

THE SYNTHETIC POSSIBILITIES OF ADDITION REACTIONS BETWEEN
COMMON ORGANOMETALLIC COMPOUNDS AND CONJUGATED ENYNES

Léone MIGINIAC

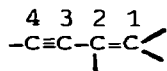
Laboratoire de Synthèse Organique, Groupe de Recherches de
Chimie Organique, Université de Poitiers, 86022 - POITIERS (France)

CONTENTS

Introduction	236
Usual methods of preparation of conjugated enynes	236
1) Hydrocarbons	236
2) α -functional conjugated enynes	238
3) α, α' -difunctional conjugated enynes	240
Addition reactions	242
<u>First part</u> - Conjugated enynes with an internal triple bond	242
A - Addition involving the 1,3-butadiene system	242
1) Hydrocarbons	242
2) α -functional enynes	244
3) α, α' -difunctional enynes	246
B - Addition involving the 1,3-butadiene system and substitution	247
1) α -functional enynes	247
2) α, α' -difunctional enynes	247
C - Addition to the triple bond	248
1) Enynes $R''''-C\equiv C-C(R')=C(R'')(R''')$	248
2) Enynes $(R'')(R''')C=C(R')-C\equiv C-C(R'''')_2-Y$	249
3) Enynes $HOCH_2-C\equiv C-CH=CH-CH_2-NR_2^t$	249
D - Addition to the triple bond and substitution	250
<u>Second Part</u> - Conjugated enynes with a terminal triple bond	251
A - Addition involving the 1,3-butadiene system	251
1) Hydrocarbons	251
2) α -functional enynes	253
B - Addition involving the 1,3-butadiene system and substitution	254
C - Addition to the triple bond	256
1) Hydrocarbons	256
2) α -functional enynes	259
D - Addition to the triple bond and substitution	260
E - Bis-addition to the triple bond and 1,3-elimination	262
Conclusion	262
Acknowledgements	263
References	263

INTRODUCTION

Conjugated enynes possess two orthogonal π -systems [1,2] :



- a 1,3-butadiene system on C(1), C(2), C(3) and C(4),

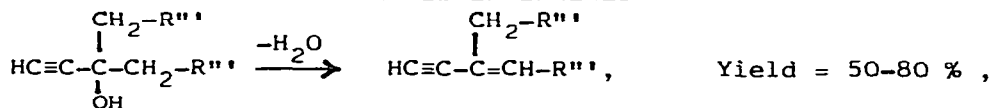
- a π -bond on C(3), C(4).

Varied organometallic derivatives R-M add easily to these compounds. In most cases, even when an excess of organometallic compound is used, a single addition is observed, either on the conjugated system or on the triple bond. In some cases, a bis-addition involving only the triple bond appears. At last, this addition may be accompanied by other reactions : substitution or elimination reactions.

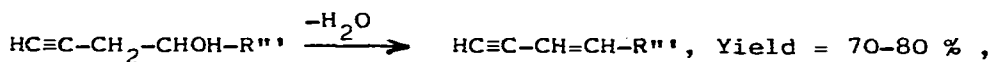
USUAL METHODS OF PREPARATION OF CONJUGATED ENYNES

1) Hydrocarbons : Five main methods may be used [1-9] :

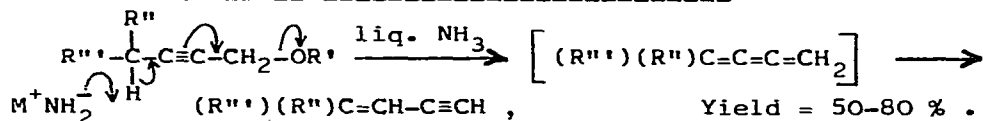
a) Dehydration of α -acetylenic alcohols :



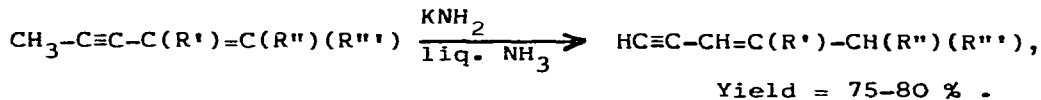
b) Dehydration of β -acetylenic alcohols :



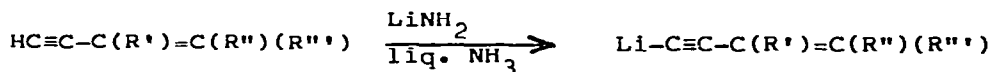
c) 1,4-elimination from an α -acetylenic ether :

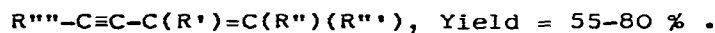
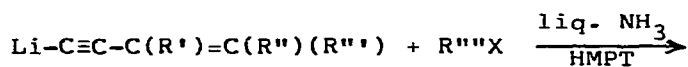


d) Prototropic rearrangement :



e) Alkylation of HC \equiv C group of a conjugated enyne :





A number of results are gathered together in Table 1.

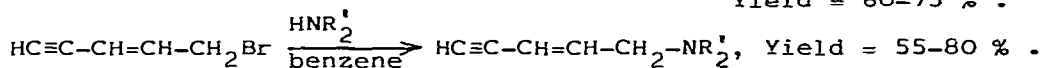
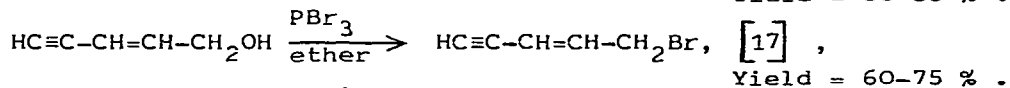
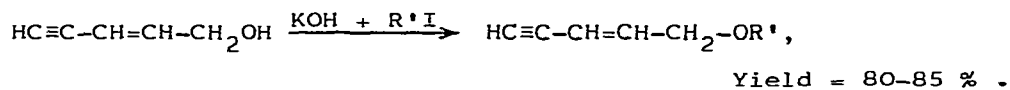
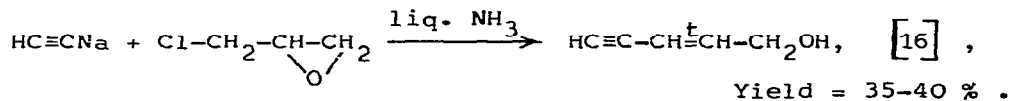
Table 1

Preparation of enynes : $R''''\text{-C}\equiv\text{C-C(R}')=\text{C(R'')}(R''')$

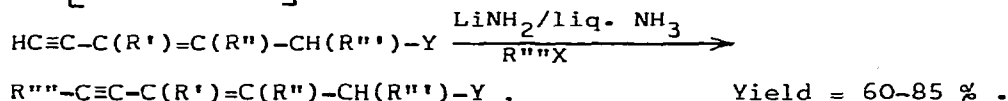
R''''	R'	R''	R'''	Method	Yield %
H [3]	CH ₃	H	H	a	62
H [2]	C ₂ H ₅	H	CH ₃	a	65
H [6]	CH(CH ₃) ₂	CH ₃	CH ₃	a	50
H [6]		(CH ₂) ₄	H	a	80
H [6]	H	H	C ₆ H ₅	b	70
H [2]	H	H	CH ₃	c	50
H [2]	H	H	nC ₄ H ₉	c	55
H [6]	H	C ₂ H ₅	C ₂ H ₅	c	80
H [6]	H	H	OC ₂ H ₅	c	70
H [6]	H	H	N(CH ₃) ₂	c	70
H [6]	H	(CH ₂) ₅		d	80
CH ₃ [7]	CH ₃	H	H	e	55
C ₂ H ₅ [7]	CH ₃	H	H	e	60
nC ₃ H ₇ [7]	CH ₃	H	H	e	65
nC ₄ H ₉ [7]	CH ₃	H	H	e	68
nC ₅ H ₁₁ [7]	CH ₃	H	H	e	70
CH ₃ [2]	C ₂ H ₅	H	CH ₃	e	55
CH ₃ [2]	CH(CH ₃) ₂	CH ₃	CH ₃	e	75
CH ₃ [3]		(CH ₂) ₄	H	e	94
CH ₃ [2]	H	H	nC ₄ H ₉	e	80
CH ₃ [2]	H	C ₂ H ₅	C ₂ H ₅	e	75

2) α -functional conjugated enynes : Three ways are generally used :

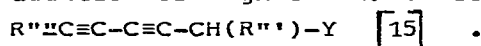
f) Preparation of an enynol and transformation of OH group into another functional group [1, 3-5, 10-15] , for instance :



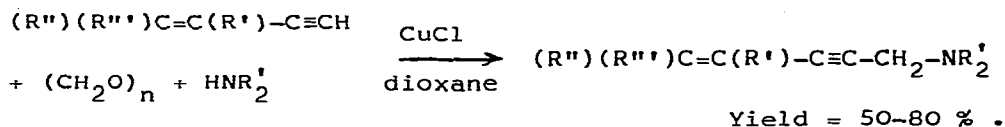
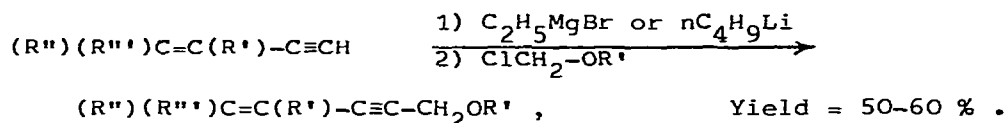
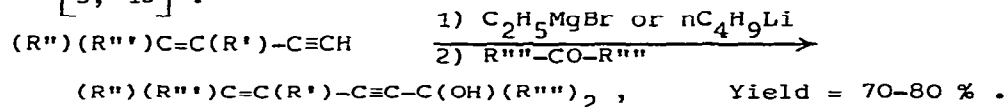
g) Alkylation of HC≡C group of an α -functional enyne [1, 3-5, 11-15] :



Remark : These α -functional enynes may be obtained also by addition of RMgX or RLi to conjugated diynes



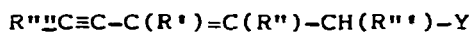
h) Functionalisation of the HC≡C group of a conjugated enyne [3, 15] :



Several results are collected in Tables 2 and 3.

