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Synthetic methodologies for carbo-substituted conjugated dienes

A A Vasil'ev, E P Serebryakov

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Abstract. The scope of this review encompasses methods and synthetic protocols leading to conjugated dienes bearing no heteroatoms in the C=C–C=C moiety. Attention is concentrated on methodologies developed during the last decade, particularly, to the metal complex-mediated synthesis. The bibliography includes 494 references.

I. Introduction

Until about 1960, the synthetic chemistry of conjugated dienes was focused mainly on their simplest representatives. Usually, these dienes were prepared either by dehydrating diols and allylic or homoallylic alcohols or by eliminating the elements of HX (X = OAlk, OCOR, OSO_2R, Hal, *etc*.) from properly selected unsaturated substrates. However, such techniques were unsuitable for the synthesis of higher homologues, because the use of these reactions resulted in mixtures of isomers.

Then, in the mid-sixties a new period in the synthesis of conjugated dienes began, as this class of compounds became increasingly in demand. This popularity was due to the fact that dienes with fixed position of configurationally defined double bonds and with various sensitive functional groups (and their combinations) had been identified by that time as fragments of many natural products. Moreover, inter- and intramolecular Diels – Alder reactions employing conjugated dienes had become widely used tools in the synthesis of cyclic molecules.

Advances in organometallic chemistry and metal complex catalysis highlighted dienes as useful four-electron π-ligands capable of forming interesting metal complexes. These aspects of diene chemistry are considered, with due attention to details, in two recently published review collections.[1,2] Finally, stereospecific 1,4-*cis* hydrogenation of conjugated dienes using chromium carbonyl complexes proved to be an efficient, preparatively viable method for stereocontrolled synthesis of alkenes.[3,4]

Abundant literature on the synthesis of conjugated dienes has been accumulated, and systematic surveys have been periodically attempted during the last thirty years. Among early sources (up to the late 1980's), the serial edition of Houben – Weyl[5] and a few monographs and collective volumes[6–9] should be mentioned, because some chapters there are dedicated to conjugated dienes. Another good source of references (not commented on) is a compendium of reactions leading to dienes.[10] Also useful is a monograph,[11] where numerous methods for constructing conjugated dienes are cited in the context of pheromone synthesis. A review on the synthesis of conjugated polyenes, where the dienes were considered as parental polyene systems,[12] was published in 1997 in a book[1] that is nearly inaccessible in Russia. This makes the appearance of an updated review quite opportune, let alone the fact that in the last four years the chemistry of conjugated dienes has been enriched with some new and interesting synthetic methods.

This review aims at a systematic survey of selective methods for obtaining conjugated carbo-substituted dienes that were elaborated between the end of 1960 and March, 2001. Methods leading to the molecules with heteroatomic substituents on the C=C–C=C unit will be mentioned just in a few exclusive cases. The description of reactions used will be focused on their preparative aspects; the mechanisms will be mentioned only when it is necessary, since most of them have been considered in detail in original publications.

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II. Elimination reactions

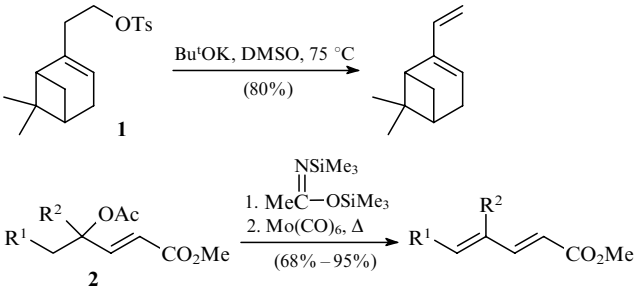
Elimination reactions leading to alkenes basically can be divided into two groups. The first group involves the ejection of a nucleofugal group and a vicinal hydrogen or metal atom. The second one involves reductive elimination of two vicinal groups. When the substrate already has a double bond adjacent to one of the groups undergoing elimination, the product of the reaction is a conjugated diene.

1. Elimination of HX

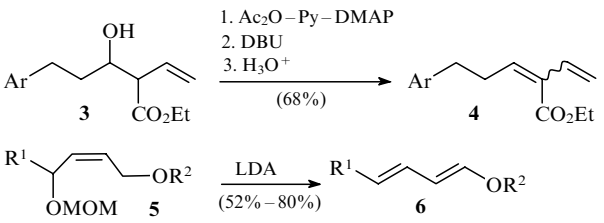
Elimination of one molecule of water from 2-methylbut-3-en-2-ol (Favorskii's method) or of two molecules of water from butane-1,3-diol (the last step in Lebedev's process) as well as catalytic

thermolysis of 4,4-dimethyl-1,3-dioxane (Farberov's method) are classical ways of obtaining dienic monomers applicable to other lower conjugated dienes. However, the conditions under which the processes are performed are too drastic to be useful for obtaining more labile, functionally substituted higher dienes.

