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Organic derivatives of manganese(II) in organic synthesis

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ABSTRACT. **Literature data on the use of organic compounds of Mn(II) as reagents for organic synthesis have been correlated. Methods of obtaining and using them in acyl-, alkenyl- and allyldemetallation reactions and in 1,2- and 1,4-additions to carbonyl substrates are considered. The reactions of manganese derivatives containing Mn–Si and Mn–Sn bonds are discussed.**

The bibliography contains 99 references.

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I Introduction

The synthesis of organic derivatives of Mn(II) with a metal–carbon bond was achieved for the first time in 1937 by Gilman and collaborators.[1] It was found that on reacting MnI_2 with 1 or 2 equiv. PhMgI red-brown solutions of the complexes PhMnI and Ph_2Mn were formed. In spite of the intensive development in recent years of the chemistry of organomanganese compounds containing carbonyl ligands,[2,3] during the period from 1937 to 1976 only a few studies were published which were devoted to the preparation and properties of derivatives of the type of RMnI, R_2Mn and R_3MnLi (R = Alk, Ar).[4–10] The main reason for this is the extremely low stability of such complexes which exist (with rare exceptions) only as solutions in ether or THF, frequently at low temperatures and for a limited time. After 1976 progress became focussed, thanks to the work of Normant and collaborators,[11–13] on the use of organic Mn(II) derivatives as efficient reagents for forming new carbon–carbon bonds. Methods have been developed for obtaining the various alkyl-, alkenyl-, aryl- and alkynylmanganese halides, the corresponding di-organo derivatives and the lithium and magnesium triorganomanganates, without isolating them in the free state. In spite of the absence of detailed information on the structure of the reagents (the formulae RMnX, R_2Mn, R_3MnLi and R_3MnMgX reflect only the ratio of the starting materials) their application has in many cases proved to be extremely successful.[14]

The main applications of Mn(II) derivatives with a Mn–C bond and also with Mn–Si and Mn–Sn bonds in synthetic organic chemistry are considered below.

II. Preparation, stability and structure of organic compounds of Mn(II)

The most general method of obtaining organic compounds of Mn(II) in ether is the reaction of RLi or RMgX with MnI_2 at 0–20 °C (R = n-alkyl, alkenyl, aryl, alkynyl) or at −30 to −50 °C (R = sec-, t-alkyl).[14,15] Complexes of the type of RMnI or R_3MnLi are obtained depending on the ratio of RLi (or RMgX) and MnI_2. It must be noted that in ether the treatment of MnI_2 with 3 equiv. RMgX does not lead to the formation of the corresponding triorganomanganate R_3MnMgX. The synthesis of the di-organo derivatives R_2Mn was in all cases carried out at temperatures below −30 °C.

$$RM + MnI_2 \xrightarrow{Et_2O} RMnI + MI,$$
$$2\,RM + MnI_2 \xrightarrow{Et_2O} R_2Mn + 2\,MI,$$
$$3\,RLi + MnI_2 \xrightarrow{Et_2O} R_3MnLi + 2\,LiI,$$
M = Li, MgCl, MgBr, MgI.

The reagents are suspensions or homogeneous red-brown solutions but occasionally, when R = CH_2=CH or Ar, they are green. They are extremely sensitive to oxygen and moisture of the air.

The use of the more readily available $MnCl_2$ and $MnBr_2$ in place of MnI_2 is less efficient due to their low solubility in Et_2O.[14] The synthesis of organic compounds of Mn(II) from $MnBr_2$ in ether is successful if the practically insoluble dibromide is replaced by the soluble complex Li_2MnBr_4, prepared by treating $MnBr_2$ with an ether solution of LiBr (the latter was obtained from metallic lithium and Br_2 in Et_2O).[16] It is also possible to use previously prepared complexes of Grignard reagents with LiBr or ether solutions of organolithium compounds containing lithium halides.

$$MnBr_2 \xrightarrow[Et_2O]{LiBr} Li_2MnBr_4 \xrightarrow[Et_2O]{RMgX} RMnBr,$$
$$RMgX \xrightarrow[Et_2O]{LiBr} \text{«}RMgX \cdot LiBr\text{»} \xrightarrow[Et_2O]{MnBr_2} RMnBr,$$
$$RX \xrightarrow[Et_2O]{Li} RLi;\ RLi \xrightarrow[Et_2O]{MnBr_2} RMnBr,$$
X= Cl, Br.

It is best to use the readily available $MnCl_2$ or its soluble complex Li_2MnCl_4 in combination with 1–3 equiv. RLi or RMgX (R is alkyl, alkenyl, aryl, alkynyl) to synthesise organic derivatives of Mn(II) in THF.[14] The reaction is effected at 20 °C and in the majority of cases leads to the formation of homogeneous yellow or

brown solutions of derivatives of RMnCl, R_2Mn or R_3MnM (M = Li, MgX). All three types of complex may be synthesised using Grignard reagents in THF (in contrast to Et_2O).

$$MnCl_2 + 2LiCl \xrightarrow{THF} Li_2MnCl_4,$$

$$RM + MnCl_2(Li_2MnCl_4) \xrightarrow{THF} RMnCl + MCl(+2\,LiCl),$$

$$2\,RM + MnCl_2(Li_2MnCl_4) \xrightarrow{THF} R_2Mn + 2\,MCl(+2\,LiCl),$$

$$3\,RM + MnCl_2(Li_2MnCl_4) \xrightarrow{THF} R_3MnM + 2\,MCl(+2\,LiCl),$$

M = Li, MgCl, MgBr, MgI.

The stability of organomanganese compounds is determined by the type of complex, the nature of the organic fragment and the solvent. The tri-organomanganates R_3MnM (M = Li, MgX) possess the greatest stability. The thermal stabilities of the RMnX complex and particularly of R_2Mn are markedly less.[14] The decomposition point of Bu_3MnLi in ether is above 35 °C and of BuMnI and Bu_2Mn it is 20 and −30 °C.

The stability of Mn(II) derivatives with a Mn−C bond depends chiefly on the ease of β-elimination determined by the presence of alkyl β-hydrogen atoms.[9,10,14,17] It was found that the stabilities of the complexes RMnX and R_2Mn increase in the folowing series of R: t-alkyl < sec-alkyl < n-alkyl < methyl, alkenyl, aryl.[14] The decomposition points of the compounds RMnI in Et_2O are

R	t-Bu	iso-Pr	n-Bu	Me, Ph, $Me_2C{=}CH$
T, °C	−35	−30	20	>35

The formation of hydride intermediates during decomposition of the manganese reagents was confirmed by the isolation of hydrogenation products of unsaturated hydrocarbons introduced into the reaction mixture.[10,18]

On changing from ether to THF a marked increase was observed in the stability of organic Mn(II) compounds which is seemingly associated with stronger coordination.[14,15] The complexes t-BuMnCl, iso-PrMnCl, n-BuMnCl and PhMnCl do not undergo marked decomposition in THF even at 66 °C. A similar effect may also be caused by certain other donor ligands. Thus the addition of 5 equiv. DMF to a solution of iso-PrMnI in Et_2O raises the decomposition temperature of the complex from −30 to 35 °C.

Allyl derivatives of manganese of the type RMnCl may be obtained by the reaction of allyl Grignard reagents with Li_2MnCl_4 in THF at −78 °C.[19] The allylmanganese halides are significantly less stable than the alkyl, alkenyl, aryl and alkynyl σ-complexes considered above. Their decomposition with the formation of a mixture of regioisomeric 1,5-dienes occurs even at −78 °C.

$$R^1CH{=}C(R^2)CH_2MgX + Li_2MnCl_4 \xrightarrow{THF}$$

$$\longrightarrow R^1CH{=}C(R^2)CH_2MnCl + Mg(X)Cl + 2\,LiCl$$

R^1, R^2 = H, Alk; X = Cl, Br.

The direct synthesis of allyl compounds of Mn(II) from metallic manganese and allyl halides is described in section III.3.