Remark : Alcohols of type : $(\text{R}'')(\text{R}''')\text{C}=\text{C}(\text{R}')-\text{C}\equiv\text{C}-\text{CH}_2\text{OH}$ have been recently prepared by reaction between vinylcopper (I) reagents and 1-bromo 3-trimethylsiloxy prop 1-yne [18] .

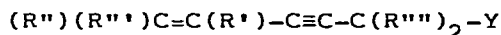
Table 2

Preparation of α -functional enynes :

R'''	R'	R''	R'''	Y	Pathway	Yield %
H [16]	H	H	H	OH	f	35
H [16]	H	H	CH ₃	OH	f	45*
H [17]	H	H	H	Br	f	60
H [5]	H	H	H	OC ₄ H ₉	f	60
H [5]	H	H	H	NH-C ₂ H ₅	f	65
H [5]	H	H	H	N(C ₂ H ₅) ₂	f	75
H [11]	H	CH ₃	H	OH	f	80
H [11]	H	CH ₃	H	Br	f	65
H [11]	H	CH ₃	H	OC ₄ H ₉	f	68
H [11]	H	CH ₃	H	NH-C ₂ H ₅	f	68
H [11]	H	CH ₃	H	N(C ₂ H ₅) ₂	f	84
H [11]	CH ₃	H	H	OH	f	60
H [11]	CH ₃	H	H	Br	f	78
H [11]	CH ₃	H	H	OC ₄ H ₉	f	52
H [11]	CH ₃	H	H	NH-C ₂ H ₅	f	45
H [11]	CH ₃	H	H	N(C ₂ H ₅) ₂	f	83
CH ₃ [5]	H	H	H	OH	g	75
CH ₃ [5]	H	H	H	Br	g	72
CH ₃ [5]	H	H	H	OC ₄ H ₉	g	85
CH ₃ [5]	H	H	H	NH-C ₂ H ₅	g	60
CH ₃ [5]	H	H	H	N(C ₂ H ₅) ₂	g	80
nC ₄ H ₉ [15]	H	H	H	OH	g	70
nC ₄ H ₉ [15]	H	H	H	Br	g	50
nC ₄ H ₉ [15]	H	H	H	N(CH ₃) ₂	g	80

* this alcohol has been obtained also by isomerisation in acidic medium of HC≡C-CHOH-CH=CH-CH₃, Yield = 85 % [14] .

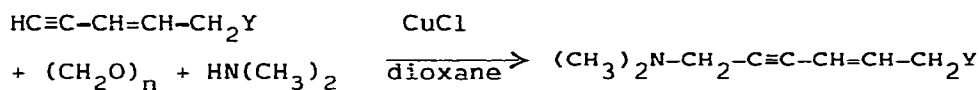
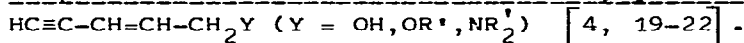
Table 3

Preparation of α -functional enynes :

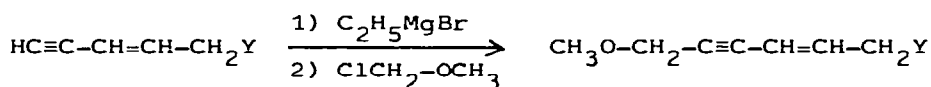
R''	R'''	R'	R''''	Y	Pathway	Yield %
H	[3]	H	H	OH	h	60
H	[3]	H	CH ₃	OH	h	80
H	[3]	CH ₃	H	OH	h	74
H	[15]	nC ₄ H ₉	H	OH	h	77
H	[15]	nC ₄ H ₉	CH ₃	OH	h	80
H	[3]	CH ₃	H	OC ₂ H ₅	h	79
H	[3]	H	CH ₃	OC ₂ H ₅	h	82
H	[15]	nC ₄ H ₉	H	OCH ₃	h	72
H	[3]	H	H	N(C ₂ H ₅) ₂	h	95
H	[3]	C ₂ H ₅	H	N(C ₂ H ₅) ₂	h	90
H	[15]	nC ₄ H ₉	H	N(CH ₃) ₂	h	83

3) α, α' -difunctional conjugated enynes

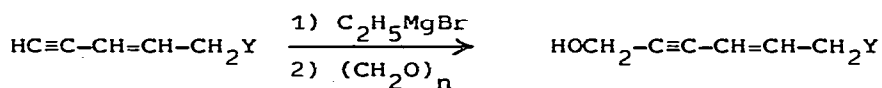
Two ways can be used :

i) Preparation from an α -functional conjugated enyne

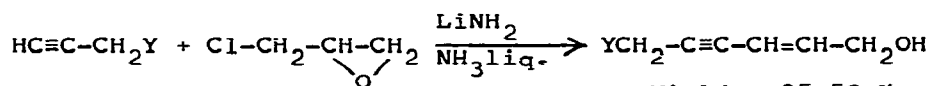
Yield = 50-76 % .



Yield = 50-60 % .

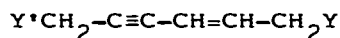


Yield = 20-40 % .

j) Preparation from epichlorhydrin and $HC\equiv C-CH_2Y$ [20-23]

Yield = 35-50 % .

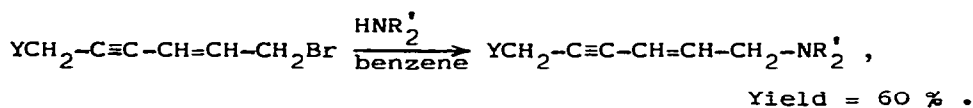
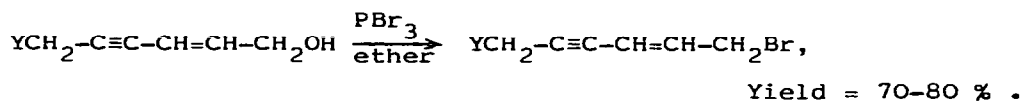
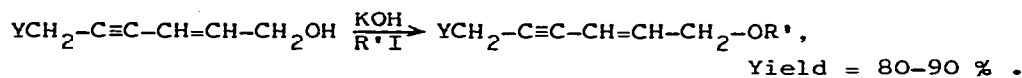
Table 4

Preparation of α, α' -difunctional enynes :

	Y'	Y	Pathway	Yield %
$N(CH_3)_2$	[20]	OH	i	20
$N(CH_3)_2$	[23]	OH	j	40
$N(C_2H_5)_2$	[19]	OH	i	76
$N(CH_3)_2$	[20]	Br	j	70
$N(CH_3)_2$	[20]	OCH_3	i	60
$N(CH_3)_2$	[20]	OCH_3	j	80
$N(CH_3)_2$	[20]	$N(CH_3)_2$	i	50
$N(CH_3)_2$	[20]	$N(CH_3)_2$	j	60
OCH_3	[21]	OH	i	50
OCH_3	[23]	OH	j	50
OCH_3	[23]	Br	j	80
OCH_3	[21]	OCH_3	i	60
OCH_3	[23]	OCH_3	j	86
OCH_3	[21]	$N(CH_3)_2$	i	20
OCH_3	[23]	$N(CH_3)_2$	j	60
OH	[19, 22]	OH	i	10-30*
OH	[23]	OH	j	35
OH	[22]	OCH_3	i	40
OH	[22]	$N(CH_3)_2$	i	30

* impure product

Then, the alcohol group can be transformed into an ether, a bromide or an amine group :



The main results appear in Table 4 .

ADDITION REACTIONS OF ORGANOMETALLIC DERIVATIVES

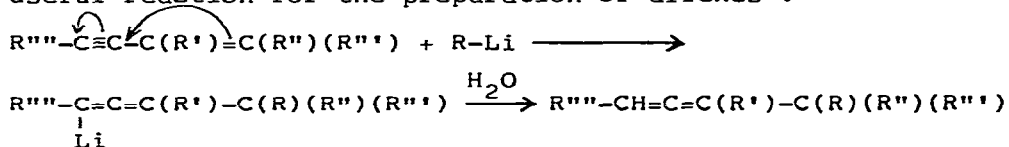
The results reported here mainly concern common organometallic derivatives such as organolithium, organomagnesium and organozinc compounds. Often, the experiments have been run with a large excess of organometallic derivative to allow for all the possibilities of addition and of the mobile hydrogen atoms, as the case may be.

First Part - Conjugated enynes with an internal triple bondA - Addition involving the 1,3-butadiene system1) Hydrocarbons - Synthesis of allenes

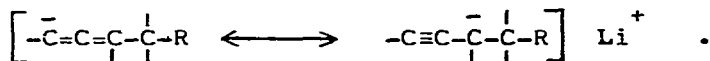
With hydrocarbons, the only reaction observed is an 1,4-addition to the 1,3-butadiene system :



The addition of organolithium compounds to enynes is a useful reaction for the preparation of allenes :



The adducts are formed in good yields (see Table 5), when R = alkyl [1, 5, 9, 24, 25], allyl [5, 9], benzyl [1, 24, 26] and phenyl [1, 24, 27]. On hydrolysis, they produce only allenic hydrocarbons; the absence of any acetylenic product from the reaction is noteworthy, inasmuch as the addition product is an organometallic compound which may well be represented by the resonance-stabilized anion :



Remark : These allenic organolithiums are very useful in synthesis [24, 28]. In various further reactions, the allenic structure is preserved : upon reaction with various aliphatic, aromatic, α -ethylenic, α -acetylenic aldehydes and ketones, they produce in good yields the expected α -allenic alcohols and with epoxides they give β -allenic alcohols ; but oxidation leads to the predominant formation of acetylenic alcohols [24, 28].