Elimination of HX from substrates of allylic or homoallylic type proceeds regiospecifically only for molecules with specific patterns of substitution, *e.g.*, for compounds **1**[13] or **2**.[14] If the substrate contains a functional group strongly stabilising only one of the possible isomeric products, this also can favour an unambiguous course of the process (*e.g.*, in the case of reactions **3** → **4**[15] and **5** → **6**[16]).

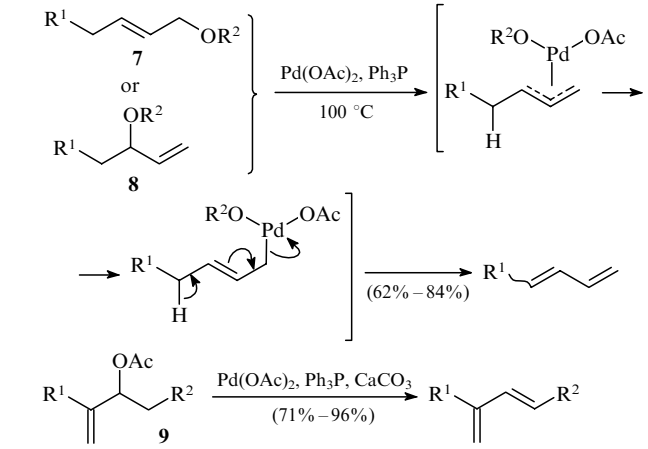


R^2 = H, CH_2R^1.



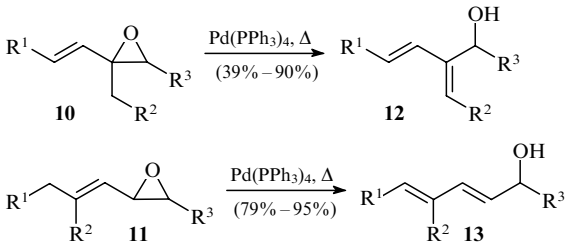
DMAP is 4-dimethyaminopyridine; DBU is 1,8-diazabicyclo-[5.4.0]undec-7-ene; MOM is methoxymethyl; LDA is lithium diisopropylamide.

Generally, elimination of HX or MX from allylic-type substrates affords isomer mixtures. However, in the presence of palladium catalysts the reaction proceeds regioselectively. In these cases substituents R^1 in starting compounds **7**–**9** can contain functional groups.[17, 18]

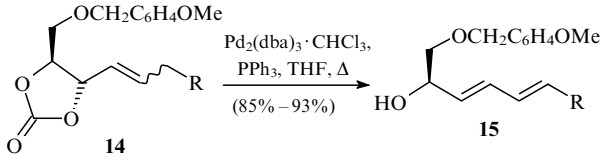


In this way neryl acetate was converted to myrcene, while geranyl acetate afforded a mixture of *cis* and *trans* isomers of β-ocymene.[19]

In the presence of palladium catalysts, the ring opening in acyclic vinylic oxiranes **10** and **11** proceeds smoothly to give α-dienols **12** and **13**.[20] The regioselectivity of these reactions depends on the position of substituents at the epoxide ring.

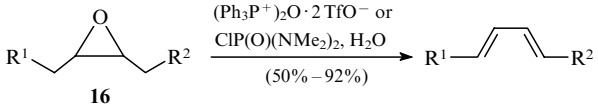


Elimination of CO_2 from alkenyl-substituted cyclic carbonates **14** takes place in the same manner, but the resulting diene **15** is obtained predominantly as the *E*,*E*-isomer whatever the configuration of the starting compound.[21]

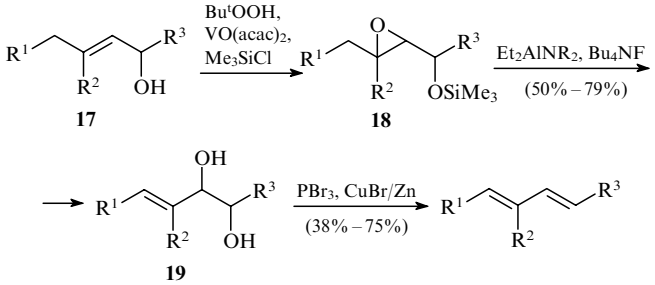


dba is dibenzylideneacetone.

