Journal of Organometallic Chemistry, 69 (1974) 1—44

Review

THE REACTIVITY OF ALLYLIC ORGANOMETALLIC COMPOUNDS OF LITHIUM, SODIUM, MAGNESIUM, ZINC, CADMIUM AND ALUMINIUM: RECENT ADVANCES

G. COURTOIS and L. MIGINIAC

Laboratoire de Synthèse Organique, Groupe de Recherches de Chimie Organique, 40, Avenue du Recteur Pineau - 86022 Poitiers (France)

(Received May 2nd, 1973; in revised form October 2nd, 1973)

Contents

Introduction

In order to restrict our subject matter within well-defined limits, the results gathered in this review cover only allylic organometallic compounds of lithium, sodium, magnesium, zinc, cadmium and aluminium. Organometallic compounds of benzylic or similar structure will not be considered here.

The methods used to prepare these allylic organometallic compounds (which are usually described and discussed in reviews dealing with the study of their reactions) have been studied and developed mainly by Young [1, 2] in the case of mixed or symmetrical organomagnesium compounds (see also [159, 160, 173]), Gaudemar in the case of mixed organozinc [3-5, 10] and mixed organoaluminium compounds [3-5, 10] (see also [199]), Thiele [6, 252] and Freon [15] in the case of symmetrical organozinc and organocadmium compounds, and Seyferth [7] and Eisch [8] in the case of organolithium compounds (see also [51, 113, 206]).

The study of the structure of these organometallic compounds has been mainly carried out using physical methods, in particular, studies using UV and visible absorption spectroscopy in the case of organomagnesium [9] and organolithium compounds [213, 214, 218, 230], studies using IR spectroscopy in the case of organomagnesium [5, 10, 11], organozinc [5, 10, 11], organoaluminium [5, 10, 11], organolithium [16, 113, 156, 213] and organosodium compounds [16, 200], studies using NMR spectroscopy in the case of organomagnesium [12, 13, 16, 179], organolithium [14, 16, 156, 157, 207, 208, 213, 216, 219, 230] and organosodium compounds [157, 219].

These studies have shown that usually attack by a primary allylic halide (or other derivative) or by its secondary (or tertiary) allylic isomer on a metal leads to the same organometallic compound which is mainly the primary allylmetallic type:

$$\begin{array}{lcl} \mathrm{RCH{=}CHCH_2X} & & \mathrm{RCH{=}CHCH_2M} \\ \text{or} & +\ \mathrm{M} \rightarrow & \updownarrows \\ \mathrm{RCHXCH{=}CH_2} & & \mathrm{CH_2{=}CHCH(R)M} \end{array}$$

We will not give a more detailed account of the conditions of preparation or of the physicochemical studies of the structure of such organometallic solutions, and we propose to deal here with the main recent results (since about 1960) on reactivity of these organometallic compounds towards various reactants

1. Hydrolysis, protolysis and deuterolysis reactions

$$\mathrm{RCH{=}CHCH_2M} + \mathrm{AH} \rightarrow \mathrm{AM} + \begin{cases} \mathrm{RCH_2CH{=}CH_2} & \text{(I)} \\ \mathrm{RCH{=}CHCH_3}\ \ \textit{cis} & \text{(II)} \\ \mathrm{RCH{=}CHCH_3}\ \ \textit{trans} & \text{(III)} \end{cases}$$

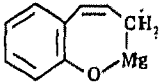
A few recent results have been gathered together in Table 1.

Usually a mixture of the three expected compounds, (I), (II) and (III), is obtained in protolysis reactions, regardless of the metal used. The composition of the mixture of the three hydrocarbons depends on the metal of the organometallic compound and on the protolytic agent, while the nature of the halogen of the organometallic compound seems not to be of importance [19, 20].

(continued on p. 5)

TABLE 1

HYDROLYSIS, PROTOLYSIS AND DEUTEROLYSIS REACTIONS

Organometallic compound, solvent	Reagent	[c]	Products, yield (%)				Ref.
			I	II	II + III	III	
	H_2O		21	61		18	125
$CH_3CH{=}CHCH_2MgBr$, ether	H_2O		75	14		11	2, 19-22
$CH_3CH{=}CHCH_2MgBr$, ether	$HClO_4$	0.5 *N*	78	10		12	
$CH_3CH{=}CHCH_2MgBr$, ether	H_2SO_4	2 *N*	83	10		7	
$CH_3CH{=}CHCH_2MgBr$, ether	H_2SO_4	6 *N*	87	7		6	
$CH_3CH{=}CHCH_2MgBr$, ether	HCl		79	12.5		8.5	
$CH_3CH{=}CHCH_2MgBr$, ether	C_2H_5OH		80	9		11	
$CH_3CH{=}CHCH_2MgBr$, ether	$C_6H_5NH_2$		85	11		4	
$CH_3CH{=}CHCH_2MgBr$, ether	CH_3COOH		90	5		5	
$CH_3CH{=}CHCH_2MgBr$, ether	$C_6H_5C{\equiv}CH$		95	4		1	
$(CH_3CH{=}CHCH_2)_2Mg$, ether	H_2O		73	15		12	25
$CH_3CH{=}CHCH_2MgBr$, THF	H_2O		55	25		20	19, 20
$CH_3CH{=}CHCH_2MgBr$, ether + HMPT ($n = 1$)[a]	H_2O		72.5	18.5		9	
$CH_3CH{=}CHCH_2MgBr$, ether + HMPT ($n = 2$)	H_2O		40	47		13	
$CH_3CH{=}CHCH_2MgBr$, ether + HMPT ($n > 5$)	H_2O		41	45		14	
$CH_3CH{=}CHCH_2MgBr$, ether + HMPT ($n > 5$)	$C_6H_5C{\equiv}CH$		36	50		14	
$C_6H_5CH{=}CHCH_2MgCl$, ether	H^+/H_2O		73		27		2, 17
$(t\text{-}BuCH_2CH{=}CHCH_2)_2Mg$, pentane	H_2O		38	19		43	231
$(t\text{-}BuCH_2CH{=}CHCH_2)_2Mg$, pentane	C_2H_5OH		45	15		40	

(continued)

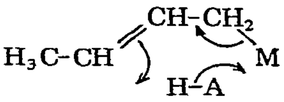
TABLE 1 *(continued)*

Organometallic compound, solvent	Reagent	[c]	Products, yield (%)				Ref.
			I	II	II + III	III	
$(t\text{-}BuCH_2CH{=}CHCH_2)_2Mg$, pentane	t-BuOH		38	15		47	
$(t\text{-}BuCH_2CH{=}CHCH_2)_2Mg$, pentane	n-BuC≡CH		100	—		—	
$(t\text{-}BuCH_2CH{=}CHCH_2)_2Mg$, ether	H_2O		70	12		18	
$(t\text{-}BuCH_2CH{=}CHCH_2)_2Mg$, ether	C_2H_5OH		90	3		7	
$(t\text{-}BuCH_2CH{=}CHCH_2)_2Mg$, ether	t-BuOH		74	5		21	
$(t\text{-}BuCH_2CH{=}CHCH_2)_2Mg$, ether	n-BuC≡CH		93	2		5	
$CH_3CH{=}CHCH_2ZnCl$, ether	H_2O		80	14		6	23
$C_6H_5CH{=}CHCH_2ZnBr$, THF	H_2O		80		20		10
$CH_3CH{=}CHCH_2CdCl$, ether	H_2O		77	13		10	23
$(CH_3CH{=}CHCH_2)_3Al_2Br_3$, ether	H_2O		mixture				22
$R_2AlC(C_6H_5)_2CH{=}CHCH_3$-*trans* (R = i-Bu, heptane)	H_2O, D_2O					100	24
$CH_3CH{=}CHCH_2Al(CH_3)_2$	CH_3OH		100				199
$C_6H_5CH{=}CHCH_2Li$, NH_3 liq.	NH_4Cl		19		81		17
$C_6H_5CH{=}CHCH_2Li$, THF	C_2H_5OH		15		85		214
Pentadienyllithium	D_2O		10	20		70	207
$t\text{-}BuCH_2CH{=}CHCH_2Li$, pentane	H_2O		2	23		75	213, 248
$t\text{-}BuCH_2CH{=}CHCH_2Li$, pentane	C_2H_5OH		3	23		74	
$t\text{-}BuCH_2CH{=}CHCH_2Li$, pentane	t-BuOH		5	16		79	
$t\text{-}BuCH_2CH{=}CHCH_2Li$, pentane	$C_6H_5C{\equiv}CH$		6	16		78	
$C_6H_5CH_2CH(C_6H_5)CH{=}CH_2$ + BuLi	H_2O, D_2O		17	78		5?	210
$C_6H_5CH{=}CHCH_2^-Na^+/NH_3$ liq.	CH_3OH		15		85		17
$C_6H_5CH{=}CHCH_2^-Na^+$/pentane	CH_3OH		16.5	14.5		69	232

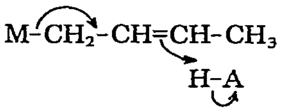
[a] n = moles of HMPT/mole of RM.

Moreover, the nature of the solvent used to prepare the organometallic compound can have considerable influence in certain cases [19, 20]. Thus, in the case of organomagnesium compounds, an increase in solvent basicity leads to a decrease in yield of (I) and an increase of (II) (*cis* compound). In the presence of a highly basic solvent, HMPT* for instance, formation of a carbanion may be considered: $CH_3\,\overset{\delta^-}{CH}\cdots CH\cdots\overset{\delta'^-}{CH_2}\;M^+$; protolysis will then occur mainly at the primary center ($\delta'^- > \delta^-$) and, moreover, the *cis*-carbanion will be favoured through interactions between the dipole of the methyl group and that of the mesomeric system. The protolysis of allylic diorganomagnesium compounds [25] gives the same results as that of the analogous organomagnesium halides.

The formation (always very important) of 1-butene from an organometallic compound derived from 1-bromo-2-butene (a mainly primary structure) can be explained, either by an S_Ei' mechanism or by an S_E2' mechanism:



S_Ei'



S_E2'

2. Reactions with metallic and metalloidal halides

This reaction has been used in the synthesis of various organometallic compounds. A few recent results have been gathered together in Table 2 (see also [241]).

It is to be noticed that in the case of dicrotylcadmium, it is imperative to operate at -25° C, otherwise decomposition will occur [15, 172].

Usually, the exchange reaction between metal or metalloidal halide and an organometallic compound will take place without any allylic rearrangement.

We note also the study of the stereochemical aspects of the action of allylic organometallic compounds (M = Mg and Li) on asymmetric silicon halides [41, 42].

3. Reactions with halogenated derivatives

The formation of hydrocarbons during the action of a metal on an allylic halide (Würtz reaction, "concurrent" with the formation of the organometallic compound [22]) on the one hand, and the coupling of allylic organometallic compounds with halogenated derivatives (Würtz reaction "consecutive" [22]) on the other, have been the subject of numerous studies:

(continued on p. 10)

---

[*] HMPT = $(Me_2N)_3PO$, hexamethylphosphoric triamide; THF = tetrahydrofuran; DMSO = dimethyl sulfoxide.

TABLE 2

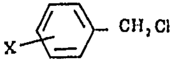
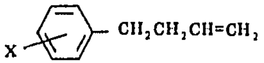
REACTIONS WITH METALLIC AND METALLOIDAL HALIDES

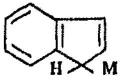
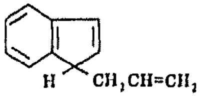
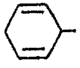
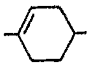
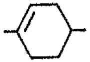
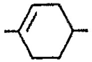
Organometallic compound	M—X	Product	Yield (%)	Ref.
$CH_2{=}CHCH_2MgCl$	$SiCl_4$	$(CH_2{=}CHCH_2)_4Si$	35	183, 235
$CH_2{=}CHCH_2MgCl$	$GeCl_4$	$(CH_2{=}CHCH_2)_4Ge$	45	183
$CH_2{=}CHCH_2MgCl$	$SnCl_4$	$(CH_2{=}CHCH_2)_4Sn$	53	183
$CH_2{=}C(CH_3)CH_2MgCl$	R_3SnCl	$CH_2{=}C(CH_3)CH_2SnR_3$	56-78	113, 243
$CH_2{=}C(CH_3)CH_2MgCl$	R_2SnCl_2	$[CH_2{=}C(CH_3)CH_2]_2SnR_2$	83	239, 243
$CH_2{=}CHCH_2MgBr$	$(CH_3)_3SiCl$	$CH_2{=}CHCH_2Si(CH_3)_3$	51	28
$CH_2{=}CHCH_2MgBr$	$(R)_3GeX$	$CH_2{=}CHCH_2GeR_3$		236
$CH_2{=}CHCH_2MgBr$	$GeCl_4$	$(CH_2{=}CHCH_2)_4Ge$		236
$CH_2{=}CHCH_2MgBr$	$(CH_3)_3SnBr$	$CH_2{=}CHCH_2Sn(CH_3)_3$	25	28
$CH_2{=}CHCH_2MgBr$	$(R)_3SnCl$	$CH_2{=}CHCH_2SnR_3$	65-72	239, 242, 243
$CH_2{=}CHCH_2MgBr$	$(R)_2SnCl_2$	$(CH_2{=}CHCH_2)_2SnR_2$	39-84	239, 242, 243
$CH_2{=}CHCH_2MgBr$	$SnCl_4$	$(CH_2{=}CHCH_2)_4Sn$	80	237, 238, 239
$CH_2{=}CHCH_2MgBr$	$(C_6H_5)_3PbCl$	$CH_2{=}CHCH_2Pb(C_6H_5)_3$	73-85	28, 242
$CH_2{=}CHCH_2MgBr$	$PbCl_4$	mixture		237
$CH_2{=}CHCH_2MgBr$	$RPCl_2$	$(CH_2{=}CHCH_2)_2PR$		239
$CH_2{=}CHCH_2MgBr$	PCl_3	$(CH_2{=}CHCH_2)_3P$		239
$CH_2{=}CHCH_2MgBr$	$RAsI_2$	$(CH_2{=}CHCH_2)_2AsR$		239
$CH_2{=}CHCH_2MgBr$	$AsCl_3$	$(CH_2{=}CHCH_2)_3As$	40	237, 239
$CH_2{=}CHCH_2MgBr$	$SbCl_3$	$(CH_2{=}CHCH_2)_3Sb$		239
$CH_2{=}CHCH_2MgBr$	$HgBr_2$	$CH_2{=}CHCH_2HgBr$		251
$CH_2{=}C(CH_3)CH_2MgBr$	$RPCl_2$	$[CH_2{=}C(CH_3)CH_2]_2PR$		239
$CH_2{=}C(CH_3)CH_2MgBr$	PCl_3	$[CH_2{=}C(CH_3)CH_2]_3P$		239

CH_2=C(CH_3)CH_2MgBr	$RAsI_2$	[CH_2=C(CH_3)CH_2]$_2$AsR		239
CH_2=C(CH_3)CH_2MgBr	$AsCl_3$	[CH_2=C(CH_3)CH_2]$_3$As		239
CH_2=C(CH_3)CH_2MgBr	$HgBr_2$	CH_2=C(CH_3)CH_2HgBr	42	251
CH_3CH=CHCH_2MgBr	$ZnBr_2$	(CH_3CH=CHCH_2)$_2$Zn		15, 172
CH_3CH=CHCH_2MgBr	$CdBr_2$	(CH_3CH=CHCH_2)$_2$Cd		15, 172
CH_3CH=CHCH_2MgBr	$HgBr_2$	CH_3CH=CHCH_2HgBr	14	251
c-C_5H_5MgBr[a]	$ZnBr_2$	c-C_5H_5ZnBr		245
c-C_5H_5MgBr	CdI_2	c-C_5H_5CdI		245
Indenyl-MgBr	$CdCl_2$	Indenyl-CdCl		245
C_6H_5CH=CHCH_2Br + Mg	R_3SnCl	R_3SnCH_2CH=CHC_6H_5	71-75	185
(t-BuCH_2CH=CHCH_2)$_2$Mg	ClSi(CH_3)$_3$	t-BuCH_2CH=CHCH_2Si(CH_3)$_3$ chiefly		231
CH_2=CHCH_2ZnBr	HgX_2	CH_2=CHCH_2HgX	69-83	10, 26, 43
CH_3CH=CHCH_2ZnBr, THF	$CdCl_2$	(CH_3CH=CHCH_2)$_2$Cd		27
CH_3CH=CHCH_2ZnBr, DMSO	$CdCl_2$	no exchange		27
CH_3CH=CHCH_2ZnBr, HMPT	$CdCl_2$	no exchange		27
(CH_2=CHCH_2)$_3Al_2Br_3$	$HgBr_2$	CH_2=CHCH_2HgBr	40	10, 43
CH_2=CHCH_2Li	(C_6H_5)$_3$SiCl	CH_2=CHCH_2Si(C_6H_5)$_3$	66	8
CH_3CH=CHCH_2Li	(CH_3)$_3$SiCl	(CH_3)$_3$SiCH_2CH=CHCH_3 (*cis* 40%, *trans* 60%)	94	14
t-BuCH_2CH=CHCH_2Li	(CH_3)$_3$SiCl	t-BuCH_2CH=CHCH_2Si(CH_3)$_3$ (*cis* + *trans*)	84	213
c-C_4H_6=C(C_6H_5)$_2$ + BuLi	(CH_3)$_3$SiCl	2-(CH_3)$_3$Si-c-C_4H_5=C(C_6H_5)$_2$	75	225
(CH_3)$_2$C=C(C_6H_5)$_2$ + BuLi	(CH_3)$_3$SiCl	(CH_3)$_3$SiCH_2C(CH_3)=C(C_6H_5)$_2$	90	225
c-$C_5H_5^-Na^+$	$ZnCl_2$	(c-C_5H_5)$_2$Zn	14	244

[a] c-C_5H_5 = cyclopentadienyl.