Only a few examples are known of the isolation of organic Mn(II) derivatives in the free state. The existence of molecular associates (dimer, trimer and polymers) has been proved for $(Me_2PhCCH_2)_2Mn$, $(Me_3SiCH_2)_2Mn$ and $(Me_3CCH_2)_2Mn$ by X-ray structural analysis.[20] Intermolecular interaction is effected by bridging bonds between the Mn atoms and CH_2 groups and is confirmed by a shift of the appropriate absorption bands in the IR spectrum. The elemental analysis of the isolated Me_2Mn and Ph_2Mn shows that they exist as associates with Mg salts.[20] On attempting to isolate Me_3MnLi a compound was obtained the composition of which corresponded to the formula $Li_2MnMe_4.0.5Et_2O$.[20]

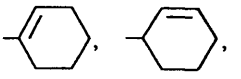
III. Reactions of organic compounds of Mn(II)

1. Alkenyl- and allyldemetallation

The first attempts to use organic compounds of Mn(II) in cross-coupling reactions generally did not give positive results. In contrast to the lithium dialkylcuprates[21,22] the alkyl derivatives of manganese of type R_3MnLi and R_2Mn gave cross-coupling products in less than 10% yield on reaction with alkyl halides.[23] Reaction with alkenyl and allyl halides (bromides and iodides) occurred relatively smoothly only in the case of the most stable Me_3MnLi.

$$Me_3MnLi + RX \xrightarrow[0°C]{Et_2O} R{-}Me$$

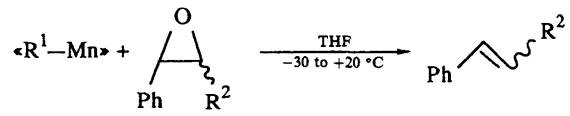
65—82%

R = , (*E*)-PhCH=CH,

(*E*)-(n-C_7H_{15})CH=CH; X = Br, I.

The main side reactions were reduction of the substrates RX to 'dimeric' products R_2 and the formation of dehalogenation products RH (when β-hydrogen atoms are present in the reagent).

The complexes MeMnCl and Bu_3MnLi may be used for deoxygenating epoxides.[24] The reaction occurs selectively under mild conditions and leads to the *trans*-olefin using either *cis*- or *trans*-oxiranes.

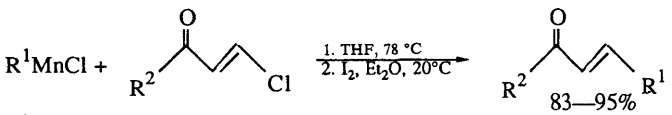


R^1	R^2	Yield of olefin, %
Me	H	63
Bu	*E*-Ph	66 (*E*:*Z* = 100:0)
Bu	*Z*-Ph	59 (*E*:*Z* = 90:10)

Further study of the cross-coupling reaction involving organomanganese compounds led to the development of efficient methods of synthesis of alkenyl- and allyl-demetallation products.

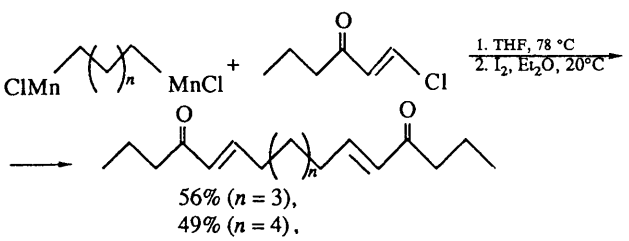
The alkyl derivatives of manganese RMnCl react with β-chlorovinyl ketones forming the corresponding β-alkyl substituted α,β-unsaturated ketones in good yield as a mixture of *trans* and *cis* isomers. The *cis* isomeric enones are readily isomerised in the presence of trace amounts of I_2.[25,26] Under the same conditions the dimanganese derivatives give unsaturated diketones as the main

product. It must be noted that replacement of halogen by alkyl using organocuprate complexes proceeds smoothly only in the case of the cyclic β-chloro-α,β-enones.[27,28]



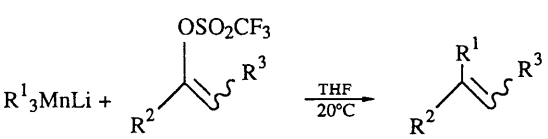
R^1 = Me, Bu, iso-Bu, sec-Bu, cyclo-C_6H_{11};

R^2 = Pr, Ph;

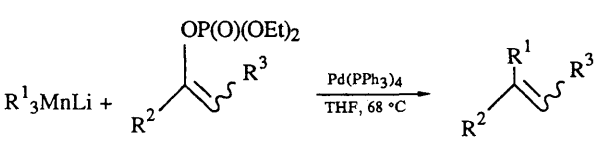


56% (n = 3),
49% (n = 4).

The formation of alkenyldemetallation products is observed in reactions of Ph_3MnLi and trialkylmanganates with enol phosphates and enol triflates.[29] the enol phosphates, unlike the enol triflates, react only in the presence of a palladium catalyst [10 mol% $Pd(PPh_3)_4$]. On changing from Me_3MnLi and Ph_3MnLi to Bu_3MnLi the yield of cross-coupling products was reduced due to the reduction side reactions.



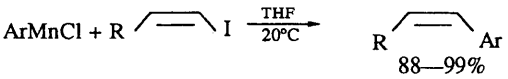
R^1 = Me, Bu, Ph;
R^2 = n-$C_{10}H_{21}$, R^3 = H; R^2, R^3 = n-C_5H_{11};



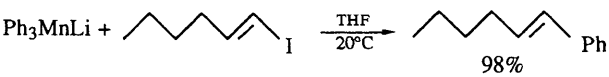
63—82% (R^1 = Me, Ph)
34—50% (R^1 = Bu)

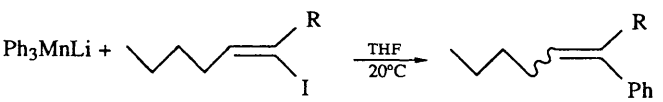
R^1 = Me, Bu, Ph; R^2 = n-C_5H_{11}, R^3 = Bu; R^2–R^3 = –$(CH_2)_{10}$– .

The cross-coupling of aryl manganese compounds with alkenyl iodides is a convenient and efficient method of synthesis of various substituted styrenes.[30] It was found that the reaction of reagents of the type of ArMnCl and Ar_3MnLi with substrates containing a 1,2-disubstituted double bond is accompanied by the complete retention of its geometry. In the case of the less reactive trisubstituted iodides a high yield of alkenyldemetallation products was achieved only when using the "ate" complexes Ar_3MnLi. The reactions lead to the formation of a mixture of stereoisomers.



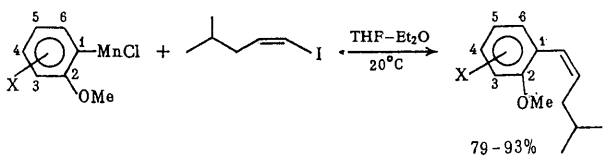
Ar = Ph, p-MeC_6H_4, p-$MeOC_6H_4$, p-ClC_6H_4,
p-BrC_6H_4, α-napthyl; R = Bu, iso-Bu.



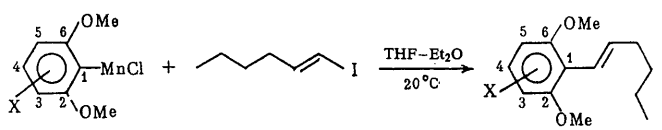


68% (R = Bu, E:Z = 38:62)
58% (R = $SiMe_3$, E:Z = 88:12)

Aryl *ortho-o*-substituted σ-complexes of manganese as well as p-$MeOC_6H_4MnCl$ undergo cross-coupling with alkenyl iodides.[31] Since the corresponding lithium reagents may readily be obtained by the *ortho* lithiation of ethers of di- and trihydroxybenzenes,[32] the combination of the stages of lithiation, transmetallation and cross-coupling is a convenient method for introducing an alkenyl fragment into aromatic polyhdyroxy compounds.



X = 3-OMe, 5-OMe, 6-OMe



88% (X = 3-OMe),
60% (X = 4-OMe)

It must be noted that the cross-coupling of aryl manganese compounds with alkenyl iodides, unlike the analogues reactions with derivatives of Li,[33] Mg,[34] Zn,[35] Al [36]and several other metals, proceeds without a catalyst (Pd or Ni complex). The corresponding organocopper reagents react with alkenyl iodides without a catalyst but under far more forcing conditions.[37]

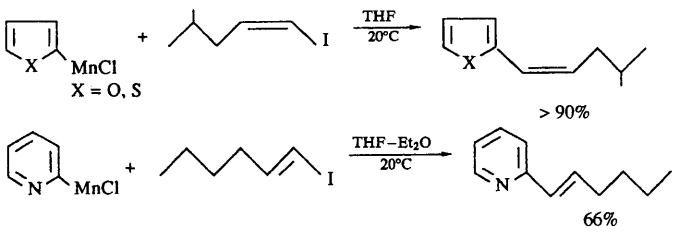
The mechanism of alkenyldemetallation seemingly includes an oxidative addition step (*a*) [the intermediate (I) containing tetravalent manganese is formed] and a reductive elimination step (*b*).[30,38]

$$Ph_3MnLi + RI \xrightarrow{(a)} \underset{(I)}{Ph_3MnR} + LiI,$$

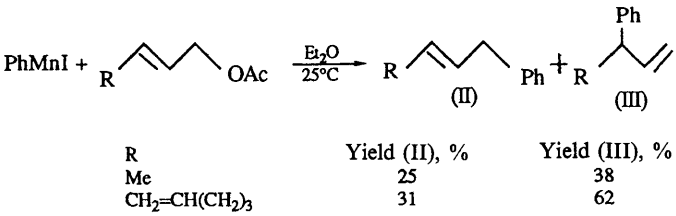
$$Ph_3MnR \xrightarrow{(b)} PhR + Ph_2Mn.$$

