling between Grignard reagents and aryl or vinyl halides [424-427]. A wide variety of $NiCl_2$-(phosphine)$_2$ complexes were studied; the ligands $Ph_3P$ (*162*), $[Ph_2PCH_2]_2CH_2$ (*163*) and $[Me_2PCH_2]_2$ (*164*) were preferred for various Grignard-halide combinations. The reaction is successful for a variety of alkyl, aryl, alkenyl, and allyl Grignard reagents. Ether as solvent and aryl or vinyl chlorides are preferred; even fluorobenzene reacts. A number of varied examples of the nickel-catalyzed coupling to heterocyclic aryl halides were reported [425]; the following is one of the more interesting:



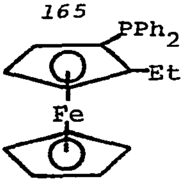
Several chiral phosphine ligands, including *165-168* were used



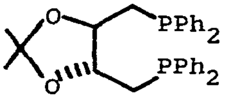
*165*



*166*



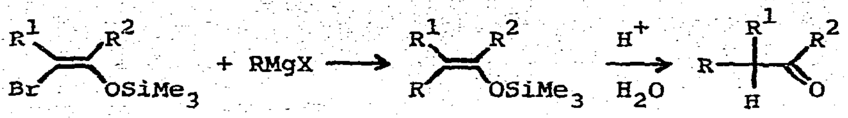
*167*



*168*

to bring about asymmetric induction in couplings. Ligands *165* and *166* were most effective, giving optical purities of 50-60%

or more [426]. This coupling reaction has also been incorporate into ketone [427] and aldehyde [428] syntheses:



$$\mathrm{BrCH{=}CHOEt} + \mathrm{RMgX} \longrightarrow \mathrm{RCH{=}CHOEt} \xrightarrow[H_2O]{H^+} \mathrm{RCH_2CHO}$$

(not stereospecific)

A nickel-catalyzed coupling combined with rearrangement is noted in section VII, A.

Aryl iodides and bromides may also be coupled with Grignard reagents in good yield using $[Ph_3P]_2PdArI$ at concentrations as low as $10^{-4}$ [429]. A mechanism similar to that drawn for iron catalysis was proposed, involving Pd(II) and Pd(0) intermediates.

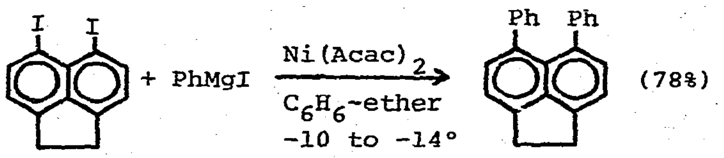
A study has also been published of the CuI or $Li_2CuCl_4$-catalyzed coupling of vinylic Grignard reagents with alkyl halides which gives yields of 82-97% [430]. The use of $MgX_2$- or LiX-CuCN complexes for coupling of Grignard reagents with organic halides or sulfonates has been patented [431].

The reaction of isopropylmagnesium chloride with various aryl or vinylic halides catalyzed by 1% of $MnCl_2$ gives reduction of the halide, accompanied in some cases by crossed coupling [432].

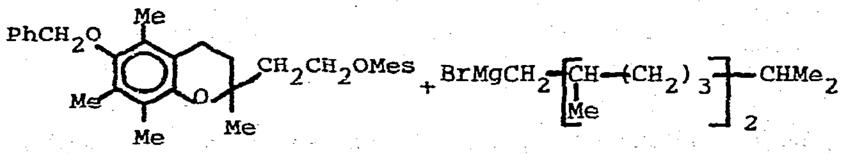
Some less routine examples of catalyzed crossed coupling are:

$$\mathrm{RMgX} + \mathrm{Br(CH_2)_nCO_2MgCl} \xrightarrow{Li_2CuCl_4} \mathrm{R{-}(CH_2)_nCO_2MgCl} \qquad [433]$$

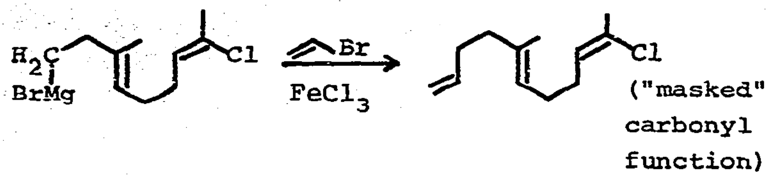
*e.g.* $R = C_5H_{11}$, n = 10 (94%); R = sec-Bu, n = 4 (88%)



[434]



$+ Li_2CuCl_2$ [435]

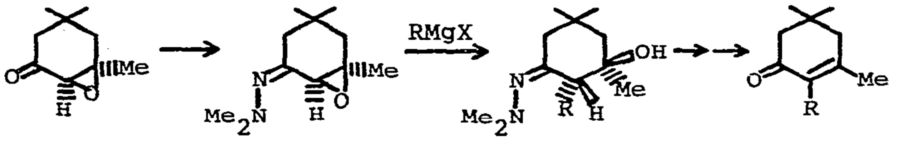


[436]

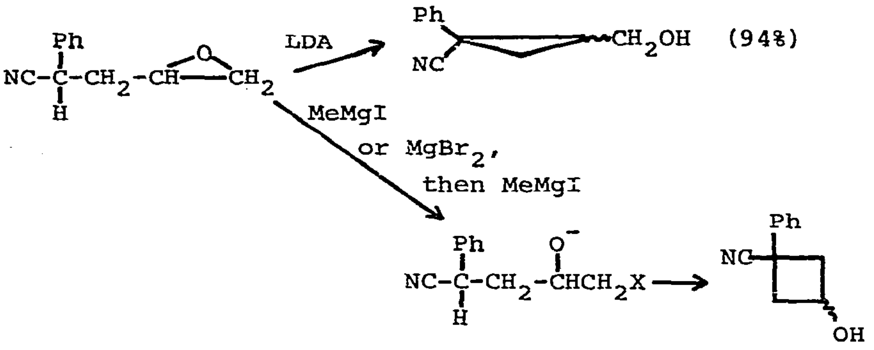
Catalyzed coupling reactions were reported in a number of previously-cited references: nickel and palladium complexes [70,97,101]; $Li_2CuCl_4$ or CuCl [78,84,85,89]; magnesium cuprate [158].

B. Reaction with Ethers, Epoxides, Acetals, etc.

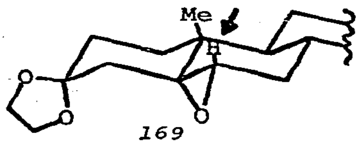
The reaction of Grignard reagents with epoxides is a step in a new synthetic sequence for α-β-unsaturated ketones originated by Stork and Ponaras [437]; *e.g.*



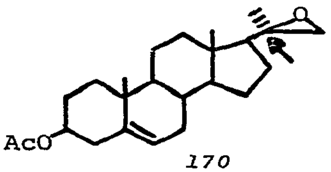
The following intramolecular epoxide cleavage depends on the base used [438]:



A steroidal epoxide *169* reacts with allylmagnesium bromide by displacement at the secondary position [439]. The epoxy acetate *170* reacted with isoamylmagnesium bromide



*169*

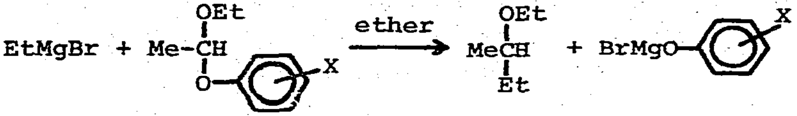


*170*

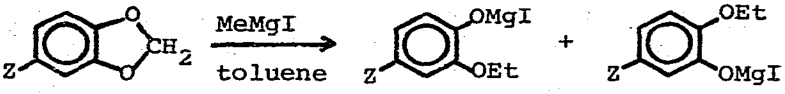
preferentially at the ester function. A small yield (5-12%) of product from addition to the *tertiary* carbon of the epoxide was isolated, along with a dimeric product of unknown structure [277].

Several reactions of epoxides with allylic and propargylic Grignard reagents are discussed in section III, D. Alkynyl Grignard reagents added normally to the primary epoxy carbon of epichlorohydrin [184].

The kinetics of the acetal reaction below appear to be second order [440]. A ρ-value of +2.35 for aryl ring substituents



is similar to +2.11 for ArOH ionization in water, and is consistent with an $S_N2$ or an unsymmetrical 4-center mechanism. The cleavage of *171* occurs preferentially at the oxygen *para* to

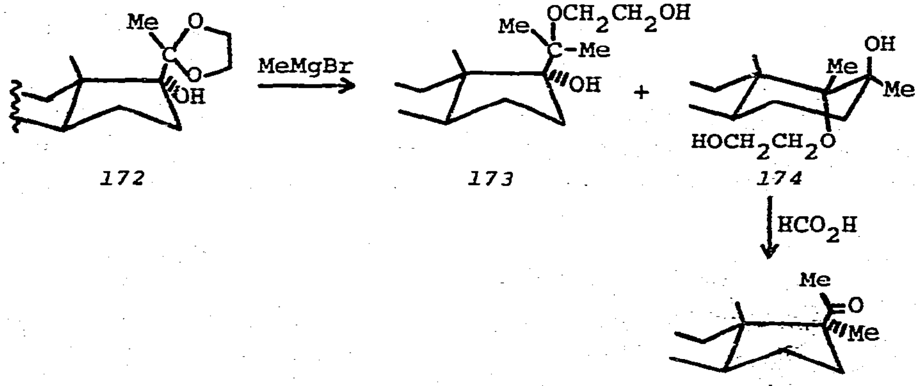


*171*

Z = Me, H, Cl

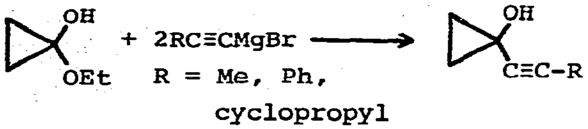
methyl and *meta* to chlorine (with reduced rate). Two moles of Grignard reagent are required, since product forms an unreactive complex with reagent [441].

A previous report that reaction of *172* yielded product *173* in two *isolable* rotameric forms has been shown incorrect [442]. The second product *174* is formed by carbonium ion rearrangement. Both products undergo pinacolic rearrangement to *175*.

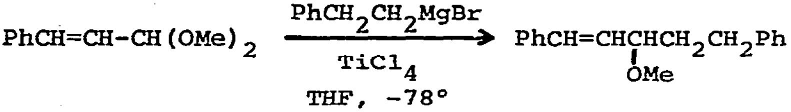


*172* *173* *174* *175*

The ethanol hemiketal of cyclopropanone reacts with displacement of the ethoxy group [443]:

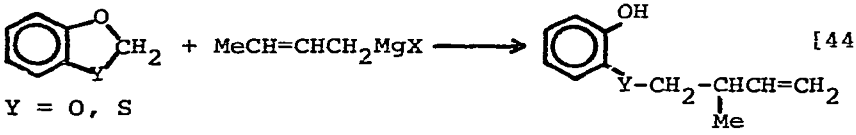


Titanium halides are reported to catalyze the displacement cf Grignard reagents with a variety of allylic acetals [444]; *e.g.*



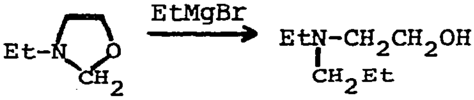
$$PhCH{=}CH{-}CH(OMe)_2 \xrightarrow[\text{TiCl}_4,\ \text{THF},\ -78°]{PhCH_2CH_2MgBr} PhCH{=}CH\underset{\displaystyle OMe}{C}HCH_2CH_2Ph$$

Displacement of the alkoxy group in several mixed systems has also been reported:

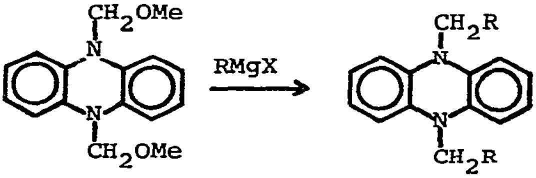


[445]

(95-97% α-methylallyl)

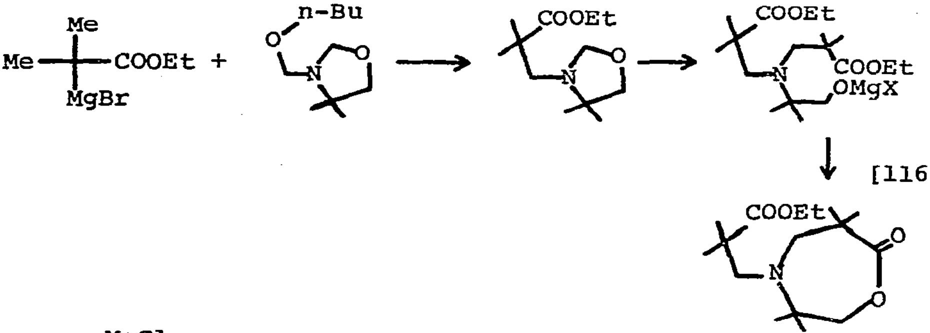


[446]

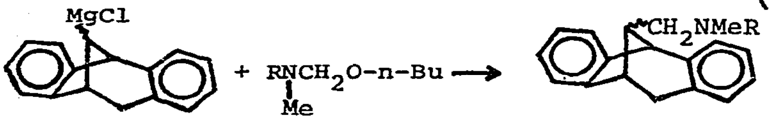


72-90%

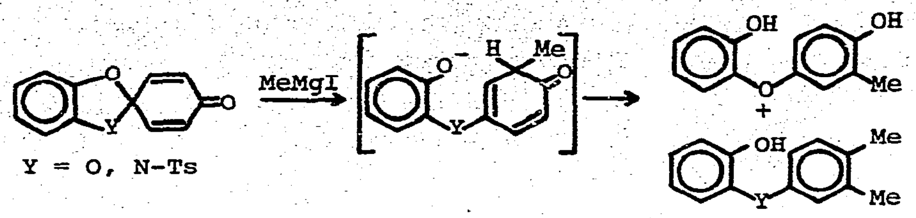
[447]



[116]

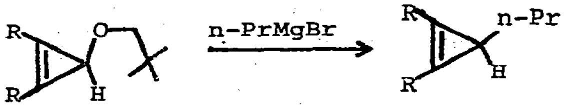


[127]

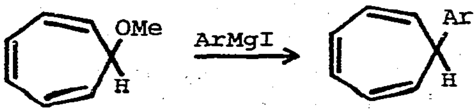


[448]

Grignard reagents reacted with cyclopropenyl and cycloheptatrienyl ethers, most probably *via* the corresponding carbonium ions [449,450].



R = Et, n-Pr

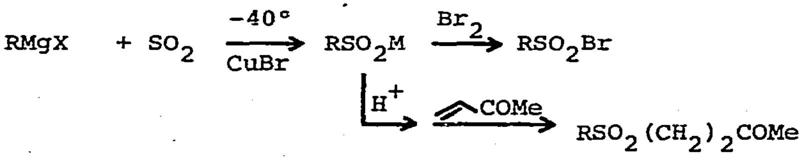


Reaction of the 1,4-diphenyl-1,3-butadiene--magnesium adduct with tetrahydrofuran [55] has been described in section III, D.

Displacement reactions of a variety of allylic, propargylic and vinyl ethers, amines, and acetates are described in sections V, B and V, C.

## C. Displacement Reactions at Sulfur

Organocuprates from Grignard reagents were reported to react with sulfur dioxide [451]:

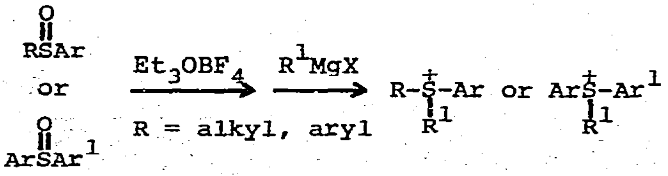


$$RMgX + SO_2 \xrightarrow[CuBr]{-40^\circ} RSO_2M \xrightarrow{Br_2} RSO_2Br$$

$$RSO_2M \xrightarrow{H^+} \xrightarrow{\text{CH}_2\text{=CHCOMe}} RSO_2(CH_2)_2COMe$$

A patent reports reaction of vinylmagnesium bromide with sulfuryl chloride [452].