TABLE 3[a]. REACTIONS WITH HALOGENATED DERIVATIVES

Organometallic compound	Halide	Products	Yield (%)	Ref.
$CH_2{=}CHCH_2MgCl$	$CH_3CH{=}CHCH_2Cl$	$CH_2{=}CH(CH_2)_2CH{=}CHCH_3 + CH_2{=}CHCH_2CH(CH_3)CH{=}CH_2$	54	28, 29
$CH_2{=}CHCH_2MgCl$	$ClCH_2CH_2N(C_2H_5)_2$	$CH_2{=}CH(CH_2)_3N(C_2H_5)_2$	85	28
$CH_2{=}CHCH_2MgCl$	$ClC(R')(R'')(R''')$	$CH_2{=}CHCH_2C(R')(R'')(R''')$	28	28
$CH_2{=}C(CH_3)CH_2MgCl$, HMPT	$R'R''C{=}CHCH_2Cl$	$CH_2{=}C(CH_3)CH_2CH_2CH{=}C(R')(R'')$	95	175
$CH_2{=}CHCH_2MgBr$	$HC{\equiv}CCH(R)Br$	$HC{\equiv}CCH(R)CH_2CH{=}CH_2$ (85%) $RCH{=}C{=}CHCH_2CH{=}CH_2$ (15%)	70	31, 32
$CH_2{=}CHCH_2MgBr$	$CH_3CH{=}CHCH_2Cl$	$CH_2{=}CHCH_2CH_2CH{=}CHCH_3$	54	29
$CH_2{=}CHCH_2MgBr$	$CH_3(CH_2)_5CHBrCH_3$	$CH_3(CH_2)_5CH(CH_3)CH_2CH{=}CH_2$	78	28
$CH_2{=}CHCH_2MgBr$	1-bromoindane	1-allylindane		177
$CH_2{=}CHCH_2MgBr$	$CF_2{=}CF_2$	$CH_2{=}CHCH_2CF{=}CFBr + CH_2{=}CHCH_2CF{=}CFCH_2CH{=}CH_2$	30, 10	33
$CH_2{=}CHCH_2MgBr$	$CF_2{=}CFCl$	$CH_2{=}CHCH_2CF{=}CFCl$	30	33
$CH_2{=}CHCH_2MgBr$	$CF_2{=}CFBr$	$CH_2{=}CHCH_2CF{=}CFBr$	40	33
$CH_2{=}CHCH_2MgBr$	 (X = CH_3, Cl, F, OCH_3)		42-76	34
$CH_3CH{=}CHCH_2MgBr$	$CH_2{=}CHCH_2Cl$	isomer *P* (8%), isomer *S* (92%)	49	29
$CH_3CH{=}CHCH_2MgBr$	$CH_2{=}CHCH_2Br$	isomer *P* (50%), isomer *S* (50%)	68	29
$CH_3CH{=}CHCH_2MgBr$	$CH_3CH{=}CHCH_2Br$	isomers *P*—*P*, *P*—*S* and *S*—*S*	58	28
$CH_3CH{=}CHCH_2MgBr$	$CH_2{=}CHCHBrCH_3$		75	28
$CH_3CH{=}CHCH_2MgBr$	$CH_3CH{=}CHCH_2Cl$		72	28
$CH_3CH{=}CHCH_2MgBr$	$CH_2{=}CHCHClCH_3$		76	28
$CH_3CH{=}CHCH_2MgBr$	$CF_2{=}CFCl$	$CH_2{=}CHCH(CH_3)CF{=}CFCl$	15	33
Geranyl MgCl	CH_3I	isomer *P* (8%), isomer *S* (92%)		188
Allylic chlorides + Mg	Allylic chlorides	Dienes	55-65	181, 182
$(CH_3)_2C{=}CHCH_2Cl$ + Mg	$(CH_3)_2C{=}CHCH_2Cl$	$(CH_3)_2C{=}CHCH_2C(CH_3)_2CH{=}CH_2$ chiefly	37-43	158, 180
$CH_2{=}CHCH{=}CHCH_2Br$ + Mg	$CH_2{=}CHCH{=}CHCH_2Br$	isomer *P*—*P* (50%), isomer *P*—*S* (50%)	80	35
$CH_2{=}CHCH_2ZnBr$	$R'CH{=}CHCH_2Br$	isomer *P*	50-80	29
$CH_2{=}CHCH_2ZnBr$	$R'CH{=}CHCH_2Cl$		55-79	29
	($R' = C_2H_5, C_4H_9, C_5H_{11}$)	isomer *P*		
$CH_2{=}CHCH_2ZnBr$	$C_6H_5CH{=}CHCH_2Br$	isomer *P* (66%), isomer *S* (34%)	78	29
$CH_2{=}CHCH_2ZnBr$	$CH_2{=}CHCH{=}CHCH_2Br$	isomer *P* (99%), isomer *S* (1%)	66	29
$CH_2{=}C(CH_3)CH_2ZnBr$	$R'CH{=}CHCH_2Br$	isomer *P*	75-81	29
$RCH{=}CHCH_2ZnBr$ ($R = C_2H_5, C_4H_9, C_5H_{11}$)	$CH_2{=}CHCH_2Br$	isomer *S*	57-82	29
$RCH{=}CHCH_2ZnBr$ ($R = C_2H_5, C_4H_9, C_5H_{11}$).	$CH_2{=}C(CH_3)CH_2Br$	isomer *S*	70-75	29
$C_6H_5CH{=}CHCH_2ZnBr$	$CH_2{=}CHCH_2Br$	isomer *P* (60%), isomer *S* (40%)	71	29
$CH_2{=}CHCH{=}CHCH_2ZnBr$	$CH_2{=}CHCH_2Br$	isomer *P* (25%), isomer *S* (75%)	45	29

$C_6H_5CH{=}CHCH_2Br$ + Zn	$C_6H_5CH{=}CHCH_2Br$	isomers *S*–*S*, *P*–*S*, *P*–*P*	76	10
$R''CH{=}C(R')CH_2M$ (R'' = H or CH_3, R' = H or CH_3, M = ZnBr, MgBr, Mg)	$ClCH_2CH{=}CHCH_2OH$	$CH_2{=}C(R')CH(R'')CH_2CH{=}CHCH_2OH$ (IV) $CH_2{=}C(R')CH(R'')CH(CH_2OH)CH{=}CH_2$ (V) $CH_2{=}C(R')CH(R'')CHOHCH_2CH{=}CH_2$ (VI) (IV) > (VI) ⋗ (V) generally	70-80	36
$C_4H_9CH{=}CHCH_2ZnBr$	$CH_2{=}CHCH_2Br$	isomer *S* (95%), isomer *P* (5%)	74	37
$C_4H_9CH{=}CHCH_2MgBr$	$CH_2{=}CHCH_2Br$	isomer *S* (61%), isomer *P* (39%)	56	
$C_4H_9CH{=}CHCH_2Li$	$CH_2{=}CHCH_2Br$	isomer *S* (30%), isomer *P* (70%)	52	
 (M = MgBr, Li)	$CH_2{=}CHCH_2Br$		70-90	177
$CH_2{=}CHCH_2Li$	$C_6H_{13}CH(CH_3)X$ (X = OTs[b], I)	$C_6H_{13}CH(CH_3)CH_2CH{=}CH_2$	65	38, 206
	R'X		28-37	209
RR'C=CHCH$_2$-mesitoate + Li	$R''R'''C{=}CHCH_2Br$	$RR'C{=}CHCH_2CH_2CH{=}CR''R''' + CH_2{=}CHC(RR')CH_2CH{=}CRR''R'''$	19-95	195
$C_6H_5SCH_2CH{=}CH_2$ + BuLi	R'X	$C_6H_5SCH(R')CH{=}CH_2 + C_6H_5SCH{=}CHCH_2R'$		215
$RSCH_2CH{=}CR'R''$ + BuLi	R'''X	$RSCH(R''')CH{=}CR'R''$		215
$>NCH_2CH{=}C(CH_3)_2$ + BuLi	R'Cl ($R'{=}(CH_3)_2C{=}CHCH_2$)	$>NCH(R')CH{=}C(CH_3)_2 + >NCH{=}CHC(R')(CH_3)_2$	23	217
$CH_3SCH{=}CHCHLiSCH_3$	$C_5H_{11}X$	$CH_3SCH{=}CHCH(C_5H_{11})SCH_3$	90	220
 $C({=}CH_2)CH_2Li$	$(CH_3)_2C{=}CHCH_2Br$	 $C({=}CH_2)CH_2C(CH_3)_2CH{=}CH_2$ +  $C({=}CH_2)CH_2CH_2CH{=}C(CH_3)_2$	42	223
$(CH_2 \cdots CH \cdots CH_2)^-Na^+$	2-bromooctane	$CH_2{=}CHCH_2CH(CH_3)C_6H_{13}$	83	202
$(CH_2 \cdots CH \cdots CH \cdots CH \cdots CH_2)^-Na^+$	$CH_2{=}CHCH_2Cl$	$CH_2{=}CHCH{=}CHCH_2CH_2CH{=}CH_2$	37	203
$(CH_2 \cdots CH \cdots CH \cdots CH \cdots CH_2)^-Na^+$	$C_6H_5CH_2Cl$	$CH_2{=}CHCH{=}CHCH_2CH_2C_6H_5 + CH_2{=}CHCH(CH{=}CH_2)CH_2C_6H_5$		203
$(R'R''C \cdots CH \cdots CH{-}R''')^-Na^+$	CH_3X (X = Cl, Br, I, SO_4, OTs[b])	$R'R''C(CH_3)CH{=}CHR''' + R'R''C{=}CHCH(CH_3)R'''$	68-100	204
$C_6H_5CH{=}CHCH_2^-Na^+$, pentane	$ClCH_2CH{=}CH_2$	isomer *P* (40%), isomer *S* (60%)	32	232
$C_6H_5CH{=}CHCH_2^-Na^+$, pentane	CH_3Br	isomer *P* (42%), isomer *S* (58%)	35	232
$C_6H_5CH{=}CHCH_2^-Na^+$, NH_3 liq.	$BrCH_2CH{=}CH_2$	isomer *P* (9%), isomer *S* (91%)	67	232
$C_6H_5CH{=}CHCH_2^-Na^+$, NH_3 liq.	CH_3Br	isomer *P* (9%), isomer *S* (91%)	70	232
$C_6H_5CH{=}CHCH_2^-Na^+$, NH_3 liq.	XCH_2COOH	isomer *P* (57%), isomer *S* (43%)	43-74	250

---

[a] For theoretical discussions, see chiefly refs. 22, 28, 29. [b] OTs = $O{-}SO_2{-}C_6H_4{-}p{\cdot}CH_3$.

$$\mathrm{RCH{=}CHCH_2X + M \rightarrow}$$

$$\left\{\begin{array}{ll} \mathrm{(RCH{=}CHCH_2)_2} & P\text{—}P \text{ “primary—primary”} \\ \mathrm{RCH{=}CHCH_2CH(R)CH{=}CH_2} & P\text{—}S \text{ “primary—secondary”} \\ \mathrm{[CH_2{=}CHCH(R)]_2} & S\text{—}S \text{ “secondary—secondary”} \end{array}\right.$$

$$\mathrm{RCH{=}CHCH_2M + R'X \rightarrow} \left\{\begin{array}{ll} \mathrm{RCH{=}CHCH_2R'} & P \\ \mathrm{CH_2{=}CHCH(R)R'} & S \end{array}\right.$$

$$\mathrm{RCH{=}CHCH_2M + R'CH{=}CHCH_2X \rightarrow} \left\{\begin{array}{ll} \mathrm{RCH{=}CHCH_2CH_2CH{=}CHR'} & P\text{—}P' \\ \mathrm{RCH{=}CHCH_2CH(R')CH{=}CH_2} & P\text{—}S' \\ \mathrm{CH_2{=}CHCH(R)CH_2CH{=}CHR'} & S\text{—}P' \\ \mathrm{CH_2{=}CHCH(R)CH(R')CH{=}CH_2} & S'\text{—}S' \end{array}\right.$$

Usually, the Würtz reaction becomes increasingly more facile as the electropositive character of the metal increases Zn < Mg < Li, and when the solvent basicity increases: furan < ether, γ-DHP* < THF, THP*, DME* < DMSO, HMPT. The nature of the halogen of the halogenated derivative plays also an important role. It is to be noticed however, that organoaluminium compounds do not seem to undergo such Würtz reactions [4, 31].

A few recent results are reported in Table 3.

We have further noticed the study of the composition of ethylenic hydrocarbon mixtures obtained by action of butenyl chlorides on crotylmagnesium bromide and on dicrotylmagnesium [39, 40].

The experiments shown in Table 4 have been carried out either with $\mathrm{(CH_3CH{=}CHCH_2)_2Mg}$ (VII), or with $\mathrm{CH_3CH{=}CHCH_2MgBr}$ (VIII).

The same authors have also studied the composition of the mixture of hydrocarbons obtained in the Würtz reaction occurring during the preparation of dicrotylmagnesium [40], as well as the influence of the nature of the solvent and of the concentration of reactants in the action of (VII) on allyl chloride [78].

TABLE 4[a]

REACTIONS OF CROTYLORGANOMAGNESIUM COMPOUNDS WITH BUTENYL CHLORIDES

Hydrocarbons obtained	R″Cl + (VII)	R′(*trans*)—Cl + (VII)	R′(*cis*)—Cl + (VII)	R′(*trans*)—Cl + (VIII)	R″Br + (VII)
R″—R″ *meso*	18%	2%	1%	2%	4%
R″—R″ racemic	19	1	1	1	4
R″—R′ (*trans*)	44	82	1	83	60
R″—R′ (*cis*)	11	1	82	1	20
R′(*trans*)—R′(*trans*)	2	6	3	3	3
R′(*trans*)—R′(*cis*)	4	7	6	6	6
R′(*cis*)—R′(*cis*)	2	1	6	4	3

[a] R″Cl = 3-chloro-1-butene; R′(*trans*)—Cl = *trans*-1-chloro-2-butene; R′(*cis*)—Cl = *cis*-1-chloro-2-butene.

---

*γ-DHP = γ-dihydropyran; THP = tetrahydropyran; DME = 1,2-dimethoxyethane.

4. Reactions with *gem*-haloethers, *gem*-aminoethers, *gem*-aminothioethers, *gem*-aminonitriles and *gem*-haloamines

Allylic organometallic compounds usually react with derivatives of the type YCH(R')Z (Y, Z = Cl, OR, $N(R)_2$, sometimes C≡N) as follows:

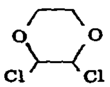
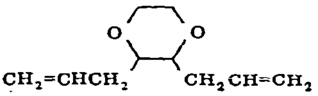
$$CH_2{=}CHCH_2M + YCH(R')Z \longrightarrow CH_2{=}CHCH_2CH(R')Z$$

(a) gem-Haloethers

A few results are given in Table 5. We notice that *gem*-haloethers are among the few halogenated derivatives that react easily with allylic organoaluminium compounds.

TABLE 5

REACTIONS WITH *gem*-HALOETHERS

Organometallic compound	Haloether	Product	Yield (%)	Ref.
$CH_2{=}CHCH_2MgBr$	$C_2H_5OCHBrCH_2Br$	$CH_2{=}CHCH_2CH(OC_2H_5)CH_2Br$	77-82	160
$CH_3CH{=}CHCH_2MgBr$	$C_4H_9OCH_2Cl$	$CH_2{=}CHCH(CH_3)CH_2OC_4H_9$	70	28
$CH_2{=}CHCH_2MgBr$			18	28
$(CH_2{=}CHCH_2)_3Al_2Br_3$	CH_3OCH_2Cl	$CH_2{=}CH(CH_2)_2OCH_3$	63	22, 43
$(CH_2{=}CHCH_2)_3Al_2Br_3$	$C_2H_5OCHBrCH_2Br$	$CH_2{=}CHCH_2CH(OC_2H_5)CH_2Br$	50	31

(b) gem-Aminoethers and gem-aminothioethers

Table 6 gathers together the results of the action of organo-zinc, -magnesium and -lithium compounds on *gem*-aminoethers and *gem*-aminothioethers.

A reaction with a preponderant, if not exclusive, allylic rearrangement can be observed. However, the yield of the product resulting from a reaction without any rearrangement increases in the sequence Zn < Mg < Li, and is also greater in the case of sulphur derivatives than of oxygen derivatives. We note that the secondary aminothioether $C_6H_5SCH_2NHC_6H_5$ makes it possible to obtain the same secondary amines as those which would result from the non-isolable imine $CH_2{=}NC_6H_5$ [44].

(c) gem-Aminonitriles

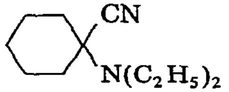
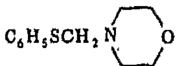
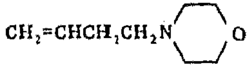
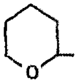
The action of allylzinc bromide on  leads to 1-diethylamino-1-allylcyclohexane in 83% yield; the same reaction is observed with allylmagnesium bromide [45]. The action of allylzinc bromide on $(CH_3)_2NCH(C_6H_5)C{\equiv}N$ also gives an amine, $(CH_3)_2NCH(C_6H_5)CH_2CH{=}CH_2$ [70].

TABLE 6

REACTIONS WITH *gem*-AMINOETHERS AND *gem*-AMINOTHIOETHERS

Organometallic compound	Aminoether	Product									Yield (%)	Ref.
CH_2=$CHCH_2ZnBr$	$C_4H_9OCH_2N(C_2H_5)_2$	CH_2=$CHCH_2CH_2N(C_2H_5)_2$									50-60	46
CH_2=$CHCH_2ZnBr$	$C_4H_9OCH(C_6H_5)N(C_2H_5)_2$	CH_2=$CHCH(C_6H_5)N(C_2H_5)_2$										
C_2H_5CH=$CHCH_2M$	$C_4H_9OCH(R')NR''R'''$ $(R' = H, C_6H_5)$	CH_2=$CHCH(C_2H_5)CHR'NR''R'''$ isomer *S* C_2H_5CH=$CHCH_2CHR'NR''R'''$ isomer *P*										46
		M = ZnBr			M = MgBr			M = Li				
		Yield (%)	%*S*	%*P*	Yield (%)	%*S*	%*P*	Yield (%)	%*S*	%*P*		
	$C_4H_9OCH_2N(C_2H_5)_2$	70	100	0	77	100	0	53	72	28		
	$C_6H_5SCH_2N(C_2H_5)_2$	60	99	1	87	96	4	85	76	24		
	$C_4H_9OCH(C_6H_5)N(CH_3)_2$	75	100	0	90	87	13	14	20	80		
	$C_4H_9SCH(C_6H_5)N(CH_3)_2$	83	99	1	67	85	15	15	11	89		
CH_2=$CHCH_2MgBr$											76	47
CH_2=$CHCH_2MgBr$	$(C_6H_5SCH_2)_2NC_6H_5$	$(CH_2$=$CHCH_2CH_2)_2NC_6H_5$									81	48
CH_2=$CHCH_2MgBr$	THP—NHC_3H_7[a]	$HO(CH_2)_4CH(NHC_3H_7)CH_2CH$=$CH_2$									93	49
CH_2=$CHCH_2MgBr$	THP—$NHCH_2CH$=CH_2	$HO(CH_2)_4CH(NHCH_2CH$=$CH_2)CH_2CH$=CH_2									90	49
C_6H_5CH=$CHCH_2ZnBr$	$C_4H_9OCH_2N(C_2H_5)_2$	CH_2=$CHCH(C_6H_5)CH_2N(C_2H_5)_2$									82	46
C_6H_5CH=$CHCH_2M$	$C_6H_5SCH_2NHC_6H_5$											
M = ZnBr		isomer *S* 100 + isomer *P* 0									67	44
M = MgBr		isomer *S* 100 + isomer *P* 0									94	44
M = Li		isomer *S* 84 + isomer *P* 16									92	44

[a] THP = tetrahydropyranyl 

(d) gem-Haloamines

$$RR'NCH(R'')X + CH_2{=}CHCH_2MgBr \rightarrow RR'NCH(R'')CH_2CH{=}CH_2$$

(20-43%) [194]

5. Reactions with ethers, peroxides and disulfides

Allylic organomagnesium and lithium compounds, in ether or THF, undergo a substitution reaction with allylic and benzylic ethers (see Table 7). Allylic magnesium compounds also react with peroxides and disulphides. However, the action of allyllithium on allylic ether in THF/TMEDA* medium at reflux leads mainly to a Wittig rearrangement [53].

6. Reactions with aldehydes and ketones

(a) Action of simple allylic organometallic compounds

The reaction:

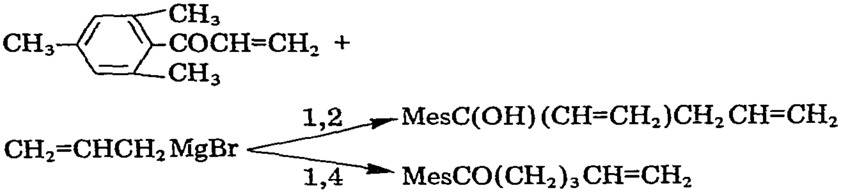
$$CH_2{=}CHCH_2M \ + \ R'COR'' \longrightarrow CH_2{=}CHCH_2C(R')(R'')OH$$

has been studied in numerous cases of aldehydes and ketones. The reaction usually occurs readily and with allylic organometallic compounds no reduction or enolization reactions are observed [22]. Table 8 gathers together a few recent results and presents yields of alcohols obtained by the action of $CH_2{=}CHCH_2M$ and $CH_2{=}C(R)CH_2M$ on various types of carbonyl derivatives.