The fact that in several cases the yield of cross-coupling product continues to grow after complete disappearance of the initial alkenyl substrate supports this scheme. A possible explanation is that step (a) proceeds at a higher rate than step (b). Furthermore the formation of dehalogenation products RH [by hydrolysis of complex (I)], the yield of which falls depending on the accumulation of compounds RPh, becomes understandable.[30]

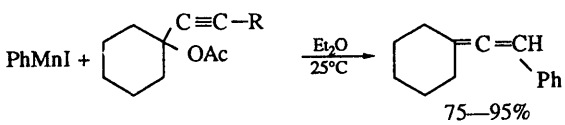
The organomanganese derivatives of furan, thiophene, pyridine and *N*-methylindole react with alkenyl iodides to give the corresponding α-alkenyl substituted O-, S- and N-containing heterocycles in high yield with complete retention of the configuration at the double bond.[39]



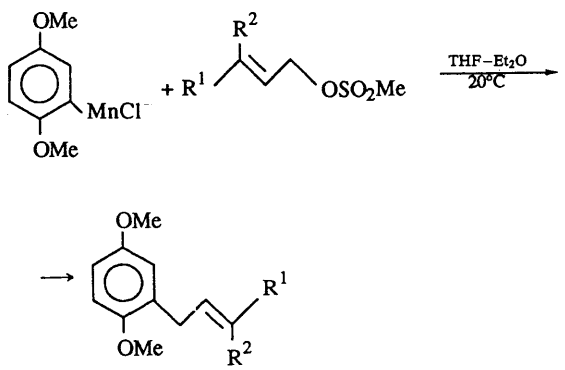
The reaction of PhMnI with allyl and propargyl acetates leads to substituted allylbenzenes and phenylallenes.[40] Unlike phenylmanganese iodide, the 2,5-dimethoxyphenyl derivative does not react with allyl acetates.[31] The synthesis of the practically important *O,O*-dimethylhydroquinones containing an allyl fragment may be effected by replacing the acetates by the corresponding mesylates.[31] The reactions take place with high regiospecificity (products of cross-coupling contain a dimethoxyphenyl group at the least substituted carbon atom of the allylic system) and are accompanied by the retention of the geometry of both *trans* and *cis* double bonds.



R	Yield (II), %	Yield (III), %
Me	25	38
CH_2=$CH(CH_2)_3$	31	62

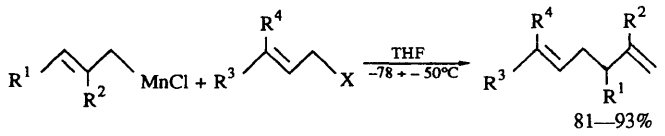


R = H, Ph, n-C_5H_{11}.



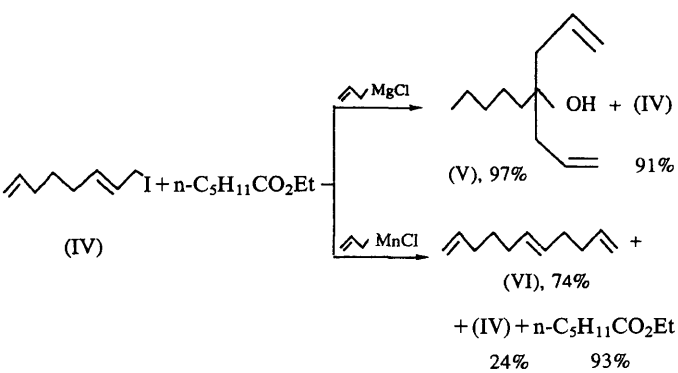
R^1 = CH_2=$CH(CH_2)_3$, R^2 = H; R^1 = H, R^2 = Bu;
R^1 = Me_2C=$CH(CH_2)_2$, R^2 = Me.

Allyl compounds of manganese of the type RMnCl may also be used in cross-coupling reactions. Their reaction with allyl bromides and iodides is effected under mild conditions and is an efficient method for synthesising 1,5-dienes.[19] The formation of allyldemetallation products occurs with the participation of the α-carbon atom of the substrate and the γ-carbon atom of the reagent with high stereoselectivity.

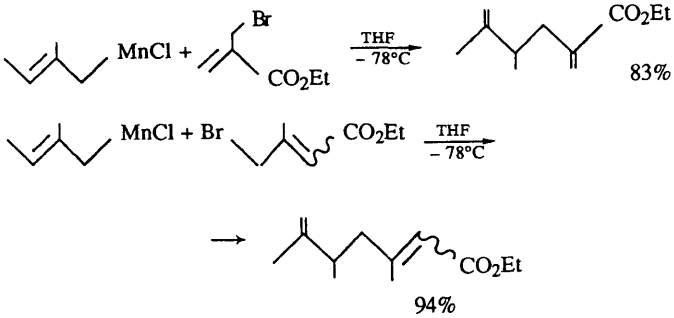


R^1, R^2 = H; R^1 = Me, R^2 = Me, Bu; R^3 = Ph, *E*-MeCH=CH, CH_2=$CH(CH_2)_3$, R^4 = H; R^3 = Me_2C=$CH(CH_2)_2$, R^4 = Me; X = Br, I.

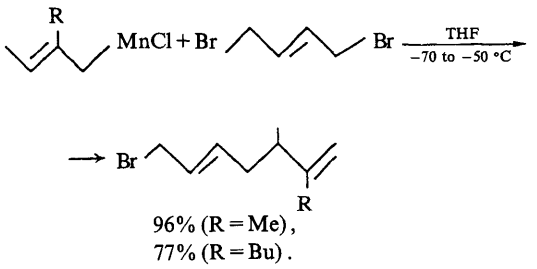
Allyl derivatives of magnesium, like the manganese derivatives, react with allyl halides giving 1,5-dienes,[41] however in contrast to the latter several functional groups are affected.[19] Treatment of an equimolar mixture of the iodide (IV) and ethyl caproate with 2 equiv. CH_2=$CHCH_2MgCl$ leads to the tertiary alcohol (V). The initial iodide is practically unreacted. Reaction of the same mixture with 2 equiv. CH_2=$CHCH_2MnCl$, on the other hand, leads to the formation of the hydrocarbon (VI) and the ester is completely unaffected. A similar result was observed in the reaction of CH_2=$CHCH_2M$ (M = MgCl, MnCl) with an equimolar mixture of the iodide (IV) and BuCN.



The inert nature of the organomanganese compounds in relation to ester groups enables cross-coupling reactions to be effected with esters of α,β-unsaturated carboxylic acids (2-methylacrylic, 3,3-dimethylacylic, tiglic, angelic) containing an allylic halogen atom which cannot be achieved using Grignard reagents.[42] In the case of alkyl 3-bromocrotonates the main course of the reaction is the formation of cyclopropanes (see section III.3).



The use of allyl complexes of manganese enables a selective monoallylation of allylic 1,4-dibromides to be effected while magnesium derivatives give chiefly diallylation products.[43]



96% (R = Me),
77% (R = Bu).

Comparatively little has been published on work devoted to the use of Mn(II) compounds as catalysts in cross-coupling reactions. It was shown that reaction of Grignard reagents RMgX (R = Ph, $PhCH_2$, $CH_2=CHCH_2$, $MeCH=CHCH_2$; X = Cl, Br) with enol triflates in the presence of 10 mol% Li_2MnCl_4 leads to the alkenyldemetallation product in 74–92% yield. On changing to MeMgI, EtMgBr and $CH_2=CHMgBr$ the yield was reduced to 6–35%.[29] Under approximately the same conditions iso-PrMgBr reacts with alkenyl and aryl halides to give mainly products of reduction.[44]

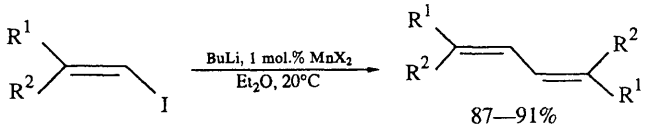
$$RX + \text{iso-PrMgBr} \xrightarrow[\text{THF, 25 to 45 °C}]{\text{1 mol.\% } MnX_2} RH \quad 65-93\%$$

R = (*E*) and (*Z*)-Bu(Et)C=CH, $Bu_2C=CH$, (*Z*)-(n-C_7H_{15})CH=CH

$CH_2=C$(n-C_8H_{17}), 4-$MeOC_6H_4$, 4-$Me_2NC_6H_4$, 2,4,6-$Me_3C_6H_2$,

α-napthyl; X = Br, I.