Sulfonium salts were formed from sulfoxides [453]:



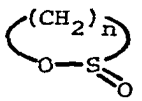
$$\overset{O}{\overset{\|}{RSAr}} \text{ or } \overset{O}{\overset{\|}{ArSAr^1}} \xrightarrow[R\,=\,\text{alkyl, aryl}]{Et_3OBF_4} \xrightarrow{R^1MgX} R\text{-}\underset{R^1}{\overset{+}{S}}\text{-}Ar \text{ or } Ar\underset{R^1}{\overset{+}{S}}\text{-}Ar^1$$

With only one aryl group present, inversion of configuration was found; otherwise the product was racemic. Dimethylsulfoxide with ethylmagnesium bromide gave some methyl ethyl sulfoxide, dimethyl sulfide, and ethylene [62].

Reactions of Grignard reagents with sulfinate esters *176*-*179* to yield sulfoxides have been reported [454,455]. A major side reaction was reduction of the sulfoxide product to a sulfide [454]. Partial kinetic resolution was reported in the reaction of racemic sulfinic esters *176*, *178*, and *179* with optically active Grignard reagents $RCHEtCH_2MgCl$ (R = Me, Ph) [455]. The (S)-Grignard reagent reacted more rapidly with (R)-sulfinate; optical purity of recovered sulfinates ranged from 8 to 64%. In reactions of optically pure *180*, asymmetric induction in the incoming group is found--as high as 60% in the allene [456].

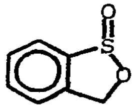
$\mathrm{Ar\overset{O}{\overset{\|}{S}}OMe}$

*176*

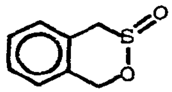


n = 3, 4

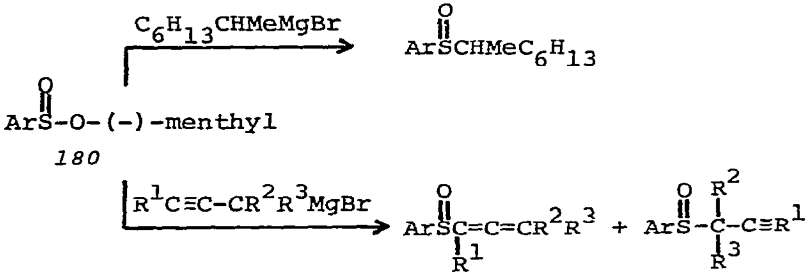
*177*



*178*



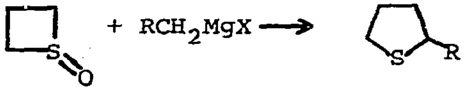
*179*



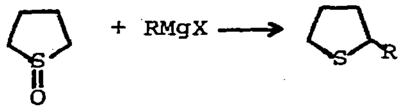
*180*

Inversion of configuration in reaction of MeMgI with thiosulfinate ArS(O)-S-*t*-Bu was used to establish its absolute configuration [457].

Substitution and ring-expansion reactions were found for cyclic sulfoxides [458]:

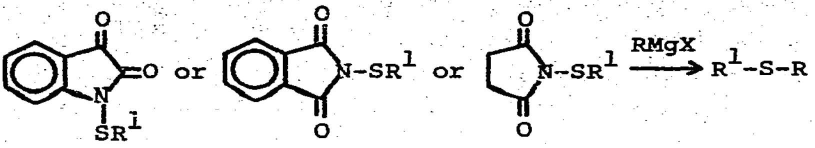


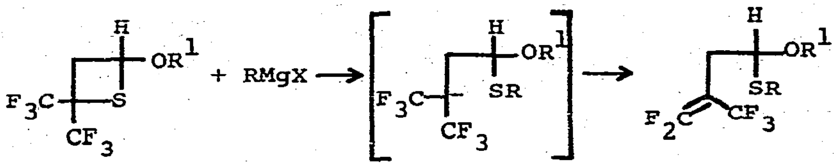
R = H, Me, Ph, o-Tol

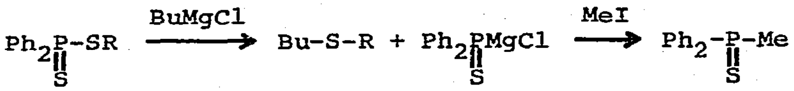


R = Me, $PhCH_2$

Nucleophilic attack on divalent sulfur occurred in th following reactions, with formation of a thioether:

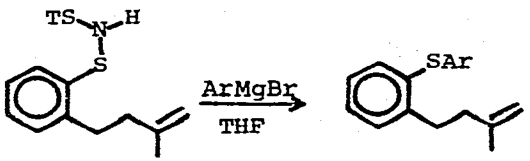


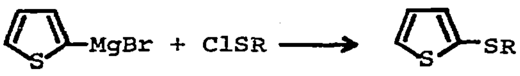




$Ph_2\underset{\|S}{P}-SR \xrightarrow{BuMgCl} Bu-S-R + Ph_2\underset{\|S}{P}MgCl \xrightarrow{MeI} Ph_2-\underset{\|S}{P}-Me$

R = Me, $PhCH_2$, Ph





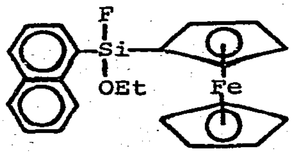
R = $CFCl_2$, $CCl_3$, $\underset{\|O}{C}F$

D. Alkylation of Other Elements

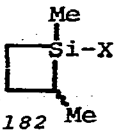
The displacement of halide ion or other leaving grou on a metalloid or metal derivative by the alkyl group of a Grignard reagent is a common preparative procedure. General synthetic or mechanistic studies, and a number of less routi examples will be cited. Other examples are referenced in sections II, C, 7 and III, D.

Group IV metals and metalloids. Reaction of n-alkyl Grignard reagents with $MeSiCl_3$ gave good yields of $RSiCl_2Me$; a second alkylation occurred with difficulty, and no tetraalkylsilane was formed [464].

The fluoroethoxy silane *181* led to unusual stereochemi



*181*



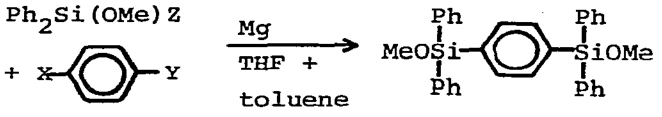
*182*

+ RMgX

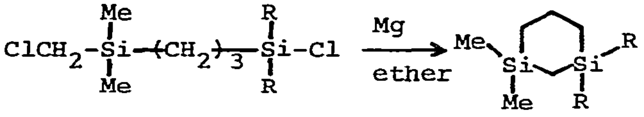
X = Cl, R = p-ani
X = OMe, O-t-Bu
R = alkyl, pheny
allyl, benzy

[465]. With Grignard reagents, ethoxy was replaced, and the stereochemistry was retention in all cases except allyl; alkyllithiums displaced fluoride with inversion. Retention of configuration was found in all displacements of *182* [466,467].

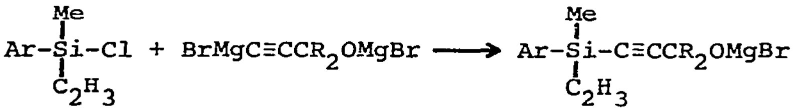
Some additional alkylations of silane derivatives are:



[468]

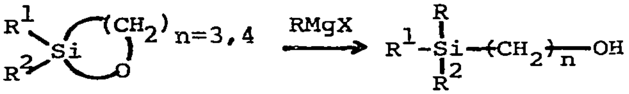


R = Me, Cl [469]



$$\text{Ar-}\underset{C_2H_3}{\overset{Me}{Si}}\text{-Cl} + BrMgC{\equiv}CCR_2OMgBr \longrightarrow \text{Ar-}\underset{C_2H_3}{\overset{Me}{Si}}\text{-}C{\equiv}CCR_2OMgBr$$

[102]



[470]

$R^1 = R^2 = Me$; $R^1$ = α-naphthyl, $R^2$ = phenyl;

R = alkyl, vinyl, allyl, benzyl

The reaction of organic compounds with halosilanes in the presence of magnesium is discussed in section II, A [38,39].

A synthetic sequence for tetraalkyltin compounds, a Mg-catalyzed oxidative addition of alkyl halides to $SnCl_2$, and an improved preparation of hexamethyldilead may also be noted:

$$Sn + RX \longrightarrow R_2SnX_2 \xrightarrow{R^1MgX} R_2SnR_2{}^1 \qquad [471]$$

$$SnCl_2 + RCl \xrightarrow[I_2]{Mg} RSnCl_3 \qquad [472]$$

$$6MeMgI + 3PbCl_2 \longrightarrow Me_6Pb_2 + 3MgCl_2 + 3MgI_2 + Pb \qquad [473]$$

*In situ* reactions of magnesium and 2-trimethylsilylallyl chloride with $Ph_3GeCl$ and $Me_3SnCl$ have been reported [474].

Earlier references cite alkylations of Si [137,139,141, 146,147,174-176], Ge [174], Sn [133,134,141,143,174], and Pb [174]

Group V. The reaction of $PCl_5$ with organomagnesium and -lithium reagents was studied [475]. Successive replacement of halogens to $R_3PCl_2$ occurs. This is hydrolyzed to $R_3PO$ or undergoes nucleophilic attack on Cl, producing RCl and $R_3P$.

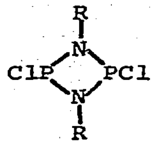
An improved method for preparing di(cyclohexyl)chlorophosphine from $PCl_3$ was published [476]. Replacement of chloro or alkoxy groups are reported for the following:

$PhC{\equiv}CP(OEt)_2$ + 2ArMgBr

[477]

$R^1SCH{=}CHPCl_2$ + 2RMgX

[478]

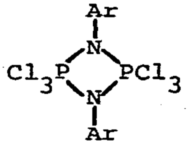


+ 2MeMgI

[479]

$Cl_2P(O){-}C(Cl){=}C(Cl)OEt$ + EtMgBr

[480]



+ RMgX (R = Et, Ph)

[481]

In [480], double alkylation on phosphorous occurs, followed by replacement of the terminal vinylic chlorine. The product in [481] was a mixture including mono- and di-alkylations of the phosphorous, and condensed product. A detailed preparation of $(C_6D_5)_3P$ from $PCl_3$ was given [482].

The reaction of $PhAsCl_2$ with a mixture of MeMgI and *i*-propyl-MgBr gave a better yield of the mixed tri-substituted arsine than a sequential synthesis [483]. Detailed procedures have been published for syntheses of $C_6F_5AsMe_2$ [484] and o-$BrC_6H_4AsMe_2$ [485]. Earlier references cited alkylation of phosphorous [103,124,141] and arsenic [136,141].

Group III. Alkylation of boron is reported in [141] and [145]. The reaction of aluminum halides with cyclohexyl Grignard reagents gave a tricyclohexylaluminum product which could not be obtained free of halide; $R_2AlCl$ and $RAlCl_2$ were prepared. Chlorocyclohexane reacted with aluminum and magnesium to form a mixture of aluminum and magnesium derivatives which could not be separated [486].

Transition elements and actinides. Titanium-magnesium complexes with nitrogen-fixing reactivity have been noted previously [153-155]. Dialkylamino organotitanium derivatives have been prepared, where the organic groups are benzyl and $Me_3SiCH_2$- [487].

Reagents from Grignard compounds and $MnI_2$ are useful for preparing ketones from acid chlorides [270].

Some reactions which have been reported are:

| | | |
|---|---|---|
| $CrCl_n$ (n = 2,3)<br>$+\ n\ MeCH{=}CH\underset{\underset{MgCl}{\mid}}{C}HMe$ | $FeCl_2$ or $MoO_2Cl_2$<br>+ 2 mesityl-MgBr | $BrCo(Acacen)PPh_3$<br>$+\ C_6F_5MgX$ |
| [488] | [489,490] | [491] |

$$Re_3Cl_9 + RMgCl \longrightarrow Re_3Cl_3R_6$$

[492]

$$ReR_5 \text{ or } ReR_4{\cdot}THF \xrightarrow{RMgCl} \underset{(\text{under } N_2)}{ReR_8N_2} \text{ or } \underset{(\text{under } O_2)}{ReOR_4} \text{ or } \underset{(\text{under Ar})}{Re_3R_{12}}$$

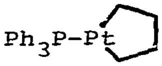
$$(\eta^5\text{-cp})_3ThCl + RMgX \longrightarrow (\eta^5\text{-cp})_3ThR \qquad [493]$$

$$Me_2AuI{\cdot}PPh_3 + CD_3MgI \longrightarrow \textit{cis}\text{-}Me_2AuCD_3{\cdot}PPh_3 \qquad [494]$$

$$(\eta^5\text{-cp})(Ph_3P)PdBr \xrightarrow[-78°]{RMgBr} (\eta^5\text{-cp})(Ph_3P)PdR \qquad [495]$$

R = Me, Bu, Ph

$$(COT)PtCl_2 + BrMg(CH_2)_4MgBr \longrightarrow \xrightarrow{Ph_3P}$$



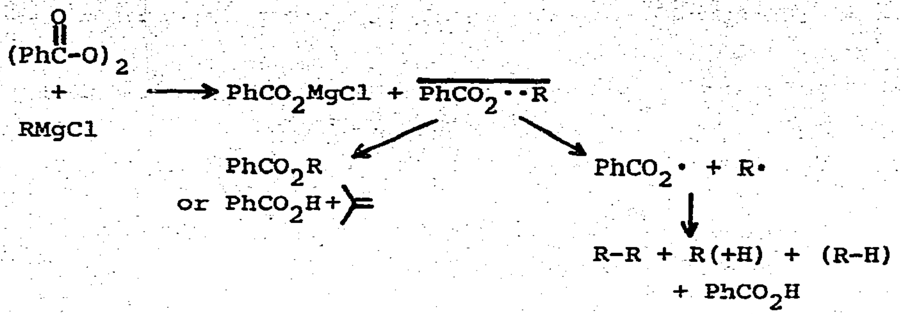
[496]

Formation of a platinum metallocycle [135] and reaction of $NiCl_2$ with 2-trimethylsilylallylmagnesium bromide [474] have been reported.

The alkylation of a transition metal intermediate has been proposed as a probable step in the crossed coupling of Grignard reagents with organic halides (see section VI, A) [422-429].

## E. Reaction with Peroxides and Disulfides

CIDNP studies have been made of the reactions of t-butyl- and benzylmagnesium chlorides with benzoyl peroxide [497,498]. Results were explained on the basis of single electron transfer to form a radical pair:

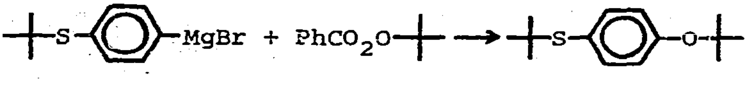


With the *t*-butyl Grignard reagent, polarization of isobutane, isobutene, and 2,3-dimethylbutane was observed; in the presence of styrene, only the isobutene was polarized. With benzylmagnesium chloride, polarization of the benzylic $CH_2$ was observed in the dimer and the ester (and in benzyl chloride which results from a pathway not clearly defined).

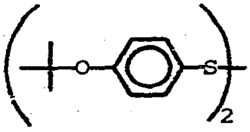
CIDNP observations in the reaction of *t*-butylmagnesium chloride with dibenzoyldisulfide were interpreted on the basis of a similar scheme [499].

A variety of techniques were used to study electron-transfer processes in reactions of Grignard reagents with peroxides [23].

Grignard reagent *183* reacted with *t*-butyl perbenzoate [502]. The disulfide *184* was formed by a Grignard reaction with elemental sulfur.