It has been found [11] that allylic organometallic compounds of type R_2M and RMX react with carbonyl derivatives to give the same quantitative results. It has been noted [15] that, even in the absence of metallic halides, allylic organo-zinc and -cadmium compounds are highly reactive toward carbonyl derivatives, in contrast to the corresponding saturated organometallic compounds.

We note also that the reactions of allylic organometallic compounds with aldehydes and ketones can be carried out successfully in solvents other than ether or THF which commonly are used for the preparation of organometallic compounds [31, 32], but that too basic a solvent can interfere with the reaction.

With α-unsaturated ketones, allylic organometallic compounds almost always give exclusive 1,2 addition [10, 22, 28, 43, 59, 60, 63, 67, 69, 71], which has often been justified by the impossibility of achieving an 8-membered cyclic electron transfer. However, an exception is referred to [62] in the case of a highly hindered ketone:



(continued on p. 17)

---

*TMEDA = tetramethylethylenediamine.

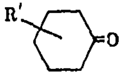
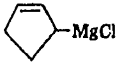
TABLE 7

REACTIONS WITH ETHERS, PEROXIDES AND DISULFIDES

Organometallic compound	Ether	Product	Yield (%)	Ref.
$CH_2=CHCH_2MgBr$	$CH_3CH=CHCH_2OC_6H_{11}$	$CH_3CH(CH=CH_2)CH_2CH=CH_2$	32	50
$CH_2=CHCH_2MgBr$	$C_6H_5CH=CHCH_2OC_6H_{11}$	$C_6H_5CH=CHCH_2CH_2CH=CH_2 + C_6H_5CH(CH=CH_2)CH_2CH=CH_2$		50
$C_6H_5CH=CHCH_2Br$ + Mg excess		$C_6H_5CH(CH=CH_2)(CH_2)_4OH$	64	185
$CH_2=CHCH_2Li$	$C_4H_9CH=CHCH_2OC_6H_5$	$C_4H_9CH=CHCH_2CH_2CH=CH_2$ (68%) + $C_4H_9CH(CH=CH_2)CH_2CH=CH_2$ (32%)	54	51
$CH_2=C(CH_3)CH_2MgBr$	t-BuOO-t-Bu	t-$BuOCH_2C(CH_3)=CH_2$ + t-BuOH	43-55	52
$CH_2=CHCH_2MgBr$	n-BuSS-Bu-n	n-$BuSCH_2CH=CH_2$ + n-BuSH	49-55	52
$CH_2=CHCH_2MgBr$	$CH_2=CHCH_2SSCH_2CH=CH_2$	$(CH_2=CHCH_2)_2S + CH_2=CHCH_2SH$	50-48	52

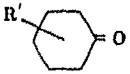
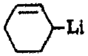
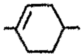
TABLE 8

REACTIONS OF ALLYLIC AND METHALLYLIC ORGANOMETALLIC COMPOUNDS WITH ALDEHYDES AND KETONES

Organometallic compound	Carbonyl compound	Yield (%)	Ref.
CH_2=$CHCH_2MgX$ (X = Cl or Br)	i-PrCO-i-Pr	80	11
CH_2=$CHCH_2MgX$	 (R′ = alkyl)	60-100	15, 55, 56, 57, 58, 64, 65
CH_2=$CHCH_2MgX$	CH_3CH=$CHCHO$	82	28, 59
CH_2=$CHCH_2MgX$	CH_2=$C(CH_3)CHO$	74	59
CH_2=$CHCH_2MgX$	CH_3COCH=CH_2	70	59
CH_2=$CHCH_2MgX$	CH_3COCH=$C(CH_3)_2$	91	59
CH_2=$CHCH_2MgX$	CH_2=$C(Cl)CHO$	73	60
CH_2=$CHCH_2MgX$	$R'COCH$=C=CH_2 (R′ = CH_3, C_2H_5, CH_2=CH)	60	61
CH_2=$CHCH_2MgX$	t-BuCO-t-Bu	57	18, 161
CH_2=$CHCH_2MgX$	Duryl-COC_6H_5	90	62
CH_2=$CHCH_2MgX$	CH_3COCH_2Cl	55	28
CH_2=$CHCH_2MgX$	HC≡CCHO	55	63
CH_2=$CHCH_2MgX$	Anthraquinone		66
	$C_6H_5COC_6H_5$	65	83
CH_2=$CHCH_2Br$ + Mg	R′CHO and R′COR″ (Saytzeff's method)	48-95	176, 195, 31
CH_2=$C(CH_3)CH_2MgX$ (X = Cl or Br)	CH_2=$CHCHO$	77	59, 60
CH_2=$C(CH_3)CH_2MgX$	CH_3CH=$CHCHO$		59
CH_2=$C(CH_3)CH_2MgX$	CH_2=$C(CH_3)CHO$	75	59
CH_2=$C(CH_3)CH_2MgX$	CH_2=$CHCOCH_3$	69	59
CH_2=$C(CH_3)CH_2MgX$	2-cyclohexenone	95	67

(continued)

TABLE 8 (continued)

Organometallic compound	Carbonyl compound	Yield (%)	Ref.
CH_2=$CHCH_2ZnBr$	R'CHO (R' = H, C_6H_5...)	52-83	10, 43
CH_2=$CHCH_2ZnBr$	R'COR" (R' and R" = alkyl, C_6H_5, C_6H_5CH=CH)	68-95	10, 43
CH_2=$CHCH_2ZnBr$	R'CHO (C_3H_7, C_6H_5)	65-75	15, 68
CH_2=$CHCH_2ZnBr$	R'COR" (R' and R" = CH_3, C_2H_5)	71-83	15, 68
CH_2=$CHCH_2ZnBr$	 (R' = alkyl)	100	15
CH_2=$CHCH_2ZnBr$	R'C≡CCHO	70	69
CH_2=$CHCH_2ZnBr$	R'$COCH_2OCH_3$ (R' = alkyl)	80	70
CH_2=$CHCH_2ZnBr$	R'$COCH_2CH_2OCH_3$	85	70
CH_2=$CHCH_2ZnBr$	Paraquinone	36	10, 43
CH_2=$CHCH_2ZnBr$	Anthraquinone	86	10, 43
CH_2=$CHCH_2Br$ + Zn	R'CHO (Saytzeff's method)	69	195
CH_2=$C(COOC_2H_5)CH_2Br$ + Zn	$>C$=O (Saytzeff's method)	42-100	196
$(CH_2$=$CHCH_2)_2Cd$	R'CHO	74-80	15
$(CH_2$=$CHCH_2)_2Cd$	R'COR"	85-89	15
$(CH_2$=$CHCH_2)_3Al_2Br_3$	R'CHO (H, C_6H_5)	33-50	10, 43
$(CH_2$=$CHCH_2)_3Al_2Br_3$	R'COR"	57-72	10, 11, 43
$(CH_2$=$CHCH_2)_3Al_2Br_3$	C_6H_5CH=$CHCHO$ abnormal reaction-hydrocarbons		43
$(CH_2$=$CHCH_2)_3Al_2Br_3$	R'C≡CCHO	50	69
CH_2=$CHCH_2Li$	R'COR"	75	54
-Li	CH_3CHO	44	222
-$C($=$CH_2)CH_2Li$	R'CHO	57-61	223, 221

A few studies have been reported which deal with stereochemistry: the attack on (+)-camphor by allylmagnesium chloride (yield 98%) occurs on the *endo* side [72]; stereoselectivity during the attack on monoalkylated cyclohexanones is different in the case of zinc and magnesium: if E is the equatorial attack and A the axial one, one finds the ratios (E/A)Zn 80/20 and (E/A)Mg 50/50 [15]; the study of steric development of the reaction between allylmagnesium bromide and 4-t-butylcyclohexanone shows that the E/A ratio varies with temperature: E/A 1.14 at -40°C, 1.06 at 0°C and 0.99 at 35°C [55]. We note that for diallylmagnesium E/A 1.25 at 0°C [73]; the attack of allylmagnesium chloride proceeds 80% *trans* in relation to the methyl group in the case of α-methylcyclopentanone [56, 57]; the attack of $CH_2{=}CHCH_2MgX$ is preferentially *trans* on 2-methoxycyclopentanone (82/18), while that of $(CH_2{=}CHCH_2)_3Al_2Br_3$ is notably less so (56/44) [155]; and the attack is only axial during the action of an allylmagnesium compound on highly hindered cyclohexanones [58].

(b) Action of substituted allylic organometallic compounds

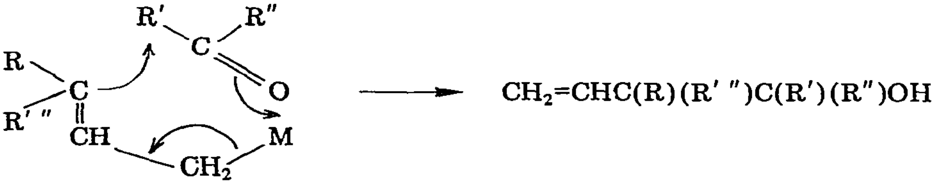
The reaction can be described in the following way:

$$RCH{=}CHCH_2M + R'COR'' \longrightarrow \begin{cases} CH_2{=}CHCH(R)C(R')(R'')OH & \text{isomer } S \\ RCH{=}CHCH_2C(R')(R'')OH & \text{isomer } P \end{cases}$$

The substituted allylic organometallic compounds react readily with the carbonyl derivatives (Table 9). Their reactivity is still high when metallic halides are absent [15].

Under the usual experimental conditions and with an unhindered carbonyl derivative, only the alcohol with secondary group is generally obtained. Given the mainly primary structure of the reactant, this corresponds to complete allylic rearrangement. The proportion of alcohol of rearrangement decreases with the steric hindrance in the neighbourhood of the carbonyl function [11, 76, 81, 82, 86-88], and with a similar steric hindrance the organozinc compound undergoes the highest decrease [11, 81, 82]. Both *cis* and *trans* forms of the allylic alcohol are obtained when there is no rearrangement. In the case of allylic magnesium compounds, the *cis/trans* ratio obtained is always > 1 [73, 76]; this is probably due to the fact that the *cis*-form of the organomagnesium compound is thermodynamically more stable [76].

To justify the preponderant, if not exclusive, yield of alcohol with secondary group, a 6-center cyclic mechanism has often been proposed [2, 10, 22, 43, 79, 118]:



The action of an α,γ-unsaturated organometallic compound on a carbonyl compound which leads to a single alcohol resulting from only one allylic rearrangement, can be rationalized in the same way:

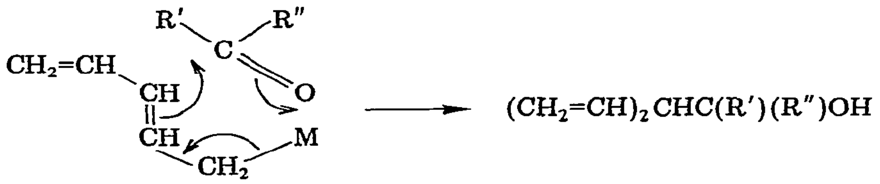
(continued on p. 20)

TABLE 9

REACTIONS OF SUBSTITUTED ALLYLIC ORGANOMETALLIC COMPOUNDS WITH ALDEHYDES AND KETONES

Organometallic compound	Carbonyl compound	Yield (%)	*S*	*P*	Ref.
$CH_3CH=CHCH_2MgX$ (X = Cl or Br)	$R'CHO$ (R' = H, alkyl, C_6H_5)	50-80	100	0	28, 74, 75
$CH_3CH=CHCH_2MgX$ (X = Cl or Br)	$R'COR''$ (primary alkyl group)	70-80	100	0	5, 11
$CH_3CH=CHCH_2MgX$ (X = Cl or Br)	C_2H_5CO-i-Pr	92	95	5	76, 77
$CH_3CH=CHCH_2MgX$ (X = Cl or Br)	i-PrCO-i-Pr	66	66	34	11, 76, 77, 40
$CH_3CH=CHCH_2MgX$ (X = Cl or Br)	i-PrCO-t-Bu	75	40	60	76, 77
$CH_3CH=CHCH_2MgX$ (X = Cl or Br)	t-BuCO-t-Bu	78	0	100	76, 77
$CH_3CH=CHCH_2MgX$ (X = Cl or Br)	$CH_2=CHCHO$	42	100	0	59
$C_2H_5CH=CHCH_2MgBr$	$R'CHO$	85	100	0	79, 80
$C_2H_5CH=CHCH_2MgBr$	$R'COR''$ (primary alkyl group)	67-92	100	0	79, 80, 81, 82
$C_2H_5CH=CHCH_2MgBr$	EtCOEt	60	100	0	198
$C_2H_5CH=CHCH_2MgBr$	i-PrCO-i-Pr	60	75	25	81, 82
$CH_3CH=CHCH(CH_3)MgCl$	$CH_2=CHCHO$	30			59
$HC\equiv CCH=CHCH_2MgBr$	$C_5H_{11}CHO$	64	100	0	79, 80
$CH_3CH=CHCH=CHCH_2MgBr$	$C_6H_{13}CHO$	64	100	0	35
$CH_2=CHCH=CHCH_2MgBr$	$C_5H_{11}CHO$	63	100	0	35
$(CH_3)_2C=CHCH_2MgBr$	$CH_2=CHCHO$	50	100	0	191
$t\text{-}BuCH=CHCH_2MgBr$	$R'COR''$		mixture		169
$(CH_3)_2C=CHCH_2Br$ + Mg	cyclohexanone	73	100	0	195
$t\text{-}BuCH_2CH=CHCH_2Mg$, ether	$CH_3COC_2H_5$		96	4	231
$t\text{-}BuCH_2CH=CHCH_2Mg$, pentane	$CH_3COC_2H_5$		70	30	231
$C_6H_5CH=CHCH_2MgX$, ether	$C_6H_5COCH_3$	"good"	100	0	246
$(CH_3CH=CHCH_2)_2Zn$	$R'CHO$ (alkyl, C_6H_5)	87-88	100	0	15, 75
$CH_3CH=CHCH_2ZnBr$	$R'COR''$ (primary alkyl group)	76	100	0	5, 10, 11, 43
$CH_3CH=CHCH_2ZnBr$	i-PrCO-i-Pr	70	2	98	11
$CH_3CH=CHCH_2ZnBr$	CH_3CO-t-Bu	70	5	95	11
$C_2H_5CH=CHCH_2ZnBr$	$C_5H_{11}CHO$	85	100	0	79, 80
$C_2H_5CH=CHCH_2ZnBr$	cyclohexanone	79	100	0	79, 80
$C_2H_5CH=CHCH_2ZnBr$	$CH_3COC_6H_5$	87	100	0	79, 80
$C_2H_5CH=CHCH_2ZnBr$	n-PrCO-n-Pr	70	83	17	81, 82
$C_2H_5CH=CHCH_2ZnBr$	i-PrCO-i-Pr	60	1	99	81, 82
$C_2H_5CH=CHCH_2ZnBr$	i-$PrCOCH_3$	73	75	25	82
$C_2H_5CH=CHCH_2ZnBr$	$CH_3COCH=C(CH_3)_2$	64	3	97	82
$CH_2=CHCH=CHCH_2ZnBr$	$R'CHO$ (R' = alkyl, C_6H_5)	75-84	100	0	79, 80, 84, 86
$CH_2=CHCH=CHCH_2ZnBr$	cyclohexanone	70	100	0	79, 80, 86
$CH_2=CHCH=CHCH_2ZnBr$	CH_3COCH_3	67	100	0	86

$CH_2=CHCH=CHCH_2ZnBr$	CH_3CO-i-Pr	90	83	17	86
$CH_2=CHCH=CHCH_2ZnBr$	i-PrCO-i-Pr	71	0	100	86
$CH_3CH=CHCH=CHCH_2ZnBr$	C_6H_5CHO	32	100	0	79, 80
$HC\equiv CCH=CHCH_2ZnBr$	R'CHO (C_5H_{11}, C_6H_5)	55-60	100	0	79, 80
$HC\equiv CCH=CHCH_2ZnBr$	cyclohexanone	37	100	0	79, 80
$(C_6H_5CH_2)_2C=CHCH_2ZnBr$	CH_3CHO	76	100	0	85
$C_6H_5CH=CHCH_2ZnBr$	R'CHO (R' = alkyl)	55-90	100	0	87
$C_6H_5CH=CHCH_2ZnBr$	CH_3COCH_3	60	100	0	87
$C_6H_5CH=CHCH_2ZnBr$	CH_3CO-i-Pr	44	62	38	87
$C_6H_5CH=CHCH_2ZnBr$	i-PrCO-i-Pr	40	0	100	87
$RC(R'')=C(R''')CH_2Br + Zn$	R'CHO and R'COR'	52-72	100	0	195
$CH_3CH=C(COOC_2H_5)CH_2Br + Zn$	cyclohexanone	78	100	0	197
$(CH_3CH=CHCH_2)_2Cd$	R'CHO (R' = alkyl)	50-86	100	0	75
$(CH_3CH=CHCH_2)_3Al_2Br_3$	R'COR'' (R', R'' = prim. or sec. alkyl)	70	100	0	5, 11
$(C_2H_5CH=CHCH_2)_3Al_2Br_3$	R'COR'' (R', R'' = prim. or sec. alkyl)	50	100	0	81
$(CH_2=CHCH=CHCH_2)_3Al_2Cl_3$	R'COR'' (R', R'' = prim. or sec. alkyl)	35-78	100	0	87
$(C_6H_5CH=CHCH_2)_3Al_2Cl_3$	R'COR'' (R', R'' = prim. or sec. alkyl)	38-42	100	0	87
$C_2H_5CH=CHCH_2Li$	$CH_3COCH=C(CH_3)_2$	82	98	2	82
$C_2H_5CH=CHCH_2Li$	CH_3CO-n-Pr	75	86	14	82
$C_2H_5CH=CHCH_2Li$	CH_3COCH_2-i-Pr	86	85	15	82
$C_2H_5CH=CHCH_2Li$	i-PrCH_2COCH_2-i-Pr	95	82	18	82
$C_2H_5CH=CHCH_2Li$	n-BuCO-n-Bu	92	79	21	82
$C_2H_5CH=CHCH_2Li$	CH_3CO-i-Pr	80	75	25	82
$C_2H_5CH=CHCH_2Li$	i-PrCO-i-Pr	88	52	48	82
$C_6H_5CH=CHCH_2Li$	$C_6H_5COC_6H_5$	41	0	100	17
t-Bu$CH_2CH=CHCH_2Li$, pentane or ether	$CH_3COC_2H_5$	75-85	55	45	213, 248
t-Bu$CH_2CH=CHCH_2Li$, pentane or ether	$CH_3COCH(CH_3)_2$	75-85	52	48	213, 248
t-Bu$CH_2CH=CHCH_2Li$, pentane or ether	i-BuCO-i-Bu	75-85	64	36	213, 248
t-Bu$CH_2CH=CHCH_2Li$, pentane or ether	i-PrCO-i-Pr	75-85	51	49	213, 248
t-Bu$CH_2CH=CHCH_2Li$, pentane or ether	t-BuCO-t-Bu	75-85	0	100	213, 248
t-Bu$CH_2CH=CHCH_2Li$, pentane or ether	$C_6H_5COC_6H_5$	75-85	0	100	213
$(LiCH_2C(CH_3)=CHCH_2)_2$	R'COR''	25-35	0	100	211
$R'R''C=CHCH_2$mesitoate + Li	R'''CHO and R'''COR''''	14-67	100	0	195
$C_6H_5CH_2CH=CH_2 + NH_2Na/NH_3$ liq.	$C_6H_5COCH_3$	60	0	100	246
$C_6H_5CH_2CH=CH_2 + NH_2Na/NH_3$ liq.	CH_3COCH_3	25	35	65	247
$C_6H_5CH_2CH=CH_2 + NH_2Na/NH_3$ liq.	$C_6H_5COC_6H_5$	75	0	100	247

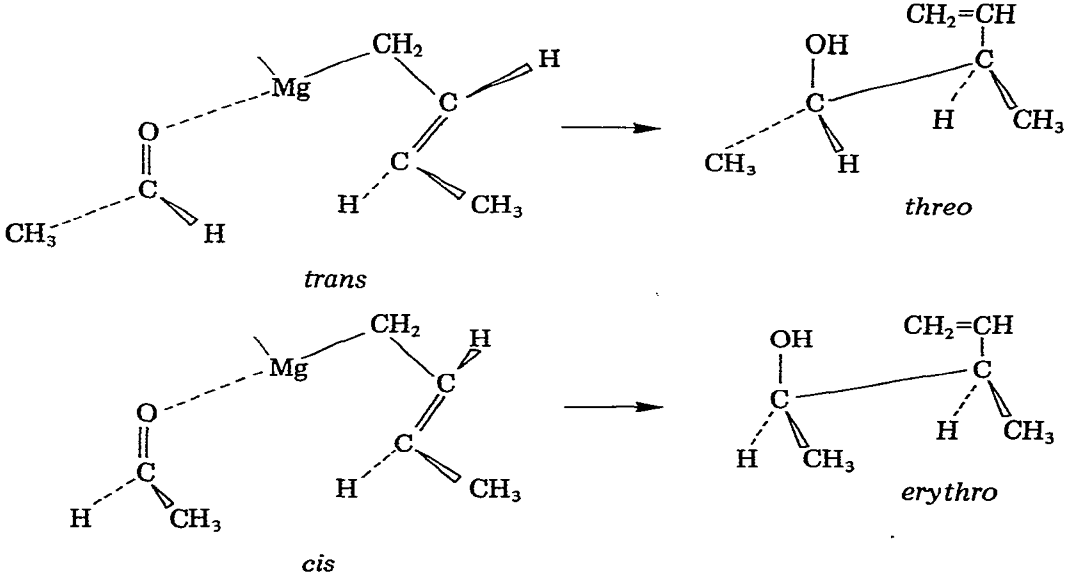


This would correspond to a 6-center cyclic mechanism with the exclusion of 4- or 8-center mechanisms [35, 79, 80, 84, 86, 87].