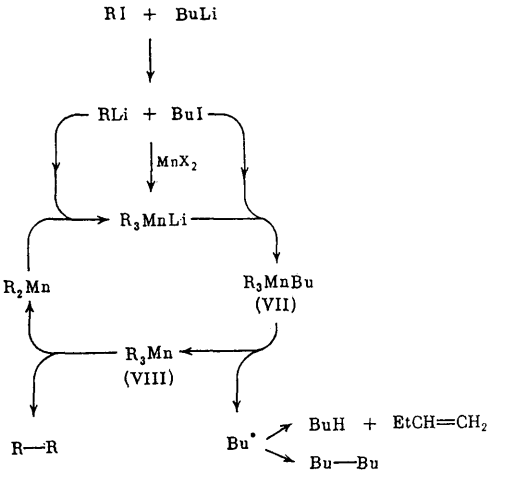
Manganese halides (1 mol% $MnCl_2$ or $MnBr_2$) efficiently catalyse the reductive 'dimerisation' of alkenyl iodides to symmetrical 1,3-dienes on treatment of the iodides with 1 equiv. n-butyllithium.[45] Both double bonds in the reaction product have the same geometry as in the substrate.



87—91%

R^1 = H, R^2 = n-C_7H_{15}; R^1 = Me, Bu, R^2 = Et; R^1 = Et, R^2 = Bu.

The mechanism proposed for the 'dimerisation' is the formation *in situ* (by metal–halogen exchange) of a lithium alkenyl derivative and butyl iodide. The successive reaction of the catalyst with the lithium reagent and BuI leads to the mixed tetraorgano-derivative (VII) containing quadrivalent manganese which is converted into the trialkenyl complex (VIII) by expulsion of a butyl radical. Decomposition of the intermediate (VIII) gives a conjugated diene and a dialkenylmanganese which continues the catalytic cycle.



2. Acyldemetallation

The acyldemetallation of organic Mn(II) derivatives is one of the most efficient and well characterised routes for using these reagents in synthesis. In comparison with organic compounds of cadmium, zinc and aluminium, which are traditionally used to obtain unsymmetrical ketones from acid chlorides or anhydrides of carboxylic acids,[46–49] the manganese reagents generally give a higher yield of ketone particularly in the case of substrates containing other reactive functional groups in place of the acid chloride (or anhydride).[14] The preferential use of the latter must be attributed to the accessibility, cheapness and lack of toxicity of the initial manganese halides, the ease of preparing reagents of various types from them, and also the possibility of carrying out the reactions at temperatures close to ambient in a relatively short time. Frequently the use of organocopper complexes gives better results,[21,50,51] however the smooth acyldemetallation of many of them occurs only at low temperatures (−78 °C) and with a large excess of reagent (unlike the manganese reagents).

The reaction of alkyl-, aryl-, alkenyl- and alkynylmanganese halides, obtained by treating MnI_2 (in ether) or Li_2MnCl_4 (in THF) with organolithium or organomagnesium compounds, with carboxylic acid chlorides leads to the formation of alkyl, aryl, alkenyl and alkynyl ketones respectively in high yield.[11,12,14,52]

$$R^1MnX + R^2COCl \xrightarrow[-10 \text{ to } +20\ °C]{Et_2O \text{ or THF}} R^1COR^2$$

R^1 = Me, Bu, n-C_7H_{15}, Ph, (*Z*)-BuCH=CH, (*Z*)-Et(Me)C=CH,

$Me_2C=CH$, $BuC\equiv C$;

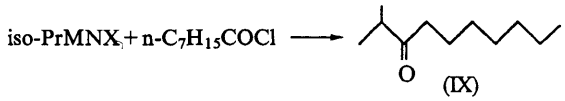
R^2 = Et, Bu, n-C_7H_{15}, iso-Pr, t-Bu, Ph, $Me_2C=CH$; X = Cl, I.

Reactions involving alkenyl derivatives of manganese are accompanied by complete retention of the double bond geometry. On changing from complexes RMnI (R = Alk) to the di-organo

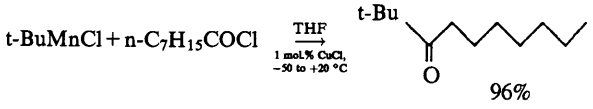
derivatives R_2Mn and the trialkylmanganates R_3MnLi the yield of ketone is reduced by 5–10%. In the case of R_2Mn two and in the case of R_3MnLi three alkyl fragments are transferred. The introduction of α,β-unsaturated acid chlorides into the reaction is only possible when two β-alkyl substituents are present in the latter. β-Monosubstituted α,β-unsaturated acid chlorides polymerise in the presence of the manganese reagents.

The initial use of Et_2O almost exclusively as solvent (in combination with MnI_2) and not THF [11,12,14] was associated with the possible opening of the tetrahydrofuran ring by an acid chloride in the presence of a Lewis acid, viz. the manganese dihalide, formed in addition to the ketone.[53] It was found subsequently that this process does not take place under the usual acyldemetallation conditions.[52]

Replacement of ether by THF enables the cheaper and more available $MnCl_2$ or its soluble complex Li_2MnCl_4 (see section II) to be used instead of MnI_2 to prepare organomanganese compounds. There are other advantages. The higher stability of the thermally unstable secondary and tertiary alkyl derivatives of manganese in an ether–THF mixture, in comparison with pure Et_2O, leads to an increase in the yield of acyldemetallation products.[14] The yield becomes practically quantitative on carrying out the reaction in THF in the presence of 1 mol% CuCl.[52]

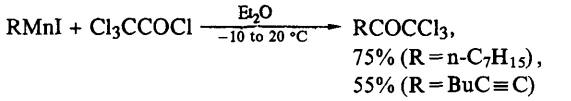


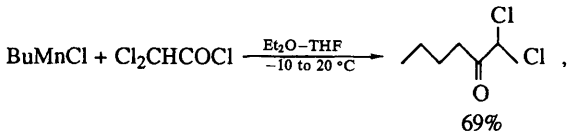
X	Solvent	T, °C	Yield of ketone (IX), %
I	Et_2O	−35	65
I	Et_2O–THF	−35	78
Cl	THF (1 mol.% CuCl)	−30 to +20	93

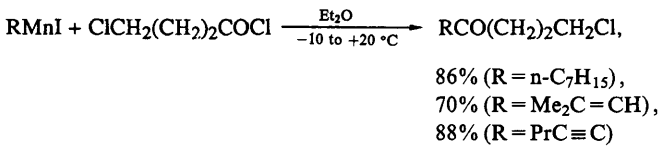


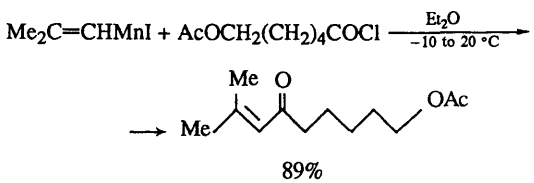
It turned out that on using THF (but no Et_2O) the addition of catalytic amounts of CuCl markedly increased the yield of ketone in reactions involving MeMnCl and also σ-complexes of manganese RMnCl (R is aryl, alkenyl).[52]

Smooth acyldemetallation is also observed in the case of more complex substrates containing other functional groups in addition to the acid chloride.[12,14,52,54,55] The acid chlorides of trichloroacetic, α,α-dichloro- and α-chlorocarboxylic acids react with organomanganese compounds to give the corresponding trichloromethyl-, α,α-dichloroalkyl- and α-chloroalkyl ketones in high yield. β-Chloro-containing acyl chlorides are subject to elimination of HCl in the presence of manganese complexes. On the other hand γ-chloro derivatives (and also substrates with a halogen atom removed even further from the COCl fragment) react in the usual way. A high yield of acyldemetallation product was also achieved on using acid chlorides of α-alkoxy- and α-alkylthiocarboxylic acids.

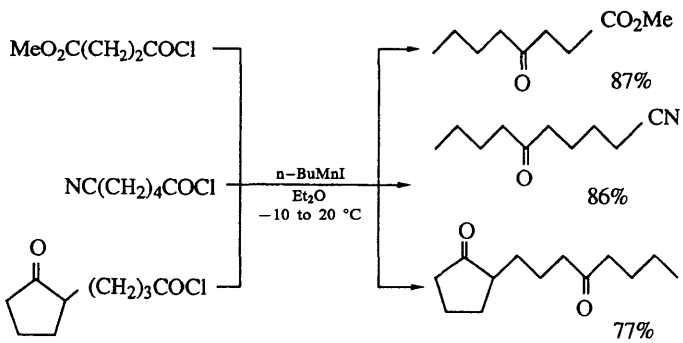




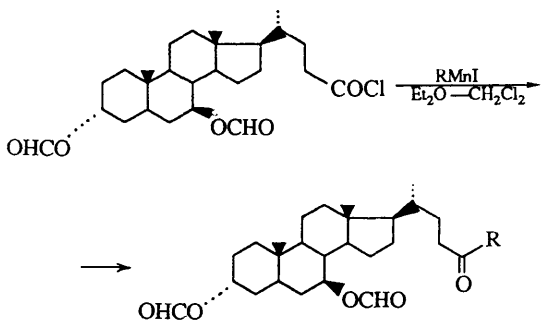




Reactions involving substrates containing ester, nitrile and keto groups are characterised by complete retention of these groupings and lead to keto-esters, ketonitriles and diketones.