Table 5
 Synthesis of allenes $R''\text{CH}=\text{C}=\text{C}(R')-\text{C}(R'')(R''')(R)$

RM		R'''	R'	R''	R'''	Yield %
$\text{CH}_2=\text{CH}-\text{CH}_2\text{MgBr}$	[9]	CH_3	H	H	$n\text{C}_4\text{H}_9$	10
$\text{CH}_3\text{CH}=\text{CH}-\text{CH}_2\text{MgBr}$	[9]	CH_3	H	H	$n\text{C}_4\text{H}_9$	45
$\text{CH}_2=\text{CH}-\text{CH}_2\text{Li}$	[9]	CH_3	H	H	$n\text{C}_4\text{H}_9$	60
$\text{C}_2\text{H}_5\text{CH}=\text{CH}-\text{CH}_2\text{Li}$	[9]	CH_3	H	H	$n\text{C}_4\text{H}_9$	56
$n\text{C}_4\text{H}_9\text{Li}$	[25]	C_2H_5	H	H	H	30-50
$(\text{CH}_3)_2\text{CH}-\text{CH}_2\text{Li}$	[25]	C_2H_5	H	H	H	30-50
$(\text{CH}_3)_3\text{CLi}$	[25]	C_2H_5	H	H	H	30-50
$\text{C}_6\text{H}_5-\text{CH}_2\text{Li}$	[26]	CH_3	H	H	H	30-50
$\text{C}_6\text{H}_5-\text{CH}_2\text{Li}$	[26]	C_2H_5	H	H	H	30-50
$p\text{-CH}_3-\text{C}_6\text{H}_4\text{Li}$	[27]	C_2H_5	H	H	H	30
$o\text{-CH}_3-\text{C}_6\text{H}_4\text{Li}$	[27]	C_2H_5	H	H	H	30
$p\text{-CH}_3\text{O}-\text{C}_6\text{H}_4\text{Li}$	[27]	C_2H_5	H	H	H	30
$\text{C}_2\text{H}_5\text{CaI}$	[31]	C_2H_5	H	H	H	20-25
$\text{C}_6\text{H}_5\text{CaI}$	[31]	C_2H_5	H	H	H	20-25
$n\text{C}_4\text{H}_9\text{CaI}$	[31]	$\text{CH}=\text{CH}-\text{CH}_3$	H	H	H	25
$(\text{C}_2\text{H}_5)_2\text{Ca}$	[31]	CH_3	H	H	H	25-30
$(\text{C}_2\text{H}_5)_2\text{Ca}$	[31]	C_6H_5	H	H	H	25-30
$(\text{C}_2\text{H}_5)_2\text{Ca}$	[31]	$\text{CH}=\text{CH}_2$	H	H	H	25-30
$(\text{C}_2\text{H}_5)_2\text{Sr}$	[32]	CH_3	H	H	H	40-50
$(\text{C}_2\text{H}_5)_2\text{Sr}$	[32]	C_2H_5	H	H	H	40-50
$(\text{C}_2\text{H}_5)_2\text{Sr}$	[32]	$n\text{C}_3\text{H}_7$	H	H	H	40-50
$(\text{C}_2\text{H}_5)_2\text{Ba}$	[33]	CH_3	H	H	H	45
$(\text{C}_2\text{H}_5)_2\text{Ba}$	[33]	$n\text{C}_4\text{H}_9$	H	H	H	45
$(\text{C}_2\text{H}_5)_2\text{Ba}$	[33]	$(\text{CH}_3)_3\text{C}$	H	H	H	45
$(\text{C}_2\text{H}_5)_2\text{Ba}$	[33]	CH_3S	H	H	H	35-40

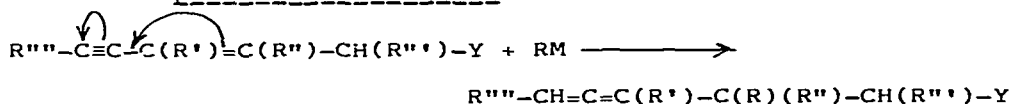
The same results are observed with allylic organomagnesium compounds [5, 9]; when R is a substituted allyl group, the reaction takes place with complete allylic rearrangement, as it is general in addition reactions of organometallic derivatives to unsaturated C-C bonds [29]. Under the usual conditions, Grignard reagents, when R is a saturated group or

benzyl group do not react [13, 30] ; the same result is observed with organozinc compounds (R = alkyl, allyl) [5, 12] .

In the other hand, organometallic compounds such as calcium, strontium and barium derivatives (R = alkyl, phenyl) do lead to allenes [31-33] .

2) α -functional enynes

a) Enynes $R'''-C\equiv C-C(R')=C(R'')-CH(R''')-Y$ - Synthesis of β -functional allenes

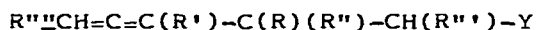


Organolithium compounds where R = alkyl or allyl [5, 15] lead to β -functional allenes (Y = OH, OR', NH-R', NR'₂) in good yields (see Table 6). It is to remark that the reaction of LiAlH₄ with these enynes lead to β -functional allenes also [24].

The same results are observed with allylic organomagnesium derivatives [5, 15] , but alkyl- and benzyl-organomagnesium compounds [13] , allyl- and alkyl-organozinc compounds [5, 12, 14, 15] do not react.

Table 6

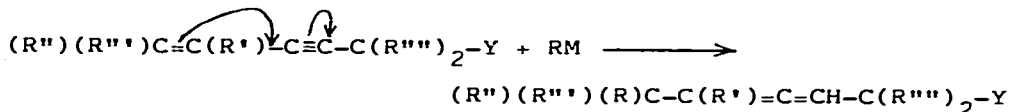
Synthesis of β -functional allenes



R-M		R'''	R'	R''	R'''	Y	Yield %
CH ₂ =CH-CH ₂ Li	[5]	CH ₃	H	H	H	OH	17
nC ₄ H ₉ Li	[5]	CH ₃	H	H	H	OH	10
CH ₂ =CH-CH ₂ MgBr	[5]	CH ₃	H	H	H	OH	45
CH ₂ =CH-CH ₂ Li	[5]	CH ₃	H	H	H	OC ₄ H ₉	77
nC ₄ H ₉ Li	[5]	CH ₃	H	H	H	OC ₄ H ₉	25
CH ₂ =CH-CH ₂ MgBr	[5]	CH ₃	H	H	H	OC ₄ H ₉	55
CH ₂ =CH-CH ₂ MgBr	[5]	CH ₃	H	H	H	NH-C ₂ H ₅	47
CH ₂ =CH-CH ₂ Li	[15]	nC ₄ H ₉	H	H	H	OH	24
nC ₄ H ₉ Li	[15]	nC ₄ H ₉	H	H	H	OH	25
CH ₂ =CH-CH ₂ MgBr	[15]	nC ₄ H ₉	H	H	H	OH	57
CH ₂ =CH-CH ₂ Li	[15]	nC ₄ H ₉	H	H	H	N(CH ₃) ₂	30
nC ₄ H ₉ Li	[15]	nC ₄ H ₉	H	H	H	N(CH ₃) ₂	20
CH ₂ =CH-CH ₂ MgBr	[15]	nC ₄ H ₉	H	H	H	N(CH ₃) ₂	15

b) Enynes (R'')(R''')C=C(R')-C≡C-C(R''')₂-Y - Synthesis of α-functional allenes

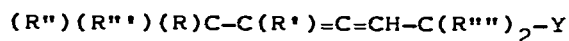
With these enynes, 1,4-addition to the conjugated system leads to α-functional allenes :



This type of addition is obtained with alkyl-lithium, calcium and barium derivatives [24, 28, 34-37]. The same result is observed with allyl-lithium, when Y is a tertiary alcohol group or a tertiary amino group [15] (see Table 7).

Table 7

Synthesis of α-functional allenes :

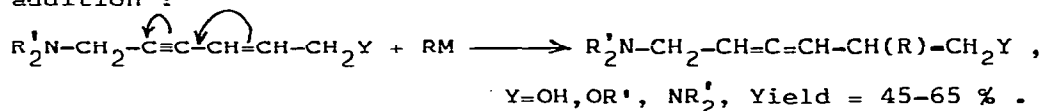


RM		R''	R'''	R'	R''''	Y	Yield %
CH ₂ =CH-CH ₂ Li	[15]	H	nC ₄ H ₉	H	CH ₃	OH	60
nC ₄ H ₉ Li	[15]	H	nC ₄ H ₉	H	CH ₃	OH	80
CH ₂ =CH-CH ₂ Li	[15]	H	nC ₄ H ₉	H	H	OH	20*
nC ₄ H ₉ Li	[15]	H	nC ₄ H ₉	H	H	OH	50*
CH ₂ =CH-CH ₂ Li	[15]	H	nC ₄ H ₉	H	H	N(CH ₃) ₂	60
nC ₄ H ₉ Li	[15]	H	nC ₄ H ₉	H	H	N(CH ₃) ₂	20
C ₂ H ₅ Li	[34]	H	H	H	CH ₃	OH	75
(CH ₃) ₂ CHLi	[34]	H	H	H	CH ₃	OH	70
(CH ₃) ₂ CH-CH ₂ Li	[34]	H	H	H	CH ₃	OH	70
nC ₅ H ₁₁ Li	[34]	H	H	H	CH ₃	OH	75
C ₂ H ₅ Li	[35]	H	H	H	H	N(C ₂ H ₅) ₂	80
(CH ₃) ₂ CHLi	[35]	H	H	H	H	N(C ₂ H ₅) ₂	80
C ₂ H ₅ CaI	[35]	H	H	H	H	N(C ₂ H ₅) ₂	25-30
(CH ₃) ₂ CHCaI	[35]	H	H	H	H	N(C ₂ H ₅) ₂	25-30
C ₂ H ₅ CaI	[36]	H	H	H	CH ₃	OH	25-30
C ₆ H ₅ CaI	[36]	H	H	H	CH ₃	OH	25-30
(C ₂ H ₅) ₂ Ba	[37]	H	H	H	H	N(CH ₃) ₂	30-50
(C ₂ H ₅) ₂ Ba	[37]	H	H	H	H	N(C ₂ H ₅) ₂	30-50

* 50/50 mixture with the conjugated diene resulting from addition on the triple bond.