But this mechanism is not the only one that has been put forward [74, 89] crotylmagnesium bromide is composed of a mixture in mobile equilibrium:

$CH_3CH=CHCH_2MgBr$ (IX) $\qquad$ $CH_2=CHCH(CH_3)MgBr$ (X)

where form (IX) would predominate in the equilibrium, thus explaining the physical properties, but where form (X) would be the more reactive, thus accounting for the preponderant formation of secondary isomers. If this hypothesis is valid, it leads to an absence of stereoselectivity during the reaction as is the case with sec-BuMgBr [74]; on the contrary, if we assume there is a cyclic electronic transfer, and if we consider the action of crotylmagnesium bromide on acetaldehyde, there are two possibilities, whether the methyl group of acetaldehyde is *trans* or *cis* compared to the methyl group of the organomagnesium compound:



The steric interactions being less important in the *trans* arrangement, this mechanism should then lead to a majority of *threo* isomer. It has been found that the reaction, when carried out at 0°C, leads to an only 2% excess of the *threo* isomer. Other authors [15, 75] also have reported this absence of stereoselectivity during the action of substituted allylic organometallic compounds on aldehydes R'CHO (Table 10).

TABLE 10

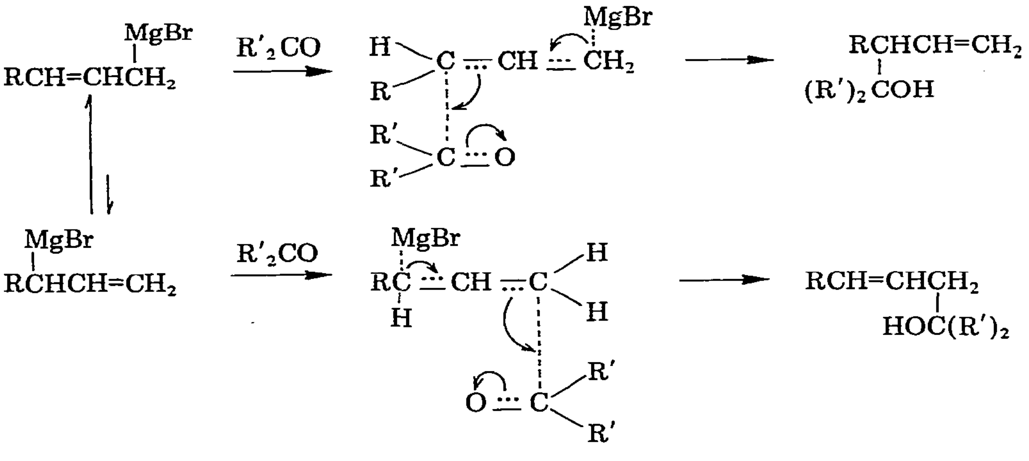
STEREOSELECTIVITY OF THE REACTION BETWEEN CROTYLORGANOMETALLIC COMPOUNDS AND ALDEHYDES

Organometallic compound		R'			
		Et	n-Pr	i-Pr	t-Bu
$CH_3CH{=}CHCH_2MgBr$	*% threo*[a]	52	51	58	75
$(CH_3CH{=}CHCH_2)_2Zn + MgBr_2$		45	46	70	82
$(CH_3CH{=}CHCH_2)_2Cd + MgBr_2$		50	51	80	86

[a] $\%\ threo = \dfrac{threo}{threo + erythro} \times 100$

The stereoselectivity of the reaction does not vary with the temperature, nor with the nature of the solvent (ether or THF); it increases as the steric hindrance of R' increases, as well as with the electronegativity of the metal Mg < Zn < Cd [15, 75].

Other experimental data [90-92, 112] have led the authors to the conclusion that allylic organomagnesium compounds react with carbonyl derivatives according to a mechanism of non-cyclic bimolecular electrophilic substitution S_E2':



Moreover, it recently has been shown that the addition of an allylic organometallic compound to a carbonyl derivative is reversible. Indeed, we can see that the proportion of alcohol with a primary group becomes greater as the reactants remain in contact longer after mixing; it seems then that the initially formed alcohol with secondary group changes, in the reaction medium, into the thermodynamically more stable alcohol with a primary group.

This phenomenon depends on the nature of the organometallic compound involved; with an organomagnesium compound, it seems to work only with hindered ketones [77, 82], whereas with an organozinc compound it is observed with all ketones and even with some aldehydes. Moreover, it has been possible to make use of this property of the organozinc compounds to prepare alcohols of exclusively $RCH=CHCH_2C(R')(R'')OH$ structure [81, 82, 86, 87, 93]. As for organolithium compounds, it has not been possible up to now to demonstrate reversibility for the addition reaction to carbonyl derivatives [82]. We shall see further on that the same phenomenon of reversibility is operative in the addition of allylic organometallic compounds to aldimines [94, 102, 103].

7. Reactions with epoxides

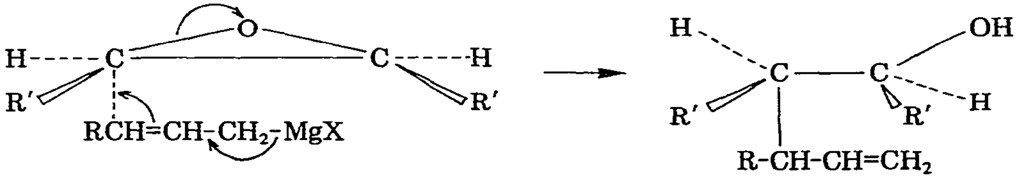
This reaction has been studied mainly in the case of organomagnesium and organozinc compounds. However, a few studies have been carried out recently with organolithium and sodium compounds (Table 11). Allylic organoaluminium compounds seem to be unreactive toward ethylene oxide [22].

Epoxides react readily with allylic organo-magnesium and -zinc compounds, and when the organometallic compound is a substituted allyl compound, the reaction takes place with complete allylic rearrangement.

The presence of metallic halides in the reaction medium has an influence on the direction of opening of styrene oxide,  $C_6H_5\underbrace{CHCH_2}_{O}$ [97, 98]. The action of diallylzinc or dicrotylzinc in the presence of metallic halides ($MgBr_2$ or $ZnBr_2$) on this epoxide leads to mixture of two alcohols: $C_6H_5CH_2CHOHCH(R)\text{-}CH=CH_2$ ($R = H, CH_3$) (XIII) and $C_6H_5CH(CH(R)CH=CH_2)CH_2OH$ (XIV). In contrast, in the absence of metallic halides, the same organometallic compounds react to form only (XIV). The formation of (XIII) can be explained by preliminary metal halide-induced isomerization of styrene oxide to phenylacetaldehyde, followed by the addition of the organometallic to the $\geq C=O$ bond. Study of electronic effects of substituents on the benzene nucleus of styrene oxide showed that the ring-opening reaction is accelerated by electron-donor substituents, and retarded by electron-withdrawing substituents [98, 99].

The opening of cyclohexene oxide by $CH_3CH=CHCH(CH_3)Mg$ compounds gives a mixture of *cis*- and *trans*-alcohols [73]. The *cis/trans* ratio is 1.9 in the case of the R_2Mg and 0.5 in the case of the RMgBr compound.

The stereochemistry of the opening of epoxides by allylic organomagnesium compounds has also been studied [100, 101]. The reaction always occurs with an inversion of the configuration of the C* of the epoxide. For instance:

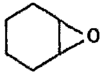
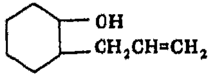
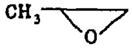
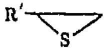
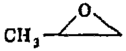
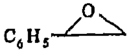
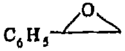


This steric consequence, which is not the one that is expected from the S_Ei' cyclic mechanism (retention of configuration), can be explained by a S_E2' mechanism with respect to organomagnesium compound, and S_N2 with respect to the epoxide. We recall that an S_E2' process was also proposed by the same

(continued on p. 25)

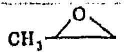
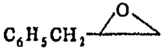
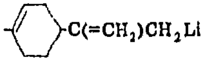
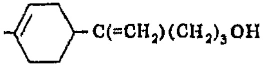
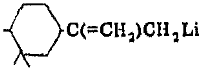
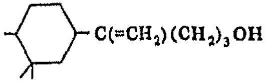
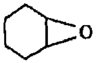
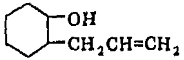
TABLE 11

REACTIONS WITH EPOXIDES

Organometallic compound	Epoxide	Products	Yield (%)	Ref.
$CH_2{=}CHCH_2MgBr$			64	28, 95, 163, 186
$CH_2{=}CHCH_2MgBr$		$CH_2{=}CHCH_2CH_2CHOHCH_3$	67	190
$CH_2{=}CHCH_2MgBr$	 $R' = Me, Bu, (CH_2)_3$	$R'CH(SH)CH_2CH_2CH{=}CH_2$		96
$CH_2{=}CHCH_2Br + Mg$		$CH_2{=}CHCH_2CH_2CH_2OH$	41-72	176
$CH_3CH{=}CHCH_2MgBr$		$CH_2{=}CHCH(CH_3)CH_2CH_2OH$	50	22
$(CH_2{=}CHCH_2)_2Zn$		$CH_3CHOHCH_2CH_2CH{=}CH_2$	26	97
$(CH_2{=}CHCH_2)_2Zn$		$C_6H_5CH(CH_2CH{=}CH_2)CH_2OH$	75	97, 98
$(CH_3CH{=}CHCH_2)_2Zn$		$C_6H_5CH(CH(CH_3)CH{=}CH_2)CH_2OH$	75	97

(continued)

TABLE 2 (continued)

Organometallic compound	Epoxide		Products	Yield (%)	Ref.
$(CH_3CH{=}CHCH_2)_2Zn$			$CH_3CHOHCH_2CH(CH_3)CH{=}CH_2$	17	97
$(CH_2{=}CHCH_2)_2M$			$C_6H_5CH_2CH(OH)CH_2CH_2CH{=}CH_2$ (M = Zn; M = Mg)	15 91	99 99
$(CH_2{=}CHCH_2)_2M$		(*cis*)	$C_6H_5CH(CH_2CH{=}CH_2)CHOHCH_3$ (XI) $C_6H_5CHOHCH(CH_3)CH_2CH{=}CH_2$ (XII) (M = Mg (XI) (61%), (XII) (39%); M = Zn (XI) (92%), (XII) (8%))		153
$(CH_2{=}CHCH_2)_2M$		(*trans*)	$C_6H_5CH(CH_2CH{=}CH_2)CHOHCH_3$ (M = Zn; M = Mg)		153
pentadienyl-Li			$(CH_2{=}CH)_2CHCH_2CH_2OH$	50·85	212
				55	223
					224
$CH_2{=}C(CH_3)CH_2Li$			$CH_2{=}C(CH_3)CH_2CH_2CH_2OH$	72	249
$CH_2\because CH\because CH_2^-Na^+$				85	163
Pentadienyl$^-$Na$^+$			$CH_2{=}CHCH{=}CH(CH_2)_3OH$ (30%) + $(CH_2{=}CH)_2CHCH_2CH_2OH$ (70%)	50·60	201
$(CH_2{=}CH)_3C^-Na^+$			$(CH_2{=}CH)_2C{=}CH(CH_2)_3OH$ (23%) + $(CH_2{=}CH)_3CCH_2CH_2OH$ (77%)	80	201

authors for the action of allylic organomagnesium compounds on carbonyl derivatives [90-92].

8. Reactions with imines

Allylic organometallic compounds (M = Zn, Mg, Li) react readily with enolizable or non-enolizable imines (see Table 13), while such reactions with organoaluminium compounds seem to be rather difficult [44].

With a substituted allylic organometallic compound, usually a mixture of two amines (XV) and (XVI) is obtained.

$$\mathrm{RCH{=}CHCH_2M + R'CH{=}NR''} \longrightarrow \begin{cases} \mathrm{CH_2{=}CHCH(R)CH(R')NHR''} & \mathrm{(XV)} \\ \mathrm{RCH{=}CHCH_2CH(R')NHR''} & \mathrm{(XVI)} \end{cases}$$

The general characteristics of this reaction have been studied [44], and it has been shown that the percentages of (XV) and (XVI) in the amine mixture vary: with the nature of the aldimine (its more or less important basic character playing a major role); with the nature of metal (Mg leading usually to more (XV) isomer than Zn and Li); with the nature of the R group of the organometallic compound (alkyl, C_6H_5); and with the *reaction time* [94].

Indeed, the addition of an allylic organometallic compound to an aldimine is characterized by *reversibility*. In the reaction medium, the initially formed amine (XV) will progressively change to amine (XVI) which is thermodynamically more stable (Table 12).

TABLE 12

REVERSIBILITY OF THE REACTION BETWEEN A SUBSTITUTED ALLYLIC ORGANOZINC COMPOUND AND AN ALDIMINE

$C_2H_5CH{=}CHCH_2ZnBr + C_6H_5CH{=}NCH_3$	Yield (%)	(XV)	(XVI)
Immediate hydrolysis	90	89%	11%
Hydrolysis after 24 h at 25°C	93	74%	26%
Hydrolysis after 72 h at 25°C	82	46%	54%
Hydrolysis after 168 h at 25°C	87	36%	64%
Hydrolysis after 48 h at 65°C	85	—	100%

This phenomenon of reversibility is easily seen with organozinc and organolithium compounds (the reverse is the case in reactions with carbonyl derivatives). It can occur, but with greater difficulty, with organomagnesium compounds [102, 192]. Finally, reversibility has been observed not only in the case of a single imine, but also during the 1,2-addition to a conjugated imine [103].

With α-unsaturated imines, it is possible to observe 1,4-addition with allylic organometallic compounds (M = Zn, Mg, Li) [103, 104]. For instance, during the action of $C_2H_5CH{=}CHCH_2M$ on $C_6H_5CH{=}CHCH{=}NCH(CH_3)_2$ we obtained: M = Zn, Yield 70% (11% 1,4 and 89% 1,2); M = Mg, Yield 85% (14% 1,4 and 86% 1,2); M = Li (Eisch), Yield 50% (100% 1,4 and no 1,2).

1,4- and 1,6-additions have also been observed in pyridinic and similar series [28, 106, 109].

(continued on p. 28)

TABLE 13

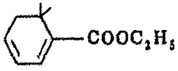
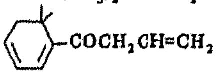
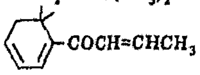
REACTIONS WITH ALDIMINES AND KETIMINES

Organometallic compound	Imine	Products	Yield (%)	Ref.
$CH_2=CHCH_2MgBr$	$(C_6H_5)_2C=NC_6H_5$	$(C_6H_5)_2C(CH_2CH=CH_2)NHC_6H_5$	87	28, 105
$CH_2=CHCH_2MgBr$	fluorenyl-$C=NC_6H_5$	fluorenyl-$C(CH_2CH=CH_2)NHC_6H_5$	87	28, 105
$CH_2=CHCH_2MgBr$	$R'CH=CHCH=NR''$ $(R' = \text{alkyl}, C_6H_5; R'' = \text{alkyl})$	$R'CH=CHCH(CH_2=CHCH_2)NHR''$	80-93	104
$C_2H_5CH=CHCH_2MgBr$	$R'CH=NR''$ $(R' = \text{alkyl}, C_6H_5; R'' = \text{alkyl}, C_6H_5)$	$R'CH[CH(C_2H_5)CH=CH_2]NHR''$ chiefly	60-91	37, 44, 102
$CH_3CH=CHCH_2MgBr$	$C_6H_5CH=NR'$	$C_6H_5CH[CH(CH_3)CH=CH_2]NHR'$	16-44	108
$CH_2=CHCH_2ZnBr$	$R'CH=CHCH=NR''$ $(R' = \text{alkyl}, C_6H_5; R'' = \text{alkyl})$	$R'CH=CHCH(CH_2=CHCH_2)NHR''$	66-91	104
$C_2H_5CH=CHCH_2ZnBr$	$R'CH=NR''$ $(R' = \text{alkyl}, C_6H_5; R'' = \text{alkyl}, C_6H_5)$	$R'CH[CH(C_2H_5)CH=CH_2]NHR'' + R'CH(CH_2CH=CHC_2H_5)NHR''$	43-95	37, 44, 102
$CH_2=CHCH_2Li$ (exchange)	i-PrCH=N-i-Pr	i-PrCH($CH_2=CHCH_2$)NH-i-Pr	70	107
$CH_2=C(CH_3)CH_2Li$ (exchange)	i-PrCH=N-i-Pr	i-PrCH[$CH_2=C(CH_3)CH_2$]NH-i-Pr	42	107
$CH_2=CHCH_2Li$ (Eisch's method)	$(C_6H_5)_2C=NC_6H_5$	$(C_6H_5)_2C(CH_2CH=CH_2)NHC_6H_5$	68	8
$CH_2=CHCH_2Li$ (Eisch's method)	$R'CH=CHCH=NR''$ $(R' = \text{alkyl}, C_6H_5; R'' = \text{alkyl})$	$R'CH(CH_2CH=CH_2)CH_2CH=NR''$	45-80	104
$C_2H_5CH=CHCH_2Li$ (Eisch)	$R'CH=NR''$ $(R' = \text{alkyl}, C_6H_5; R'' = \text{alkyl}, C_6H_5)$	$R'CH[CH(C_2H_5)CH=CH_2]NHR'' + R'CH(CH_2CH=CHC_2H_5)NHR''$	30-95	37, 44, 104