The possibility of retaining two formate ester groups is shown using a steroid acid chloride as an example.[56]



88% (R = iso-Bu),
78.5% (R = Me_2C=CH),
73.5% (R = PrC≡C)

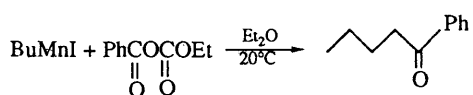
The less reactive carboxylic acid anhydrides[14,15,54,57] have been used in this reaction in addition to acid chlorides. Symmetrical anhydrides react with the complexes RMnI (in Et_2O) or RMnCl (in THF) to give the corresponding ketones in high yield. The yield of acyldemetallation product was reduced somewhat on replacing RMnX derivatives (R = Alk; X = Cl, I) by trialkyl manganates R_3MnM (M = Li, MgBr). It is reported that the latter react with transfer of all three organic fragments.

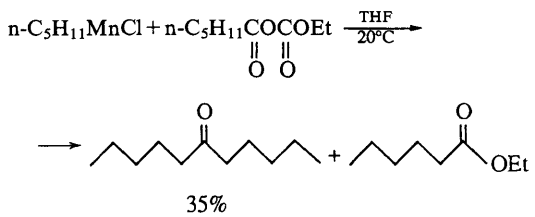
$$R^1MnX + (R^2CO)_2O \xrightarrow[20°C]{Et_2O \text{ or } THF} R^1COR^2$$
81—96%

$R^1 = n\text{-}C_7H_{15}$, Ph;
R_2 = Et, iso-Pr, iso-Bu, t-Bu;
X = Cl, I.

The reaction of $n\text{-}C_7H_{15}MnI$ with the mixed anhydride of a carboxylic acid and pivalic acid proceeds exclusively by replacing the t-butyl carboxylate group and leads to heptyl pentyl ketone (72% yield).[15]

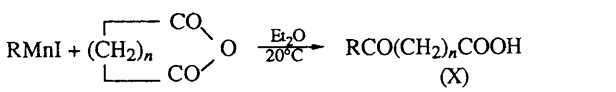
Acyl ethyl carbonates, which may readily be obtained by treating carboxylic acids with phosgene in the presence of Et_3N, are efficient substrates for carrying out the acyldemetallation of organomanganese compounds.[14,15] These derivatives react with RMnI complexes in ether giving the corresponding ketones in high yield. On using THF or a THF—Et_2O mixture as solvent the yield of ketone was reduced due to a side reaction forming an ethyl ester.





The use of other mixed anhydrides of the form $R^1C(O)OC(O)ZR^2$ (ZR^2 = OMe, OPh, SEt) and $RC(O)OP(O)(OMe)_2$ in place of acyl ethyl carbonates gives poorer results.[15]

The reactions of alkyl σ-complexes of manganese with cyclic anhydrides of dicarboxylic acids is a convenient method of synthesising aliphatic keto-acids.[54]

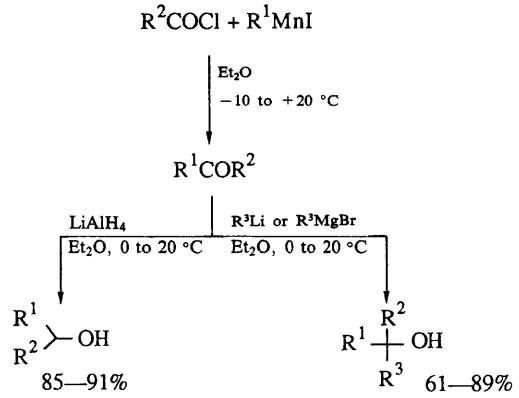


R	*n*	Yield (X), %
$n\text{-}C_7H_{15}$	2	77
n-Bu	3	55

The reaction of alkyl-, aryl- and alkenylmanganese iodides with ethyl chloroformate leads to the ethyl esters of alkyl-, aryl- and alkenylcarboxylic acids.[13]

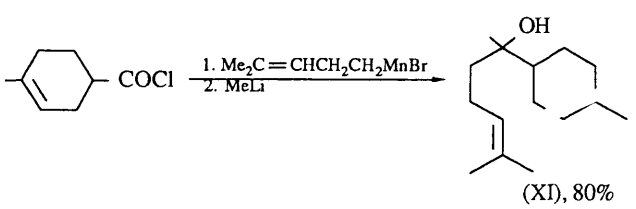
$$RMnI + ClCOOEt \xrightarrow[20\ °C]{Et_2O} RCOOEt$$
83% (R = $n\text{-}C_7H_{15}$),
77% (R = Ph),
70% ($R = Me_2C{=}CH$)

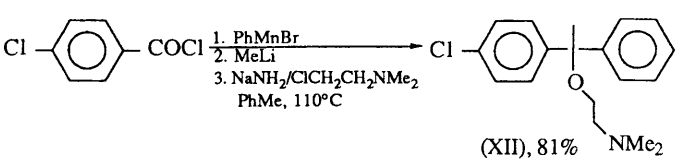
A more detailed study of the acyldemetallation of organomanganese compounds revealed several interesting features.[58] It turned out that the difference in reaction rates of RMnI derivatives with the initial acid chloride and with the ketone isolated from the reaction mixture was too small to guarantee conduct of the acylation without subsequent condenstion with the formation of a tertiary alcohol (which is observed in practically every case). In the reaction of BuMnI with BuCOCl (ether, 20 °C) the yield of BuCOBu is 80 and 92% after 5 and 10 min but in the reaction of BuMnI with BuCOBu the yield of Bu_3COH is 78 and 81% after the same times. It was shown that the acyldemetallation product formed *in situ* is a complex of the ketone with the metal halides present in solution (MnX_2 + LiX or MnX_2 + MgX_2, whre X = Cl, Br, I) which are practically unreactive towards RMnI unlike the free ketone. Treatment of such a complex with the more reactive organic compounds of lithium and magnesium and with $LiAlH_4$ and $NaBH_4$ leads to the formation of tertiary and secondary alcohols respectively in high yield. Various tertiary alcohols may therefore be synthesised directly from acid chorides by the sequential action on them of first organomanganese compounds and then organolithium or organomagnesium reagents.[58]



R^1 = Et, Bu, iso-Bu, $n\text{-}C_7H_{15}$;
R^2 = Et, iso-Bu, t-Bu, $n\text{-}C_5H_{11}$, Ph, $Me_2C{=}CH$;
R^3 = Me, Et, Bu, sec-Bu, Ph, $Me_2C{=}CH$, $MeCH{=}CH$, $CH_2{=}CHCH_2$.

The procedure developed has been used successfully to obtain biologically active compounds, viz. the diastereomeric (±-α-bisabolols (XI) and (±)-chlorphenoxamine (XII).[59]





3. 1,2- And 1,4-addition

The reaction of organomanganese compounds with aldehydes and ketones occurs similarly to the corresponding reaction of organolithium and organomagnesium compounds and leads to secondary or tertiary alcohols in high yield.[14,60,61] However, the σ-complexes of manganese react significantly more selectively than the lithium or magnesium derivatives. They are inert towards esters, nitriles and apparently several other functional groups, the preservation of which during a condensation at an aldehyde or ketone group has been shown in only a few examples.[14,62]

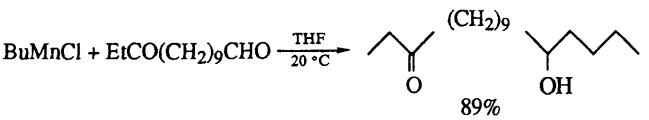
Reaction of alkyl-, alkenyl-, aryl- and alkynylmanganese halides with an equimolar mixture of an aldehyde and a ketone occurs only with the aldehyde. The initial ketone does not react.[60,61]

$$R^1MnX + R^2CHO + R^3COR^4 \longrightarrow R^1R^2CHOH + R^3COR^4$$
82—99%

R^1 = Me, Bu, n-C_7H_{15}, Ph, $Me_2C{=}CH$, $BuC{\equiv}C$;
R^2 = Bu, n-C_6H_{13}, t-Bu, Ph, $Me_2C{=}CH(CH_2)_2C(Me){=}CH$;
$R^3 = R^4$ = Pr; R^3 = Me, R^4 = n-C_5H_{11}; R^3 = Pr, R^4 = Ph;
$R^3 - R^4 = -(CH_2)_5-$; $R^3 = Me_2C{=}CH$, R^4 = n-C_7H_{15}.