*183*



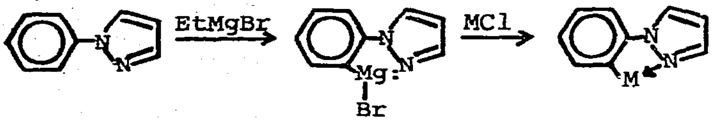
*184*

## F. Reaction As a Base; Metallation

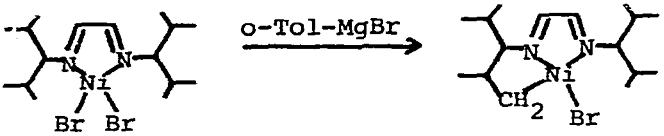
Preparation of a number of organomagnesium compounds by proton removal from an organic substrate has been discussed in sections II, B [61-65] and II, C, 4 [115,117-119].

Phenylmagnesium bromide reacts with acetylene in the presence of secondary and tertiary amines to form complexes of the di-(bromomagnesium) derivative of acetylene. The diethylamine complex was isolated and characterized [501]. Kinetics of the reaction were studied [502-504]. The catalytic activity of amines was directly related to basicity, and was less important in the more basic THF as solvent. Disproportionation of an initially-formed mono-magnesium derivative was proposed.

Cyclic metal complexes were formed by proton abstraction:

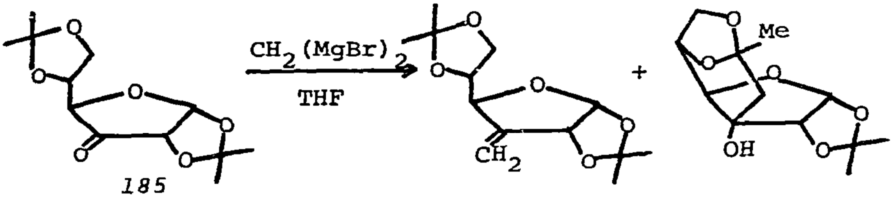


[505]



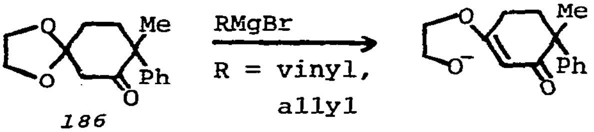
[506]

The latter example is noteworthy in that there is no apparent activation of the proton abstracted. Another unusual attack on an unactivated carbon was reported as a side-process in the Wittig-type reaction of *185*; the abnormal product was absent when the reagent was prepared and used *in situ* [140].



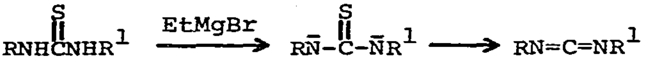
*185*

Proton abstraction from *186* and *187* leads to elimination:



*186*

[507]

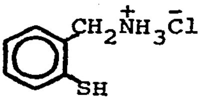


$$\underset{\textit{187}}{\mathrm{RNH\overset{S}{\overset{\|}{C}}NHR^1}} \xrightarrow{\mathrm{EtMgBr}} \mathrm{R\bar{N}\text{-}\overset{S}{\overset{\|}{C}}\text{-}\bar{N}R^1} \longrightarrow \underset{33\text{-}61\%}{\mathrm{RN{=}C{=}NR^1}}$$

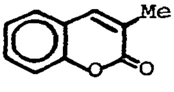
[508]

Elimination, with cleavage of an oxazoline ring, is also a probable mechanistic step in the ketone synthesis in [178] (see section V, A).

Formation of the di-magnesium salt from *188* leads to a



*188*



*189*

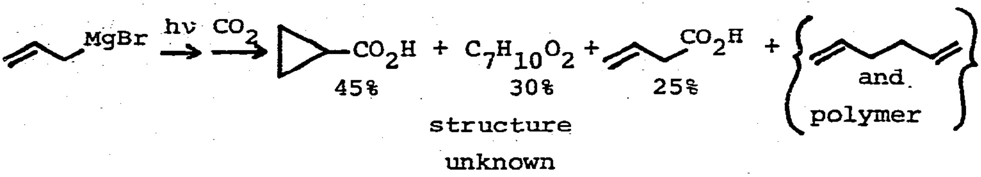
nucleophile useful for further transformations [509]. Proton abstraction from the methyl group of *189* was favored by a deficiency of magnesium [284]. Only enolization was observed in the reaction of rotenone with MeMgI [510].

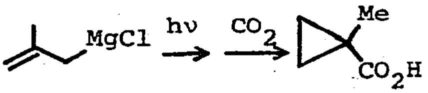
## VII. Other Reactions of Organomagnesium Compounds

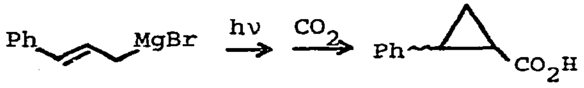
### A. Rearrangements of Organomagnesium Compounds

Reviews which include material on rearrangement have been cited in section I, A [7,20].

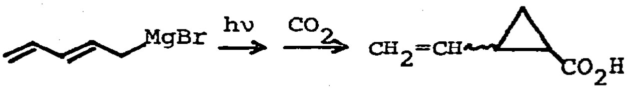
The most novel development in rearrangement chemistry is the finding by Cohen and Yogev that allylic magnesium compounds are photocyclized (quartz) to cyclopropyl derivatives [166]. The following examples were studied:







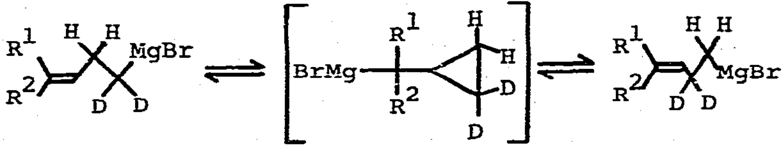
*trans:cis* = 49:1



*trans:cis* = 6:1

No cyclization was observed thermally at temperatures up to 200°.

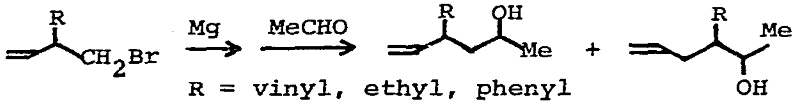
Maercker and Streit have published results of a study of the rearrangement [511]:



*190*

The existence of *190* as an intermediate with finite lifetime rather than a transition state is inferred from the occurrence of *cis-trans* isomerization ($R^1 = H$, $R^2 = Me$) at a rate very similar to that of label rearrangement. The substituent effect on rate ($R^1 = R^2 = H > R^1 = H, R^2 = Me > R^1 = R^2 = Me$) is inconsistent with a radical mechanism of rearrangement. Slowness of the compound with $R^1$ = *t*-Bu indicates considerable steric hindrance to cyclization. The rate shows a steady decrease on variation of the solvent from 100% ether to 100% THF, an increase with HMPA, and a linear increase with increasing concentration. The results were interpreted in terms of a bimolecular mechanism involving $RMg^+$ and $RMgX_2^-$.

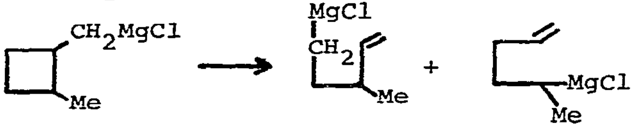
Rearrangements in a similar system have also been investigated by Migianiac [512]:



R = vinyl, ethyl, phenyl

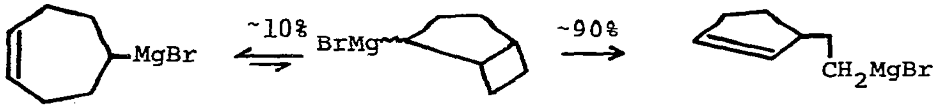
Rearranged product was found only for R = vinyl. Rearrangement apparently occurred during formation of the Grignard reagent, possibly by a radical mechanism; reflux for 3 hr before reaction with acetaldehyde did not change the product ratio. However, there were also isolated substantial amounts of monomeric and dimeric hydrocarbons and alcohols corresponding formally to hydrolysis, coupling and oxygenation of rearranged and unrearranged skeletons.

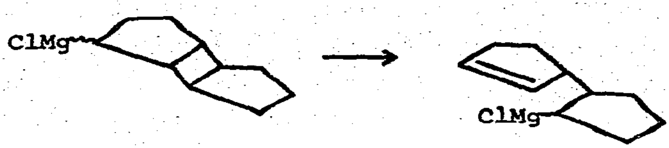
Further evidence against a radical mechanism for rearrangement of Grignard reagent *after formation* came from a study of the system [513]:



The primary Grignard reagent comprised >98% of the cleavage product, whereas the corresponding free radical was shown to cleave mostly in the direction to form a secondary radical. The direction of ring cleavage was also considered to be inconsistent with a single electron transfer mechanism.

Related rearrangement processes involving cleavage of the four-membered ring in bicyclo[3.2.0]heptyl ring systems have been reported [165]:



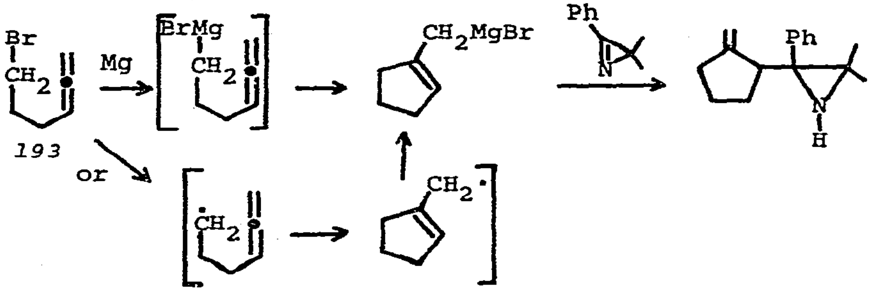


*192*

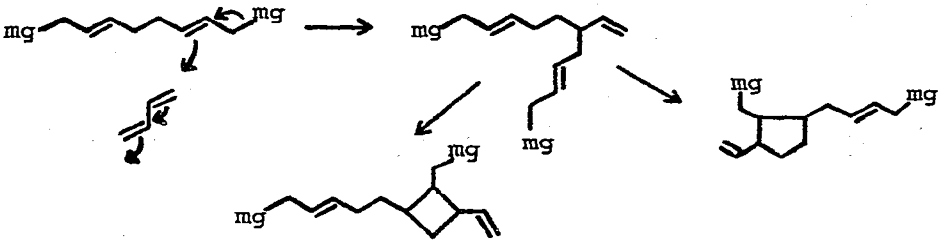
R = Me, Et

In the rearrangement of *191*, cleavage to the cycloheptenyl isomer occurs reversibly to a small extent. Consideration of the rates of the cleavage processes led to the proposal that the preferred geometry of the rearrangement transition state was one in which the C-Mg and C=C bonds are approximately perpendicular. Cleavage of the stereoisomer of *192* with an *endo* alkoxy group appears to be accelerated, and may be a concerted fragmentation process.

The product from a Grignard reagent prepared from bromide *193* indicates cyclization either during or after formation of the Grignard reagent [36]:

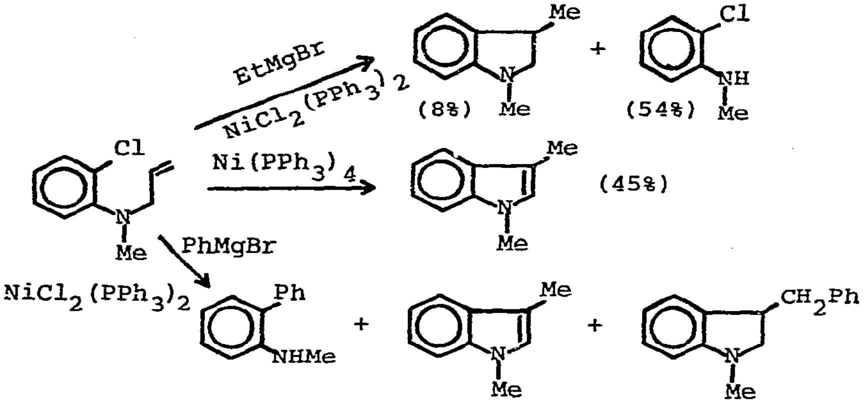


Rearrangement was also apparent in the 3:1 and 4:1 adducts of butadiene with magnesium [54]. The following addition and cyclization processes appear to be indicated in formation of the trimer, based on hydrolysis products:



The 3:1 adduct reacted less readily with a fourth mole of butadiene, and the 4:1 adduct was completely inert to further addition. The hydrolysis products had two rings and no allylic C-Mg bonds, indicating a second cyclization.

Cyclizations under conditions of the nickel complex-catalyzed coupling reaction (see VI, A) most probably involve rearrangement of an organonickel intermediate [514,515]:



## B. Catalysis of Polymerization and Other Reactions

The year 1976 saw great activity in the patent literature in the area of multi-component alkene polymerization and copolymerization catalysts including an organomagnesium compound in their formulation. These catalysts are described as solids formed by interaction of the magnesium organometallic or halide with a titanium or vanadium compound, generally along with other components such as organoaluminum, boron, or berylium compounds, siloxanes or other silicon or tin derivatives, and frequently a Lewis base or alcohol. It is not clear whether the catalyst is actually an organomagnesium material; in some cases the magnesium salt may function primarily as support. Polymerization occurs when the alkene is treated with the catalyst and an aluminum alkyl; often polymerization was done under $H_2$. In various cases, claims were made for high polymer yield and molecular weight, high stereospecificity or broad molecular weight range. Because of their number, the patents will not be referenced individually; however, a list of Chemical Abstracts numbers is included as Ref 516.

Magnesium-containing catalysts for the polymerization of alkenes in a dry fluidized bed are described [517,518]. A granular reducing agent for preparation of polymerization catalysts was prepared by polymerization of a small amount of ethylene by a system $TiCl_4$-$Ti(OEt)_4$-EtMgCl-$H_2$ [519].

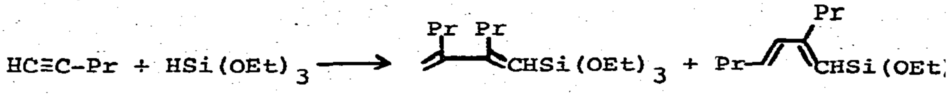
Two studies appeared in the periodical literature on ethylene polymerization with organomagnesium-containing catalysts A high-activity catalyst from $TiCl_4$, $Et_2AlCl$, and $Ph_2Mg$ produced 20 to 30 kg of polymer per gram of catalyst. The catalyst produces polymer of very high molecular weight; polymerization at 90-130° under $H_2$ produced a lower molecular weight polymer of "standard commercial properties" [520]. Polymer produced with such a catalyst had minimal branching, one terminal vinyl group, and a narrow molecular weight range [521].

Catalysts for diene polymerization which contained organomagnesium components were reported to have high specificit for *trans*-1,4-polymer [522,523]. Mixtures of dialkylmagnesium with barium alkoxides also functioned effectively [524,525].

The use of organomagnesium compounds as amionic polymerization catalysts has also appeared both in the periodical and patent literature. Methyl methacrylate polymerization by *t*-butylmagnesium chloride was studied mechanistically as a function of temperature and organometallic composition [526,527]. Under the conditions studied, only di-*t*-butylmagnesium initiated polymerization; *t*-BuMgCl and *t*-BuOMgCl were inactive. Mechanisms based on the coordination of magnesium to ether or monomer were proposed for initiation, propagation and termination, and to explain the variation in stereochemistry of the polymer. The structures of methyl acrylate polymers produced by various catalysts (including PhMgBr) were compared [528].

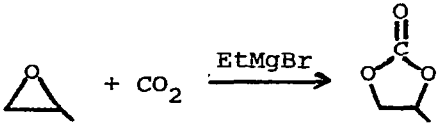
A polymerization of ε-caprolactam with Grignard reagent catalysts [529] and a block terpolymer from polyether, methyl terephthalate and caprolactam using ethylmagnesium bromide [530] have been patented. A complex of diethylmagnesium, resorcinol, and water produces an alternating $CO_2$-propylene oxide copolymer [531].