TABLE 14

REACTIONS WITH ACIDS, ACID ANHYDRIDES, ACID CHLORIDES, ESTERS AND AMIDES

Organometallic compound	Reagent	Products	Yield (%)	Ref.
$CH_2=CHCH_2MgBr$	$HCOOC_2H_5$	$CH_2=CHCH_2CHOHCH_2CH=CH_2$	35	111, 176
$CH_2=CHCH_2MgBr$	$C_2H_5OCH_2COOC_3H_7$	$C_2H_5OCH_2C(OH)(CH_2CH=CH_2)_2$	90	28
$CH_2=CHCH_2MgBr$	*N*-methylphthalimide	ring structure retained	52	18
$CH_2=CHCH_2MgBr$	*N*-methylsuccinimide	ring structure retained	52	18
$CH_2=CHCH_2MgBr$	*N*-methylglutarimide	$CH_3CH=CHCO(CH_2)_3CONHCH_3$	41	162
$CH_2=CHCH_2MgBr$	$CH_3CH=CHCOO_sC_4H_9$	$CH_3CH=CHC(OH)(CH_2=CHCH_2)_2$		71
$CH_2=CHCH_2Br + Mg$	maleate or fumarate	tetraallylglycol	18-45	189
$CH_3CH=CHCH_2MgBr$	$RCON(R')_2$	$CH_3CH_2CH=CHCOR$	20	88

$C_2H_5CH{=}CHCH_2MgBr$	$HCOOC_2H_5$	$[CH_2{=}CHCH(C_2H_5)]_2CHOH$	80	79, 80
$C_2H_5CH{=}CHCH_2MgBr$	$HCON(CH_3)_2$	$[CH_2{=}CHCH(C_2H_5)]_2CHOH$	30	79, 80
$HC{\equiv}CCH{=}CHCH_2MgBr$	$HCOOC_2H_5$	$[CH_2{=}CHCH(C{\equiv}CH)]_2CHOH$	56	79, 80
$(CH_3)_2C{=}CHCH_2MgCl$	$RCOCl$	$RCOC(CH_3)_2CH{=}CH_2$		193
$CH_2{=}CHCH_2ZnBr$	$(CH_3CO)_2O$	$CH_3C(OH)(CH_2CH{=}CH_2)_2$	77	43
$CH_2{=}CHCH_2ZnBr$	$CH_3COOC_2H_5$	$CH_3C(OH)(CH_2CH{=}CH_2)_2$	70	43
$CH_2{=}CHCH_2ZnBr$	CH_3COONa	$CH_3C(OH)(CH_2CH{=}CH_2)_2$	53	43
$CH_2{=}CHCH_2ZnBr$	$HCOOC_2H_5$	$CH_2{=}CHCH_2CHOHCH_2CH{=}CH_2$	69	111
$CH_2{=}CHCH_2ZnBr$	$C_2H_5OCH_2COOC_2H_5$	$C_2H_5OCH_2C(OH)(CH_2CH{=}CH_2)_2$	76	70
$CH_2{=}CHCH_2ZnBr$	$CH_3O(CH_2)_2COOCH_3$	$CH_3O(CH_2)_2C(OH)(CH_2CH{=}CH_2)_2$	93	70
$C_2H_5CH{=}CHCH_2ZnBr$	$HCOOC_2H_5$	$[CH_2{=}CHCH(C_2H_5)]_2CHOH$	86	79, 80
$C_2H_5CH{=}CHCH_2ZnBr$	$C_2H_5OCH_2COOC_2H_5$	$[CH_2{=}CHCH(C_2H_5)]_2C(OH)CH_2OC_2H_5$	84	70
$CH_2{=}CHCH{=}CHCH_2ZnBr$	$HCOOC_2H_5$	$[CH_2{=}CHCH(CH{=}CH_2)]_2CHOH$	80	79, 80
$(CH_2{=}CHCH_2)_2Zn$	CH_3COOCH_3	$CH_3C(OH)(CH_2CH{=}CH_2)_2$	53	15
$(CH_3CH{=}CHCH_2)_2Zn$	CH_3COOCH_3	$CH_3C(OH)[CH(CH_3)CH{=}CH_2]_2$	64	15
$(CH_2{=}CHCH_2)_2Cd$	CH_3COOCH_3	$CH_3C(OH)(CH_2CH{=}CH_2)_2$	65	15
$(CH_2{=}CHCH_2)_3Al_2Br_3$	$CH_3COOC_2H_5$	$CH_3C(OH)(CH_2CH{=}CH_2)_2$	75	43
$(CH_2{=}CHCH_2)_3Al_2Br_3$	CH_3COONa	$CH_3C(OH)(CH_2CH{=}CH_2)_2$	48	43
$(CH_2{=}CHCH_2)_3Al_2Br_3$	CH_3COCl	$CH_3C(OH)(CH_2CH{=}CH_2)_2$	64	43
$(CH_2{=}CHCH_2)_3Al_2Br_3$	$HCOOC_2H_5$	$CH_2{=}CHCH_2CHOHCH_2CH{=}CH_2$	65	43
$C_2H_5CH{=}CHCH_2M$	CH_3COOCH_3	$[CH_2{=}CHCH(C_2H_5)]_2C(OH)(CH_3)$ $CH_2{=}CHCH(C_2H_5)C(OH)(CH_3)CH_2CH{=}CHC_2H_5$ Mg, 95/5; Zn, 65/35; Al, 100/0	50-80	198
$C_2H_5CH{=}CHCH_2M$	CH_3COO-i-Pr	$[CH_2{=}CHCH(C_2H_5)]_2C(OH)(CH_3)$ $CH_2{=}CHCH(C_2H_5)C(OH)(CH_3)CH_2CH{=}CHC_2H_5$ $(C_2H_5CH{=}CHCH_2)_2C(OH)(CH_3)$ Zn, 0/60/40; Al, 94/6/0	55-70	198
$(CH_3)_2C{=}CHCH_2Li$	$RCOOH$	$RCOC(CH_3)_2CH{=}CH_2 + RCOCH_2CH{=}C(CH_3)_2$		110
$CH_2{=}CHCH_2Li$		 + 	86	154

9. Reactions with acids, acid anhydrides, acid chlorides, esters and amides

Allylic organometallic compounds (M = Zn, Mg, Al, Li) react readily with acids and derived functions (Table 14). Particularly, the allylic organozinc compounds, in contrast to their saturated homologs, react well with esters, acid anhydrides and acid chlorides. However, the allylic organozinc and aluminium compounds do not react with *N,N*-dialkyl acetamides [10, 22, 43].

Moreover, it has been shown recently that a reaction between a substituted allylic organozinc compound and an ester can be a reversible process [198].

The 1,4-addition of allylic organometallic compounds to diethyl alkylidenemalonates and to allylic amides [114-117] has been demonstrated. For instance:

$$(CH_3)_2C{=}C(COOC_2H_5)_2 + RCH{=}CHCH_2M \rightarrow CH_2{=}CHCH(R)C(CH_3)_2CH(COOC_2H_5)_2$$

This 1,4-addition is *usually the exclusive process*, no matter whether one starts with an alkylidenemalonate, an alkylidenecyanoacetate or an allylic amide (Table 15). However, in some cases, and under certain experimental conditions (low temperature), it is possible to observe the formation of the 1,2-addition product [115]:

$$\begin{aligned} &\text{i-Pr}(CH_3)C{=}C(CN)COOC_2H_5 + CH_2{=}CHCH_2MgBr \rightarrow \\ &\qquad CH_2{=}CHCH_2C(CH_3)(\text{i-Pr})CH(CN)COOC_2H_5 \quad + \\ &\qquad \text{i-Pr}(CH_3)C{=}C(CN)C(OH)(CH_2CH{=}CH_2)_2 \end{aligned}$$

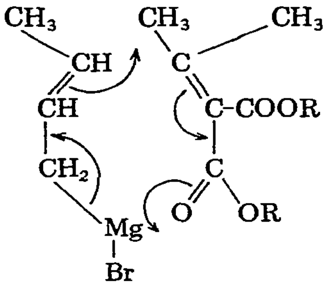
at 0°C exclusively the 1,4-product; at -50°C 55% 1,2- and 45% 1,4-product.

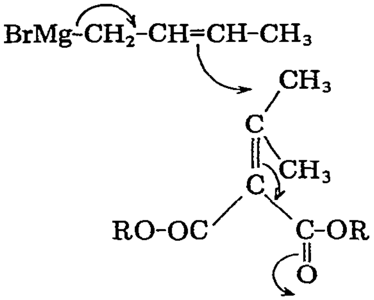
TABLE 15

REACTIONS WITH ALKYLIDENEMALONATES, ALKYLIDENECYANOACETATES AND ALLYLIC AMIDES

Organometallic compound	Reagent	Product		Yield (%)	Ref.
		1,2-addition	1,4-addition		
$CH_2{=}CHCH_2MgBr$	$R'R''C{=}C(COOC_2H_5)_2$	0	100	50	114
$CH_2{=}CHCH_2MgBr$	$R'R''C{=}C(CN)COOC_2H_5$	0	100	25-45	115
$CH_2{=}CHCH_2MgBr$	$R'CH{=}CHCON(C_2H_5)_2$	0	100	50	116
$CH_2{=}CHCH_2MgBr$	$(CH_3)_2C{=}C(COOR)_2$	0	100		117
$CH_3CH{=}CHCH_2MgBr$	$(CH_3)_2C{=}C(COOR)_2$	0	100		117
$CH_3CH{=}CHCH_2MgBr$	$R'CH{=}CHCON(C_2H_5)_2$	0	100	85	116
$C_2H_5CH{=}CHCH_2MgBr$	$R'CH{=}CHCON(C_2H_5)_2$	0	100	85	116
$CH_2{=}CHCH_2ZnBr$	$R'R''C{=}C(COOC_2H_5)_2$	0	100	80	114
$CH_2{=}CHCH_2ZnBr$	$R'R''C{=}C(CN)COOC_2H_5$	0	100	25-45	115
$CH_2{=}CHCH_2ZnBr$	$R'CH{=}CHCON(C_2H_5)_2$	0	100	traces	116

To rationalize this 1,4-addition, two paths have been proposed [117]: either an 8-membered cyclic pathway (which is quite unlikely) or an S_E2' mechanism similar to the one proposed for simple carbonyl derivatives [90-92].





10. Reactions with orthoformates

Allylic organomagnesium compounds react with ethyl orthoformate to give acetals in good yields [28, 118, 119]. Allylaluminium bromide reacts in similar fashion [31].

With a substituted allylic organometallic compound, the reaction occurs mainly with complete allylic rearrangement [28]:

$$CH_3CH{=}CHCH_2MgBr + HC(OC_2H_5)_3 \rightarrow CH_2{=}CHCH(CH_3)CH(OC_2H_5)_2$$

11. Reactions with nitriles

While allylic organoaluminium compounds seem not to react with nitriles [10, 22, 43] apart from polymerization, allylic organo-zinc, -magnesium and -lithium compounds react readily with nitriles to give an ethylenic ketone (see Table 16).

Normally, after hydrolysis, a β-ethylenic ketone is obtained, with complete allylic rearrangement [37, 120]:

$$RCH{=}CHCH_2M + R'C{\equiv}N \rightarrow CH_2{=}CHCH(R)COR'$$

but the product isomerizes into an α-ethylenic ketone, $H_3CCH{=}C(R)COR'$, if the reaction time is increased [37, 120]. The ease with which this isomerization occurs seems also to depend on the nature of the metal: Zn < Mg < Li [37]. An unsaturated alkoxy ketone (a mixture of α- and β-ethylenic compounds) is obtained from the reaction of an α-alkoxynitrile with $RCH{=}CHCH_2M$, ($M = Zn$, Mg), when a reverse addition procedure is used (adding the organometallic to the nitrile) [70].

A primary amine can be obtained by the action of an excess of the organometallic reagent, prepared from an unsubstituted allylic halide on a nitrile [28, 37, 227] and on an alkoxynitrile [28, 70, 227, 228], but this has not been observed, up to now, with substituted allylic organometallic compounds.

$$CH_2{=}CHCH_2M + R'C{\equiv}N \rightarrow CH_2{=}CHCH_2C(R'){=}NM + CH_2{=}CHCH_2M \rightarrow$$

$$(CH_2{=}CHCH_2)_2C(R')N(M)_2 \xrightarrow{H_2O} (CH_2{=}CHCH_2)_2C(R')NH_2$$

Finally, as far as the reaction mechanism is concerned, a 6-membered cyclic pathway has been proposed [10, 22] but an S_E2' mechanism also can be considered [120].

TABLE 16

REACTIONS WITH NITRILES

Organometallic compound	Reagent	Product	Yield (%)	Ref.
$CH_2{=}CHCH_2MgBr$	$C_2H_5OCH_2CH_2C{\equiv}N$	α- and β-ethylenic ketones + primary amine	30	70
$CH_2{=}CHCH_2MgBr$ (excess)	$CH_3OCH_2C{\equiv}N$	$CH_3OCH_2C(CH_2CH{=}CH_2)_2NH_2$	39	70
$CH_2{=}CHCH_2MgBr$ (excess)	$C_2H_5OCH_2C{\equiv}N$	$C_2H_5OCH_2C(CH_2CH{=}CH_2)_2NH_2$	79	28
$CH_2{=}CHCH_2MgBr$ (excess)	$R'CH_2C{\equiv}N$	$R'CH_2C(CH_2CH{=}CH_2)_2NH_2$	45-55	28
$CH_3CH{=}CHCH_2MgBr$	$CH_3C{\equiv}N$	$CH_3CH{=}C(CH_3)COCH_3$ (84%) + $CH_2{=}CHCH(CH_3)COCH_3$ (16%)	45	120
$CH_3CH{=}CHCH_2MgBr$	$C_6H_5C{\equiv}N$	$CH_3CH{=}C(CH_3)COC_6H_5$	78	120
$C_2H_5CH{=}CHCH_2MgBr$	$R'C{\equiv}N$	α- and β-ethylenic ketones	19-35	37
$CH_2{=}CHCH_2ZnBr$	$CH_3C{\equiv}N$	$CH_2{=}CHCH_2COCH_3$	47	43
$CH_2{=}CHCH_2ZnBr$	$ROCH(R')C{\equiv}N$	α- and β-ethylenic ketones	48-57	70
$CH_2{=}CHCH_2ZnBr$	$RO(CH_2)_2C{\equiv}N$	α- and β-ethylenic ketones	57	70
$CH_2{=}CHCH_2ZnBr$ (excess)	CH_3OCH_2CN	$CH_3OCH_2C(CH_2CH{=}CH_2)_2NH_2$	45	70
$C_2H_5CH{=}CHCH_2ZnBr$	$R'C{\equiv}N$	α- and β-ethylenic ketones	45-59	37
$C_2H_5CH{=}CHCH_2ZnBr$	CH_3OCH_2CN	α- and β-ethylenic ketones	53	70
$C_2H_5CH{=}CHCH_2Li$	$R'C{\equiv}N$	α-ethylenic ketone	20-36	37

12. Reactions with iminoethers, amidines and iminohalides

Allylic organometallic compounds (M = Zn, Mg, Li, Al) react easily with iminoethers (yield 60-80%) [121] to produce a secondary amine, without stopping at an intermediate step:

$$2\ CH_2{=}CHCH_2M\ +\ C_6H_5N{=}CHOC_2H_5 \longrightarrow C_6H_5NHCH(CH_2CH{=}CH_2)_2$$

For this reaction, two paths have been proposed [121-123]:

$$RM + C_6H_5N{=}CHOC_2H_5 \left[\begin{array}{l} \xrightarrow{1} C_6H_5N(M)CH(R)OC_2H_5 \rightarrow C_6H_5N{=}CHR \\ \xrightarrow{2} C_6H_5N{=}C(M)OC_2H_5 \qquad\ \rightarrow C_6H_5N{=}C: \end{array}\right.$$

Path 1 corresponds to a normal addition to the $>C{=}N$ bond followed by the addition of a second mole of organometallic compound to the imine. Path 2 corresponds to the abstraction of a proton by the organometallic compound; then the isonitrile reacts with two moles of organometallic compound to give the amine.

It seems that path 1 is the more likely, for, during the action of allylic organometallic compounds on isonitriles, the yields of the expected amines are very low [123], whereas this reaction with iminoethers or aldimines gives amines with yields of about 80%. Moreover, the reaction between the allylic organometallic compounds and substituted iminoethers, $C_6H_5N{=}C(R')OC_2H_5$, gives excellent yields, although these compounds can only lead, in intermediate position, to an imine [128].

When the organometallic compound has a substituted allylic group, the reaction gives a mixture of three amines (XVII), (XVIII), (XIX), their proportion varying according to the nature of the metal:

$$R''OCH{=}NR' + RCH{=}CHCH_2M \longrightarrow$$

$$\left\{\begin{array}{ll} R'NHCH(CH(R)CH{=}CH_2)_2 & (XVII) \\ R'NHCH(CH(R)CH{=}CH_2)CH_2CH{=}CHR & (XVIII) \\ R'NHCH(CH_2CH{=}CHR)_2 & (XIX) \end{array}\right.$$

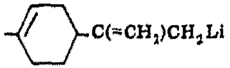
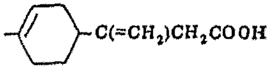
M	Yield (%)	(XVII)	(XVIII)	(XIX)
ZnBr	91	2	76	22
MgBr	60	95	5	0
Li	96	69	30	1

Moreover, in the case of zinc, the reaction is *reversible*, the proportion of amine (XIX) increasing with the length of time the reactants are in contact [102, 121].

The results observed with the amidine $C_6H_5N{=}CHN(CH_3)_2$ are quite comparable with those observed with $C_6H_5N{=}CHOC_2H_5$ [121].

In the same way, iminochlorides $RN{=}C(Cl)R'$ can react with allylmagnesium bromide [124].