X	Solvent	T, °C	Additive
Cl	THF	20	LiCl or MgClBr
Br	Et_2O	20	LiBr
I	Et_2O	−50	MgBrI

Under the same conditions aliphatic ketoaledhydes give secondary ketoalcohols.

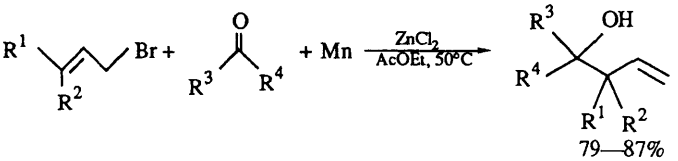


The temperature for carrying out a chemoselective condensation is determined by the reactivity of the manganese derivative which in its turn depends on the nature of the solvent and the metal salts in solution. It was found that complexes RMnX (X = Br, I) in ether in the presence of MgX_2 are more reactive than in the presence of LiX.[61] The reason for this is apparently that MgX_2, being a stronger Lewis acid, is coordinated at the oxygen atom of the carbonyl group, increasing its electrophilicity.

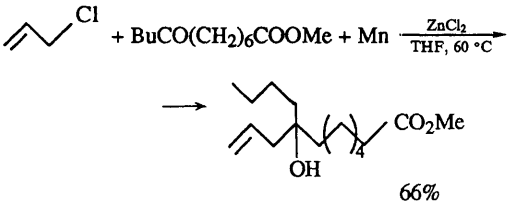
It is known that organic derivatives of trialkoxytitanium are used most frequently to achieve a high chemoselectivity in reactions of this type.[63—65] Organic compounds of Mn(II) at the same selectivity (>99%) give secondary alcohols in higher yield (5—10% more on average). In addition the reaction of σ-complexes containing alkenyl and secondary alkyl fragments becomes possible (the corresponding titanium reagents are unstable even at −78 °C.

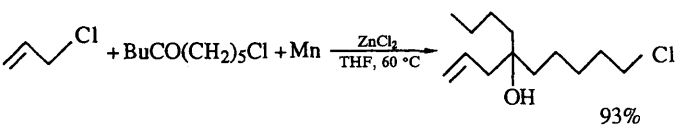
Allylmanganese halides, unlike alkyl-, alkenyl-, aryl- and alkynylmanganese halides, may be obtained by direct synthesis from metallic manganese and allyl halides.[66—68] The synthesis of allylmanganese halides in the presence of a carbonyl substrate, such as an aldehyde or ketone, is the most expedient and preparatively convenient.[67,68] This modification enables both the decomposition of the unstable allyl manganese complexes and the formation of 1,5-dienes by the Wurtz reaction, which reduce the yield of condensation products, to be reduced to a minimum.

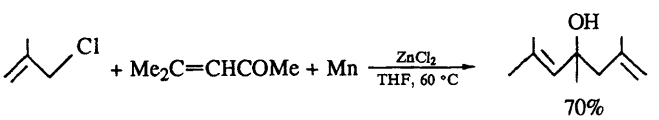
Heating the carbonyl compound, allyl halide and metallic manganese in ethyl acetate or THF in the presence of 10 mol% $ZnCl_2$ leads to the preparation of the corresponding homoallyl alcohols in high yield.[68]



$R^1 = R^2$ = H, R_1 = Me, R^2 = H, Me;
R^3 = H, R^4 = n-C_6H_{13}, t-Bu, Ph;
R^3 = Me, R^4 = n-C_7H_{15}, $R^3 = R^4$ = Bu.



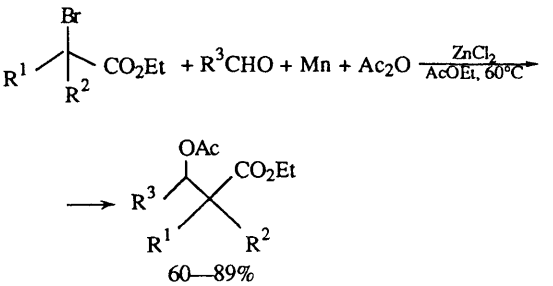




The reaction is characterised by complete retention of ester and dimethylacetal groups, and of alkyl and aryl halogen atoms in the initial aldehyde or ketone. On using α,β-unsaturated ketones only 1,2-addition is observed. Crotyl and isoprenyl bromides react giving condensation products formed from the most substituted carbon atom of the allyl fragment.

Carrying out the reaction in THF in the absence of $ZnCl_2$ requires the use of a large excess (6—7 equiv.) of both manganese and allyl halide.[67] Furthermore, it is necessary to add 1 equiv. I_2 to the reaction mixture to achieve a high yield of the homoallyl alcohol.

In the presence of metallic manganese and 10 mol% $ZnCl_2$ it is possible to effect the condensation of α-bromocarboxylic acid esters with aldehydes and ketones by a type of Reformatsky reaction.[68] The use of acetic anhydride to acylate the alkoxide formed *in situ* inhibits the retroaldol reaction.

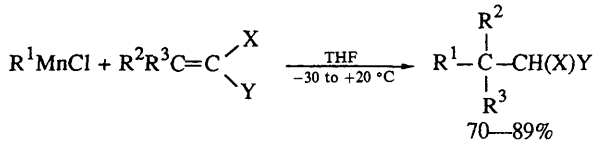


R^1 = H, R^2 = H, n-C_6H_{13}; $R^1 = R^2$ = Me;
R^3 = n-C_6H_{13}, t-Bu, Ph.

The conjugate addition of σ-complexes of Mn(II) to an α,β-unsaturated carbonyl substrate was described for the first time by Gilman and collaborators[4] for the reaction of PhMnI and PhCH=CHCOPh. A detailed study of the reaction of alkyl-, aryl- and alkenylmanganese compounds with 2-cyclohexenone showed their unsuitability for the smooth synthesis of 3-substituted cyclohexanones. The latter were obtained in relatively low yield as a result of the competing processes of 1,2-addition and reductive dimerisation with the formation of 3,3′-bis(cyclohexanone).[69] The product ratio depended markedly on the type of complex (RMnX, R_2Mn, R_3MnLi or R_3MnMgX) and the nature of the solvent (Et_2O or THF).

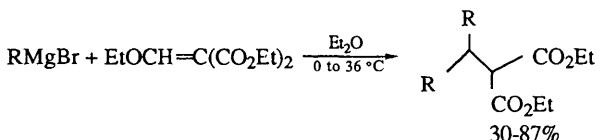
The reaction of cyclic α,β-unsaturated ketones with RMgX (R = Alk, Ar; X = Br, I) catalysed by manganese salts also proceeds nonselectively.[69–71]

In contrast to the α,β-enones, substrates containing a double bond activated by two electron-accepting groups (alkylidenemalonic, -cyanoacetic and -acetoacetic esters) react with RMnCl derivatives (R is alkyl, alkenyl, aryl, alkynyl) obtained from $MnCl_2$ and RMgCl in THF, forming conjugate addition products in high yield.[72] The yield is reduced when using the corresponding lithium reagents instead of RMgCl to obtain the organomanganese compounds.

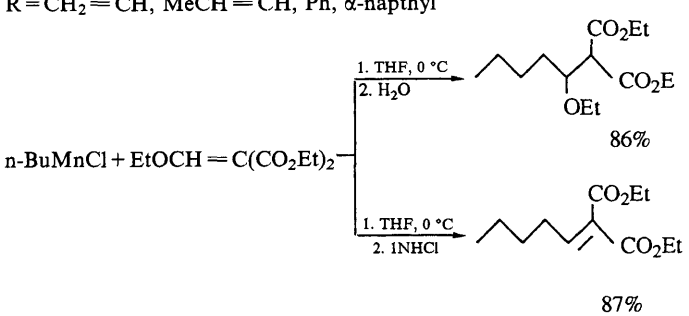


R^1 = Me, Bu, iso-Pr, $Me_2C=CH$, Ph, $BuC\equiv C$;
R^2 = H, R^3 = Me, Pr, Ph; R^2, R^3 = Me;
X, Y = CO_2Et, CN, COMe.