3) α, α' -difunctional enynesa) Enynes $R_2^1N-CH_2-C\equiv C-CH=CH-CH_2Y$ - Synthesis of α -allenic δ -functional amines

When the functional group next to the triple bond is an amino group, the corresponding enynes give only the 1,4-addition :

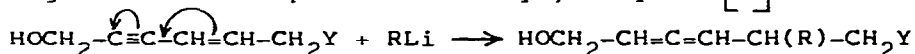


Alkyl and allyl-lithium derivatives react in this manner in good yields [20] ; alkyl- and allyl-magnesium compounds lead to the same result and when R is a substituted allyl group, the reaction proceeds with complete allylic rearrangement. Allyl-zinc compounds do not react, even on heating for a long time.

This is a very convenient method for preparing α, β' -difunctional allenes. Several results are collected in Table 8.

b) Enynes $HOCH_2-C\equiv C-CH=CH-CH_2Y$ - Synthesis of α -allenic δ -functional alcohols

Analogous results were obtained with α, α' -difunctional conjugated enynes which possess one OH group next to the triple bond (see Table 8), but only in the case of reactions with organolithium compounds (R= alkyl, allyl) [22] :



Yield = 40-65 % .

Table 8

Synthesis of α, β' -difunctional allenes $Y^1CH_2-CH=C=CH-CH(R)-CH_2Y$

RM		Y'	Y = OH Yield %	Y = OCH ₃ ³ Yield % ³	Y = N(CH ₃) ₂ ² Yield % ²
CH ₂ =CH-CH ₂ Li	[20]	N(CH ₃) ₂	25*	45	25
C ₄ H ₉ Li	[20]	N(CH ₃) ₂	30	47	20
CH ₃ CH=CH-CH ₂ Li	[20]	N(CH ₃) ₂	45*	70	45
CH ₂ =CH-CH ₂ MgBr	[20]	N(CH ₃) ₂	50*	64	45
C ₄ H ₉ MgBr	[20]	N(CH ₃) ₂	15	18	15
CH ₃ CH=CH-CH ₂ MgBr	[20]	N(CH ₃) ₂	63*	85	50
CH ₂ =CH-CH ₂ Li	[22]	OH	10	59**	30**
C ₄ H ₉ Li	[22]	OH	-	25**	-
CH ₃ CH=CH-CH ₂ Li	[22]	OH	-	65	55

*10-25% of vinylallenic amine resulting from an 1,2-elimination is also obtained. ** 5-10% of allene resulting from an 1,4-addition and a substitution of the OH group is also formed.

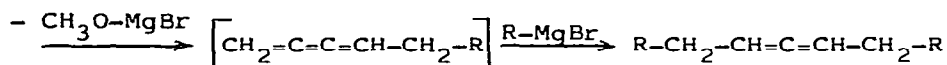
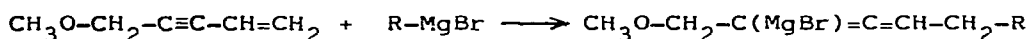
B - Addition involving the 1,3-butadiene system and substitution

The 1,4-addition can be accompanied by a substitution reaction of a good leaving group, when this group is located in the α -position to the triple bond.

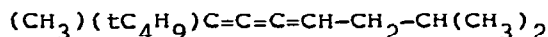
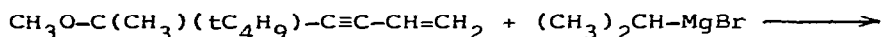
This behaviour has been noted with α -functional and with α,α' -difunctional enynes, particularly when they possess an alkoxy group.

1) α -functional enynes $R'''-CH=CH-C\equiv C-C(R'''')_2-Y$ $Y=Cl, OR'$

This type of reaction may be observed among other reactions, when Grignard reagents $R-MgBr$ are allowed to react with such enynes [38] :



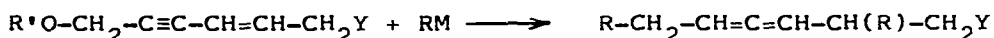
This mechanism is proved by the fact that the cumulene can be obtained when the structure shows steric hindrance, for instance :



Analogous results are observed with alkyl-lithium and allyl-magnesium compounds [15] .

2) α,α' -difunctional enynes

a) Enynes $R'OCH_2-C\equiv C-CH=CH-CH_2Y$ - Synthesis of β -functional allenes



Alkyl and allyl-lithium compounds react in this manner with good yields (see Table 9) ; alkyl- and allyl-magnesium compounds lead to the same result and, when R is a substituted allyl group, the reaction proceeds with complete allylic rearrangement [21]. Allyl-zinc compounds do not react, even on heating for a long time.

Table 9

Synthesis of β -functional allenes $R-CH_2-CH=C=CH-CH(R)-CH_2Y$ from $Y'CH_2-C\equiv C-CH=CH-CH_2Y$

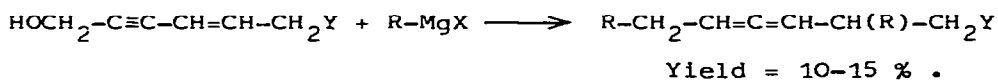
RM	Y'	Y = OH Yield %	Y = OCH ₃ Yield %	Y = N(CH ₃) ₂ Yield %	
CH ₂ =CH-CH ₂ Li	[21]	OCH ₃	25	36	30
C ₄ H ₉ Li	[21]	OCH ₃	20	30	-
CH ₃ CH=CH-CH ₂ Li	[21]	OCH ₃	20	45	10
CH ₂ =CH-CH ₂ MgBr	[21]	OCH ₃	50	60	42
C ₄ H ₉ MgBr	[21]	OCH ₃	-	10	-
CH ₃ CH=CH-CH ₂ MgBr	[21]	OCH ₃	55	65	50
CH ₂ =CH-CH ₂ MgBr	[22]	OH	10*	12*	5*
CH ₃ CH=CH-CH ₂ MgBr	[22]	OH	10*	15*	5*

* in these cases, 30-45 % of dienic products is also formed (see Table 11).

Probably, the mechanism involves a 1,4-addition, then a 1,2-elimination to give a cumulene and, finally, another addition of R-M [21, 38].

b) Enynes HOCH₂-C≡C-CH=CH-CH₂Y

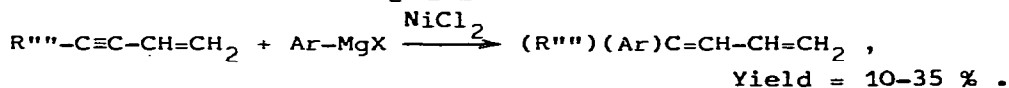
The same behaviour is noted for a minor part (see Table 9) of the reaction between allyl-magnesium derivatives and α, α' -difunctional enynes which possess one group OH next to the triple bond [22]:



C - Addition to the triple bond

1) Enynes R'''-C≡C-C(R')=C(R'')(R''') - Synthesis of conjugated dienes

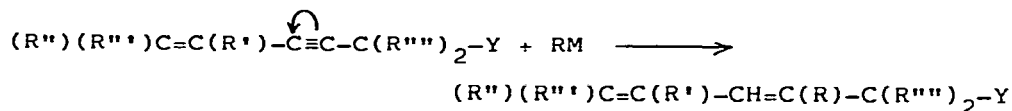
Under the usual conditions, Grignard reagents do not react [30], but addition to the triple bond may be observed in the presence of NiCl₂ [39]:



Yet, under similar conditions, alkylmagnesium halides lead to the polymerisation of conjugated enynes [39].

2) Enynes (R'')(R''')C=C(R')-C≡C-C(R''')₂-Y - Synthesis of α-functional conjugated dienes

With allyl-magnesium derivatives [15] and organocuprates (R)₂CuMgBr [40], a single addition on the triple bond is observed, leading to α-functional conjugated dienes:

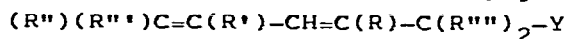


This addition is observed also when LiAlH₄ is allowed to react with these enynes [24]. In individual cases, organozinc compounds (R = allyl) and organolithium compounds (R = alkyl, allyl) can lead to analogous results (see Table 10).

With organomagnesium compounds, this reaction proceeds by trans-addition [15], whereas with organocuprates both cis- and trans-addition occur [40].

Table 10

Synthesis of α-functional conjugated dienes

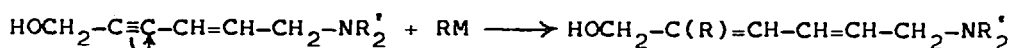


RM		R''	R'''	R'	R''''	Y	Yield %
CH ₂ =CH-CH ₂ MgBr	[15]	H	nC ₄ H ₉	H	H	OH	40
CH ₂ =CH-CH ₂ ZnBr	[15]	H	nC ₄ H ₉	H	H	OH	5
CH ₂ =CH-CH ₂ MgBr	[15]	H	nC ₄ H ₉	H	H	N(CH ₃) ₂	25
(C ₄ H ₉) ₂ CuMgCl	[40]	H	H	H	H	OC ₂ H ₅	60
CH ₂ =CH-CH ₂ Li	[15]	H	nC ₄ H ₉	H	H	OH	20*
C ₄ H ₉ Li	[15]	H	nC ₄ H ₉	H	H	OH	50*

* 50/50 mixture with allene resulting from an 1,4-addition on butadiene system.

3) Enynes HOCH₂-C≡C-CH=CH-CH₂-NR'₂ - Synthesis of α,α'-difunctional dienes

4 3 2 1



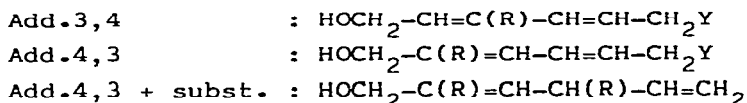
This 4,3-addition has been observed with allyl-magnesium compounds, concurrently with 1,4-addition to the conjugated system and substitution [22]; with allyl-zinc derivatives, it is the only reaction obtained, but the group R often adds on either side of the triple bond (see Table 11).