TABLE 17. REACTIONS WITH CARBON DIOXIDE

Organometallic compound	Acids	Yield (%)	Ref.
$CH_2=C(CH_3)CH_2MgCl$	$CH_2=C(CH_3)CH_2COOH$	40	178
$CH_3CH=CHCH_2MgBr$	$CH_2=CHCH(CH_3)COOH$	75	28, 170
$C_2H_5CH=CHCH_2MgBr$	$CH_2=CHCH(C_2H_5)COOH$	50	79, 80
$CH_3CH=CHCH(CH_3)MgBr$	$CH_3CH=CHCH(CH_3)COOH$		73
$(CH_3)_2C=CHCH_2MgCl$	$(CH_3)_2C(COOH)CH=CH_2$	64	180, 193
$RCH=CHCH_2MgX$ (Cl, Br)	$CH_2=CHCH(R)COOH$	50	2
		55	83, 233
$C_6H_5CH=CHCH_2MgCl$, ether	$C_6H_5CH(COOH)CH=CH_2$	75	17, 171
$CH_2=CHCH_2MgOCH_3$	$CH_2=CHCH_2COOH$	15	125
$CH_2=C(R)CH_2MgOC_6H_5$	$CH_2=C(R)CH_2COOH$	66	125
$C_6H_5CH=CHCH_2MgOC_6H_5$	$C_6H_5CH=CHCH_2COOH$ (40%) + $CH_2=CHCH(C_6H_5)COOH$ (60%)	65	125
$CH_3O(CH_2)_3CH=CHCH_2MgCl$	$CH_3O(CH_2)_3CH(CH=CH_2)COOH$	38	174
Geranyl-MgCl	$CH_3CR(COOH)CH=CH_2$	28	187
$(t\text{-}BuCH_2CH=CHCH_2)_2Mg$, pentane	$t\text{-}BuCH_2CH(CH=CH_2)COOH$ (98%) + $t\text{-}BuCH_2CH=CHCH_2COOH$ (2%)		231
$(CH_2=CHCH_2)_2Zn$	$CH_2=CHCH_2COOH$	100	126
$(CH_3CH=CHCH_2)_2Zn$	$CH_2=CHCH(CH_3)COOH$	100	126
$[CH_2=C(CH_3)CH_2]_2Zn$	$CH_2=C(CH_3)CH_2COOH$	100	126
$CH_2=CHCH_2ZnBr$	$CH_2=CHCH_2COOH$	70	10, 43
$C_2H_5CH=CHCH_2ZnBr$	$CH_2=CHCH(C_2H_5)COOH$	53	79, 80
$CH_2=CHCH=CHCH_2ZnBr$	$(CH_2=CH)_2CHCOOH$	31	79, 80
$(CH_2=CHCH_2)_2Cd$	$CH_2=CHCH_2COOH$	100	126
$(CH_3CH=CHCH_2)_2Cd$	$CH_2=CHCH(CH_3)COOH$	100	126
$[CH_2=C(CH_3)CH_2]_2Cd$	$CH_2=C(CH_3)CH_2COOH$	100	126
$t\text{-}BuCH_2CH=CHCH_2Li$	$t\text{-}BuCH_2CH=CHCH_2COOH$ + $t\text{-}BuCH_2CH(COOH)CH=CH_2$	75	213
$CH_2=C(CH_3)CH_2Li$	$CH_2=C(CH_3)CH_2COOH$	60	249
$C_6H_5CH=CHCH_2Li$, ether	$C_6H_5CH(COOH)CH=CH_2$ + $C_6H_5CH=CHCH_2COOH$	48-57	17
		19	223
$(CH_2=CH)_2CH^-Na^+$	$(CH_2=CH)_2CHCOOH$	13	205
$(CH_2=CH)_2CH^-Na^+$	$CH_2=CHCH=CHCH_2COOH$	61	203
$C_6H_5CH=CHCH_2^-Na^+$, pentane	$C_6H_5CH=CHCH_2COOH$ + $C_6H_5CH(CH=CH_2)COOH$	50	17

13. Reactions with *O*-alkylated oximes

Allylic organometallic compounds (M = Mg, Zn, Al, Li) react with *O*-alkylated oximes [44].

The reaction with an organometallic compound prepared from allyl bromide gives three compounds:

$$C_6H_5CH{=}NOC_4H_9 + 2\,CH_2{=}CHCH_2M \longrightarrow \left\{ \begin{array}{ll} C_6H_5CH(CH_2CH{=}CH_2)NHOC_4H_9 & \text{(XX)} \\ C_6H_5CH(CH_2CH{=}CH_2)NHCH_2CH{=}CH_2 & \text{(XXI)} \\ C_6H_5NHCH(CH_2CH{=}CH_2)_2 & \text{(XXII)} \end{array} \right.$$

Product (XXII) corresponds to the intervention of a Beckmann type rearrangement during the addition.

The nature of the metal (Mg, Zn, Al, Li) plays an important role in the formation of one or the other of these three compounds. Moreover, when the organometallic compound is a substituted allyl, the formation of compounds with primary or secondary structure can be observed.

14. Reactions with carbon dioxide, carbonates and chloroformates

The action of carbon dioxide on allylic organometallic compounds has been studied mainly in order to prepare β-ethylenic acids rather than to produce tertiary alcohols.

The carbonation of organoaluminium compounds is difficult and leads to tertiary alcohols [10, 22, 43]. Organozinc compounds are not carbonated at normal pressure [43], but their carbonation, as well as that of organomagnesium compounds, can be achieved by using solid carbon dioxide in great excess in a pressure vessel (see Table 17).

In the substituted allylic series, the reaction usually occurs with a complete allylic rearrangement except in cases of high steric hindrance.

The action of allylic organometallic compounds on carbon dioxide derivatives such as $CO(OC_2H_5)_2$ and $ClCOOC_2H_5$ can also be used to prepare tertiary alcohols:

$CH_2{=}CHCH_2Br + Mg + O{=}C(OC_2H_5)_2 \rightarrow (CH_2{=}CHCH_2)_3COH$ (70%) [176, 234]
$CH_2{=}CHCH_2ZnBr + O{=}C(OC_2H_5)_2 \rightarrow (CH_2{=}CHCH_2)_3COH$ (51%) [43]
$(CH_2{=}CHCH_2)_3Al_2Br_3 + ClCOOC_2H_5 \rightarrow (CH_2{=}CHCH_2)_3COH$ (66%) [43]

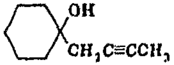
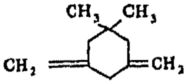
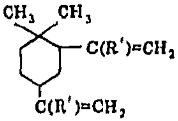
$$C_2H_5CH{=}CHCH_2M + ClCOOC_2H_5 \xrightarrow{\text{15 h at } 40^\circ} \left\{ \begin{array}{ll} [CH_2{=}CHCH(C_2H_5)]_3COH & \text{(XXIII)} \\ [CH_2{=}CHCH(C_2H_5)]_2C(OH)CH_2CH{=}CHC_2H_5 & \text{(XXIV)} \\ [CH_2{=}CHCH(C_2H_5)]C(OH)[CH_2CH{=}CHC_2H_5]_2 & \text{(XXV)} \end{array} \right. \quad [198]$$

(30-55%)

[(XXIII)/(XXIV)/(XXV) for M = Mg 55/45/0, for M = Zn 0/42/58, for M = Al 75/25/0]

TABLE 18

REACTIONS OF ORGANOMAGNESIUM COMPOUNDS WITH ETHYLENIC AND ACETYLENIC COMPOUNDS

Organometallic compound	Reagent	Product	Yield (%)	Ref.
$CH_2=CHCH_2MgBr$	$R'CH=C(R'')CHOHR'''$	$CH_2=CHCH_2C(R'')(CH_2R')CHOHR'''$	5 to 50	129, 131, 184
$CH_2=CHCH_2MgBr$	$(C_6H_5)_2C(OH)CH_2CH=CH_2$	$(C_6H_5)_2C(OH)(CH_2)_4CH=CH_2$	70	130
$CH_2=CHCH_2MgCl$	$R'C\equiv CCHOHR''$	$R'CH=C(CH_2=CHCH_2)CHOHR''$	22-85	132, 133
$CH_2=CHCH_2MgCl$	$R'C\equiv CCH_2CHOHR''$	$R'C(CH_2CH=CH_2)=CHCH_2CHOHR'' + R'CH=C(CH_2CH=CH_2)CH_2CHOHR''$	68-75	132, 133
$CH_2=CHCH_2MgCl$	$C_6H_5C\equiv CCH_2CH_2OH$	$C_6H_5CH=C(CH_2CH=CH_2)CH_2CH_2OH$	40	132
$CH_2=CHCH_2MgCl$	$R'C\equiv CCH_2CH_2CH_2OH$	$R'C(CH_2=CHCH_2)=CH(CH_2)_2CH_2OH$	7	133
$CH_2=CHCH_2CH_2MgBr$			60	134
$CH_2=CHCH_2MgBr$	$HC\equiv CCH=CHCH_2OH$	$HC\equiv CCH_2CH(CH_2CH=CH_2)CH_2OH + CH_2=C=CHCH(CH_2CH=CH_2)CH_2OH$	50-78	135, 138
$CH_2=CHCH_2MgCl$	$CH_2=C=CHCH_2OH$	$CH_2=CHCH_2CH_2CH=CHCH_2OH + CH_2=C(CH_2CH=CH_2)CH=CH_2$	2	136
$CH_2=CHCH_2MgCl$	$CH_2=C=CHCH_2CH_2OH$	$CH_3C(CH_2CH=CH_2)=CHCH_2CH_2OH + CH_2=C(CH_2CH=CH_2)CH_2CH_2OH$	50	136
$CH_2=CHCH_2MgBr$	$HC\equiv CCH=CHCH_2OBu$	$HC\equiv CCH_2CH(CH_2CH=CH_2)CH_2OBu + CH_2=C=CHCH(CH_2CH=CH_2)CH_2OBu$	83	138
$CH_2=CHCH_2MgCl$	$C_6H_5CH=CHCH_2NH_2$	$C_6H_5CH_2CH(CH_2CH=CH_2)CH_2NH_2$	23	137
$CH_2=CHCH_2MgCl$	$C_6H_5CH=CHCH_2N(CH_3)_2$	$C_6H_5CH_2CH(CH_2CH=CH_2)CH_2N(CH_3)_2$	44	137
$CH_2=CHCH_2MgCl$	$C_6H_5C\equiv CCH_2N(CH_3)_2$	$C_6H_5CH=C(CH_2CH=CH_2)CH_2N(CH_3)_2$	51	137
$CH_2=CHCH_2MgBr$	$HC\equiv CCH=CHCH_2N(R')C_2H_5$ $(R' = H, Et)$	$HC\equiv CCH_2\text{-}CH(CH_2CH=CH_2)CH_2N(R')C_2H_5 + CH_2=C=CHCH(CH_2CH=CH_2)CH_2N(R')C_2H_5$	68-70	138
$CH_3CH=CHCH_2MgBr$	$CH_2=CHCH_2OH$	$CH_2=CHCH(CH_3)CH(CH_3)CH_2OH$		129
$CH_3CH=CHCH_2MgBr$	$(C_2H_5)_2C(OH)CH(CH_3)CH=CH_2$	$(C_2H_5)_2C(OH)CH(CH_3)(CH_2)_2CH(CH_3)CH=CH_2$		28
$CH_2=CHCH_2MgCl$	$CH_2=C(R')(R'')$ (under 30-45 atm pressure)	$CH_2=CHCH_2CH_2CH(R')(R'')$	28-41	139
$CH_2=C(CH_3)CH_2MgCl$	$CH_2=C(R')(R'')$ (under 30-45 atm pressure)	$CH_2=C(CH_3)CH_2CH_2CH(R')(R'')$	33-82	139
$CH_3CH=CHCH_2MgCl$	$CH_2=C(R')(R'')$ (under 30-45 atm pressure)	$CH_2=CHCH(CH_3)CH_2CH(R')(R'') + CH_3CH=CHCH_2CH_2CH(R')(R'')$	18-56	139
$CH_2=C(CH_3)CH_2MgCl$	$CH_2=C=CH_2$		44	140
$CH_2=C(CH_3)CH_2MgCl$	$CH_2=C(R')CH=CH_2$		40-42	140

On the other hand, use of a deficiency of the organometallic reactant leads to esters in its reactions with chloroformates:

$RCH{=}CHCH_2MgBr + ClCOOC_2H_5 \rightarrow CH_2{=}CHCH(R)COOC_2H_5$ [187]

15. Reactions with iminocarbonates, isoureas, guanidines and carbodiimides

Allylic organometallic compounds (M = Zn, Mg, Li) react readily with iminocarbonates such as $C_6H_5N{=}C(OC_2H_5)_2$ [127, 128]; this reaction could in principle lead to three types of compounds:

$C_6H_5N{=}C(OC_2H_5)_2 + CH_2{=}CHCH_2M \rightarrow C_6H_5N{=}C(OC_2H_5)CH_2CH{=}CH_2$ (XXVI) (1)
(XXVI) + $CH_2{=}CHCH_2M \rightarrow C_6H_5N{=}C(CH_2CH{=}CH_2)_2$ (XXVII) (2)
(XXVII) + $CH_2{=}CHCH_2M \rightarrow C_6H_5NHC(CH_2CH{=}CH_2)_3$ (XXVIII) (3)

In fact, it gives only amine (XXVIII) in the case of $CH_2{=}CHCH_2M$ (yield 63-93%), while a mixture of imino ether (XXVI) (with complete allylic rearrangement) and of the amine (XXVIII) can be obtained in the case of $RCH{=}CHCH_2M$.

The reaction is more difficult to achieve in the case of isoureas such as $C_6H_5N{=}C(OC_2H_5)N(CH_3)_2$, and even more so in the case of guanidines such as $C_6H_5N{=}C[N(CH_3)_2]_2$ [128]; thus, allylic organozinc compounds are practically without effect, while organo-magnesium and -lithium compounds mainly lead to step 1 (here it is an amidine) and give comparatively little amine (step 3). It is to be noted that the amidine obtained at step 1 usually possesses a conjugated structure resulting from the isomerization of the allyl group to a propenyl group:

$$C_6H_5N{=}C(OC_2H_5)N(CH_3)_2 + CH_2{=}CHCH_2Li \rightarrow C_6H_5N{=}C(CH{=}CHCH_3)N(CH_3)_2 \quad (81\%)$$

Carbodiimides, R′N=C=NR′ (R′ = $(CH_3)_2CH$, C_6H_5, cyclohexyl), can react only once, even when a large excess of the allylic organometallic compound (M = Zn, Mg, Li) is used [128]; the amidines thus produced possess a conjugated structure, as, here again, the allyl group isomerizes to a propenyl group:

$$CH_2{=}CHCH_2M + C_6H_{11}N{=}C{=}NC_6H_{11} \rightarrow C_6H_{11}NHC(CH{=}CHCH_3){=}NC_6H_{11}$$

(M = Zn, yield 86%; M = Mg, yield 60%; M = Li, yield 74%)

In the same way, phenyl isocyanate reacts with only one molar equivalent of $CH_2{=}CHCH_2M$ [2].

16. Reactions with isolated unsaturated carbon—carbon bonds

Although only recently discovered, the addition of allylic organo-magnesium, and -zinc compounds, and sometimes -lithium and -aluminium compounds, to isolated unsaturated carbon—carbon bonds has already prompted numerous research studies and very interesting applications have been developed (see Tables 18 and 19).

Two types of reaction mechanisms have been proposed for the addition of

(continued on p. 38)

TABLE 19

REACTIONS OF ALLYLIC ORGANOMETALLIC COMPOUNDS (M = Zn, Al, Li) WITH ETHYLENIC, ACETYLENIC AND ALLENIC COMPOUNDS

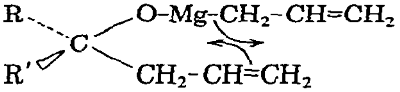
Organometallic compound	Reagent	Product	Yield (%)	Ref.
$CH_2{=}CHCH_2ZnBr$	$H_2C{=}CHCH_2OH$	$CH_3CH(CH_2CH{=}CH_2)CH_2OH$	23	141
$CH_2{=}CHCH_2ZnBr$	$H_2C{=}CHCH_2CH_2OH$	$CH_3CH(CH_2CH{=}CH_2)CH_2CH_2OH$	5	141
$CH_2{=}CHCH_2ZnBr$	$HC{\equiv}CCH_2OH$	$CH_2{=}C(CH_2CH{=}CH_2)CH_2OH + CH_3C(CH_2CH{=}CH_2)_2CH_2OH$	62	142
$CH_2{=}CHCH_2ZnBr$	$HC{\equiv}CCH{=}CHCH_2OH$	$CH_2{=}C(CH_2CH{=}CH_2)CH{=}CHCH_2OH$	63	135, 138
$CH_2{=}CHCH_2ZnBr$	$CH_2{=}CHCH_2OBu$	$CH_3CH(CH_2CH{=}CH_2)CH_2OBu$	5	141
$CH_2{=}CHCH_2ZnBr$	$CH_2{=}CHCH_2CH_2OBu$	$CH_3CH(CH_2CH{=}CH_2)CH_2CH_2OBu$	7	141
$CH_2{=}CHCH_2ZnBr$	$HC{\equiv}CCH{=}CHCH_2OBu$	$CH_2{=}C(CH_2CH{=}CH_2)CH{=}CHCH_2OBu$	57	138
$CH_2{=}CHCH_2ZnBr$	$CH_2{=}CH(CH_2)_nNEt_2$	$CH_2{=}CH(CH_2)_{n+3}NEt_2$	5-65	45, 141, 143
$CH_2{=}CHCH_2ZnBr$	$-CH{=}CCHCHNEt$	$CH_2{=}CHCH_2CHCHCHCHNEt$ generally		45
$CH_2{=}CHCH_2ZnBr$	$HC{\equiv}C(CH_2)_nNEt_2$	$CH_2{=}C(CH_2CH{=}CH_2)(CH_2)_nNEt_2$	25-70	45, 144
$CH_2{=}CHCH_2ZnBr$	$CH_3C{\equiv}C(CH_2)_nNEt_2$	$CH_3C(CH_2CH{=}CH_2){=}CH(CH_2)_nNEt_2$	25-65	45, 144
$CH_2{=}CHCH_2ZnBr$	$HC{\equiv}CCH_2NEt$	$CH_2{=}C(CH_2CH{=}CH_2)CH_2NEt + CH_3C(CH_2CH{=}CH_2)_2CH_2NEt$	32-43	45
$CH_2{=}CHCH_2ZnBr$	$HC{\equiv}CCHCHNEt$	$CH_2{=}C(CH_2CH{=}CH_2)CHCHNEt$	52-60	45
$CH_2{=}CHCH_2ZnBr$	$CH_2{=}C{=}C(CH_3)CH_2NEt$	$CH_2{=}CHCH_2CH_2CH{=}C(CH_3)CH_2NEt$	43-72	45, 145
$CH_2{=}CHCH_2ZnBr$	$CH_2{=}C{=}CH(CH_2)_2NEt_2$	$\left\{\begin{array}{l}CH_2{=}CHCH_2CH_2CH{=}CH(CH_2)_2NEt\ +\\CH_2{=}CHCH_2C(CH_3){=}CH(CH_2)_2NEt\end{array}\right.$	46	45, 145
$CH_2{=}CHCH_2ZnBr$	$HC{\equiv}CCH{=}CHCH_2N(R')Et$	$\left\{\begin{array}{l}CH_2{=}C(CH_2CH{=}CH_2)CH{=}CHCH_2N(R')Et\ +\\CH_3C(CH_2CH{=}CH_2)_2CH{=}CHCH_2N(R')Et\end{array}\right.$	35-60	45, 135, 138
$C_2H_5CH{=}CHCH_2ZnBr$	$CH_2{=}CHCH_2CH_2NEt_2$	$CH_2{=}CHCH(Et)(CH_2)_4NEt_2$	70	45, 141, 143
$C_2H_5CH{=}CHCH_2ZnBr$	$CH_3C{\equiv}C(CH_2)_2NEt_2$	$CH_2{=}CHCH(Et)C(CH_3){=}CH(CH_2)_2NEt_2$	65	45, 144
$C_2H_5CH{=}CHCH_2ZnBr$	$CH_2{=}C{=}C(CH_3)CH_2NEt_2$	$CH_2{=}CHCH(Et)CH_2CH{=}C(CH_3)CH_2NEt_2$	56	45, 145