Catalysts described for other processes have also involved organomagnesium components. A catalyst from $CH_2$=$CHCH_2$-$CH_2MgBr$ and ($\eta^5$-cp)$TiCl_3$ principally dimerizes ethylene to butenes [532]. Catalysts prepared from BuMgBr or other organometallic components and nickel acetylacetonate catalyze hydrosilylation of isoprene and piperylene, and a hydrosilylation-dimerization of 1-pentyne [533]:



Catalysts prepared from reaction of Grignard reagents and $WCl_6$ or $MoCl_5$, deposited on silica or incorporated into a polymeric support, act with metal halides ($AlCl_3$, $TiCl_4$, etc.) to catalyze olefin dismutation reactions [534,535].

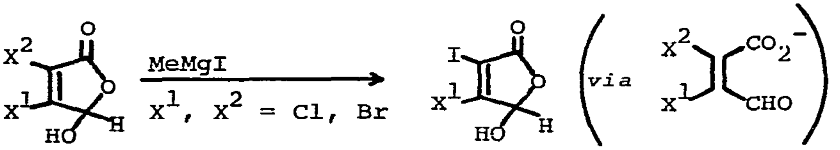
A process has been patented in which alkyl or aryl Grignard reagents catalyze reaction between epoxides and $CO_2$ [536]; *e.g.*



C. Reaction of the Halide Ion of Grignard Reagents as a Nucleophile

Halogen exchange between alkyl fluorides and Grignard reagents has been reported [537]. Halide reactivity followed the order $Cl^- < Br^- < I^-$. In a series of silyl-substituted fluorides, $Me_3Si(CH_2)_nF$, the rate increased with decreasing chain length ($C_5 < C_3 < C_1$), and the rate was increased relative to $n$-$C_7H_{15}F$. Neopentyl fluoride was unreactive [538].

Halide exchange was also observed for [539]:



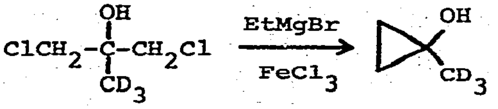
Cleavage of an α-lactam by halide ion was noted previously [289,290].

D. Miscellaneous Reactions

Other reactions with metal salts. In addition to transition metal-catalyzed crossed coupling reaction with alkyl halides (section VI, A), alkylation of metal or metalloids (see section VI, D), and possible catalysis of single electron transfer pathways (section IV, A), some other reactions may be noted.

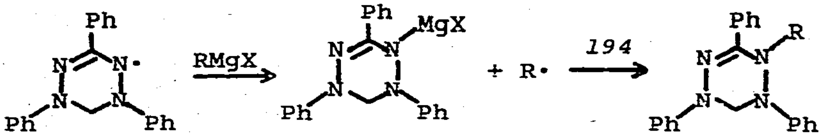
Fauvarque has studied reactions of $PhPdI(PPh_3)_2$ with Grignard reagents [540]. Reducing Grignard reagents rapidly and quantitatively form benzene and the corresponding alkene, even at -70°. The ligand (biphos) suppresses reaction. Non-reducing Grignard reagents (Me, Ph, benzyl, allyl, phenylethynyl) give mainly crossed coupling with the phenyl of the complex, accompanied by some biphenyl. Crossed coupling of these occurs best in a catalytic reaction with $Pd(PPh_3)_4$.

An experimental procedure for coupling of p-tolylmagnesium bromide to the corresponding biphenyl with thallium[I]bromide was published [541]. Silver triflate was used to oxidatively couple alkyl di-organomagnesium compounds to cycloalkanes [138]. Cyclization by means of a Kharasch reaction has been reported [253]:



The reaction of the complex $Mo(CO)_5(PR_2Cl)$ (R = Me, Ph) with ethylmagnesium bromide led to unanticipated coupling to a P-P bonded dimer [542].

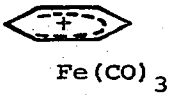
<u>Reaction with radicals, oxidizing agents, cations, etc.</u> The stable free radical *194* reacts with Grignard reagents, probably initially by single electron transfer [543]. With



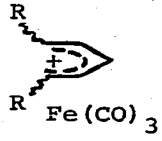
*194* *195*

aryl Grignard reagents, no *195* is isolated, but the corresponding biphenyl forms almost quantitatively. In another oxidation, phenylmagnesium bromide reacts with tetranitromethane in THF or MeCN to yield benzene and $Mg[C(NO_2)_3]_2$; the mechanism may again involve electron transfer [544]. Similar reactions are found with $N_2O_4$ and $XC(NO_2)_3$.

With cationic iron complexes *196* and *197*, dialkylcadmium



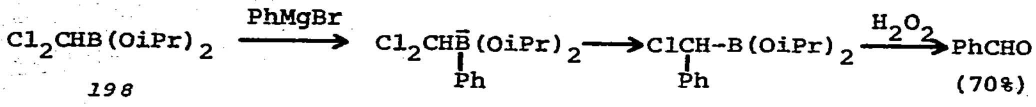
*196*



*197*

compounds (from $2RMgX + CdCl_2$) react with alkylation of the least hindered terminus, yielding a dimer complex; Grignard reagents lead to decomposition without alkylation [545].

In a new aldehyde synthesis, an organometallic compound reacts with the borate ester *198* [546]:

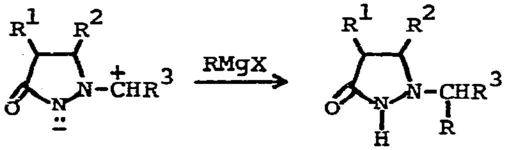


$$Cl_2CHB(OiPr)_2 \xrightarrow{PhMgBr} Cl_2\underset{\displaystyle Ph}{CH\bar{B}}(OiPr)_2 \longrightarrow Cl\underset{\displaystyle Ph}{CH}\text{-}B(OiPr)_2 \xrightarrow{H_2O_2} PhCHO$$

198

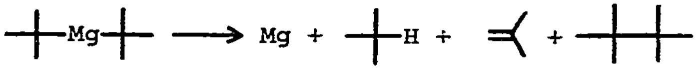
(70%)

Coupling with azomethine imines occurred non-stereospecifically [547]:



The reaction of surface groups on graphite and carbon with MeMgI was studied [548]. Cyclic esters were considered responsible for surface acidity.

Thermal decomposition. A review of metal alkyls considers thermal decomposition reactions [6]. The decomposition of di-t-butylmagnesium was studied [549]:



Analysis of $\Delta S^{\ddagger}$ and the ratio of disproportionation to combination indicates a radical mechanism. A CIDNP multiplet effect in the monomeric products indicated a non-cage radical process. Similar results were found for Zn, but the polarization with Hg favored a cage mechanism.

Acknowledgement: The assistance of the University of Wisconsin-Milwaukee Library Data Search Service is gratefully acknowledged.

## References

1. A. Bruylants, Bull. Cl. Sci., Acad. R. Belg., 62 (1976) 531.
2. T. Urbański, Chem. Br., 12 (1976) 191.
3. L. Espada Recarey, Quim. Ind. (Madrid), 22 (1976) 77.
4. R. D. Rieke, Top. Curr. Chem., 59 (1975) 3.
5. H. Hashimoto, Yuki Gosei Kagaku Kyokai Shi, 34 (1976) 246; Chem. Abs., 85 (1976) 94418.
6. P. J. Davidson, M. F. Lappert, and R. Pearce, Chem. Rev., 76 (1976) 219.
7. A. K. Prokof'ev, Usp. Khim., 45 (1976) 1028.
8. M. Okubo and K. Maruyama, Kagaku (Kyoto), 30 (1975) 780, 878, and 947; Chem. Abs., 84 (1976) 179629, 179630, and 179631.
9. K. Tamao and M. Kumada, Kagaku (Kyoto), 30 (1975) 832; Chem. Abs., 84 (1976) 179028.
10. M. Schlosser, New Synthetic Methods, 2 (1975) 1.
11. I. P. Beletskaya, G. A. Artamkina, and O. A. Reutov, Usp. Khim., 45 (1976) 661.
12. G. Boireau, D. Abenhaim, J. L. Namy, and E. Henry-Basch, Zh. Org. Khim., 12 (1976) 1841.
13. J. G. Tillet, Chem. Rev., 76 (1976) 747.
14. A. V. Fokin and A. F. Kolomiets, Usp. Khim., 45 (1976) 71.
15. M. E. Volpin and I. S. Kolmnikov, Organomet. React., 5 (1975) 313.
16. R. C. Duty and B. R. Ryder, J. Chem. Educ., 53 (1976) 457.
17. T. Holm, Chem. Abs., 86 (1977) 4846.
18. L. M. M. Thiessen, Diss. Abstr. Int. C, 37 (1976) 153.
19. G. R. Buske, Diss. Abs., 36B (1976) 4479.
20. C. E. Cannon, Diss. Abs., 36B (1976) 6161.
21. P. D. Livant, Diss. Abs., 37B (1976) 233.
22. R. B. Banks, Diss. Abs., 37B (1976) 2849.
23. W. A. Nugent, Diss. Abs., 37B (1977) 5671.
24. C. W. Wilkins, Jr., Diss. Abs., 37B (1977) 5676.
25. D. A. Hutchison, Diss. Abs., 36B (1976) 3387.
26. R. G. Lawler and P. Livant, J. Am. Chem. Soc., 98 (1976) 3710.
27. B. J. Schaart, H. W. H. J. Bodewitz, C. Blomberg, and F. Bickelhaupt, J. Am. Chem. Soc., 98 (1976) 3712.
28. S. Bank and D. A. Suckett, J. Am. Chem. Soc., 98 (1976) 7742.
29. E. C. Ashby, T. L. Wiesemann, J. S. Bowers, Jr., and J. T. Laemmle, Tetrahedron Lett., 21 (1976).
30. E. C. Ashby, J. D. Buhler, I. G. Lopp, T. L. Wiesemann, J. S. Bowers, Jr., and J. T. Laemmle, J. Am. Chem. Soc., 98 (1976) 6561.

31. C. C. Lee and E. C. F. Ko, Can. J. Chem., 54 (1976) 3041.
32. G. R. Buske and W. T. Ford, J. Org. Chem., 41 (1976) 1998.
33. M. Lequan, F. Meganem, and Y. Besace, J. Organomet. Chem., 113 (1976) C13.
34. D. A. Evans and J. M. Hoffman, J. Am. Chem. Soc., 98 (1976) 1983.
35. G. Piancatelli and A. Scettri, Tetrahedron, 32 (1976) 1745.
36. M. L. Roumestant, S. Arseniyadis, J. Gore, and A. Laurent, J. Chem. Soc., Chem. Commun., (1976) 479.
37. F. T. Bond, C.-Y. Ho, and O. McConnell, J. Org. Chem., 41 (1976) 1416.
38. M. Bolourtchian and A. Saednya, C. R. Hebd. Seances Acad. Sci., Ser. C, 283 (1976) 545.
39. L. Rösch, W. Erb, and H. Müller, Z. Naturforsch., B: Anorg. Chem., Org. Chem., B31 (1976) 281.
40. M. T. Rahman and H. Gilman, J. Indian Chem. Soc., 53 (1976) 269.
41. S. Umio, I. Ueda, and T. Kanaya, Japan Kokai, 76 39,214 (1976); Chem. Abs., 86 (1977) 189475.
42. S. Oowaki and S. Kitamura, Japan Kokai, 76 16,637 (1976); Chem. Abs., 85 (1976) 46208.
43. J. Vit, Brit. Patent 1,449,139 (1976); Chem. Abs., 86 (1977) 72856g.
44. U. R. Ghatak, S. K. Alam, P. C. Chakraborti, and B. C. Ranu, J. Chem. Soc., Perkin Trans. 1, (1976) 1669.
45. A. I. Ratanova and N. S. Imyanitov, Zh. Prikl. Khim. (Leningrad), 49 (1976) 1864.
46. Oxon Italia S.p.A., Ger. Offen. 2,625,216 (1976); Chem. Abs., 86 (1977) 140234.
47. J. Mayer, V. Sopara, and J. Michalsky, Czech 161,568 (1975); Chem. Abs., 85 (1976) 159422r.
48. V. G. Bondarenko, V. A. Kholodnov, T. A. Kholodnova, M. V. Sokolov, and L. A. Musyakov, Zh. Prikl. Khim. (Leningrad), 49 (1976) 936.
49. M. S. Newman and R. Kannan, J. Org. Chem., 41 (1976) 3356.
50. R. L. Hillard III and K. P. C. Volhardt, J. Am. Chem. Soc., 98 (1976) 3579.
51. A. Maercker and H.-J. Jaroschek, J. Organomet. Chem., 108 (1976) 145.
52. G. F. Luteri and W. T. Ford, J. Organomet. Chem., 105 (1976) 139-43.
53. A. Maercker and H.-J. Jaroschek, J. Organomet. Chem., 116 (1976) 21.

54. K. Fujita, Y. Ohnuma, H. Yasuda, and H. Tani, J. Organomet. Chem., 113 (1976) 201.
55. R. Baker, R. C. Cookson, and A. D. Saunders, J. Chem. Soc. Perkin Trans. 1, (1976) 1809.
56. S. Akutagawa and S. Otsuka, J. Am. Chem. Soc., 98 (1976) 7420.
57. P. Markov, L. Dimitrova, and Kh. Ivanov, Monatsh. Chem., 107 (1976) 619.
58. M. T. Rahman and A. F. M. Salahuddin, Tetrahedron Lett., (1976) 1235.
59. L. D. Wescott, Jr., C. Williford, F. Parks, M. Dowling, and S. Sublett, J. Am. Chem. Soc., 98 (1976) 7853.
60. E. J. Corey, R. L. Danheiser, and S. Chandrasekaran, J. Org. Chem., 41 (1971) 260.
61. M. T. Rahman and H. Gilman, J. Indian Chem. Soc., 53 (1976) 582.
62. N. A. Nesmeyanov, V. A. Kalyavin and O. A. Reutov, Dokl. Akad. Nauk SSSR, 230 (1976) 1353.
63. A. C. W. Curran, U. S. Patent 3,963,722 (1976); Chem. Abs., 86 (1977) 5334.
64. G. T. Pearce, W. E. Gore, and R. M. Silverstein, J. Org. Chem., 41 (1976) 2797.
65. K. Taguchi, A. Yamamoto, and T. Ishihara, Japan. Kokai 76 138,608 (1976); Chem. Abs., 87 (1977) 5376h.
66. N. Matsumura, Y. Yagyu, and E. Imoto, Nippon Kagaku Kaishi, (1976) 1801; Chem. Abs., 86 (1976) 55189.
67. J.-L. Lemberton, G. Perot, M. Guisnet, and R. Maurel, Bull. Soc. Chim. Fr., (1976) 359.
68. D. Seeback, K.-H. Geiss, and M. Pohmakotr, Angew. Chem. Int. Ed. Engl., 15 (1976) 437.
69. P. G. Harrison and J. A. Richards, J. Organomet. Chem., 108 (1976) 35.
70. R. L. Clough, P. Mison, and J. D. Roberts, J. Org. Chem., 41 (1976) 2252.
70a. S. A. Reyba, Span. Patent 407,655 (1975); Chem. Abs., 84 (1976) 180062.
71. G. R. Buske and W. T. Ford, J. Org. Chem., 41 (1976) 1995.
72. D. B. Malpass, Ger. Offen. 2,515,351; Chem. Abs., 86 (1976) 72857h.
73. C. G. Screttas, U.S. Patent 3,932,545 (1976); Chem. Abs., 85 (1976) 33177.
74. K. V. Werner, J. Fluorine Chem., 8 (1976) 451.