Table 11

Various products resulting from addition on the triple bond of $\text{HOCH}_2\text{-C}\equiv\text{C-CH=CH-CH}_2\text{Y}$ [22]

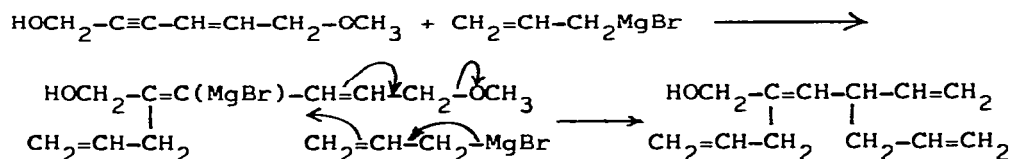
RM	Y	Add. 3,4	Add. 4,3	Add. 4,3 + subst.
$\text{CH}_2=\text{CH-CH}_2\text{MgBr}$	$\text{N(CH}_3)_2$	0	37*	0
$\text{CH}_3\text{-CH=CH-CH}_2\text{MgBr}$	$\text{N(CH}_3)_2$	0	45*	0
$\text{CH}_2=\text{CH-CH}_2\text{ZnBr}$	$\text{N(CH}_3)_2$	5	45	0
$\text{CH}_3\text{-CH=CH-CH}_2\text{ZnBr}$	$\text{N(CH}_3)_2$	0	35	0
$\text{CH}_2=\text{CH-CH}_2\text{MgBr}$	OH	0	0	30*
$\text{CH}_3\text{-CH=CH-CH}_2\text{MgBr}$	OH	0	0	35*
$\text{CH}_2=\text{CH-CH}_2\text{ZnBr}$	OH	0	0	20
$\text{CH}_3\text{-CH=CH-CH}_2\text{ZnBr}$	OH	0	0	30
$\text{CH}_2=\text{CH-CH}_2\text{MgBr}$	OCH_3	0	0	30*
$\text{CH}_3\text{-CH=CH-CH}_2\text{MgBr}$	OCH_3	0	0	40*
$\text{CH}_2=\text{CH-CH}_2\text{ZnBr}$	OCH_3	15	0	20
$\text{CH}_3\text{-CH=CH-CH}_2\text{ZnBr}$	OCH_3	20	0	30

* In these cases, 5-10 % of allene resulting from an 1,4-addition on butadiene system and substitution of OH group is also formed.



D - Addition on the triple bond and substitution

This behaviour has been observed with α, α' -difunctional conjugated enynes, when the group next to the triple bond is a OH group and when the group located next to the double bond is a good leaving group [22]; thus, allyl-magnesium and allyl-zinc compounds react in this manner and produce α, δ -dienic alcohols (Table 11), for instance :

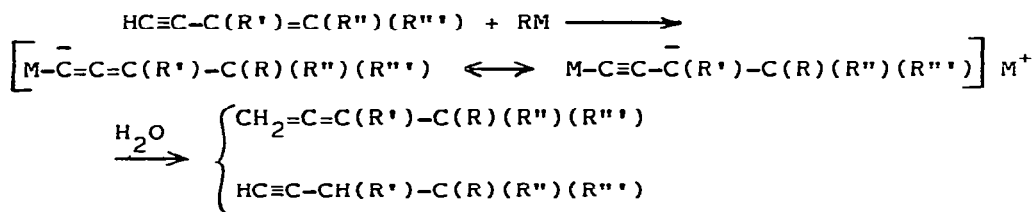


Second Part - Conjugated enynes with a terminal triple bond

A - Addition involving the 1,3-butadiene system

1) Hydrocarbons - Synthesis of alkynes and allenes

The reaction takes place according to the following general scheme [5 - 9] :



The organolithium compounds (R = allyl, alkyl) react easily to give only alkynes, which thus appear as resulting from an 1,2-addition on the ethylenic bond ; when R is a substituted allylic group, the reaction takes place mainly with allylic rearrangement.

It is an easy way to obtain β -branched terminal alkynes from varied enynes (see Table 12), but the yield decreases when the steric hindrance increases.

Table 12

Synthesis of 1-alkynes $\text{HC}\equiv\text{C}-\text{CH}(\text{R}')-\text{C}(\text{R})\text{C}(\text{R}'')(\text{R}''')$

RLi		R'	R''	R'''	Yield %
$\text{CH}_2=\text{CH}-\text{CH}_2\text{Li}$	[5, 9]	H	H	nC_4H_9	40
$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2\text{Li}$	[6]	H	H	nC_4H_9	45
$\text{C}_2\text{H}_5-\text{CH}=\text{CH}-\text{CH}_2\text{Li}$	[5, 9]	H	H	nC_4H_9	33
$\text{nC}_4\text{H}_9\text{Li}$	[5, 9]	H	H	nC_4H_9	40
$\text{CH}_2=\text{CH}-\text{CH}_2\text{Li}$	[6]	H	H	C_6H_5	10
$\text{nC}_4\text{H}_9\text{Li}$	[6]	H	H	C_6H_5	15
$\text{CH}_2=\text{CH}-\text{CH}_2\text{Li}$	[6]		$(\text{CH}_2)_4$	H	30
$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2\text{Li}$	[6]		$(\text{CH}_2)_4$	H	40
$\text{nC}_4\text{H}_9\text{Li}$	[6]		$(\text{CH}_2)_4$	H	42
$\text{CH}_2=\text{CH}-\text{CH}_2\text{Li}$	[6]	H		$(\text{CH}_2)_5$	26
$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2\text{Li}$	[6]	H		$(\text{CH}_2)_5$	12
$\text{nC}_4\text{H}_9\text{Li}$	[6]	H		$(\text{CH}_2)_5$	≤ 10
$\text{CH}_2=\text{CH}-\text{CH}_2\text{Li}$	[6]	H	C_2H_5	C_2H_5	25
$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2\text{Li}$	[6]	H	C_2H_5	C_2H_5	-
$\text{nC}_4\text{H}_9\text{Li}$	[6]	H	C_2H_5	C_2H_5	≤ 10

The organomagnesium reagents react easily and produce always a mixture of an alkyne and an allene. The reaction takes place with various Grignard reagents (R = allyl, alkyl, benzyl), but it is necessary to use more drastic conditions [13], for instance 40h at 105°C instead of 24h at 20° or 35°C, with saturated or benzylic than with allylic organomagnesium derivatives; when R is a substituted allyl group, the reaction takes place with complete allylic rearrangement.

The ratio alkyne/allene depends on several factors :

- nature of the R', R'' and R''' groups of the enyne,
- nature of the R group of the Grignard reagent,
- experimental conditions,

but it does not depend on the E or Z configuration of the double bond [9].

Finally, the results gathered in Table 13 also show that the yield decreases with increasing steric hindrance.

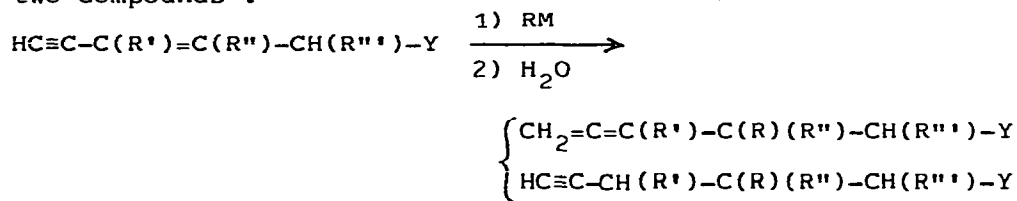
Table 13

Synthesis of 1-alkynes $\text{HC}\equiv\text{C}-\text{CH}(\text{R}')-\text{C}(\text{R})(\text{R}'')(\text{R}''')$ and 1-allenes $\text{CH}_2=\text{C}=\text{C}(\text{R}')-\text{C}(\text{R})(\text{R}'')(\text{R}''')$

RMgBr		R'	R''	R'''	yield %	alkyne %	allene %
$\text{CH}_2=\text{CH}-\text{CH}_2\text{MgBr}$	[9]	H	H	nC_4H_9	40	75	25
$\text{CH}_3\text{CH}=\text{CH}-\text{CH}_2\text{MgBr}$	[6]	H	H	nC_4H_9	65	64	36
$\text{C}_2\text{H}_5\text{CH}=\text{CH}-\text{CH}_2\text{MgBr}$	[9]	H	H	nC_4H_9	44	75	25
$\text{C}_2\text{H}_5\text{MgBr}$	[13]	H	H	nC_4H_9	40	95	5
$(\text{CH}_3)_2\text{CHMgBr}$	[13]	H	H	nC_4H_9	43	95	5
$\text{C}_6\text{H}_5-\text{CH}_2\text{MgBr}$	[13]	H	H	nC_4H_9	10	100	0
$\text{CH}_2=\text{CH}-\text{CH}_2\text{MgBr}$	[6]	H	H	C_6H_5	50	87	13
$\text{CH}_2=\text{CH}-\text{CH}_2\text{MgBr}$	[6]		$(\text{CH}_2)_4$	H	26	52	48
$\text{CH}_3\text{CH}=\text{CH}-\text{CH}_2\text{MgBr}$	[6]		$(\text{CH}_2)_4$	H	5	99	1
$\text{CH}_2=\text{CH}-\text{CH}_2\text{MgBr}$	[6]	H		$(\text{CH}_2)_5$	32	61	39
$\text{CH}_3\text{CH}=\text{CH}-\text{CH}_2\text{MgBr}$	[6]	H		$(\text{CH}_2)_5$	10	99	1
$\text{CH}_2=\text{CH}-\text{CH}_2\text{MgBr}$	[6]	H	C_2H_5	C_2H_5	15	70	30

2) α -functional enynes - Synthesis of γ -functional alkynes and β -functional allenes

As previously, the reaction can lead to a mixture of two compounds :

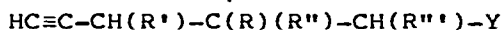


The organolithium compounds (R = allyl, vinyl, alkyl) react easily to give only γ -functional alkynes (alcohols, ethers, tertiary amines) [5, 10, 11].