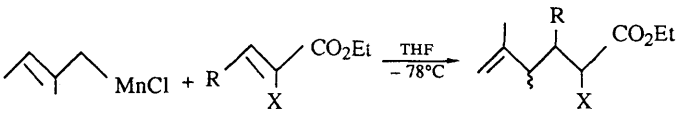
The initial Grinard reagents also give β-substituted alkylmalonic or alkylcyanoacetic esters on reaction with alkylidenemalonates or alkylidenecyanoacetates[73,74] though often in significantly lower yield (particularly with β,β-disubstituted substrates).[72] An even more clear difference in behaviour of the manganese and magnesium derivatives is displayed in reactions involving diethyl (ethoxymethylene)-malonate.[72,73,75]



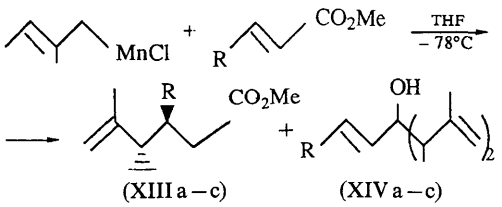
R = $CH_2=CH$, MeCH=CH, Ph, α-napthyl



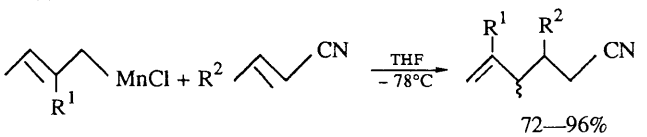
The introduction of γ-substituted allylic organomanganese compounds into the reaction leads to the formation of 1,4-addition products involving exclusively the γ-carbon atom of the reagent.[76] The esters of alkylidenemalonic, alkylidenecyanoacetic, maleic and fumaric acids containing a doubly activated double bond give 1,4-addition products. In contrast methyl crotonate, methyl 2-hexenoate and methyl cinnamate give the 1,2-addition products, the tertiary alcohols (XIVa–c), in addition to the 1,4-addition products (XIIIa–c). On changing from the ester to the nitrile the analogous 1,2-addition process does not take place.



R = n-C_6H_{13}, *E*-MeCH=CH; X = CO_2Et, CN.



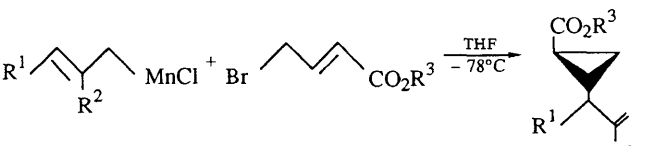
Compound	R	Yield (XIII), %	Yield (XIV), %
(a)	Me	69	18
(b)	Pr	45	39
(c)	Ph	27	36



R^1 = H, Me, Bu; R^2 = Me, Pr, Ph.

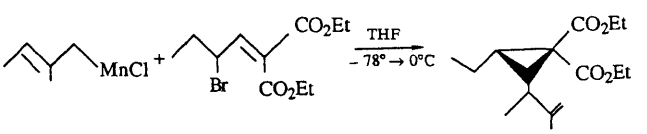
The reaction of allylic organomanganese compounds with esters of α,β-unsaturated monocarboxylic acids is characterised by a high stereoselectivity. Each of the products (XIIIa) and (XIIIb) is a single diastereomer with an *anti* disposition of alkyl groups at the β- and γ-carbon atoms.[77] The configuration of compounds (XIIIa) and (XIIIb) was confirmed by converting them into the 3,4-*cis* isomers of 3-alkyl-5-iodo-4,5-dimethylpentanolide by saponification and iodolactone formation.

The reaction of allylic complexes of manganese with alkyl 4-bromocrotonates is accompanied by cyclisation of the manganese enolates formed initially and leads to esters of allyl substituted cyclopropanecarboxylic acids.[42,78]



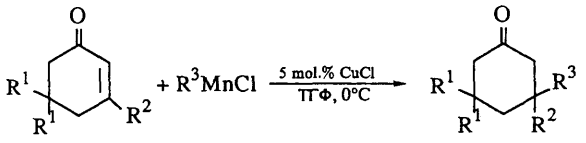
$R^1=R^2$=H; R^1 = Me, R^2 = H, Me, Bu; R^3 = Me, iso-Pr.

γ-Bromo-containing alkylidenemalonates and alkylidenecyano-acetates react similarly.[42]

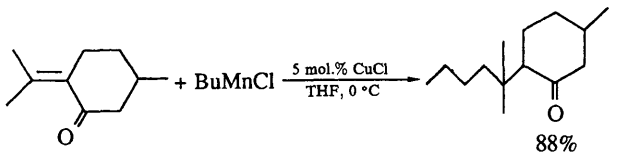


It should be noted that the corresponding α-, β- and γ-substituted crotonic acids give products of cross-coupling or condensation at the ester group (see section III.1).

The problem of the selective 1,4-addition of organomanganese reagents to α,β-unsaturated ketones may be resolved by conducting the reaction in the presence of catalytic quantities of copper salts.[79] The reaction of BuMnCl with 2-cyclohexenone (THF, 0 °C) leads to the preparation of 3-butylcyclohexanone in no more than 10% yield,[69] but in the presence of 0.1–5 mol% CuCl its yield becomes practically quantitative. The reactions of alkyl-, aryl- and alkenylmanganese chlorides with various conjugated enones (including those containing a tri- and even a tetrasubstituted double bond) catalysed by CuCl are efficient methods of synthesis of the corresponding β-branched alkyl ketones.

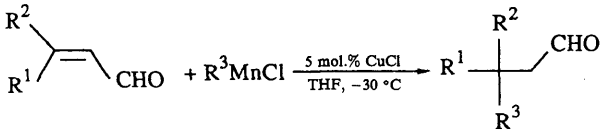


R^1 = H, R^2 = H, Me; R^1 = R^2Me;
R^3 = Me, n-Bu, iso-Pr, t-Bu, Ph, Me_2C=CH, PrCH=CH.



It must be recorded that the yield of 1,4-addition products when using RMnX is significantly greater in many cases than when using organocopper reagents of the type RCu, R_2CuLi and $R_2Cu(CN)Li_2$ and Grignard reagents under conditions of copper salt catalysis.[80]

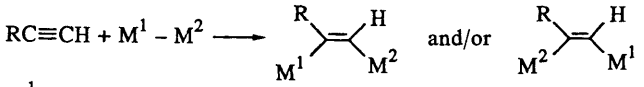
In the presence of catalytic quantities of CuCl the conjugated addition of manganese σ-complexes to β-mono- and β,β-disubstituted α,β-unsaturated aldehydes (the α,β-disubstituted substrates react giving a mixture of products of 1,4-addition and condensation at the aldehyde group).[81] The reaction course indicated is effected for organocopper compounds only on promotion with Me_3SiCl and leads to the formation of enol silyl ethers.[82,83]



R^1 = H: R^2 = Me, Bu, n-C_7H_{15}, Ph;
R^1 = Me: R^2 = Me, Bu, n-C_7H_{15}, Ph, MeCH=CH;
R^1 = Me_2C=CH$(CH_2)_2$, R^2 = Me;
R^3 = Me, Pr, n-C_7H_{15}, Me_2C=CH$(CH_2)_2$, Ph.

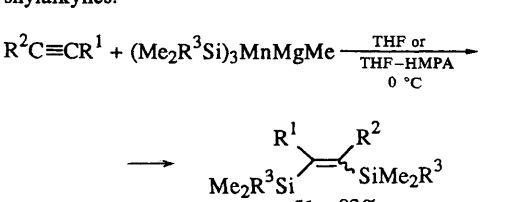
IV. Reactions of manganese derivatives containing Mn–Si and Mn–Sn bonds

The regio- and stereoselective addition of reagents with Si–Mg, Si–Al, Si–Zn,[84–86] Si–Cu,[87] Sn–Mg, Sn–Al, Sn–Zn,[88] or Sn–Cu [89,90] bonds to acetylene with the formation of 1,2-dimetallated alkenes has a high synthetic potential due to the possibility of further selective conversions at each of the two metal–carbon bonds.



M^1 = Me_2PhSi, Me_3Sn, Bu_3Sn, Ph_3Sn;
M^2 = MeMg, Et_2Al, $^1/_2Zn$, Cu, $^1/_2Cu$.

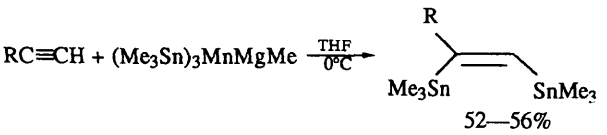
It was found that, in contrast to the "ate" complexes of manganese mentioned above, both $(Me_3Si)_3MnMgMe$ and $(Me_2PhSi)_3MnMgMe$, prepared by sequential treatment of Me_3SiLi or $Me_2PhSiLi$ with 1 equiv. MeMgI and 0.33 equiv. $MnCl_2$, give 1,2-disilylation products on reaction with terminal and 1-trimethylsilylalkynes.[91,92]



[(*E*)/(*Z*) from 33 : 67 to 65 : 35]

R^1 = H: R^2 = Me_3Si, n-C_6H_{13}, Ph, $PhCH_2O(CH_2)_2$, $(THP)O(CH_2)_2$;
R^1 = Me_3Si: R^2 = n-C_6H_{13}, $PhCH_2O(CH_2)_2$.
$(THP)O(CH_2)_2$(where THP is tetrahydropyranyl); R^3 = Me, Ph.