75. P. Moreau, G. Dalverny, and A. Commeyras, J. Chem. Soc., Chem. Commun., (1976) 174.
76. O. M. Khodkevich, L. F. Rybakova, M. V. Stepanov, E. M. Panov, V. A. Chernoplekova, T. A. Starostina, and K. A. Kocheshkov, Dokl. Akad. Nauk SSSR, 229 (1976) 645.
77. M. Protiva, M. Rajsner, K. Sindelar, and I. Cervena, Czech. Patent 160,865 (1975); Chem. Abs., 86 (1977) 89608.
78. N. V. Kuznetsov and R. A. Myrsina, USSR 503,845 (1976); Chem. Abs., 84 (1976) 135109.
79. V. M. Bulina, A. S. Kovaleva, L. L. Ivanov, Yu. B. Pyatnova, and Yu. A. Kondrat'eva, USSR Patent 456,516 (1976); Chem. Abs., 86 (1977) 139390.
80. C. A. Henrick and J. B. Siddall, U.S. Patent 3,943,157; Chem. Abs., 85 (1976) 5189.
81. M. Rosenberger and G. Saucy, U. S. Patent 3,960,895 (1976); Chem. Abs., 85 (1976) 124238.
82. M. Rosenberger and G. Saucy, U. S. Patent 3,950,358 (1976); Chem. Abs., 85 (1976) 46940.
83. H. Hikino, K. Mohri, Y. Hikino, S. Arihara, T. Takemoto, H. Mori, and K. Shibato, Tetrahedron, 32 (1976) 3015.
84. N. Cohen, W. F. Eichel, R. J. Lopresti, C. Neukom, and G. Saucy, J. Org. Chem., 41 (1976) 3512.
85. N. Cohen and G. Saucy, Ger. Offen. 2,602,507 (1976); Chem. Abs., 85 (1976) 159423.
86. K. Tamaki, N. Naito, and K. Fujii, Yuki Gosei Kagaku Kyokai Shi, 34 (1976) 162.
87. W. Biernacki and W. Sobotka, Rocz. Chem., 50 (1976) 1323.
88. R. E. Schaub and M. J. Weiss, U. S. Patent 3,932,472 (1976); Chem. Abs., 85 (1976) 123425.
89. P. Bakuzis, M. L. F. Bakuzis, C. C. Fortes, and R. Santos, J. Org. Chem., 41 (1976) 2769.
90. K. Kihira, T. Kuramoto, and T. Hoshita, Steroids, 27 (1976) 383.
91. S. Kumar, C. M. Gupta, and N. Anand, Indian J. Chem., Sect. B, 14B (1976) 303.
92. J. C. Stowell, J. Org. Chem., 41 (1976) 560.
93. M. Hayashi, S. Kori, H. Miyake, and T. Yamato, Japan. Kokai 76 82,245 (1976); Chem. Abs., 86 (1977) 43265.
94. A. A. Ponaras, Tetrahedron Lett., (1976) 3105.
95. P. Dodman and J. C. Tatlow, J. Fluorine Chem., 8 (1976) 263.
96. E. I. Stout, W. M. Doane, and V. C. Trinkus, Carbohydrate Res., 50 (1976) 282.

97. S. Kijima, I. Yamatsu, K. Hamamura, N. Minami, Y. Yamagishi, and Y. Inai, Japan. Kokai 76 100,009 (1976); Chem. Abs., 86 (1977) 106832.

98. G. Piancatelli and A. Scettri, Gazz. Chim. Ital., 106 (1976) 167.

99. Sandoz Ltd., Neth. Appl. 75 02,524 (1976); Chem. Abs., 86 (1977) 72207w.

100. P. L. Anderson and J. Nadelson, Gen. Offen. 2,509,472 (1976); Chem. Abs., 86 (1976) 16655.

101. S. Kijima and K. Hamamura, Japan. Kokai, 76 11,724 (1976); Chem. Abs., 84 (1976) 179877a.

102. D. A. Shabanova, E. M. Movsum-Zade, I. A. Shikhiev, and Ya. F. Nasirov, Azerb. Khim. Zh., (1976) 31; Chem. Abs., 87 (1977) 53420q.

103. P. Loeliger and E. Fluckiger, Org. Synth., 55 (1976) 127.

104. J. Freedman, U. S. Patent 3,993,757 (1976); Chem. Abs., 86 (1977) 155531.

105. C. L. Zirkle, Ger. Offen. 2,549,841 (1976); Chem. Abs., 85 (1976) 78025.

106. R. P. Pioch and K. K. Schmiegel, U. S. Patent 3,962,257 (1976); Chem. Abs., 85 (1976) 159894w.

107. J. C. Madelmont, J. Organomet. Chem., 116 (1976) 15.

108. R. B. Garland and R. Pappo, Ger. Offen 2,539,300 (1976); Chem. Abs., 85 (1976) 21717.

109. A. Marxer, Ger. Offen 2,602,918 (1976); Chem. Abs., 86 (1977) 16548.

110. Y. Yoshioka, Japan. Kokai 76 88,979 (1976); Chem. Abs., 86 (1977) 89878p.

111. C. Wiaux-Zamar, J.-P. Dejonghe, L. Ghosez, J. F. Normant, and J. Villieras, Angew. Chem., 88 (1976) 417; Int. Ed. Engl., 15 (1976) 317.

112. K. Akiba, K. Ishikawa, and N. Inamoto, Chem. Lett. (1976) 1111

113. Merck and Co., Inc., Austrian Patent 330,165 (1976); Chem. Abs., 85 (1976) 142906.

114. V. J. Bauer and R. W. Kosley, Jr., U. S. Patent 3,985,889 (1976); Chem. Abs., 86 (1977) 55302.

115. M. Bellassoued, F. Dardoize, F. Gaudemar-Bardone, M. Gaudemar, and N. Goasdoue, Tetrahedron, 32 (1976) 2713.

116. P. Y. Johnson and D. J. Kerkman, J. Org. Chem., 41 (1976) 1768.

117. F. Ghozland, Y. Maroni-Barnaud, and P. Maroni, Bull. Soc. Chim. Fr., (1976), 978 and 983.

118. R. Meyer and Y. Maroni-Barnaud, C. R. Hebd. Seances Acad. Sci., Ser. C, 283 (1976) 75.

119. H. Naarmann, H. Pohlemann, C. Rüchardt, S. Abuhantasch, and W. Duismann, Ger. Offen. 2,522,141 (1976); Chem. Abs., 86 (1977) 73642.

120. S. Watanabe, T. Fujita, K. Suga, and H. Koiso, Nippon Kagaku Kaishi, (1976) 1251; Chem. Abs., 86 (1977) 43151.

121. S. Watanabe, K. Suga, T. Fujita, and H. Koiso, Isr. J. Chem., 13 (1975) 257.

122. K. D. Smith and J. L. Atwood, Inorg. Synth., 16 (1976) 137.

123. D. Braun and W. Euler, Makromol. Chem., 177 (1976) 1373.

124. K. Paciorek, U. S. Pat. Appl. 706,424 (1976); Chem. Abs., 87 (1977) 40200.

125. A. Mukoo, Y. Mori, and H. Morishita, Japan. Kokai, 76 04180 (1976); Chem. Abs., 85 (1976) 5519r.

126. W. J. Hammar, U. S. Patent 3,949,091 (1976); Chem. Abs., 85 (1976) 20953.

127. W. J. Hammar, U. S. Patent 3,969,467 (1976); Chem. Abs., 85 (1976) 159770.

128. S. Gronowitz and K. Pettersson, J. Heterocycl. Chem., 13 (1976) 1099.

129. D. W. Slocum and P. L. Gierer, J. Org. Chem., 41 (1976) 3668.

130. M. Ban, Y. Baba, K. Miura, Y. Kondo, K. Suzuki, and M. Hori, Chem. Pharm. Bull., 24 (1976) 1679; Chem. Abs., 85 (1976) 177290.

131. T. Frejd, Chem. Scr., 10 (1976) 133.

132. R. V. Semenovich, Mater. Vses. Nauchn. Stud. Konf. Khim., 13th (1975) 5.

133. E. J. Bulten and H. A. Budding, J. Organomet. Chem., 110 (1976) 167.

134. H. G. Kuivila, J. L. Considine, R. H. Sarma, and R. J. Mynott, J. Organomet. Chem., 111 (1976) 179.

135. J.X. McDermott, J.F. White, and G. M. Whitesides, J. Am. Chem. Soc., 98 (1976) 6521.

136. J. B. Lambert and H.-N. Sun, J. Organomet. Chem., 117 (1976) 17.

137. H. Sakurai and M. Murakami, Bull. Chem. Soc. Jpn., 49 (1976) 3185.

138. G. M. Whitesides and F. D. Gutowski, J. Org. Chem., 41 (1976) 2882.

139. M. S. Malinovskii, N. G. Krivosheeva, V. G. Dryuk, and

O. D. Gnovitskaya, Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol., 19 (1976) 581; Chem. Abs., 85 (1976) 124013.

140. J. Yoshimura, K. Sato, H. Wakai, and M. Funabashi, Bull. Chem. Soc. Jpn., 49 (1976) 1169.

141. F. Bickelhaupt, G. Jongsma, P. deKoe, R. Lourens, N. R. Mast, G. L. vanMourik, H. Vermeer, and R. J. M. Weustink, Tetrahedron, 32 (1976) 1921.

142. G. van Koten and J. G. Noltes, J. Organomet. Chem., 104 (1976) 127.

143. E. J. Bulten, H. F. M. Gruter, and H. F. Martens, J. Organomet. Chem., 117 (1976) 329.

144. M. J. Carter and I. Fleming, J. Chem. Soc., Chem. Commun., (1976) 679.

145. S. P. Hopper, M. J. Tremelling, J. S. Fine, D. S. Gilbert, R. J. Ginsberg, A. M. Macchiarulo, and J. C. Petchler, Synth. React. Inorg. Met.-Org. Chem., 6 (1976) 373.

146. O. G. Yarosh, M. G. Voronkov, and E. O. Tsetlina, Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 1633.

147. I. M. Gverdtsiteli, N. D. Quang, T. P. Doksopulo, and A. V. Vannikov, Zh. Obshch. Khim., 46 (1976) 610.

148. L. I. Zakharkin, V. N. Kalinin, V. A. Pankratov, and V. V. Korshak, Izv. Akad. Nauk. SSSR, Ser. Khim., (1976) 217.

149. G. B. McVicker, Inorg. Synth., 16 (1976) 56.

150. M. L. H. Green, T. Luong-thi, G. A. Moser, I. Packer, F. Petit, and D. M. Roe, J. Chem. Soc., Dalton Trans., (1976) 1988.

151. K. Jacob, Z. Chem., 16 (1976) 196.

152. A. N. Nesmeyanov, N. E. Kolobova, Yu. V. Makarov, E. I. Kazimirchuk, and K. N. Anisimov, Izv. Acad. Nauk. SSSR, Ser Khim., (1976) 159.

153. S. Tyrlik and I. Wolochowicz, Bull. Acad. Pol. Sci., Ser. Sci. Chim., 24 (1976) 349.

154. F. W. Van Der Weij and J. H. Teuben, J. Organomet. Chem., 105 (1976) 203.

155. P. Sobota, B. Jezowska-Trzebiatokowska, and Z. Janas, J. Organomet. Chem., 118 (1976) 253.

156. E. Colomer and R. Corriu, J. Chem. Soc., Chem. Commun., (1976) 176.

157. M. Baudler and C. Grunner, Z. Naturforsch. B: Anorg. Chem., Org. Chem., B31 (1976) 1311.

158. D. E. Bergbreiter and J. M. Killough, J. Org. Chem., 41 (1976) 2750.

159. J. Kuyper and K. Vrieze, J. Chem. Soc., Chem. Commun., 64 (1976).

160. J. Kuyper, P. C. Keijzer and K. Vrieze, J. Organomet. Chem., 116 (1976) 1.

161. K. Kress and A. Novak, J. Organomet. Chem., 121 (1976) 7.

162. J. Kress, J. Organomet. Chem., 111 (1976) 1.

163. R. Petiaud, P. Ciaudy, and Q.-T. Pham, Eur. Polym. J., 12 (1976) 441.

164. H. O. Desseyn, L. M. Thiessen, and F. C. Alderweireldt, Proc. Int. Conf. Coord. Chem., 16th, (1974) R79; Chem. Abs., 85 (1976) 141151.

165. E. A. Hill, R. J. Theissen, C. E. Cannon, R. Miller, R. B. Guthrie, and A. T. Chen, J. Org. Chem., 41 (1976) 1191.

166. S. Cohen and A. Yogev, J. Am. Chem. Soc., 98 (1976) 2013.

167. V. G. Genchel, E. V. Evstigneeva, and N. V. Petrova, Zh. Fiz. Khim., 50 (1976) 1909; Chem. Abs., 85 (1976) 176875.

168. C. Chevrot, M. Troupel, J.-C. Folest, and J. Perichon, Bull. Soc. Chim. Fr., (1976) 2015.

169. C. Chevrot, J.-C. Folest, M. Troupel, and J. Perichon, Bull. Soc. Chim. Fr., (1976) 1388.

170. K. Manning. E. A. Petch, H. M. M. Shearer, K. Wade, and G. Whitehead, J. Chem. Soc., Chem. Commun., 107 (1976).

171. C. P. Baskin, C. F. Bender, R. R. Lucchese, C. W. Bauschlicher, Jr., and H. F. Schaeffer III, J. Mol. Struct., 32 (1976) 125.

172. G. Simons, M. E. Zandler, and E. R. Talaty, J. Am. Chem. Soc., 98 (1976) 7869.

173. J.-M. Lehn and G. Wipff, J. Am. Chem. Soc., 98 (1976) 7498.

174. E. Matarasso-Tchiroukhine and P. Cadiot, J. Organomet. Chem., 121 (1976) 169.

175. H. Sakurai, Y. Kudo, and H. Miyoshi, Bull. Chem. Soc. Jpn., 49 (1976) 1433.

176. J.-P. Pillot, J. Dunogues, and R. Calas, Tetrahedron Lett., (1976) 1871.

177. R. P. Gregson and R. N. Mirrington, Aust. J. Chem., 29 (1976) 2037.

178. C. Lion and J.-E. Dubois, Bull. Soc. Chim. Fr., (1976) 1875.

178a. C. W. Spangler, Tetrahedron, 32 (1976) 2681.

179. M. Schlosser and J. Hartman, J. Am. Chem. Soc., 98 (1976) 4675.

180. C. Chuit, G. Cahiez, J. Normant, and J. Villeras, Tetrahedron, 32 (1976) 1675.

181. S. F. Karaev, I. A. Shikhiev, and A. K. Khabibova, Izv.

Vyssh, Uchebn. Zaved., Khim. Khim. Tekhnol., 19 (1976) 208; Chem. Abs., 85 (1976) 32491.

182. S. F. Karaev, M. M. Movsumzade, and A. S. Kyazimov, Zh. Obshch. Khim., 46 (1976) 855.

183. R. Arous-Chtara, M. Gandemar, and J.-L. Moreau, C. R. Hebd. Seances Acad. Sci., Ser. C, 282 (1976) 687.

184. P. H. M. Schreurs, A. J. deJong, and L. Brandsma, Recl. Trav. Chim. Pays-Bas, 95 (1976) 55.

185. K. Kondo and M. Matsumoto, Tetrahedron Lett., (1976) 4363.

186. K. Kondo, S. Dobashi, and M. Matsumoto, Chem. Lett., (1976) 1077.

187. F. Toda and Y. Takahara, Bull. Chem. Soc. Jpn., 49 (1976) 2515.

188. M. L. Roumestant, M. Malacria, J. Gore, J. Grimaldi, and M. Bertrand, Synthesis, (1976) 755.

189. M. L. Roumestant, P. Place, and J. Gore, Tetrahedron Lett., (1976) 677.

190. A. Doutheau and J. Goré, C. R. Hebd. Seances Acad. Sci., Ser. C, 283 (1976) 355.

191. S. Nunomoto and Y. Yamashita, Nippon Kagaku Kaishi, (1976) 1583; Chem. Abs., 86 (1977) 71251u.

192. I. Partchamazad, M. Khosrovi, and R. Iranpour, C. R. Hebd. Seances Acad. Sci., Ser. C, 282 (1976) 69.

193. M. Sainsbury and R. F. Schinazi, J. Chem. Soc., Perkin Trans. 1, (1976) 1155.

194. Yu. P. Dormidontov, I. I. Lapkin, and V. S. Russkikh, Tr. Ural'sk. Un-tov. Organ. Khimiya, (1975) 198; Chem. Abs., 85 (1977) 89524.