This is an easy way to obtain β -branched γ -functional terminal alkynes from varied enynes, but the yield varies widely according to the steric hindrance next to the functional group (see Table 14).

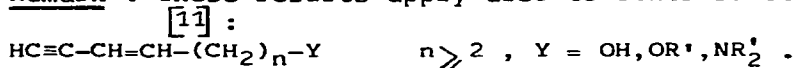
Table 14 -

Synthesis of γ -functional 1-alkynes



RLi		R'	R''	R'''	Y	Yield %
CH ₂ =CH-CH ₂ Li	[5, 11]	H	H	H	OH	50
CH ₂ =CH-CH ₂ Li	[11]	H	CH ₃	H	OH	52
CH ₂ =CH-CH ₂ Li	[11]	CH ₃	H	H	OH	46
CH ₃ CH=CH-CH ₂ Li	[5]	H	H	H	OH	58
nC ₄ H ₉ Li	[5]	H	H	H	OH	14
CH ₂ =C(CH ₃)Li	[5]	H	H	H	OH	10
CH ₂ =CH-CH ₂ Li	[5]	H	H	H	OC ₄ H ₉	35
CH ₂ =CH-CH ₂ Li	[11]	H	CH ₃	H	OC ₄ H ₉	25
CH ₂ =CH-CH ₂ Li	[11]	CH ₃	H	H	OC ₄ H ₉	48
nC ₄ H ₉ Li	[5]	H	H	H	OC ₄ H ₉	24
CH ₂ =CH-CH ₂ Li	[5]	H	H	H	N(C ₂ H ₅) ₂	42
CH ₂ =CH-CH ₂ Li	[11]	H	CH ₃	H	N(C ₂ H ₅) ₂	5
CH ₂ =CH-CH ₂ Li	[11]	CH ₃	H	H	N(C ₂ H ₅) ₂	5
nC ₄ H ₉ Li	[5]	H	H	H	N(C ₂ H ₅) ₂	44

Remark : These results apply also to other functional enynes



The organomagnesium reagents produce generally a mixture of a γ -functional alkyne and a β -functional allene [5, 10, 11, 13]. The reaction may take place with various Grignard reagents (R = allyl, vinyl, alkyl, benzyl), but it is more difficult with saturated or benzylic derivatives [13]; when R is a substituted allyl group, a complete allylic rearrangement is observed.

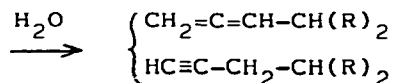
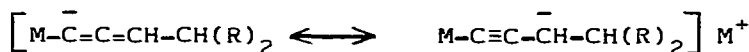
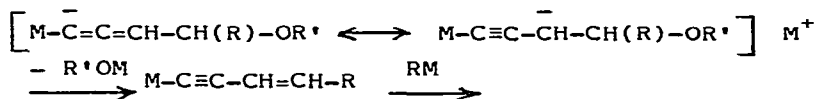
The ratio alkyne/allene depends mainly on the nature of Y group [11] and varies slightly with several other factors :
 - the nature of the R', R'' and R''' groups of the enyne,
 - the nature of the R group of the Grignard reagent,
 - experimental conditions,
 but it does not depend on the E or Z configuration of the ethylenic bond.

The results which appear in Table 15 show that this reaction is general, but the yield decreases markedly with increasing steric hindrance.

Remark : These results extend to other functional enynes [11] :
 $\text{HC}\equiv\text{C}-\text{CH}=\text{CH}-(\text{CH}_2)_n-\text{Y}$, $n \geq 2$, $\text{Y} = \text{OH}, \text{OR}', \text{NH}-\text{R}', \text{NR}'_2$.

B - Addition involving the 1,3-butadiene system and substitution

Such behaviour is observed when organolithium and organomagnesium compounds are allowed to react with functional enynes such as $\text{HC}\equiv\text{C}-\text{CH}=\text{CH}-\text{OR}'$ [6, 7]; the presumed mechanism is :



Organolithium derivatives (R = allyl, alkyl) produce β -branched 1-alkynes only, while organomagnesium compounds (R = allyl) lead to a mixture of β -branched 1-alkynes and α -branched terminal allenes (see Table 16).

Table 15

Synthesis of γ -functional 1-alkynes $\text{HC}\equiv\text{C}-\text{CH}(\text{R}')-\text{C}(\text{R})(\text{R}'')-\text{CH}(\text{R}''')-\text{Y}$ and β -functional 1-allenes $\text{CH}_2=\text{C}=\text{C}(\text{R}')-\text{C}(\text{R})(\text{R}'')-\text{CH}(\text{R}''')-\text{Y}$

RMgBr		R'	R''	R'''	Y	Yield %	alkyne %	allene %
$\text{CH}_2=\text{CH}-\text{CH}_2\text{MgBr}$	[5]	H	H	H	OH	77	30	70
$\text{CH}_2=\text{CH}-\text{CH}_2\text{MgBr}$	[11]	H	CH_3	H	OH	77	40	60
$\text{CH}_2=\text{CH}-\text{CH}_2\text{MgBr}$	[11]	CH_3	H	H	OH	75	35	65
$\text{CH}_3\text{CH}=\text{CH}-\text{CH}_2\text{MgBr}$	[5]	H	H	H	OH	78	35	65
$\text{CH}_2=\text{CHMgBr}$	[5]	H	H	H	OH	63	39	61
$\text{CH}_2=\text{C}(\text{CH}_3)\text{MgBr}$	[5]	H	H	H	OH	43	40	60
$\text{C}_2\text{H}_5\text{MgBr}$	[13]	H	H	H	OH	55	45	55
$(\text{CH}_3)_2\text{CHMgBr}$	[13]	H	H	H	OH	50	45	55
$\text{C}_6\text{H}_5-\text{CH}_2\text{MgBr}$	[13]	H	H	H	OH	15	50	50
$\text{CH}_2=\text{CH}-\text{CH}_2\text{MgBr}$	[5]	H	H	H	OC_4H_9	83	40	60
$\text{CH}_2=\text{CH}-\text{CH}_2\text{MgBr}$	[11]	H	CH_3	H	OC_4H_9	51	45	55
$\text{CH}_2=\text{CH}-\text{CH}_2\text{MgBr}$	[11]	CH_3	H	H	OC_4H_9	78	40	60
$\text{C}_2\text{H}_5\text{MgBr}$	[13]	H	H	H	OC_4H_9	15	60	40
$(\text{CH}_3)_2\text{CHMgBr}$	[13]	H	H	H	OC_4H_9	20	65	35
$\text{CH}_2=\text{CH}-\text{CH}_2\text{MgBr}$	[5]	H	H	H	$\text{NH}-\text{C}_2\text{H}_5$	68	80	20
$\text{CH}_2=\text{CH}-\text{CH}_2\text{MgBr}$	[11]	H	CH_3	H	$\text{NH}-\text{C}_2\text{H}_5$	40	75	25
$\text{CH}_2=\text{CH}-\text{CH}_2\text{MgBr}$	[11]	CH_3	H	H	$\text{NH}-\text{C}_2\text{H}_5$	49	83	17
$\text{C}_2\text{H}_5\text{MgBr}$	[13]	H	H	H	$\text{NH}-\text{C}_2\text{H}_5$	36	60	40
$(\text{CH}_3)_2\text{CHMgBr}$	[13]	H	H	H	$\text{NH}-\text{C}_2\text{H}_5$	30	65	35
$\text{C}_6\text{H}_5-\text{CH}_2\text{MgBr}$	[13]	H	H	H	$\text{NH}-\text{C}_2\text{H}_5$	0	-	-
$\text{CH}_2=\text{CH}-\text{CH}_2\text{MgBr}$	[5]	H	H	H	$\text{N}(\text{C}_2\text{H}_5)_2$	68	67	33
$\text{CH}_2=\text{CH}-\text{CH}_2\text{MgBr}$	[11]	H	CH_3	H	$\text{N}(\text{C}_2\text{H}_5)_2$	5	60	40
$\text{CH}_2=\text{CH}-\text{CH}_2\text{MgBr}$	[11]	CH_3	H	H	$\text{N}(\text{C}_2\text{H}_5)_2$	9	67	33
$\text{C}_2\text{H}_5\text{MgBr}$	[13]	H	H	H	$\text{N}(\text{C}_2\text{H}_5)_2$	40	65	35
$(\text{CH}_3)_2\text{CHMgBr}$	[13]	H	H	H	$\text{N}(\text{C}_2\text{H}_5)_2$	50	67	33
$\text{C}_6\text{H}_5-\text{CH}_2\text{MgBr}$	[13]	H	H	H	$\text{N}(\text{C}_2\text{H}_5)_2$	25	100	0

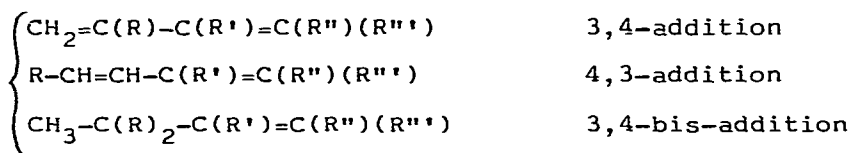
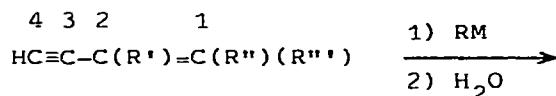
Table 16

Synthesis of 1-alkynes $\text{HC}\equiv\text{C}-\text{CH}_2-\text{CH}(\text{R})_2$
and 1-allenes $\text{CH}_2=\text{C}=\text{CH}-\text{CH}(\text{R})_2$

RM		Yield %	alkyne %	allene %
$\text{CH}_2=\text{CH}-\text{CH}_2\text{Li}$	[6]	15	100	0
$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2\text{Li}$	[6]	10	100	0
$n\text{C}_4\text{H}_9\text{Li}$	[6]	10	100	0
$\text{CH}_2=\text{CH}-\text{CH}_2\text{MgBr}$	[6]	48	85	15
$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2\text{MgBr}$	[6]	18	90	10

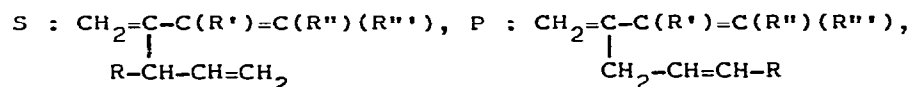
C - Addition to the triple bond

1) Hydrocarbons - Synthesis of conjugated dienes



The allylic organozinc compounds [5-9] lead to dienes resulting from 3,4-addition. With some enynes ($\text{R}'=\text{R}''=\text{H}$, $\text{R}'''=\text{H}$, alkyl) and when a large excess of organozinc compound is used, an alkene resulting from a double addition may also be produced (see Table 17).