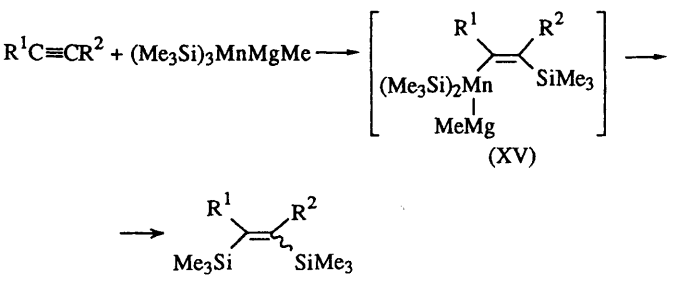
The stannylmanganese complex $(Me_3Sn)_3MnMgMe$ reacts analogously.



R = n-$C_{10}H_{21}$, $PhCH_2O(CH_2)_2$, $(THP)O(CH_2)_2$.

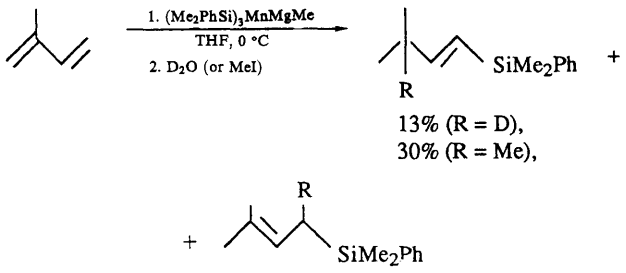
Replacement of $(Me_3Si)_3MnMgMe$ by the lithium derivative $(Me_3Si)_3MnLi$ leads, after hydrolysis, to a mixture of mono- and disilyated alkenes.

The reaction mechanism obviously includes a step for the *syn* addition of the Mn–Si fragment to the triple bond and the reductive elimination of zero-valent manganese from the alkenylmanganate intermediate (XV).

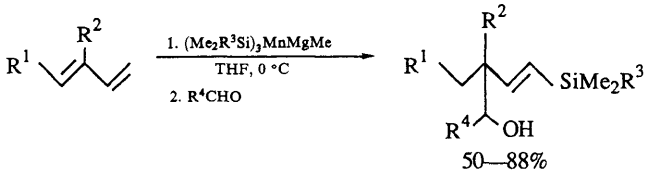


The proposed scheme is confirmed by the formation on reaction of $PhCH_2O(CH_2)_2C$≡CMe and $(Me_3Si)_3MnMgMe$, after treatment with H_2O, D_2O and MeI, of the (*E*)-isomeric products of hydrolysis, deuterolysis and methylation of the complex (XV) (R^1 = $PhCH_2O(CH_2)_2$, R^2 = Me) at the C–Mn bond.[92]

The reaction of $(Me_2PhSi)_3MnMgMe$ with 1,3-dienes (butadiene, isoprene, *trans*-piperylene) and subsequent deuterolysis gives in each case a mixture of γ-deuteroalkyenyl- and α-deuteroallylsilanes.[92,93] An analogous picture is also observed on replacing D_2O by MeI.



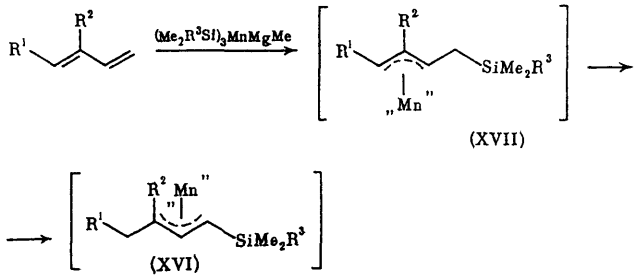
The use of aldehydes and ketones as electrophiles leads exclusively to the preparation of γ-substituted alkenylsilanes in high yield.



$R^1 = H$, $R^2 = H$, Me; $R^1 = Me$, $R^2 = H$; $R^3 = Me$, Ph;
$R^4 = Bu$, n-C_8H_{17}, Ph, *E*-MeCH=CH, *E*-PhCH=CH, Ph.

We note that, in contrast to the complexes $(Me_3Si)_3MnMgMe$ and $(Me_2PhSi)_3MnMgMe$, the lithium manganate reagents $(Me_3Si)_3MnLi$ and $(Me_2PhSi)_3MnLi$ do not react with conjugated dienes under the same conditions.

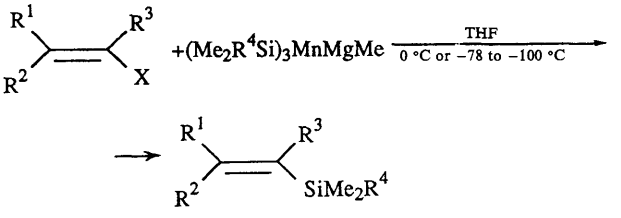
The synthesis of the indicated products of deuterolysis, alkylation and condensation indicates the participation of the allyl manganese intermediate (XVI) in the reaction. It is most probably formed by silylmanganation of the monosubstituted double bond in the diene and further isomeriation of complex (XVII) to complex (XVI) as a result of reversible β-elimination–addition of an Mn–H fragment.[92,93]



„Mn" = $(Me_2R^3Si)_2MnMgMe$

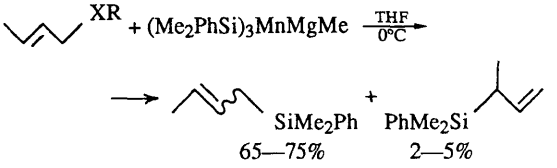
It is known that the diethylaluminosilane $Me_2PhSiAlEt_2$ is an efficient reagent for obtaining alkenyl- and allylsilanes from enol and allyl phosphates.[94,95] The silylmanganates $(Me_3Si)_3MnMgMe$ and $(Me_2PhSi)_3MnMgMe$ may also be used successfully for this purpose.

The reaction of these derivatives with alkenyl halides (bromides and iodides) is effected under mild conditions and leads to the corresponding alkenylsilanes in high yield.[92,96] In the cross-coupling process complete retention of both *trans* and *cis* geometry of the double bond is observed (to retain the *cis* geometry it is necessary to reduce the temperature from 0 to −78 or −100 °C). Alkenyl sulphides, enol phosphates and enol triflates also react in addition to the alkenyl halides.

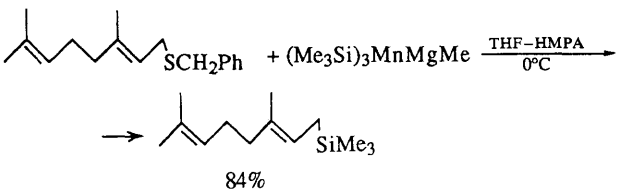


$R^1 = Me$, n-C_6H_{13}, n-$C_{10}H_{21}$, Ph, $R^2 = R^3 = H$;
$R^1 = R^3 = H$, $R^2 =$ n-$C_{10}H_{21}$, Ph;
$R^1 = Me$, n-$C_{10}H_{21}$, $R^2 = Me$, $R^3 = H$;
$R^1 = R^2 = H$, $R^3 = Pr$, n-C_6H_{13}, n-$C_{10}H_{21}$;
$R^1 - R^3 = -(CH_2)_4-$, $-(CH_2)_6-$, $R^2 = H$;
$R^4 = Me$, Ph;
X = Br, I, SMe, SPh, $OP(O)(OEt)_2$, $OP(O)(OPh)_2$, OSO_2CF_3.

Allyl sulphides and allylethers react forming allylsilanes.[92,96] Monosubstituted (α or γ) substrates give a mixture of regioisomeric silylation products with a predominance of the compound in which the Si atom is bound to the least substituted carbon atom of the allyl fragment. It should be noted that the regioselectivity of cross-coupling is significantly greater when using silylmanganate reagents than when using the complex $Me_2PhSiAlEt_2$.[92]



XR = SPh, OCH_2Ph, $OSiMe_2Bu$-t.



V. Conclusion

The organic compounds of Mn(II) are therefore efficient reagents for the selective formation of a carbon–carbon bond in acyl-, alkenyl- and allyldemetallation, and in 1,4- and 1,2-addition to aldehydes, ketones and esters. The availability and cheapness of the initial manganese halides, the possibility of obtaining *in situ* complexes of various types and their inertness towards several functional groups favourably distinguish the manganese derivatives from the corresponding derivatives of many other metals.

In addition, as follows from the data presented above, only a few examples are known of the use of manganese reagents in the synthesis of biologically active natural compounds. The stereochemistry of the condensation reactions involving γ-substituted σ-allylic complexes of Mn(II) (simple diastereoselectivity[97]) and α-chiral aldehydes and ketones (1,2-asymmetric induction[98]) are practically uninvestigated. The synthesis of organomanganese compounds from organic reagents containing aluminium or zinc has not as yet been described. The latter may contain functional groups.[99] The chemistry of enolates of Mn(II) is almost completely unstudied.

It may be expected that the development of these and other routes will enable organic derivatives of Mn(II) to be applied even more successfully to the solution of the problems of fine organic synthesis.

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