195. R. V. Basova and A. A. Arest-Yabubovich, Vysokomol. Soedin., Ser. B, 18 (1976) 107; Chem. Abs., 84 (1976) 151072.

196. R. Baker, R. C. Cookson, and A. D. Saunders, J. Chem. Soc., Perkin Trans. 1, (1976) 1815.

197. R. A. Benkeser and M. P. Siklosi, J. Org. Chem., 41 (1976) 3212.

198. T. Holm, Acta Chem. Scand., Ser. B, 30 (1976) 985.

199. F. Bernadou and L. Miginiac, Tetrahedron Lett., 3083 (1976).

200. K. Yoshida, M. Ogasawara, and H. Yoshida, Hokkaido Daigaku Kogakubu Kenkyu Hokoku, 78 (1976) 155.

201. A. Staško, A. Tkáč, Ľ. Malík, and V. Adamčík, J. Magn. Reson., 21 (1976) 463.

202. C. L. Kwan and J. K. Kochi, J. Am. Chem. Soc., 98 (1976) 4903.

203. S. G. Boots, M. R. Boots, K. E. Gayer, and P. E. Marecki, J. Pharm. Sci., 65 (1976) 1374.

204. V. V. Bazyl'chik, E. A. Ionova, and I. I. Bardyshev, Vestsi Akad. Navuk BSSR, Ser. Khim. Navuk, (1976) 112; Chem. Abs., 86 (1977) 140262.

205. N. T. Anh and O. Eisenstein, Tetrahedron Lett., (1976) 155.

206. A. V. Bogatskii, Yu. Yu. Samitov, M. Bartok, S. A. Petrash, A. I. Gren, and G. Bozoki-Bartok, Zh. Org. Khim., 12 (1976) 215.

207. A. V. Bogatskii, S. A. Petrash, and M. Bartok, Dopov. Akad. Nauk Ukr., RSR, Ser. B: Geol., Khim. Biol. Nauki, (1976) 793; Chem. Abs., 86 (1977) 16228.

208. C. Alvarez Ibarra, F. Fernandez Gonzalez, and R. Perez-Ossorio, An. Quim., 72 (1976) 661.

209. S. Sawada, H. Kajiwara, and S. Yamana, Bull. Kyoto Univ. Educ., Ser. B, 47 (1975) 13; Chem. Abs., 85 (1976) 20472.

210. P. Chautemps and J.-L. Pierre, C. R. Hebd. Seances Acad. Sci., Ser. C, 282 (1976) 349.

211. H. Kimoto, H. Muramatsu, and K. Inukai, Bull. Chem. Soc. Jpn., 49 (1976) 1642.

212. C. N. Sukenik and R. G. Bergman, J. Am. Chem. Soc., 98 (1976) 6613.

213. M. le Plouzennec, F. le Moigne, and R. Dabard, J. Organomet. Chem., 111 (1976) C38.

214. Y. Osawa, T. Makino, K. Shibata, C. M. Weeks, and W. L. Duax, J. Chem. Soc., Chem. Commun., (1976) 991.

215. W. R. Nes and T. E. Varkey, J. Org. Chem., 41 (1976) 1652.

216. C. Byon and M. Gut, J. Org. Chem., 41 (1976) 3716.

217. T. Nagase, T. Aratani, and M. Hazama, Japan. Kokai 75 137,911 (1975); Chem. Abs., 85 (1976) 32608.

218. A. I. Meyers and J. Slade, Synth. Commun., 6 (1976) 601.

219. J. Huet, Y. Maroni-Barnaud, N. T. Anh, and J. Seyden-Penne, Tetrahedron Lett., (1976) 159.

220. M. Gaudemar, Tetrahedron, 32 (1976) 1689.

221. W. T. Wipke and P. Gund, J. Am. Chem. Soc., 98 (1976) 8107.

222. B. L. Shapiro and M. J. Shapiro, J. Org. Chem., 41 (1976) 1522.

223. B. L. Shapiro and T. W. Proulx, Org. Magn. Reson., 8 (1976) 40.

224. Yu. V. Tomilov, V. A. Smit, and O. M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 2512.

225. A. Fischli, H. Hoffmann, and P. M. Müller, Helv. Chim. Acta, 59 (1976) 1661.

226. J. Yoshimura, K. Mikami, K. Sato, and C. Shin, Bull. Chem. Soc. Jpn., 49 (1976) 1686.

227. A. A. Akhrem, L. I. Ukhova, G. P. Kukso, S. M. Volkov, N. I. Garbuz, and L. P. Solovei, Khim. Geterotsikl. Soedin., (1976) 1529.

228. D. Avnir and J. Blum, J. Heterocycl. Chem., 13 (1976) 619.

229. J. P. Barnier and J. M. Conia, Bull. Soc. Chim. Fr., (1976) 281.

230. J. Hambrecht and H. Straub, Tetrahedron Lett., (1976) 1079.

231. D. Lenoir, W. Röll, and J. Ipaktschi, Tetrahedron Lett., (1976) 3073.

232. V. I. Mel'nikova, A. E. Grigor'ev, and K. K. Pivnitskii, Zh. Obshch. Khim., 46 (1976) 1425.

233. Roussel-UCLAF, Fr. Demande 2,275,438 (1976).

234. K. Ikawa, K. Tokuyama, M. Kiyokawa, N. Maezono, N. Tokuno, T. Maeda, and I. Uno, Japan. Kokai 76 118,769 (1976); Chem. Abs., 86 (1977) 171263t.

235. T. Shibata and H. Mori, Japan. Kokai, 76 11,115 (1976); Chem. Abs., 85 (1976) 143362k.

236. S. Takeo and H. Mori, Japna. Kokai 76 11,114 (1976); Chem. Abs., 85 (1976) 124242.

237. G. Saucy, U. S. Publ. Pat. Appl. B 450,693 (1976); Chem. Abs., 84 (1976) 180478.

238. L. M. Morozovskaya, E. S. Belen'kaya, L. I. Klimova, and G. S. Grinenko, Khim.-Farm. Zh., 10 (1976) 64; Chem. Abs., 87 (1977) 53483.

239. A. R. Miller and D. Y. Curtin, J. Am. Chem. Soc., 98 (1976) 1860.

240. N. M. Abed, Indian J. Chem., Sect. B, 14B (1976) 428.

241. F. Bohlmann and G. Fritz, Chem. Ber., 109 (1976) 3371.

242. Y. Diab, J. C. Duplan, and A. Laurent, Tetrahedron Lett., (1976) 1093.

243. J. S. Nicholson and J. L. Turner, Ger. Offen. 2,613,817; Chem. Abs., 86 (1977) 29501.

244. V. Dave and E. W. Warnhoff, Tetrahedron Lett., (1976) 4695.

245. A. Meyer, M. Flammang, and C.-G. Wermuth, Synthesis, (1976) 832.

246. T. R. Kasturi and V. K. Sharma, Indian J. Chem., Sect. B, 14B (1976) 731.

247. M. S. Mashevskaya, P. A. Petyunin, and V. V. Mashevskii, Tr. Permsk. Gos. S-Kh. Inst., 118 (1976) 60.

248. F. Troxler, Ger. Offen. 2,552,563 (1976); Chem. Abs., 85 (1976) 94226.

249. V. A. Andryushina, E. V. Popova, O. S. Anisimova, and G. S. Grinenko, Zh. Org. Khim., 12 (1976) 897.
250. A. C. White and R. M. Black, U. S. Publ. Pat. Appl. B 490,812 (1976); Chem. Abs., 85 (1976) 117505z.
251. M. Yoshioka, Y. Sendo, and M. Murakami, Ger. Offen. 2,554,862 (1976); Chem. Abs., 86 (1977) 29837q.
252. P. J. Beeby, U. S. Patent 3,983,113 (1976); Chem. Abs., 86 (1977) 29853.
253. X. Creary, J. Org. Chem., 41 (1976) 3740.
254. Y. Izuka, G. Tsukamoto, and Y. Sawa, Japan. Kokai 76 149,239 (1976); Chem. Abs., 87 (1977) 52943.
255. L. A. Paquette, W. P. Melega, and J. D. Kramer, Tetrahedron Lett., (1976) 4033.
256. T. Shono, I. Nishiguchi, and M. Nitta, Chem. Lett., (1976) 1319.
257. K. Saigo, K. Kawata, and T. Mukaiyama, Chem. Lett., (1976) 771.
258. J. F. Hansen and S. Wang, J. Org. Chem., 41 (1976) 3635.
259. M. Matsui, Y. Nakahara, and K. Mori, Japan. Kokai, 76 13,763 (1976); Chem. Abs., 85 (1976) 32823s.
260. Y. Kitahara, M. Oda, S. Miyakoshi, and S. Nakanishi, Tetrahedron Lett., (1976) 2149.
261. P. C. Traas, H. Boelens, and H. J. Takken, Recl. Trav. Chim. Pays-Bas, 95 (1976) 57.
262. L. Lombardo and F. Sondheimer, Tetrahedron Lett. (1976) 3841.
263. J. Nieuwstad, A. P. G. Kieboom, A. J. Breijer, J. van Linden, and H. van Bekkum, Recl. Trav. Chim. Pays-Bas, 95 (1976) 225.
264. G. Stork and S. Raucher, J. Am. Chem. Soc., 98 (1976) 1583.
265. L. I. Zakharkin and V. S. Kirillova, Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 1107.
266. N. M. Loim, L. A. Malutschenko, Z. N. Parnes, and D. N. Kursanov, J. Organomet. Chem., 108 (1976) 363.
267. V. I. Savin, Zh. Org. Khim., 12 (1976) 1857.
268. F. G. Kathawala, U. S. Patent 3,962,459 (1976); Chem. Abs., 85 (1976) 68300.
269. M. S. Newman, V. Sankaran, and D. R. Olson, J. Am. Chem. Soc., 98 (1976) 3237.
270. G. Cahiez, A. Masuda, D. Bernard, and J. F. Normant, Tetrahedron Lett., (1976) 3155.
271. F. Huet, M. Pellet, and J.-M. Conia, Tetrahedron Lett., (1976) 3579.

272. Yu. G. Gololobov and L. I. Nesterova, Khim. Geterotsikl. Soedin., (1976) 1697.

273. K. Suga, S. Watanabe, T. Fujita, and K. Yoshida, Yuki Gosei Kagaku Kyokai Shi, 34 (1976) 661; Chem. Abs., 86 (1977) 71834.

274. S. Watanabe, T. Fujita, K. Suga, and T. Yokoyama, J. Appl. Chem. Biotechnol., 25 (1975) 733.

275. N. F. Albertson and W. F. Michne, U. S. Patent 3,976,653 (1976); Chem. Abs., 86 (1977) 16556.

276. I. S. Berdinskii, P. T. Pavlov, and E. Yu. Posyagina, USSR Patent 537,069 (1976); Chem. Abs., 87 (1977) 52926.

277. Zh. S. Sydykov and G. M. Segal, Izv. Akad. Nauk. SSSR, Se Khim., (1976) 1426.

278. Italfarmaco S. p. A., Belg. Patent 831,390 (1975); Chem. Abs., 85 (1976) 123436.

279. N. V. Kuznetsov, R. A. Myrsina, and N. Kh. Guznenok, Ukr. Khim. Zh. (Russ. Ed.), 42 (1976) 515; Chem. Abs., 85 (1976 94508.

280. S. Yamada, N. Oh-hashi, and K. Achiwa, Tetrahedron Lett., (1976) 2557.

281. K. Ikawa, K. Tokuyama, H. Maezono, T. Maeda, I. Ube, T. Mikami, T. Nishino, and Y. Miichi, Japan. Kokai 75 126,672 (1975); Chem. Abs., 85 (1976) 21112.

282. S. Benetti, R. Chiron, and Y. Graff, C. R. Hebd. Seances Acad. Sci., Ser. C, 283 (1976) 351.

283. M. Abou-Assali, C. Decoret, J. Royer, and J. Dreux, Tetrahedron, 32 (1976) 1655.

284. M. Abou-Assali, J. Royer, and J. Dreux, Tetrahedron, 32 (1976) 1661.

285. R. A. Archer, U. S. Patent 3,953,603 (1976); Chem. Abs., 85 (1976) 25405d.

286. L. S. Harris, H. G. Pars, R. K. Razdan, and J. C. Sheehan, U. S. Patent 3,972,880 (1976); Chem. Abs., 86 (1977) 43684

287. G. Saucy and J. W. Scott, U. S. Patent 3,984,428 (1976); Chem. Abs., 86 (1977) 90129.

288. N. Cohen, M. Rosenberger, and G. Saucy, U. S. Patent 3,994,930 (1976); Chem. Abs., 86 (1977) 121628.

289. H. E. Baumgarten, D. G. McMahan, V. J. Elia, B. I. Gold, V. W. Day and R. O. Day, J. Org. Chem., 41 (1976) 3798.

290. E. R. Talaty, L. M. Pankow, K. E. Garrett, C. M. Utermoehl and K. W. Knutson, Tetrahedron Lett., (1976) 4797.

291. D. M. McDaniel and S. Benisch, J. Heterocycl. Chem., 13 (1976) 405.

292. F. P. Hauck and J. E. Sundeen, U. S. Patent 3,963,724 (1976); Chem. Abs., 85 (1976) 160062e.

293. S. J. Goddard, U. S. Patent 3,992,189 (1976); Chem. Abs., 86 (1977) 89604w.

294. W. J. Houlihan, U. S. Patent 3,947,460 (1976); Chem. Abs., 85 (1976) 21091.

295. M. Chastrette, R. Amouroux, and M. Subit, Fr. Demande 2,292,690 (1976); Chem. Abs., 86 (1977) 170884.

296. H. H. Zoorob and E. S. Ismail, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 13B (1976) 1680.

297. G. G. DeAngelis and H. J. E. Hess, U. S. Patent 3,950,525 (1976); Chem. Abs., 85 (1976) 78153.

298. A. E. Kemppainen, M. J. Thomas, and P. J. Wagner, J. Org. Chem., 41 (1976) 1294.

299. A. T. Tosunyan, M. R. Bagdasaryan, V. N. Mndzhoyan, and S. A. Vartanyan, Arm. Khim. Zh., 29 (1976) 59; Chem. Abs., 85 (1976) 77974h.