When R is a substituted allyl group, the reaction leads to a mixture of two products S and P (reaction with and without allylic rearrangement) :

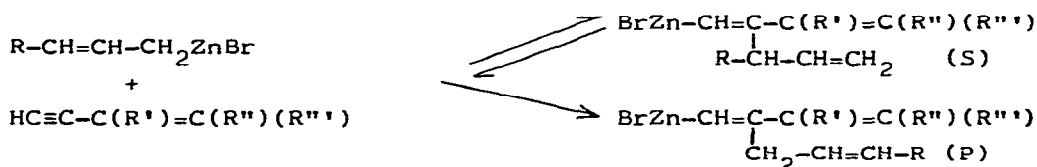


and the ratio S/P varies according to the experimental conditions (Table 18) : this fact can be explained by the reversible character of the reaction [8], which allows the formation of the thermodynamic isomer P from the kinetic isomer S :

Table 17

Synthesis of conjugated dienes $\text{CH}_2=\text{C}(\text{R})-\text{C}(\text{R}')=\text{C}(\text{R}'')(\text{R}''')$
and alkenes $\text{CH}_3-\text{C}(\text{R})_2-\text{C}(\text{R}')=\text{C}(\text{R}'')(\text{R}''')$

RM		R'	R''	R'''	diene yield %	alkene yield %
$\text{CH}_2=\text{CH}-\text{CH}_2\text{ZnBr}$	[6]	H	H	H	29	21
$\text{CH}_2=\text{CH}-\text{CH}_2\text{ZnBr}$	[6]	H	H	nC_4H_9	43	22
$\text{CH}_2=\text{CH}-\text{CH}_2\text{ZnBr}$	[6]	H	H	C_6H_5	40	0
$\text{CH}_2=\text{CH}-\text{CH}_2\text{ZnBr}$	[6]	$(\text{CH}_2)_4$		H	70	10
$\text{CH}_2=\text{CH}-\text{CH}_2\text{ZnBr}$	[6]	H		$(\text{CH}_2)_5$	35	0
$\text{CH}_2=\text{CH}-\text{CH}_2\text{ZnBr}$	[6]	H	C_2H_5	C_2H_5	20	0
$\text{CH}_2=\text{CH}-\text{CH}_2\text{ZnBr}$	[6]	H	H	OC_2H_5	25	30
$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2\text{ZnBr}$	[6]	H	H	nC_4H_9	40	0
$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2\text{ZnBr}$	[6]		$(\text{CH}_2)_4$	H	45	0
$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2\text{ZnBr}$	[6]	H		$(\text{CH}_2)_5$	23	0
$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2\text{ZnBr}$	[6]	H	H	OC_2H_5	78	0
$\text{C}_2\text{H}_5-\text{CH}=\text{CH}-\text{CH}_2\text{ZnBr}$	[5]	H	H	nC_4H_9	55	0
$\text{C}_7\text{H}_{15}\text{CuMgBr}_2$	[40]	H	H	H	42	0
$\text{C}_7\text{H}_{15}\text{CuMgBrCl}$	[40]	H	H	H	40	0
$(\text{C}_7\text{H}_{15})_2\text{CuLi}, \text{LiI}$	[40]	H	H	H	29	0
$(\text{C}_7\text{H}_{15})_2\text{CuMgCl}, \text{MgClBr}$	[40]	H	H	H	40-70	0
$(\text{C}_6\text{H}_{11})_2\text{CuMgCl}$	[41]	H	H	H	90	0
$(\text{C}_2\text{H}_5)_2\text{CuMgCl}$	[41]	CH_3	H	H	85	0
$(\text{nC}_4\text{H}_9)_2\text{CuMgCl}$	[41]	CH_3	H	H	95	0
$(\text{C}_2\text{H}_5)_2\text{CuMgCl}$	[41]	$\text{c-C}_6\text{H}_{11}$	H	H	88	0
$(\text{C}_2\text{H}_5)_2\text{CuMgCl}, 2\text{LiBr}$	[41]	C_6H_5	CH_3	H	80	0
$(\text{nC}_4\text{H}_9)_2\text{CuMgCl}, 2\text{LiBr}$	[41]	C_6H_5	CH_3	H	85	0



Other organometallic derivatives such as organo-copper (I) reagents, organohomocuprates $[\text{RCuR}]\text{MgX}$ and organoheterocuprates $[\text{RCuBr}]\text{MgX}$ [40, 41] react also with conjugated enynes to lead only to the product resulting from a 3,4-addition, when R is a primary alkyl group (see Table 17).

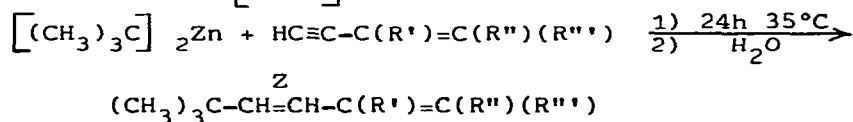
Table 18

Synthesis of conjugated dienes with a substituted allyl group
 $\text{CH}_2=\text{C}(\text{R})-\text{C}(\text{R}')=\text{C}(\text{R}'')(\text{R}''')$

RM	R'	R''	R'''	Conditions after reaction at 20°C	yield %	S*% P*%
$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2\text{ZnBr}$ [6]	H	H	$n\text{C}_4\text{H}_9$	6h 25°C	40	91 9
				6h 50°C	52	75 25
$\text{C}_2\text{H}_5-\text{CH}=\text{CH}-\text{CH}_2\text{ZnBr}$ [8, 9]	H	H	$n\text{C}_4\text{H}_9$	6h 20°C	55	95 5
				2h 65°C	53	70 30
				8h 65°C	50	65 35
$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2\text{ZnBr}$ [6]		$(\text{CH}_2)_4$	H	6h 25°C	45	48 52
				6h 50°C	51	30 70
$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2\text{ZnBr}$ [6]	H		$(\text{CH}_2)_5$	6h 25°C	23	65 35
				6h 50°C	30	47 53
$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2\text{ZnBr}$ [6]	H	H	OC_2H_5	6h 25°C	78	95 5
				6h 50°C	53	75 25

* S : $\text{CH}_2=\underset{\text{R}-\text{CH}-\text{CH}=\text{CH}_2}{\text{C}}-\text{C}(\text{R}')=\text{C}(\text{R}'')(\text{R}''')$; P : $\text{CH}_2=\underset{\text{CH}_2-\text{CH}=\text{CH}-\text{R}}{\text{C}}-\text{C}(\text{R}')=\text{C}(\text{R}'')(\text{R}''')$

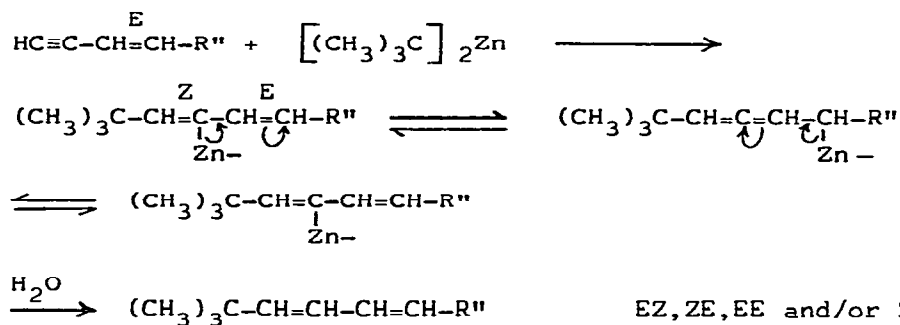
Di-t-butylzinc has a different behaviour, since it shows only 4,3-addition [12, 14] :



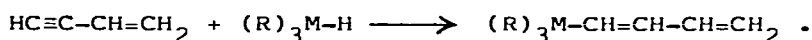
For instance, $\text{R}'=\text{R}''=\text{H}$, $\text{R}'''=n\text{C}_4\text{H}_9$, Yield = 30 %.

$\text{R}', \text{R}''=(\text{CH}_2)_4$, $\text{R}''' = \text{H}$, Yield = 55 %.

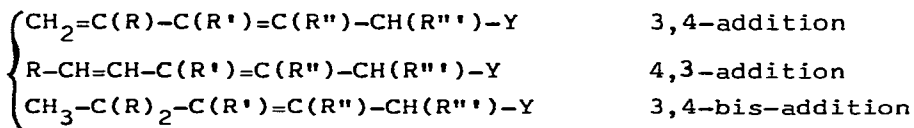
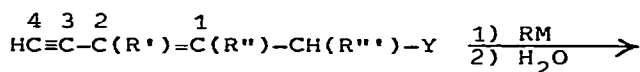
This addition is stereoselective (trans-addition) when the reaction is carried out at room temperature or by refluxing in ether during several hours ; but the reaction is not stereoselective in refluxing THF and, starting from an enyne E for instance, it is possible to obtain a mixture of four stereoisomers EZ, ZE, EE and ZZ. This result can be explained by an allylic rearrangement of the intermediate organozinc compound :



Other organometallic reagents such as organo-copper (I) reagents, organohomocuprates and organoheterocuprates [41] react with conjugated enynes to lead mainly to the product of 4,3-addition when R is a secondary or tertiary alkyl group. Finally, silanes [42], germanes [43, 44], stannanes [45] $(\text{R})_3\text{MH}$ and alanes $(\text{R})_2\text{MH}$ [46] react in the same manner:



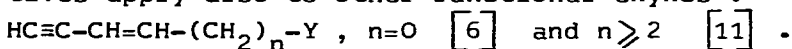
2) α -functional enynes - Synthesis of α -functional conjugated dienes



The allylic organozinc derivatives [5, 10, 11] react easily to lead to conjugated dienes resulting from 3,4-addition: sometimes 3,4-bis-addition occurs (see Table 19). When R is a substituted allyl group, the reaction proceeds with complete allylic rearrangement.