$CH_2{=}CHCH_2ZnBr$	$CH_2{=}CHCH_2ZnBr$	$CH_2{=}C(CH_2CH{=}CH_2)CH_2ZnBr$	45	146, 147
$CH_2{=}CHCH_2ZnBr$	$CH_3CH{=}CHCH_2ZnBr$	$CH_2{=}C[CH(CH_3)CH{=}CH_2]CH_2ZnBr$	10	146, 147
$CH_2{=}CHCH_2ZnBr$	$C_6H_5C{\equiv}CMgBr$	$CH_2{=}CHCH_2C(C_6H_5){=}CH_2 + (CH_2{=}CHCH_2)_2C(C_6H_5)CH_3$	22-65	142
$CH_2{=}CHCH_2ZnBr$	$CH(R'){=}C(R'')MgBr$	$CH_2{=}CHCH_2CH(R')CH_2R''$	24-58	142
$CH_3CH{=}CHCH_2ZnBr$	$C_6H_5C{\equiv}CH$	$CH_2{=}C(C_6H_5)CH(CH_3)CH{=}CH_2$	52	142
$CH_2{=}CHCH_2ZnBr$	$R'C{\equiv}CH$ (R' = n-Bu, i-Bu, sec-Bu, t-Bu)	$R'C(CH_2CH{=}CH_2){=}CH_2$ (chiefly) + $R'C(CH_2CH{=}CH_2)_2CH_3$	35-57	226
$CH_3CH{=}CHCH_2ZnBr$	$BuC{\equiv}CH$	$BuC(CH(CH_3)CH{=}CH_2){=}CH_2 + BuC(CH_2CH{=}CHCH_3){=}CH_2$	56	226
$C_2H_5CH{=}CHCH_2ZnBr$	$BuC{\equiv}CH$	$BuC[CH(C_2H_5)CH{=}CH_2]{=}CH_2 + BuC(CH_2CH{=}CHC_2H_5){=}CH_2$	52	226
$CH_2{=}CHCH_2al$ (al = $^1/3$ Al)	$CH_2{=}CHCH_2al$	$CH_2{=}CHCH_2CH(CH_2al)_2$	—	148
$CH_2{=}C(CH_3)CH_2al$	$C_6H_{13}CH{=}CH_2$	$alCH_2CH(C_6H_{13})CH_2C(CH_3){=}CH_2$	67	148
$CH_2{=}CHCH_2Li$	$CH_2{=}CHCHOHCH_3$	$CH_2{=}CHCH_2CH(CH_3)CHOHCH_3$	—	149
$CH_2{=}CHCH_2Li$	$HC{\equiv}CCH{=}CHCH_2OH$	$HC{\equiv}CCH_2CH(CH_2CH{=}CH_2)CH_2OH$	50	135, 138
$CH_2{=}CHCH_2Li$	$HC{\equiv}CCH{=}CHCH_2OBu$	$HC{\equiv}CCH_2CH(CH_2CH{=}CH_2)CH_2OC_4H_9$	35	138
$CH_2{=}CHCH_2Li$	$HC{\equiv}CCH{=}CHCH_2NEt_2$	$HC{\equiv}CCH_2CH(CH_2CH{=}CH_2)CH_2N(C_2H_5)_2$	42	135, 138
$CH_2{=}CHCH_2Li$	$C_6H_5CH{=}CHCH_2N^+R_3, X^-$	addition then 1,3-elimination  $C_6H_5\underset{CH_2}{CHCH}CH_2CH{=}CH_2$	15-35	150
$t\text{-}BuCH_2CH{=}CHCH_2Li$	butadiene	two products with 12 C atoms, corresponding to monoadditions *P* (40%) and *S* (60%)		213
$CH_2{=}CHCH_2M$	$BuCH{=}CHC{\equiv}CH$			138, 226
M = ZnBr		$BuCH{=}CHC(CH_2CH{=}CH_2){=}CH_2$	59	
M = MgBr		$BuCH(CH_2CH{=}CH_2)CH_2C{\equiv}CH$ + allenic	12-37	
M = Li		$BuCH(CH_2CH{=}CH_2)CH_2C{\equiv}CH$	30-40	

allylic organomagnesium compounds to unsaturated alcohols (ethylenic, acetylenic and allenic).

(a) Concerted intramolecular mechanism [130, 134]

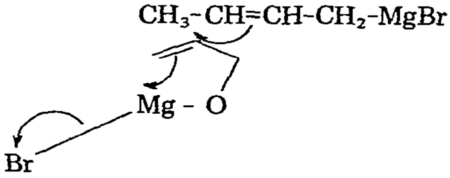
To explain the facile addition of allylmagnesium bromide to an allylic alcohol, in which the allyl group adds to the terminal ethylenic carbon, the following formation of magnesium alcoholate from diallylmagnesium has been proposed:



This leads to formation of a carbon—magnesium bond close to the site of unsaturation. There is electrophilic assistance by the metal group (in agreement with the solvent effects), and therefore an easy addition of the organometallic compound to the double bond through a 4-membered cyclic pathway. This mechanism is not unlike the intramolecular mechanism proposed for the cyclization of ethylenic, acetylenic and allenic organomagnesium compounds [152, 164, 165-168]. In the acetylenic series, a stereochemical study carried out by Eisch and Husk [130] seems to show that it is also a *cis*-addition.

(b) Concerted intermolecular mechanism [129, 131, 149]

To explain the easy addition of allylmagnesium bromide to an allylic alcohol, in which the allyl group adds to the non-terminal ethylenic carbon, a mechanism has been proposed in which the metal group of the alcoholate provides internal electrophilic assistance (which is in agreement with the kinetic data and the solvent effects), thus facilitating the external attack by a mole of the organometallic reagent.



This *trans*-addition mechanism is in agreement with the stereochemistry of the product obtained in this reaction, and with the fact that substituents placed directly on the double bond must hinder the addition.

In the acetylenic and allenic series, a mechanism of *trans*-addition [132, 133, 136] is also proposed on the basis of a stereochemical study.

The results obtained [45, 135, 141, 143-145] during the action of allylic organozinc compounds on ethylenic, acetylenic and allenic amines, and more particularly those concerning the greater or lesser ease of reaction according to the value of n in $R'CH{=}CH(CH_2)_nN(R'')_2$ and $R'C{\equiv}C(CH_2)_nN(R'')_2$, the influence of the presence and of the nature of substituents, the influence of the presence of an acidic hydrogen, either on the carbon chain or on the heteroatom, the influence of conjugation, and the influence of the nature of the solvent, show that in case of amines, the reaction mechanisms must be quite similar to those proposed for the action of organomagnesium compounds on unsaturated alcohols.

A stereochemical study carried out with the three amines: $CH_3C\equiv CCH_2CH_2N(C_2H_5)_2$; $CH_3C\equiv CCH_2CH_2CH_2N(C_2H_5)_2$ and $CH_2{=}C{=}CHCH_2CH_2N(C_2H_5)_2$ leads in the three cases to about 2/3 of *cis*-addition and 1/3 of *trans*-addition, and these percentages do not change when the heating time and the concentrations of the reactants are varied.

These results can be explained either by the simultaneous intervention of two types of mechanisms, inter- and intra-molecular, or by the intervention of a single mechanism which proceeds stepwise rather than in a concerted manner, which would make it possible to have both a *cis*- and a *trans*-addition at the same time.

17. Oxidation reactions

Allylic organometallic compounds (M = Zn, Mg, Al, Li) are oxidized by the atmospheric oxygen or by a stream of pure O_2, to give mainly alcohols.

Allylic organozinc compounds (as well as saturated dialkylzincs) are easily oxidizable [29]. Oxidation by merely bubbling air through their solutions is an easy route to allyl alcohols from allylzinc bromide, and to a mixture of two alcohols from the substituted allylic organometallic compounds (yield 70-75%) [29]:

$$CH_3CH{=}CHCH_2ZnBr \xrightarrow{\text{air}} CH_3CH{=}CHCH_2OH + CH_2{=}CHCHOHCH_3$$

$$CH_2{=}CHCH{=}CHCH_2ZnBr \xrightarrow{\text{air}} CH_2{=}CHCH{=}CHCH_2OH + CH_2{=}CHCHOHCH{=}CH_2$$

A detailed study [151] of the oxidation of organometallic compounds (M = Zn, Mg, Al) derived from 1-bromo-2-butene by a dry air stream has shown that, together with the expected alcohols, it is possible to isolate diene hydrocarbons (Table 20). According to the authors [151], the presence of dienes involves the formation of radical-type species at a certain step of the oxidation reaction. Moreover, the presence of $CoCl_2$ favors the formation of dienes, but does not change the composition of the alcohol mixture.

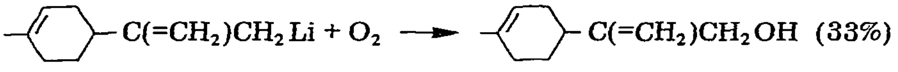
TABLE 20

OXIDATION OF CROTYLORGANOMETALLIC COMPOUNDS

Organometallic compound	Crotyl- — MgBr, ether	$(Crotyl)_2Mg$, ether	$(Crotyl)_2Mg$, ether/$CoCl_2$	$(Crotyl)_3 \cdot Al_2Br_3$, ether	Crotyl- — ZnBr, ether	Crotyl — ZnBr, THF
Alcohols, yield (%)	85	78	65	74	92	97
(XXIX) (%)	43.5	48.5	48.5	53.5	38	39.5
(XXX) (%)	26.5	22	22	31.5	35	31.5
(XXXI) (%)	30	29.5	29.5	15	27	29
Dienes, yield (%)	15	22	35	26	8	3
(XXXII) (%)	25	18.5	17.5	18.5	17.5	—
(XXXIII) (%)	18	19.5	30	39.5	40.5	—
(XXXIV) (%)	22.5	26	21	14	14	—
(XXXV) (%)	5.5	4.5	8	11	8	—
(XXXVI) (%)	15.5	16	13	12.5	12	—
(XXXVII) (%)	13.5	15.5	10.5	4.5	8	—

(XXIX), $CH_2=CHCHOHCH_3$; (XXX), $CH_3CH=CHCH_2OH$ (*trans*); (XXXI), $CH_3CH=CHCH_2OH$ (*cis*); (XXXII), $CH_2=CHCH(CH_3)CH(CH_3)CH=CH_2$; (XXXIII), $CH_2=CHCH(CH_3)CH_2CH=CHCH_3$ (*trans*); (XXXIV), $CH_2=CHCH(CH_3)$-$CH_2CH=CHCH_3$ (*cis*); (XXXV), $CH_3CH=CH(CH_2)_2CH=CHCH_3$ (*trans—trans*); (XXXVI), $CH_3CH=CH(CH_2)_2CH=CHCH_3$ (*cis—trans*); (XXXVII), $CH_3CH=$ $CH(CH_2)_2CH=CHCH_3$ (*cis—cis*)

The oxidation of allylic organolithium compounds has also been achieved:



(33%) [223]

This account of recent results on the reactivity of allylic organometallic compounds is certainly not exhaustive. However, it shows clearly the importance and the new character of the results that have been achieved in this field of research since 1960.

Acknowledgements

We express our deepest thanks to Professor Ph. Miginiac for the fruitful discussions we had with him, and the Centre National de la Recherche Scientifique for the research grant made to one of us (G.C.).

References

1 W.G. Young, J.F. Lane, A. Loshokoff and S. Winstein, J. Amer. Chem. Soc., 59 (1937) 2441.
2 R.H. Dewolfe and W.G. Young, Chem. Rev., 56 (1956) 753-901.
3 M. Gaudemar and Ch. Prévost, C.R. Acad. Sci. Paris, Ser. C, 239 (1954) 282.
4 M. Gaudemar, Ann. Chim. (Paris), [13] 1 (1956) 161.
5 M. Gaudemar, Bull. Soc. Chim. Fr., (1958) 1475.
6 K.H. Thiele and P. Zdunneck, J. Organometal. Chem., 4 (1965) 10.
7 D. Seyferth and M.A. Weiner, J. Org. Chem., 24 (1959) 1395; Org. Synth., Vol. 41, J. Wiley, London, 1961, p. 30.
8 J.J. Eisch and A.M. Jacobs, J. Org. Chem., 28 (1963) 2145.
9 R.H. Dewolfe, D.L. Hagmann and W.G. Young, J. Amer. Chem. Soc., 79 (1957) 4795.
10 M. Gaudemar, Bull. Soc. Chim. Fr., (1962) 974.
11 B. Gross and Ch. Prévost, Bull. Soc. Chim. Fr., (1967) 3605, 3610.
12 J.E. Nordlander, W.G. Young and J.D. Roberts, J. Amer. Chem. Soc., 83 (1961) 494.
13 G.M. Whitesides, J.E. Nordlander and J.D. Roberts, J. Amer. Chem. Soc., 84 (1962) 2010.
14 D. Seyferth and T.F. Jula, J. Organometal. Chem., 8 (1967) P13.
15 D. Abenhaïm, E. Henry-Basch and P. Freon, Bull. Soc. Chim. Fr., (1969) 4038, 4042.
16 H.E. Zieger and J.D. Roberts, J. Org. Chem., 34 (1969) 1976.
17 H.F. Herbrandson and D.S. Mooney, J. Amer. Chem. Soc., 79 (1957) 5809.
18 W. Flitsch, Ann. Chem., 684 (1965) 141; Angew. Chem. Int. Ed. Engl., 4 (1965) 1085.
19 C. Agami, M. Andrac and Ch. Prévost, C.R. Acad. Sci. Paris, Ser. C., 262 (1966) 852.
20 C. Agami, M. Andrac and Ch. Prévost, Bull. Soc. Chim. Fr., (1966) 1915.
21 K.W. Wilson, J.D. Roberts and W.G. Young, J. Amer. Chem. Soc., 72 (1950) 215 and 218.
22 Ch. Prévost, M. Andrac, F. Gaudemar, M. Gaudemar, B. Gross, L. Miginiac and Ph. Miginiac, Bull. Soc. Chim. Fr., (1959) 679; (1963) 1385.
23 C. Agami, M. Andrac and Ch. Prévost, Bull. Soc. Chim. Fr., (1966) 2596.
24 J.J. Eisch and G.R. Husk, J. Organometal. Chem., 4 (1965) 415.
25 C. Agami, Ch. Prévost and Ch. Brun, Bull. Soc. Chim. Fr., (1967) 706.
26 M. Gaudemar, C.R. Acad. Sci. Paris, Ser. C, 254 (1962) 1100.
27 C. Agami and Ch. Prévost, C.R. Acad, Sci. Paris, Ser. C, 263 (1966) 304.
28 R.A. Benkeser, Synthesis, 7 (1971) 347.
29 Ch. Prévost, L. Miginiac and Ph. Miginiac, Bull, Soc. Chim. Fr., (1964) 2485.
30 R. Koppang, A.C. Ranade and H. Gilman, J. Organometal. Chem., 22 (1970) 1.
31 L. Miginiac, Ann. Chim. (Paris), [13] 6 (1961) 1071.
32 L. Miginiac, Bull. Soc. Chim. Fr., (1963) 1449.
33 P. Tarrant and J. Hayes, J. Org. Chem., 30 (1965) 1485.
34 M.M. Martin and G.J. Gleicher, J. Amer. Chem. Soc., 86 (1964) 233.

35 Ph. Miginiac, Ann. Chim. (Paris), [13] 7 (1962) 445.
36 Ch. Prévost and Ph. Miginiac, Bull. Soc. Chim. Fr., (1966) 704.
37 Ph. Miginiac, C.R. Acad. Sci. Paris, Ser. C, 266 (1968) 1614.
38 W.D. Korte, L. Kiner and W.C. Kaska, Tetrahedron Letters, (1970) 603.
39 S. Czernecki, G. Georgoulis, B. Gross and Ch. Prévost, C.R. Acad. Sci. Paris, Ser. C, 264 (1967) 918.
40 S. Czernecki, G. Georgoulis, B. Gross and Ch. Prévost, Bull. Soc. Chim. Fr., (1968) 3713, 3720.
41 R. Corriu and J.P. Massé, Chem. Commun., (1970) 213.
42 R. Corriu and J.P. Massé, J. Organometal. Chem., 34 (1972) 221.
43 M. Gaudemar, Bull. Soc. Chim. Fr., (1963) 1475.
44 B. Mauzé and L. Miginiac, Bull. Soc. Chim. Fr., (1968) 3832.
45 B. Mauzé, C. Nivert and L. Miginiac, J. Organometal. Chem., 44 (1972) 69.
46 B. Mauzé and L. Miginiac, Bull. Soc. Chim. Fr., (1968) 2544.
47 I.E. Pollak, A.D. Trifunac and G.F. Grillot, J. Org. Chem., 32 (1967) 272.
48 I.E. Pollak and G.F. Grillot, J. Org. Chem., 32 (1967) 2892.
49 Ch. Glacet and R. Coupe, Bull. Soc. Chim. Fr., (1963) 2468.
50 A. Tambuté, Thesis 3me cycle, (1969) Paris.
51 Ph. Miginiac, Bull. Soc. Chim. Fr., (1968) 4156.
52 A.W.P. Jarnie and D. Skelon, J. Organometal. Chem., 30 (1971) 145.
53 G. Courtois and L. Miginiac, Tetrahedron Letters, (1972) 2411.
54 D. Seyferth and M.A. Weiner, Org. Synth., Vol. 41, J. Wiley, London 1961, p. 30.
55 M. Cherest and H. Felkin, Tetrahedron Letters, (1968) 2205.
56 J.P. Battioni, W. Chodkiewicz and P. Cadiot, Bull. Soc. Chim. Fr., (1969) 976.
57 J.P. Battioni, W. Chodkiewicz and P. Cadiot, C.R. Acad. Sci. Paris, Ser. C, 264 (1967) 991.
58 A. Sevin and W. Chodkiewicz, Bull. Soc. Chim. Fr., (1969) 4023.
59 A. Viola and I.J. Iorio, J. Amer. Chem. Soc., 89 (1967) 3462.
60 C.W. Spangler and G.F. Woods, J. Org. Chem., 28 (1963) 2245.
61 M. Bertrand and J.L. Gras, Bull. Soc. Chim. Fr., (1962) 2136.
62 W.A. De Meester and R.C. Fuson, J. Org. Chem., 30 (1965) 4332.
63 A. Viola and J.H. MacMillan, J. Amer. Chem. Soc., 92 (1970) 2404.
64 F. Roquet, J.P. Battioni, M.L. Capmau and W. Chodkiewicz, C.R. Acad. Sci. Paris, Ser. C, 268 (1969) 1449.
65 J.P. Battioni and W. Chodkiewicz, C.R. Acad, Sci. Paris, Ser. C, 269 (1969) 1556.
66 W. Chodkiewicz, Bull. Soc. Chim. Fr., (1961) 663.
67 L. Mandell and J.M. Brodman, J. Org. Chem., 31 (1966) 591.
68 D. Abenhaïm, E. Henry-Basch and P. Fréon, C.R. Acad. Sci. Paris, Ser. C, 264 (1967) 1313.
69 M. Gaudemar and S. Travers, C.R. Acad. Sci. Paris, Ser. C, 262 (1966) 139.
70 L. Miginiac and M. Lanoiselée, Bull. Soc. Chim. Fr., (1971) 2716 and Thesis 3me cycle, (1968) Poitiers.
71 J. Munch-Petersen, Bull. Soc. Chim. Fr., (1966) 471.
72 M.L. Capmau, W. Chodkiewicz and P. Cadiot, Bull. Soc. Chim. Fr., (1968) 3233.
73 H. Felkin, C. Frajerman and Y. Gault, Chem. Commun., 3 (1966) 75.
74 Y. Gault and H. Felkin, Bull. Soc. Chim. Fr., (1960) 1342.
75 D. Abenhaïm and E. Henry-Basch, C.R. Acad. Sci. Paris, Ser. C, 267 (1968) 87.
76 R.A. Benkeser, W.G. Young, W.E. Broxterman, D.A. Jones and S.J. Piaseczynski, J. Amer. Chem. Soc., 91 (1969) 132.
77 R.A. Benkeser and W.E. Broxterman, J. Amer. Chem. Soc., 91 (1969) 5162.
78 A. Brisset, S. Czernecki and G. Georgoulis, C.R. Acad. Sci. Paris, Ser. C, 272 (1971) 115.
79 L. Miginiac, Ph. Miginiac and Ch. Prévost, Bull. Soc. Chim. Fr., (1965) 3560.
80 L. Miginiac, Ph. Miginiac and Ch. Prévost, C.R. Acad. Sci. Paris, Ser. C, 260 (1965) 1442.
81 F. Barbot and Ph. Miginiac, C.R. Acad. Sci. Paris, Ser. C, 272 (1971) 1682.
82 Ph. Miginiac, Bull. Soc. Chim. Fr., (1970) 1077.
83 S. Branner-Jørgensen and A. Berg, Acta Chem. Scand., 20 (1966) 2192.
84 L. Miginiac and Ph. Miginiac, C.R. Acad. Sci. Paris, Ser. C, 258 (1964) 236.
85 Ch. Prévost, L. Miginiac and M. François, C.R. Acad. Sci. Paris, Ser. C, 262 (1966) 488.
86 F. Gérard and Ph. Miginiac, C.R. Acad. Sci. Paris, Ser. C, 273 (1971) 674.
87 F. Gérard and Ph. Miginiac, C.R. Acad. Sci. Paris, Ser. C, 275 (1972) 1129.
88 M. Andrac, Ann. Chim. (Paris), [13] 9 (1964) 287.
89 Y. Gault, C.R. Acad. Sci. Paris, Ser. C, 250 (1960) 2584.
90 H. Felkin and C. Frajerman, Tetrahedron Letters, (1970) 1045.
91 H. Felkin, Y. Gault and G. Roussi, Tetrahedron, 26 (1970) 3761.
92 M. Cherest, H. Felkin and C. Frajerman, Tetrahedron Letters, (1971) 379.
93 Ph. Miginiac, Bull. Soc. Chim. Fr., (1968) 4675.
94 L. Miginiac and B. Mauzé, Bull. Soc. Chim. Fr., (1968) 4673.
95 Belgium Patent 628790 (1963); Chem. Abstr., 60 (1964) 10735.
96 V.I. Dronov and V.P. Krivonokov, Chem. Abstr., 74 (1971) 53430z, 87725q.
97 D. Abenhaïm, E. Henry-Basch and P. Fréon, C.R. Acad. Sci. Paris, Ser. C, 267 (1968) 655.
98 D. Abenhaïm, E. Henry-Basch and P. Fréon, Bull. Soc. Chim. Fr., (1970) 179.
99 G. Boireau, J.L. Namy, D. Abenhaïm, E. Henry-Basch and P. Fréon, C.R. Acad. Sci. Paris, Ser. C, 269 (1969) 1565.
100 H. Felkin and G. Roussi, Tetrahedron Letters, (1965) 4153.
101 H. Felkin, C. Frajerman and G. Roussi, Bull. Soc. Chim. Fr., (1970) 3704.