300. Y. Iizuka, T. Tayama, and S. Miura, Japan. Kokai 75 117,784 (1975); Chem. Abs., 84 (1976) 180282.

301. N. Aikawa, H. Takayanagi, and Y. Izuka, Japan. Kokai 76 34,171 (1976); Chem. Abs., 85 (1976) 94236.

302. N. L. Holy, Synth. Commun., 6 (1976) 539.

303. D. Michelot, R. Lorne, C. Huynh, and S. Julia, Bull. Soc. Chim. Fr., (1976) 1482.

304. R. Chaabouni, A. Laurent, and B. Marquet, Tetrahedron Lett., (1976) 3149.

305. W. J. Stec and K. Lesiak, J. Org. Chem., 41 (1976) 3757.

306. W. J. Stec, K. Lesiak, and M. Sudol, Synthesis, (1975) 785.

307. A. Tzikas, C. Tamm, A. Boller, and A. Fürst, Helv. Chim. Acta, 59 (1976) 1850.

308. Y. Takehisa, Y. Kawazoe, and T. Taguchi, Chem. Pharm. Bull., 24 (1976) 1691; Chem. Abs., 86 (1977) 42745.

309. K. Imai, Y. Kawazoe, and T. Taguchi, Chem. Pharm. Bull., 24 (1976) 1083.

310. J. F. W. Keana, T. D. Lee, and E. M. Bernard, J. Am. Chem. Soc., 98 (1976) 3052.

311. M. Guyot and M. Dvolaitzky, C. R. Hebd. Seances Acad. Sci., Ser. C, 283 (1976) 649.

312. D. St. C. Black and A. B. Boscacci, Aust. J. Chem., 29 (1976) 2511.

313. T. D. Lee and J. F. W. Keana, J. Org. Chem., 41 (1976) 3237.

314. Aktieselskabet Grindstedvaerket, Neth. Appl. 75 13,754 (1976); Chem. Abs., 86 (1977) 140098.

315. D. St. C. Black, V. M. Clark, R. S. Thakur, and A. Todd, J. Chem. Soc., Perkin Trans. 1, (1976) 1951.

316. L. B. Volodarskii, V. V. Martin, and V. S. Kobrin, Zh. Org. Khim., 41 (1976) 2267.

317. L. M. Yagupol'skii, M. M. Kremlev, V. A. Khranovskii, and Yu. A. Fialkov, Zh. Org. Khim., 12 (1976) 1372.

318. L. A. Rozov, Yu. V. Zeifman, N. P. Gambaryan, Yu. A. Cheburkov, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 2750.

319. K. Okuhara, J. Org. Chem., 41 (1976) 1487.

320. H. G. Richey, Jr., C. W. Wilkins, Jr., B. S. Brown, and R. E. Moore, Tetrahedron Lett., (1976) 723.

321. G. Ple, Bull. Soc. Chim. Fr., (1975) 2213.

322. R. Gelin and M. Albrand, C. R. Hebd. Seances Acad. Sci., Ser. C, 283 (1976) 755.

323. H. Klein, H. Eijsinga, H. Westmijze, J. Meijer, and P. Vermeer, Tetrahedron Lett., (1976) 947.

324. H. Westmijze, J. Meijer, H. J. T. Bos, and P. Vermeer, Recl. Trav. Chim. Pays-bas, 95 (1976) 299.

325. H. Westmijze, J. Meijer, H. J. T. Bos, and P. Vermeer, Recl. Trav. Chim. Pays-Bas, 95 (1976) 304.

326. J. K. Crandall and F. Collonges, J. Org. Chem., 41 (1976) 4089.

327. Y. Frangin and M. Gaudemar, Bull. Soc. Chim., Fr., (1976) 1173.

328. Y. Frangin, E. Favre, and M. Gaudemar, C. R. Hebd. Seances Acad. Sci., Ser. C, 282 (1976) 277.

329. D. Mesnard and L. Miginiac, J. Organomet. Chem., 117 (1976) 99.

330. L. N. Cherkasov, R. S. Razina, and Kh. V. Bal'yan, Izv. Vyssn. Uchebn. Zaved., Khim. Khim. Tekhnol., 19 (1976) 1456; Chem. Abs., 86 (1977) 72050.

331. M. Michman, B. Steinberger, and S. Gershoni, J. Organomet. Chem., 113 (1976) 293.

332. L. M. Zubritskii, L. N. Cherkasov, T. N. Fomina, and Zh. V. Bal'yan, Zh. Obshch. Khim., 46 (1976) 441.

333. S. I. Radchenko, L. N. Cherkasov, and A. A. Petrov, Zh. Org. Khim., 12 (1976) 909.

334. J. Meijer, H. Westmijze, and P. Vermeer, Recl. Trav. Chim. Pays-Bas, 95 (1976) 102.

335. R. B. Miller and T. Reichenbach, Synth. Commun., 6 (1976) 319.

336. G. Courtois and L. Miginiac, J. Organomet. Chem., 117 (1976) 201.

337. M. S. Sargsyan and Sh. O. Badanyan, Arm. Khim. Zh., 29 (1976) 167; Chem. Abs., 85 (1976) 20525h.

338. F. Delbecq and J. Gore, Angew. Chem. Int. Ed. Engl., 15 (1976) 496.

339. F. Coulomb-Delbecq, J. Goré, and M.-L. Roumestant, Bull. Soc. Chim. Fr., (1976) 533.

340. F. Coulomb-Delbecq and J. Goré, Bull. Soc. Chim. Fr., (1976) 541.

341. J.-L. Moreau and M. Gaudemar, J. Organomet. Chem., 108 (1976) 159.

342. G. Tadema, P. Vermeer, J. Meijer, and L. Brandsma, Recl. Trav. Chim. Pays-Bas, 95 (1976) 66.

343. P. Metzner, J. Vialle, and A. Vibet, Tetrahedron Lett., (1976) 4295.

344. S. Masson, M. Saquet, and A. Thuillier, Tetrahedron Lett., (1976) 4179.

345. D. Paquer and S. Smadja, Recl. Trav. Chim. Pays-Bas, 95 (1976) 175.

346. M. Saquet, C. R. Hebd. Seances Acad. Sci., Ser. C, 283 (1976) 641.

347. J.-L. Burgot, J. Masson, P. Metzner, and J. Vialle, Tetrahedron Lett., (1976) 4297.

348. J.-L. Burgot, J. Masson, and J. Vialle, Tetrahedron Lett., (1976) 4775.

349. S. Hashimoto, S. Yamada, and K. Koga, J. Am. Chem. Soc., 98 (1976) 7450.

350. C. Jallabert, H. Riviere, and P. W. Tang, J. Organomet. Chem., 104 (1976) 1.

351. T. T. Takahashi and J. T. Satoh, Bull. Chem. Soc. Jpn., 49 (1976) 1089.

352. J. Cairns, C. L. Hewett, R. T. Logan, G. McGarry, D. F. M. Stevenson, and G. F. Woods, J. Chem. Soc., Perkin Trans. 1, (1976) 1558.

353. P. M. Wege, R. D. Clark and C. H. Heathcock, J. Org. Chem., 41 (1976) 3144.

354. J.-B. Wiel and F. Rouessac, J. Chem. Soc., Chem. Commun., (1976) 446.

355. M. I. Ali, A.-E. M. Abd-Elfattah, and H. A. Hammouda, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 31B (1976) 254.

356. N. Cohen, U. S. Patent 3,971,809 and 3,933,870 (1976);

Chem. Abs., 85 (1976) 177782n and 84 (1976) 135942p.

357. N. Arumugam and P. Shenbagamurthi, Indian J. Chem., Sect. B, 14B (1976) 946.

358. V. A. Mironov, A. D. Fedorovich, V. I. Pchelintsev, and A. A. Akhrem, Vesti Akad. Navuk B SSR, Ser. Khim. Navuk, (1976) 63; Chem. Abs., 84 (1976) 150046.

359. H. Yanagisawa and H. Nakao, Tetrahedron Lett., (1976) 1815.

360. P. Courbis and G. Peiffer, C. R. Hebd. Seances Acad. Sci., Ser. C, 282 (1976) 57.

361. N. Mông Lân and C. Wentrup, Helv. Chim. Acta, 59 (1976) 206

362. N. A. E. Kassab, S. O. A. Alla, and H. A. R. Ead, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 31B (1976) 380.

363. N. Latif, N. Mishriky, and E. El-Bayouki, Egypt. J. Chem., 17 (1974) 879.

364. D. C. Aldridge, G. C. Crawley, and C. J. Strawson, Ger. Offen. 2,543,150 (1976); Chem. Abs., 85 (1976) 46625r.

365. H. C. Gardner and J. K. Kochi, J. Am. Chem. Soc., 98 (1976) 558.

365a. D. Cabaret, J. Capillon, and J. P. Guette, J. Organomet. Chem., 113 (1976) 215.

366. Y. Ittah and I. Shahak, Synthesis, (1976) 320.

367. R. B. Gammill and T. A. Bryson, Synth. Commun., 6 (1976) 20

368. N. Kato, Y. Fukazawa, and S. Itô, Tetrahedron Lett., (1976) 2045.

369. E. Elkik and Imbeaux-Oudotte, Bull. Soc. Chim. Fr., (1976) 439.

370. E. Piers, C. K. Lau, and I. Nagakura, Tetrahedron Lett., (1976) 3233.

371. K. Matoba, T. Maeda, K. Nagase, and T. Yamazaki, Chem. Pharm. Bull., 24 (1976) 165.

372. P. De Clercq, M. De Smet, K. Legein, F. Vanhulle, and M. Vandewalle, Bull. Soc. Chim. Belg., 85 (1976) 503.

373. G. W. Griffin, D. M. Chihal, J. Perreten, and N. S. Bhacca, J. Org. Chem., 41 (1976) 3931.

374. T. Shono, I. Nishiguchi, and M. Okawa, Chem. Lett., (1976) 573.

375. C. S. Markos, U. S. Patent 3,974,143 (1976); Chem. Abs., 86 (1977) 29997s.

376. H.-D. Becker and K. Gustafsson, J. Org. Chem., 41 (1976) 214

377. A. K. Fateen, S. M. A. R. Omaran, A. M. Kaddah, and A. H. Moustafa, Indian J. Chem., Sect. B, 14B (1976) 276.

378. A. K. Fateen, S. A. R. Omran, N. Shams, and A. M. Kaddah, Indian J. Chem., Sect. B, 14B (1976) 99.

379. W. I. Awad, F. G. Baddar, S. M. A. R. Omran, and S. Antonious, Egypt. J. Chem., 17 (1974) 555.
380. A. M. Simonov, Yu. V. Koshchienko, G. M. Suvorova, B. A. Tertov, and E. N. Malysheva, Khim. Geterotsikl. Soedin., (1976) 1391.
381. A. F. M. Fahmy and N. F. Aly, Bull. Chem. Soc. Jpn., 49 (1976) 3191.
382. A. W. H. Wardrop, G. L. Sainsbury, J. M. Harrison, and T. D. Inch, J. Chem. Soc., Perkin Trans. 1, (1976) 1279.
383. A. H. Harash, M. H. Elnagdi, and A. A. A. Elbanani, Indian J. Chem., Sect. B, 14B (1976) 567.
384. J. Szabo and I. Varga, Acta Chim. Acad. Sci. Hung., 88 (1976) 61; Chem. Abs., 85 (1976) 21262.
385. C. Berti, M. Colonna, L. Greci, and L. Marchetti, Tetrahedron, 32 (1976) 2147.
386. T. Higashino, Y. Iwai, and E. Hayashi, Chem. Pharm. Bull., 24 (1976) 3120; Chem. Abs., 86 (1977) 171372c.
387. D. Bryce-Smith, P. J. Morris, and B. J. Wakefield, J. Chem. Soc. Perkin Trans. 1, (1976) 1977.
388. R. E. Lyle and D. L. Comins, J. Org. Chem., 41 (1976) 3250.
389. D. Redmore, U. S. Patent 3,998,833 (1976).
390. N. Abe, Heterocycles, 4 (1976) 221.
391. N. Vinot and P. Maitte, Bull. Soc. Chim. Fr., (1976) 251.
392. M. M. M. Sallam, Y. A. Ibrahim, and S. A.-L. Abdel-Hady, Helv. Chim. Acta, 59 (1976) 1093.
393. Ciba-Geigy A.-G., Swiss 576,963 (1976); Chem. Abs., 85 (1976) 177267y.
394. M. N. Berezhnaya, Issled. Obl. Sint. Katal. Org. Soedin., (1975) 8; Chem. Abs., 86 (1977) 139766.
395. H. Pirelahi, Y. Abdoh, and A. Afzali, Tetrahedron Lett., (1976) 4609.
396. I. Degani and R. Fochi, J. Chem. Soc., Perkin Trans. 1, (1976) 1886.
397. G. Bartoli and G. Rosini, Synthesis, (1976) 270.
398. W. J. J. M. Sprangers, A. P. van Swieten, and R. Luow, Chimia, 30 (1976) 199.
399. W. J. J. M. Sprangers and R. Louw, J. Chem. Soc., Perkin Trans. 2, (1976) 1895.
400. T. Yamamoto, T. Kohara, and A. Yamamoto, Chem. Lett., (1976) 1217.
401. B. George and E. P. Papadopoulos, J. Org. Chem., 41 (1976) 3233.

402. H. A. Selling and H. J. Mak, Synth. Commun., 6 (1976) 129.

403. M. Ballester, J. Riera, and C. Onrubia, Tetrahedron Lett., (1976) 945.

404. V. I. Savin and Yu. P. Kitaev, Zh. Org. Khim., 12 (1976) 28

405. V. I. Savin, A. G. Abul'khanov, and Yu. P. Kitaev, Zh. Org. Khim., 12 (1976) 434.

406. V. I. Savin and Yu. P. Kitaev, Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 1282.

407. N. Busch, J. Moleyre, J. Simond, R. Bondivenne, C. Labrid, and G. Dureng, Eur. J. Med. Chem.-Chim. Ther., 11 (1976) 20.

408. R. Paul, O. Riobé, and M. Maumy, Org. Synth., 55 (1976) 62.

409. I. Jezo, Chem. Zvesti, 29 (1975) 714; Chem. Abs., 85 (1976) 32588.

410. S. D. Shiyan, O. E. Lakhtina, M. L. Shul'man, and A. Ya. Khorlin, Izv. Akad. Nauk. SSSR, Ser. Khim., (1976) 197.

411. H. Straub, Tetrahedron Lett., (1976) 3513.

412. M. Flammang, C. R. Hebd. Seances Acad. Sci., Ser. C, 283 (1976) 593.

413. G. M. Mkryan, A. M. Mkrtchyan, and S. M. Gasparyan, Zh. Org. Khim., 12 (1976) 2066.

414. R. Rossi and R. Giorgi, Gazz. Chim. Ital., 106 (1976) 215.

415. A. H. A. Tinnemans and W. H. Laarhoven, J. Chem. Soc., Perkin Trans. 2, (1976) 1104.

416. F. Alvarez, U. S. Patent 3,975,432 (1976); Chem. Abs., 86 (1977) 89463.

417. N. de Kimpe, R. Verhé, L. De Buyck, H. Hasma, and N. Schamp, Tetrahedron, 32 (1976) 2457.

418. M. Prochazka, Collect. Czech. Chem. Commun., 41 (1976) 1557.

419. Italchemi S. p. A.-Instituto Chimico Farmaceutico, Belg. 834,591 (1976); Chem. Abs., 85 (1976) 192888v.

420. H. Takayangi and N. Aikawa, Japan. Kokai 76 63,178 (1976); Chem. Abs., 86 (1977) 72461z.

421. T. C. Flood, F. J. DiSanti, and D. L. Miles, Inorg. Chem., 15 (1976) 1910.

422. R. Scott Smith and J. K. Kochi, J. Org. Chem., 41 (1976) 502.

423. D. J. Pasto, G. F. Hennion, R. H. Shults, A. Waterhouse, and S.-K. Chou, J. Org. Chem., 41 (1976) 3496.

424. K. Tamao, K. Sumitani, Y. Kiso, M. Zembayashi, A. Fujioka, S. Kodama, I. Nakajima, A. Minato, and M. Kumada, Bull. Chem. Soc. Jpn., 49 (1976) 1958.

425. K. Tamao, S. Kodama, I. Nakajima, T. Nokatsuka, A. Minato,

and M. Kumada, Hukusokan Kagaku Toronkai Koen Yoshishu, 8th, (1975) 174; Chem. Abs., 85 (1976) 5468.