Other organometallic derivatives such as organocopper (I) reagents react in the same manner [40].

Remark: The results obtained with allylic organozinc derivatives apply also to other functional enynes:



Di-t-butylzinc leads to conjugated dienes corresponding to 4,3-addition [12, 14]. This addition is stereoselective (trans-addition) when the reaction is carried out at room

Table 19

Synthesis of α -functional conjugated dienes
 $\text{CH}_2=\text{C}(\text{R})-\text{C}(\text{R}')=\text{C}(\text{R}'')-\text{C}(\text{R}''')-\text{CH}(\text{R}'''')-\text{Y}$ and α -functional alkenes $\text{CH}_3-\text{C}(\text{R})_2-\text{C}(\text{R}')=\text{C}(\text{R}'')-\text{CH}(\text{R}''')-\text{Y}$

RM		R'	R''	R'''	Y	diene yield %	alkene yield %
$\text{CH}_2=\text{CH}-\text{CH}_2\text{ZnBr}$	[5]	H	H	H	OH	63	14
$\text{CH}_3\text{CH}=\text{CH}-\text{CH}_2\text{ZnBr}$	[5]	H	H	H	OH	74	0
$\text{CH}_2=\text{CH}-\text{CH}_2\text{ZnBr}$	[11]	H	H	H	OC_4H_9	57	≤ 5
$\text{CH}_2=\text{CH}-\text{CH}_2\text{ZnBr}$	[5]	H	H	H	$\text{NH}-\text{C}_2\text{H}_5$	40	18
$\text{CH}_2=\text{CH}-\text{CH}_2\text{ZnBr}$	[5]	H	H	H	$\text{N}(\text{C}_2\text{H}_5)_2$	15	14
$\text{CH}_2=\text{CH}-\text{CH}_2\text{ZnBr}$	[11]	H	CH_3	H	OH	41	0
$\text{CH}_2=\text{CH}-\text{CH}_2\text{ZnBr}$	[11]	H	CH_3	H	OC_4H_9	40	0
$\text{CH}_2=\text{CH}-\text{CH}_2\text{ZnBr}$	[11]	H	CH_3	H	$\text{NH}-\text{C}_2\text{H}_5$	29	0
$\text{CH}_2=\text{CH}-\text{CH}_2\text{ZnBr}$	[11]	H	CH_3	H	$\text{N}(\text{C}_2\text{H}_5)_2$	5	0
$\text{CH}_2=\text{CH}-\text{CH}_2\text{ZnBr}$	[11]	CH_3	H	H	OH	65	0
$\text{CH}_2=\text{CH}-\text{CH}_2\text{ZnBr}$	[11]	CH_3	H	H	OC_4H_9	53	0
$\text{CH}_2=\text{CH}-\text{CH}_2\text{ZnBr}$	[11]	CH_3	H	H	$\text{NH}-\text{C}_2\text{H}_5$	60	0
$\text{CH}_2=\text{CH}-\text{CH}_2\text{ZnBr}$	[11]	CH_3	H	H	$\text{N}(\text{C}_2\text{H}_5)_2$	10	0
$(\text{C}_4\text{H}_9)_2\text{CuMgCl}$	[40]	H	H	H	OC_2H_5	55	0

temperature or in refluxing ether ; it is a very convenient method to prepare α -functional conjugated dienes (Table 20) : $(\text{CH}_3)_3\text{C}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}_2\text{Y}$ ZE from enynes $\text{HC}\equiv\text{C}-\text{CH}=\text{CH}-\text{CH}_2\text{Y}$ E .

In refluxing THF, the reaction is not stereoselective and can lead to a mixture of four stereoisomers ZE, EZ, ZZ and EE (see Table 20).

D - Addition to the triple bond and substitution - Synthesis of conjugated dienes

This behaviour has been sometimes observed with organozinc derivatives and α -functional enynes, when Y is a good leaving group, for instance :

Reaction of di-*t*-butylzinc with an enynic ether [14] :

this reaction can be explained by the following mechanism :

Table 20

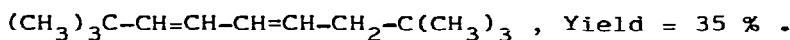
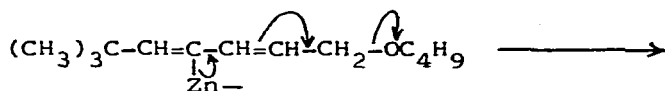
Synthesis of α -functional conjugated dienes

$(\text{CH}_3)_3\text{C}-\text{CH}=\text{CH}-\text{C}(\text{R}')=\text{C}(\text{R}'')-\text{CH}(\text{R}''')-\text{Y}$ ZE , EZ , ZZ and/or EE ,
 from di-*t*-butyl zinc, according to conditions a (ether,
 24h 35°C) or conditions b (THF, 48h 65°C) [14] .

Conditions	R'	R''	R'''	Y	yield %	ZE %	EZ %	ZZ %	EE %
a	H	H	H	OH	45	100	0	0	0
b	H	H	H	OH	70	20	80	0	0
a*	H	H	H	OH	15	0	0	100	0
b*	H	H	H	OH	5	50	0	50	0
a	H	H	CH ₃	OH	60	100	0	0	0
b	H	H	CH ₃	OH	72	23	35	42	0
a*	H	H	CH ₃	OH	40	0	0	100	0
b*	H	H	CH ₃	OH	30	50	0	50	0
a	CH ₃	H	H	OH	50	100	0	0	0
b	CH ₃	H	H	OH	65	16	0	32	52
a	H	H	H	NH-C ₂ H ₅	40	100	0	0	0
b	H	H	H	NH-C ₂ H ₅	35	10	42	35	13
a*	H	H	H	NH-C ₂ H ₅	10	0	0	100	0
b*	H	H	H	NH-C ₂ H ₅	5	10	40	40	10
a	H	H	H	N(C ₂ H ₅) ₂	37	100	0	0	0
b	H	H	H	N(C ₂ H ₅) ₂	40	20	35	30	15
a*	H	H	H	N(C ₂ H ₅) ₂	42	0	0	100	0
b*	H	H	H	N(C ₂ H ₅) ₂	35	24	31	35	10
a	CH ₃	H	H	N(C ₂ H ₅) ₂	40	100	0	0	0
b	CH ₃	H	H	N(C ₂ H ₅) ₂	50	24	22	46	8
a	H	H	H	OC ₄ H ₉	41	100	0	0	0
b**	H	H	H	OC ₄ H ₉	35	-	-	-	-

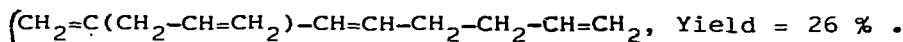
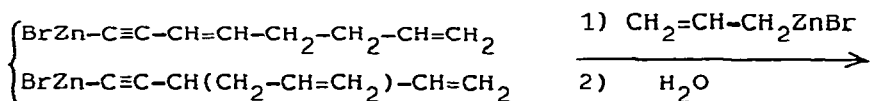
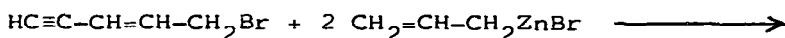
* from enyne of stereochemistry Z ; from enyne E in the other cases .

** in this case, an allene (mixture of isomers) is obtained resulting from an addition on the triple bond and substitution of group Y.



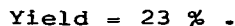
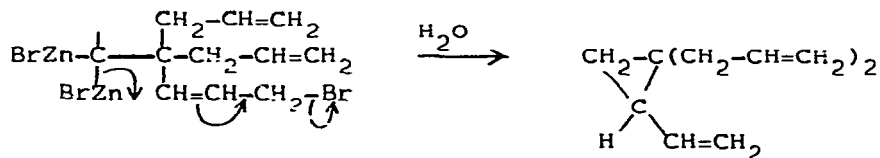
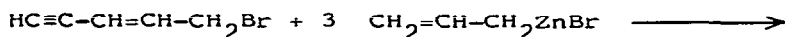
Reaction of allylzinc bromide with an enynic bromide [47]

Addition to the triple bond and substitution (S_{N}^2 and $\text{S}_{\text{N}}^{2'}$) occur in this reaction, together with the formation of a cyclopropane (see the following paragraph) :



E - Bis-addition to the triple bond and 1,3-elimination - Synthesis of vinylcyclopropanes

By reaction with a large excess of allylzinc bromide, enynic bromides can lead to vinylcyclopropanes [47] :



This reaction constitutes a potential method of access to varied vinylcyclopropanes.

CONCLUSION

The synthetic possibilities of addition reactions between common organometallic compounds and conjugated enynes are

numerous ; it is possible to carry out easily many regioselective and often stereoselective preparations of :

- internal allenes (hydrocarbons, monofunctional and difunctional derivatives),
- conjugated dienes (hydrocarbons, monofunctional and difunctional products),
- terminal alkynes (hydrocarbons and monofunctional derivatives),
- terminal allenes (hydrocarbons and monofunctional products),
- and, in some cases, particular unsaturated structures such as polyethylenic hydrocarbons and vinylcyclopropanes.

The results collected in this review complete those obtained by addition reactions of organometallic reagents (lithium [48, 49] , magnesium [49-51] , zinc [49, 52-54] , copper [49, 55]) to functionalised (or non-functionalised), terminal (or non-terminal) alkynes.

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