102 B. Mauzé and L. Miginiac, Bull. Soc. Chim. Fr., (1973) 1832.
103 B. Mauzé and L. Miginiac, Bull. Soc. Chim. Fr., (1973) 1838.
104 B. Mauzé and L. Miginiac, Bull. Soc. Chim. Fr., (1973) 1082.
105 H. Gilman and J.J. Eisch, J. Amer. Chem. Soc., 79 (1957) 2150.
106 H. Gilman, J.J. Eisch and T. Soddy, J. Amer. Chem. Soc., 79 (1957) 1245; 81 (1959) 4000.
107 J. Huet, Bull. Soc. Chim. Fr., (1964) 952.
108 J.L. Moreau and M. Gaudemar, C.R. Acad. Sci. Paris, Ser. C, 275 (1972) 1201.
109 J.J. Eisch and R.L. Harrell, J. Organometal. Chem., 21 (1970) 21.
110 A. Birch, J. Corrie and G. Rao, Aust. J. Chem., 23 (1970) 1811.
111 G. Peiffer, C.R. Acad. Sci. Paris, Ser. C, 262 (1966) 501.
112 H. Felkin, C. Frajerman and G. Roussi, Ann. Chim. (Paris), [14] 6 (1971) 17.
113 D. Seyferth and M.A. Weiner, J. Org. Chem., 26 (1961) 4797.
114 G. Daviaud and Ph. Miginiac, Bull. Soc. Chim. Fr., (1970) 1617.
115 G. Daviaud and Ph. Miginiac, C.R. Acad. Sci. Paris, Ser. C, 272 (1971) 969.
116 G. Daviaud and Ph. Miginiac, Tetrahedron Letters, (1971) 3251.
117 G.A. Holmberg and R. Sjöholm, Acta Chem. Scand., 24 (1970) 3490.
118 W.G. Young and J.D. Roberts, J. Amer. Chem. Soc., 68 (1946) 649, 1472.
119 H.H. Inhoffen, F. Bohlmann and E. Reinefeld, Chem. Ber., 82 (1949) 313.
120 H. Felkin and G. Roussi, C.R. Acad. Sci. Paris, Ser. C, 266 (1968) 1552.
121 J. Pornet and L. Miginiac, C.R. Acad. Sci. Paris, Ser. C, 271 (1970) 381.
122 N. Koga, G. Koga and J.P. Anselme, Tetrahedron Letters, (1970) 3309.
123 J. Pornet and L. Miginiac, Tetrahedron Letters, (1971) 967.
124 R. Koppang, A.C. Ranade and H. Gilman, J. Organometal. Chem., 22 (1970) 1.
125 A. Maercker, J. Organometal. Chem., 18 (1969) 249.
126 K.H. Thiele, J. Köhler and P. Zdunneck, Z. Chem., 7 (1967) 307.
127 J. Pornet and L. Miginiac, C.R. Acad. Sci. Paris, Ser. C, 273 (1971) 1763.
128 J. Pornet and L. Miginiac, Bull. Soc. Chim. Fr., (1974) 551, 638.
129 M. Cherest, H. Felkin, C. Frajerman, C. Lion, G. Roussi and G. Swierczewski, Tetrahedron Letters, (1966) 875.
130 J.J. Eisch and G.R. Husk, J. Amer. Chem. Soc., 87 (1965) 4194.
131 H. Felkin and C. Kaeseberg, Tetrahedron Letters, (1970) 4587.
132 H.G. Richey and F.W. Von Rein, J. Organometal. Chem., 20 (1969) P32.
133 F.W. Von Rein and H.G. Richey, Tetrahedron Letters, (1971) 3777, 3781.
134 J.J. Eisch and J.H. Merkley, J. Organometal. Chem., 20 (1969) P27.
135 B. Mauzé, G. Courtois and L. Miginiac, C.R. Acad. Sci. Paris, Ser. C, 274 (1972) 679.
136 H.G. Richey and S.S. Szucs, Tetrahedron Letters, (1971) 3785.
137 H.G. Richey, W.F. Erickson and A.S. Heyn, Tetrahedron Letters, (1971) 2183.
138 G. Courtois and L. Miginiac, J. Organometal. Chem., in press.
139 H. Lehmkuhl and D. Reinher, J. Organometal. Chem., 25 (1970) C47.
140 H. Lehmkuhl and D. Reinher, J. Organometal. Chem., 34 (1972) 1.
141 B. Mauzé, G. Courtois and L. Miginiac, C.R. Acad. Sci. Paris, Ser. C, 269 (1969) 1225.
142 M. Gaudemar, C.R. Acad. Sci. Paris, Ser. C, 273 (1971) 1669.
143 B. Mauzé and L. Miginiac, Bull. Soc. Chim. Fr., (1968) 462.
144 B. Mauzé, C. Nivert and L. Miginiac, C.R. Acad. Sci. Paris, Ser. C, 271 (1970) 698.
145 C. Nivert and L. Miginiac, C.R. Acad. Sci. Paris, Ser. C, 272 (1971) 1996.
146 G. Courtois and L. Miginiac, Bull. Soc. Chim. Fr., (1969) 3330.
147 G. Courtois and L. Miginiac, J. Organometal. Chem., 52 (1973) 241.
148 H. Lehmkuhl and R. Reinher, J. Organometal. Chem., 23 (1970) C25.
149 H. Felkin, G. Swierczewski and A. Tambuté, Tetrahedron Letters, (1969) 707.
150 G. Courtois and L. Miginiac, C.R. Acad. Sci. Paris, Ser. C, 273 (1971) 68.
151 S. Czernecki, G. Georgoulis, B. Gross and Ch. Prévost, C.R. Acad. Sci. Paris, Ser. C, 266 (1968) 1617.
152 H.G. Richey, E.A. Hill and T.C. Rees, J. Org. Chem., 28 (1963) 2161.
153 D. Abenhaïm, J.L. Namy and G. Boireau, Bull. Soc. Chim. Fr., (1971) 3254.
154 G. Buchi and H. Wuest, Helv. Chim. Acta, 54 (1971) 1767.
155 D. Guillerm-Dron, M.L. Capmau and W. Chodkiewicz, C.R. Acad. Sci. Paris, Ser. C, 273 (1971) 759.
156 P. West, J.I. Purmort and S.V. McKinley, J. Amer. Chem. Soc., 90 (1968) 797.
157 H.H. Freedman, V.R. Sandel and B.P. Thill, J. Amer. Chem. Soc., 89 (1967) 495, 1763.
158 A.F. Thomas and W. Pawlak, Helv. Chim. Acta, 54 (1971) 1822.
159 G.M. Whitesides, J.E. Nordlander and J.D. Roberts, Disc. Faraday Soc., 34 (1962) 185.
160 O. Grummit, E.P. Budewitz and C.C. Chudd, Organic Syntheses, Coll. Vol. IV, J. Wiley, London, 1963, p. 749.
161 A.M. Kurishko and N.A. Lipatnikov, Chem. Abstr., 54 (1960) 7530.
162 R. Lukes and M. Cerny, Collect. Czech. Chem. Commun., 24 (1959) 2722.
163 R.L. Letsinger, J.G. Traynham and E. Bobko, J. Amer. Chem. Soc., 74 (1952) 399.
164 J.D. Roberts and al., J. Amer. Chem. Soc., 82 (1960) 2646.
165 E.A. Hill and J.A. Davidson, J. Amer. Chem. Soc., 86 (1964) 4663.
166 H.G. Richey and A.M. Rothman, Tetrahedron Letters, (1968) 1457.
167 H.G. Richey and W.C. Kossa, Tetrahedron Letters, (1969) 2313.
168 H.G. Richey and T.C. Rees, Tetrahedron Letters, (1966) 4297.
169 M. Cherest and H. Felkin, Tetrahedron Letters, (1971) 379, 383.
170 J.D. Roberts and W.G. Young, J. Amer. Chem. Soc., 67 (1945) 148.

171 L.E. Friedrich and R.A. Cormier, J. Org. Chem., 36 (1971) 3011.
172 J. Cason and R. Fessenden, J. Org. Chem., 25 (1960) 477.
173 J.C.H. Hwa and H. Sims, Org. Synth., Vol. 41 (1961) p. 49.
174 R.L. Letsinger and A.W. Schnizer, J. Org. Chem., 16 (1951) 704.
175 G. Stork, P.A. Grieco and M. Gregson, Tetrahedron Letters, (1969) 1393.
176 M.P. Dreyfuss, J. Org. Chem., 28 (1963) 3 269.
177 J. Quéré and E. Maréchal, Bull. Soc. Chim. Fr., (1969) 4087.
178 R.B. Wagner, J. Amer. Chem. Soc., 71 (1949) 3214.
179 J.E. Nordlander and J.D. Roberts, J. Amer. Chem. Soc., 81 (1959) 1769.
180 H. Kwart and R.K. Miller, J. Amer. Chem. Soc., 76 (1954) 5403.
181 A.L. Henne, H. Chanan and A. Turk, J. Amer. Chem. Soc., 63 (1941) 3474.
182 A. Turk and H. Chanan, Org. Synth., Coll. Vol. III, J. Wiley, London, 1955, p. 121; see also L. Lizzani, R. Luft and J.P. Rabine, Bull. Soc. Chim. Fr., (1971) 4589.
183 M. Fishwick and M.G.H. Wallbridge, J. Organometal. Chem., 25 (1970) 69.
184 W.I. Fanta and W.F. Herman, J. Org. Chem., 37 (1972) 1624.
185 Y. Tanigawa, I. Moritani and S. Nishida, J. Organometal. Chem., 28 (1971) 73.
186 Y. Yamamoto, R.J. Gargiulo and D.S. Tarbell, J. Org. Chem., 36 (1971) 846.
187 D. Barnard and L. Bateman, J. Chem. Soc., (1950) 932.
188 L. Bateman and J.I. Cunneen, J. Chem. Soc., (1950) 941.
189 S.T. Ioffe and A.N. Nesmeyanov, in A.N. Nesmeyanov and K.A. Kocheshkov (Editors), Methods of Elemento-Organic Chemistry, Vol. 2, North-Holland Publ. Comp., Amsterdam, 1967, p. 292.
190 T.J. Cogdell, J. Org. Chem., 37 (1972) 2541.
191 T.W. Gibson and W.F. Erman, J. Org. Chem., 37 (1972) 1148.
192 J.J. Eisch and D.R. Comfort, J. Organometal. Chem., 43 (1972) C17.
193 S. Engel and M.A. Schexnayder, J. Amer. Chem. Soc., 94 (1972) 4357.
194 H. Boehme, M. Haake and G. Auterhoff, Synthesis, (1972) 636.
195 J.A. Katzenellenbogen and R.S. Lenox, J. Org. Chem., 38 (1973) 326.
196 E. Öhler, K. Reininger and U. Schmidt, Angew. Chem. Int. Ed. Engl., 9 (1970) 457.
197 A. Löffler and A.S. Dreiding, Chimia, 23 (1969) 413.
198 F. Barbot, Thesis 3me cycle, Poitiers, 1972.
199 A. Stefani and P. Pino, Helv. Chim. Acta, 55 (1972) 1110.
200 E.J. Lanpher, J. Amer. Chem. Soc., 79 (1957) 5578.
201 J.G. Berger, E.L. Strogryn and A.A. Zimmerman, J. Org. Chem., 29 (1964) 950.
202 R.L. Letzinger and J.G. Traynam, J. Amer. Chem. Soc., 72 (1950) 849.
203 R. Paul and S. Tchelitcheff, Bull. Soc. Chim. Fr., (1948) 108.
204 W.S. Murphy, R. Boyce and E.A. O'Riordan, Tetrahedron Letters, (1971) 4157.
205 R.S. Taylor and R. Connor, J. Org. Chem., 6 (1941) 696.
206 L.H. Sommer and W.D. Korte, J. Org. Chem., 35 (1970) 22.
207 R.B. Bates, D.W. Gosselink and J.A. Kaczynski, Tetrahedron Letters, (1967) 199, 205.
208 C.S. Johnson, M.A. Weiner, J.S. Waugh and D. Seyferth, J. Amer. Chem. Soc., 83 (1961) 1306.
209 G. Brieger and D.W. Anderson, Chem. Commun., (1970) 1325.
210 R.M. Magid and S.E. Wilson, Tetrahedron Letters, (1971) 19.
211 K. Suga and S. Watanabe, Synthesis, (1971) 91.
212 R.H. Bates, S. Brenner and C.M. Cole, J. Amer. Chem. Soc., 94 (1972) 2130.
213 W.H. Glaze, J.E. Hanicak, M.L. Moore and J. Chaudhuri, J. Organometal. Chem., 44 (1972) 39, 49.
214 R. Waack and M.A. Doran, J. Amer. Chem. Soc., 85 (1963) 1651.
215 J.F. Biellmann and J.B. Ducep, Tetrahedron Letters, (1968) 5629.
216 W.H. Glaze and P.C. Jones, Chem. Commun., (1969) 1434.
217 M. Julia, F. Le Goffic and L. de Matos, C.R. Acad. Sci. Paris, Ser. C, 270 (1970) 838, 954.
218 J.W. Burley and R.N. Young, Chem. Commun., (1970) 991, J. Chem. Soc., C, (1971) 3780.
219 J.W. Burley, R. Ife and R.N. Young, Chem. Commun., (1970) 1256.
220 E.J. Corey, B.W. Erickson and R. Noyori, J. Amer. Chem. Soc., 93 (1971) 1724.
221 R.J. Crawford, J. Org. Chem., 37 (1972) 3543.
222 L.A. Paquette, S.E. Wilson and R.P. Henzel, J. Amer. Chem. Soc., 93 (1972) 7771.
223 R.J. Crawford, W.F. Erman and C.D. Broaddus, J. Amer. Chem. Soc., 94 (1972) 4298.
224 G.L. Hodgson, D.F. MacSweeney and T. Money, Tetrahedron Letters, (1972) 3683.
225 E. Dunkelblum and C. Brenner, Tetrahedron Letters, (1973) 669.
226 F. Bernadou, B. Mauzé and L. Miginiac, C.R. Acad. Sci. Paris, Ser. C, 276 (1973) 1645.
227 H.R. Henze, B.B. Allen and W.B. Leslie, J. Amer. Chem. Soc., 65 (1943) 87.
228 B.B. Allen and H.R. Henze, J. Amer. Chem. Soc., 61 (1939) 1790; H.R. Henze and T.R. Thompson, J. Amer. Chem. Soc., 65 (1943) 1422.
229 R. Boyce, W.S. Murphy and K.P. Klein, J. Chem. Soc. Perkin I, (1972) 1292.
230 W.H. Glaze, J.E. Hanicak, J. Chaudhuri, M.L. Moore and D.P. Duncan, J. Organometal. Chem., 51 (1973) 13.
231 W.H. Glaze and C.R. Daniel, J. Organometal. Chem., 51 (1973) 23.
232 R.Y. Mixer and W.G. Young, J. Amer. Chem. Soc., 78 (1956) 3379.
233 A. Maercker and R. Geuss, Chem. Ber., 106 (1973) 795.
234 G. Peiffer and H. Driguez, C.R. Acad. Sci. Paris, Ser. C, 267 (1968) 773.
235 D.T. Hurd and G.F. Roedel, Ind. Eng. Chem., 40 (1948) 2078.
236 P. Mazerolles and M. Lesbre, C.R. Acad. Sci. Paris, Ser. C, 248 (1959) 2018.
237 K.V. Vijayaraghavan, J. Indian Chem. Soc., 22 (1945) 135, 141, 227.

238 M.M. Koton and T.M. Kiseleva, Obshch. Khim., 27 (1957) 2553.
239 W.J. Jones, W.C. Davies, S.T. Bowden, C. Edwards, V.E. Davis and L.H. Thomas, J. Chem. Soc., (1947) 1446.
240 A.E. Borisov, N.V. Novikova and A.N. Nesmeyanov, Izv. Akad. Nauk SSSR Ser. Khim., (1963) 1506.
241 M. Dub, Organometallic compounds, 2nd ed., Springer-Verlag, Vol. II and III, 1967-1968.
242 H. Gilman and J.J. Eisch, J. Org. Chem., 20 (1955) 763.
243 W.T. Schwartz and H.W. Post, J. Organometal. Chem., 2 (1964) 357.
244 E.O. Fischer, H.P. Hofman and A. Frieber, Z. Naturforsch., B, 14 (1959) 599.
245 Brit. Patent 768.083 Feb. (1957) 13; Chem. Abstr., 51 (1957) 15584d.
246 R.H. Dewolfe, D.E. Johnson, R.I. Wagner and W.G. Young, J. Amer. Chem. Soc., 79 (1957) 4798.
247 T.W. Campbell and W.G. Young, J. Amer. Chem. Soc., 69 (1947) 3066.
248 W.H. Glaze, D.J. Berry and D.P. Duncan, J. Organometal. Chem., 52 (1973) 233.
249 M. Schlosser and J. Hartmann, Angew. Chem. Int. Ed. Engl., 12 (1973) 508.
250 A.L. Henne and W.G. Finnegan, J. Amer. Chem. Soc., 71 (1949) 296.
251 W. Kitching, M.L. Bullpitt, P.D. Sleezer, S. Winstein and W.G. Young, J. Organometal. Chem., 34 (1974) 233.
252 K.H. Thiele, G. Engelhardt, J. Köhler and M. Arnstedt, J. Organometal. Chem., 9 (1967) 385.