426. T. Hayashi, M. Tajika, K. Tamao, and M. Kumada, J. Am. Chem. Soc., 98 (1976) 3718.

427. K. Tamao, M. Zembayashi, and M. Kumada, Chem. Lett., (1976) 1239.

428. K. Tamao, M. Zembayashi, and M. Kumada, Chem. Lett., (1976) 1237.

429. A. Sekiya and N. Ishikawa, J. Organomet. Chem., 118 (1976) 349.

430. F. Derguini-Boumechal and G. Linstrumelle, Tetrahedron Lett., (1976) 3225.

431. R. L. Carney, U. S. Patent 3,948,803 (1976); Chem. Abs., 84 (1976) 170295b.

432. G. Cahiez, D. Bernard, and J. F. Normant, J. Organomet. Chem., 113 (1976) 107.

433. T. A. Baer and R. L. Carney, Tetrahedron Lett., (1976) 4697.

434. R. L. Clough, W. J. Kung, R. E. Marsh, and J. D. Roberts, J. Org. Chem., 41 (1976) 3603.

535. N. Cohen, G. Saucy, and K.-K. Chan, Ger. Offen. 2,602,509 (1976); Chem. Abs., 86 (1977) 55601c.

436. M. Julia and J. D. Fourneron, Tetrahedron, 32 (1976) 1113.

437. G. Stork and A. A. Ponaras, J. Org. Chem., 41 (1976) 2937.

438. B. Corbel and T. Durst, J. Org. Chem., 41 (1976) 3648.

439. D. J. Collins, C. M. Horn, and V. J. Welker, Aust. J. Chem., 29 (1976) 2077.

440. P. Beltrame, G. Gelli, and A. Loi, J. Chem. Soc., Perkin Trans. 2, (1976) 1001.

441. P. Beltrame, G. Gelli, A. Lai, and M. Monduzzi, J. Org. Chem., 41 (1976) 580.

442. Y. Osawa, T. Makino, and C. M. Weeks, J. Chem. Soc., Chem. Commun., (1976) 990.

443. J. Salaün, J. Org. Chem., 41 (1976) 1237.

444. T. Mukaiyama and H. Ishikawa, Japan. Kokai, 76 125012 Chem. Abs., 86 (1977) 171070.

445. S. Cabiddu, E. Marongiu, S. Melis, and F. Sotgiu, J. Organomet. Chem., 116 (1976) 275.

446. M. J. Soulal and E. A. Twamley, Brit. 1,441,749 (1976); Chem. Abs., 86 (1977) 4929h.

447. G. P. Bettinetti, S. Maffei, and S. Pietra, Synthesis, (1976) 748.

448. I. G. C. Coutts and M. Hamblin, J. Chem. Soc., Chem. Commun., 58 (1976).

449. P. O. I. Virtanen, P. Nousiainen, and J. Vaskuri, Finn. C Lett., (1976), 12; Chem. Abs., 84 (1976) 179226.

450. R. A. Olofson, K. D. Lotts, and G. N. Barber, Tetrahedron Lett., (1976) 3779.

451. C. Cahiez, D. Bernhard, J. F. Normant, and J. Villeras, J. Organomet. Chem., 121 (1976) 123.

452. Yu. G. Skrypnik, USSR Patent 514,815 (1976); Chem. Abs., 85 (1976) 108299y.

453. K. K. Andersen, R. L. Caret, and D. L. Ladd, J. Org. Chem 41 (1976) 3096.

454. D. N. Harpp, S. M. Vines, J. P. Montillier, and T. H. Cha J. Org. Chem., 41 (1976) 3987.

455. W. H. Pirkle and M. S. Hoekstra, J. Am. Chem. Soc., 98 (1976) 1832.

456. M. Cincuini, S. Colonna, F. Cozzi, and C. J. M. Stirling, J. Chem. Soc., Perkin Trans. 1, 2061 (1976).

457. M. Mikolajczyk and J. Drabowicz, J. Chem. Soc., Chem. Com (1976) 220.

458. N. A. Nesmeyanov and V. A. Kalyavin, Tezisy Dokl. Nauchn. Sess. Khim. Tekhnol. Org. Soedin. Sery Sernistykh Neftei, 13th, (1974), 163; Chem. Abs., 86 (1977) 29554.

459. M. Furukawa, T. Suda, and S. Hayashi, Chem. Pharm. Bull., 24 (1976) 1708; Chem. Abs., 86 (1977) 72349.

460. T. Kitazume, T. Okaka, R. Takei, and N. Ishikawa, Bull. Chem. Soc. Jpn., 49 (1976) 2491.

461. K. Goda, R. Okazaki, K.-Y. Akiba, and N. Inamoto, Tetrahe Lett., (1976) 181.

462. M. Murase, M. Kitano, M. Kise, and H. Murai, Chem. Lett., (1976) 349.

463. A. Haas and V. Hellwig, Chem. Ber. 109 (1976) 2475.

464. K. A. Andrianov, B. A. Izmailov, N. P. Minyaeva, N. V. Tsvetkova, and E. A. Prozumentova, Zh. Obshch. Khim., 46 (1976) 2255.

465. C. Brelière, R. J. P. Corriu, and G. Royo, J. Chem. Soc., Chem. Commun., (1976) 906.

466. J. Dubac, P. Mazerolles, and P. Fagoaga, C. R. Hebd. Seances Acad. Sci., Ser. C, 282 (1976) 253.

467. B. G. McKinnie, N. S. Bhacca, F. K. Cartledge, and J. Fayssoux, J. Org. Chem., 41 (1976) 1534.

468. C. Mirko, V. Bazant, M. Dvorak, and J. Cermak, Czech. 160,397 (1975); Chem. Abs., 85 (1976) 124129.

469. R. Dedeyne and M. J. O. Anteunis, Bull. Soc. Chim. Belg., 85 (1976) 319.

470. R. J. P. Corriu, A. Kpoton, J. Barrau, and J. Satge, J. Organomet. Chem., 114 (1976) 21.
471. P. Fostein and J. C. Pommier, J. Organomet. Chem., 114 (1976) C7.
472. S. Matsuda and H. Kudara, Ger. Offen. 2,545,065 (1976); Chem. Abs., 86 (1977) 106782.
473. D. P. Arnold and P. R. Wells, J. Organomet. Chem., 111 (1976) 269.
474. K. H. Pannell, M. F. Lappert, and K. Stanley, J. Organomet. Chem., 112 (1976) 37.
475. B. V. Timokhin, V. I. Dmitriev, E. F. Grechkin, and A. V. Kalabina, Zh. Obshch. Khim., 46 (1976) 490.
476. F. Marschner, H. Kessel, and H. Goetz, Phosphorus, 6 (1976) 135.
477. J. C. Willians, Jr., W. D. Hounshell, and A. M. Aguiar, Phosphorus, 6 (1976) 169.
478. A. F. Kolomietx, A. V. Fokin, L. S. Rudnitskaya, and A. A. Krolevets, Izv. Acad. Nauk SSSR, Ser. Khim., (1976) 171.
479. O. Scherer and G. Schnabl, Chem. Ber., 109 (1976) 2996.
480. V. M. Ismailov, T. A. Babaeva, and L. M. Gyul'akhmedov, Tezisy Resp. Nauchn. Konf. Molodykh Uch.-Khim. Azerb., (1974) 87; Chem. Abs., 87 (1977) 23395.
481. A. M. Islam, E. H. Ibrahim, and I. M. Abd Ellah, Egypt. J. Chem., 17 (1974) 117.
482. V. D. Bianco and S. Doronzo, Inorg. Synth., 16 (1976) 160.
483. L. B. Ionov, L. A. Kunitskaya, I. P. Mukanov, and Yu. F. Gatilov, Zh. Obshch. Khim., 46 (1976) 68.
484. J. L. Peterson and D. W. Meek, Inorg. Synth., 16 (1976) 180.
485. W. Levason and C. A. McAuliffe, Inorg. Synth., 16 (1976) 184.
486. V. P. Mardykin and T. S. Pritytskaya, Zh. Obshch. Khim., 46 (1976) 1085.
487. H. Bürger and C. Kluess, J. Organomet. Chem., 108 (1976) 69.
488. I. F. Gavrilenko, N. N. Stefanovskaya, G. N. Bondarenko, E. I. Tinyakova, and B. A. Dolgoplosk, Dokl. Akad. Nauk SSSR, 228 (1976) 351.
489. B. Machelett, Z. Chem., 16 (1976) 116.
490. B. Heyn and R. Hoffmann, Z. Chem., 16 (1976) 195.
491. P. Royo and J. Sancho, Transition Met. Chem. (Weinheim, Ger.), 1 (1976) 212; Chem. Abs., 86 (1977) 155785.
492. K. Mertis, A. F. Masters, and G. Wilkinson, J. Chem. Soc., Chem. Commun., (1976) 858.
493. T. J. Marks and W. A. Wachter, J. Am. Chem. Soc., 98 (1976) 703.

494. S. Komiya, T. A. Albright, R. Hoffmann, and J. K. Kochi, J. Am. Chem. Soc., 98 (1976) 7255.

495. K. Turner and H. Felkin, J. Organomet. Chem., 121 (1976) C29.

496. J. X. McDermott, J. F. White, and G. M. Whitesides, J. Am. Chem. Soc., 98 (1976) 6521.

497. V. I. Savin, I. D. Temyachev, and F. D. Yambushev, Zh. Org. Khim., 12 (1976) 275.

498. V. I. Savin and Yu. P. Kitaev, Zh. Obshch. Khim., 46 (1976) 385.

499. V. I. Savin and Yu. P. Kitaev, Zh. Org. Khim., 12 (1976) 269.

500. F. Marcuzzi and G. Melloni, Synthesis, (1976) 451.

501. V. Pallin and M. Lopp, Tarta Ulik. Toimetised, Uch. Zap. Tartus. Un-ta, (1976) 91; Chem. Abs., 87 (1977) 6053.

502. S. Viirlaid, V. Pallin, and A. Tuulmets, Tartu Ulik. Toimetised, Uch. Zap. Tartus. Un-ta, (1976) 95; A. Tuulmets, personal communication.

503. V. Pallin, A. Laene, J. Tammaru, and A. Tuulmets, Reakts. Sposobn. Org. Soedin., 13 (1976) 139.

504. M. Lopp, E. Otsa, V. Pallin, and A. Tuulmets, Reakts. Sposobn. Org. Soedin., 13 (1976) 506.

505. H. Drevs, Z. Chem., 16 (1976) 493.

506. H. tom Dieck and M. Svoboda, Chem. Ber., 109 (1976) 1657.

507. T. Sone, S. Terashima, and S. Yamada, Chem. Pharm. Bull., 24 (1976) 1293; Chem. Abs., 85 (1976) 108807.

508. S. Sakai, T. Fujinami, N. Otani, and T. Aizawa, Chem. Lett., (1976) 811.

509. R. Boudet and D. Bourgoin-Legay, C. R. Hebd. Seances Acad. Sci., Ser. C, 282 (1976) 249.

510. G. R. Brown and B. Wright, Experientia, 32 (1976) 277.

511. A. Maercker and W. Streit, Chem. Ber., 109 (1976) 2064.

512. F. Gerard and P. Miginiac, J. Organomet. Chem., 111 (1976) 17.

513. E. A. Hill, A. T. Chen, and A. Doughty, J. Am. Chem. Soc., 98 (1976) 167.

514. M. Mori, K. Chiba, and Y. Ban, Hukusokan Kagaku Toronkai Koen Yoshishu, 8th (1975) 179; Chem. Abs., 84 (1976) 179995.

515. M. Mori and Y. Ban, Tetrahedron Lett., 1803 (1976).

516. Chem. Abs., 84 (1976) 180899; 85 (1976) 6392, 6394, 6399, 22124, 33704, 78677, 78681, 78685, 78691, 109199, 124694, 124696, 143824, 143833, 149646, 160880, 178204, 193341, 193344; 86 (1977) 5980, 17316, 17329, 30316, 44226, 44227, 44229, 55966, 90613, 156225.

517. L. Havas, F. Caumartin, and C. Raufast, Ger. Offen. 2,623,432 (1976); Chem. Abs., 86 (1977) 44234.

518. F. Caumartin and L. Havas, Ger. Offen. 2,623,693 (1976); Chem. Abs., 86 (1977) 44233.

519. M. Araro, Ger. Offen. 2,535,956 (1976); Chem. Abs., 85 (1976) 6391.

520. Ph. Radenkov, L. Petrov, S. Karaenev, and R. Kyrtcheva, Eur. Polym. J., 12 (1976) 427.

521. T. Petrova, Eur. Polym. J., 12 (1976) 571.

522. S. Arita, Japan. Kokai 76 67,387 (1976); Chem. Abs., 85 (1976) 94944r.

523. Texas-U. S. Chemical Co., Japan. Kokai 76 08152 (1976); Chem. Abs., 85 (1976) 160876.

524. Z. M. Baidakova, E. V. Kristal'nyi, and A. A. Arest-Yakubovich, Vysokomol. Soedin., Ser. A, 18 (1976) 2036.

525. Z. M. Baidakova, E. V. Kristal'nyi, R. V. Basova, and A. A. Arest-Yakubovich, Vysokomol. Soedin., Ser. B, 18 (1976) 75.

526. R. Petiand and Q.-T. Pham, Eur. Polym. J., 12 (1976) 449.

527. R. Petiaud and Q.-T. Pham, Eur. Polym. J., 12 (1976) 455.

528. L. I. Mekenitskaya, L. K. Golova, and Yu. B. Amerik, Vysokomol. Soedin., Ser. A, 18 (1976) 1799.

529. M. Ogasa, M. Matsumoto, M. Nishiyama, K. Tanaka, and Y. Akimoto, Japan. Kokai 76 71,395 (1976); Chem. Abs., 85 (1976) 125311p.

530. R. M. Hedrick and J. D. Gabbert, U. S. Patent 3,993,709 (1976); Chem. Abs., 86 (1977) 73388.

531. W. Kuran, S. Pasynkiewicz, J. Skupinska, and A. Rokicki, Makromol. Chem., 177 (1976) 11.

532. P. N. Hung, M. Roussel, C. Roque, and Y. Chauvin, Fr. Demande 2,299,339 (1976); Chem. Abs., 87 (1977) 23502a.

533. Dow Corning, Ltd., Brit. Patent 1,438,949 (1976); Chem. Abs., 85 (1976) 161580.

534. A. D. Shebaldova, V. I. Mar'in, G. G. Nasledskova, M. L. Khidekel, T. A. Popova, and V. A. Akchurin, Neftekhimiya, 16 (1976) 533; Chem. Abs., 85 (1976) 176747.

535. A. D. Shebaldova, V. I. Mar'in, M. L. Khidekel', I. V. Kalechits, and S. N. Kurskov, Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 2509.

536. A. Kumura, J. Harada, Y. Takeshita, and K. Watanabe, Japan. Kokai 76 80,856 (1976); Chem. Abs., 85 (1976) 143782.

537. J. Vclak, M. G. Voronkov, and F. Pukhnarevich, Collect. Czech. Chem. Commun., 41 (1976) 131.

538. J. Vcelak, L. Roman, and V. Chvalovsky, Collect. Czech. Chem. Commun., 41 (1976) 2708.

539. E. Beska and P. Rapos, J. Chem. Soc., Perkin Trans. 1, (1976) 2470.

540. J.-F. Fauvarque and A. Jutand, Bull. Soc. Chim. Fr., (1976) 765.

541. L. F. Elsom, A. McKillop, and E. C. Taylor, Org. Synth., 55 (1976) 48.

542. C. M. Bartish and C. S. Kraihanzel, J. Organomet. Chem., 112 (1976) C31.

543. Y. Miura, Y. Morimoto, and M. Kinoshita, Bull. Chem. Soc. Jpn., 49 (1976) 253.

544. S. A. Shevelava, R. V. Kolesnikov, A. A. Fainzil'berg, and I. P. Beletskaya, Kratk. Tezisy-Vses. Soveshch. Probl. Mekh. Geteroliticheskikh Reakts., (1974) 36; Chem. Abs., 85 (1976) 124080.

545. A. J. Birch and A. J. Pearson, J. Chem. Soc. Perkin Trans. 1, (1976) 954.

546. M. W. Rathke, E. Chao, and G. Wu, J. Organomet. Chem., 122 (1976) 145.

547. H. Dorn and H. Graubaum, J. Prakt. Chem., 318 (1976) 253.

548. S. S. Barton and B. H. Harrison, Carbon, 13 (1975) 283.

549. R. Benn, Chem. Phys., 15 (1976) 369.