Epoxides **16** (substituents R^1 and R^2 can contain ester groupings) undergo regiospecific formal dehydration mediated by organophosphorus reagents.[22, 23]



A three-step protocol of formal α,α′-elimination of water from allylic alcohols **17** is based on their chemoselective epoxidation in the presence of a silylating agent and vanadium catalysts.[24, 25] Subsequent opening of the epoxide ring in compounds **18** by mild Lewis acids proceeds regiospecifically (the ejection of proton occurs exclusively from the substituent lying in the *trans*-position relative to the silyloxy group), and affords unsaturated diols **19**. Finally, circumventional elimination of vicinal hydroxy groups from **19** gives an additional double bond. In this way nerol is readily transformed to myrcene, and geraniol to *trans*-β-ocymene.



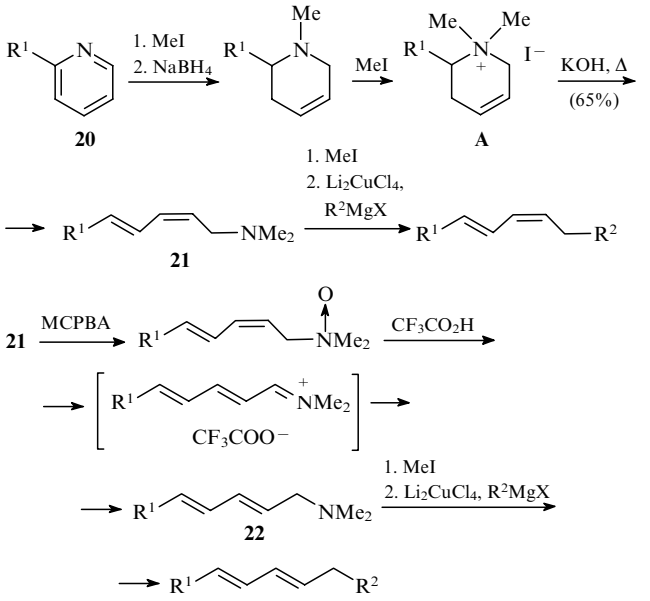
2. Deamination

An interesting method for the conversion of pyridines **20** into allylic (*Z*,*E*)-dienylamines **21** begins with quaternisation of their nitrogen atom followed by reduction, another methylation and subsequent Hofmann degradation of the resulting intermediate **A** (Scheme 1).[26, 27] Then, after yet another quaternisation, the amino group of compound **21** can be replaced by a carbonaceous substituent. The intermediate *Z*,*E*-dienes **21** can be isomerised to give the corresponding *E*,*E*-dienes **22** by treating the corresponding *N*-oxides with trifluoroacetic acid, and subsequently by reductive substitution. This protocol was employed in the synthesis of insect pheromones.[27]

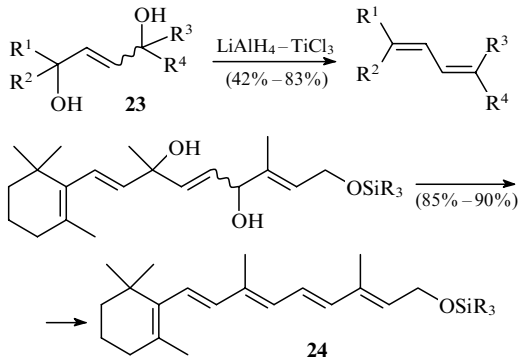
3. Reductive elimination

The reduction of alk-2-ene-1,4-diols[28] **23** or of the respective ethers[29, 30] in the system $LiAlH_4 – TiCl_3$ was used in the synthesis of retinoids **24**[31, 32] and other natural products.[30, 33]

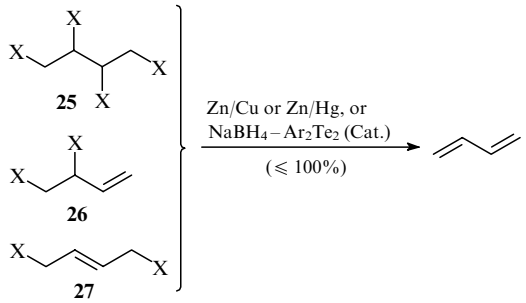
Scheme 1



MCPBA is *m*-chloroperbenzoic acid.

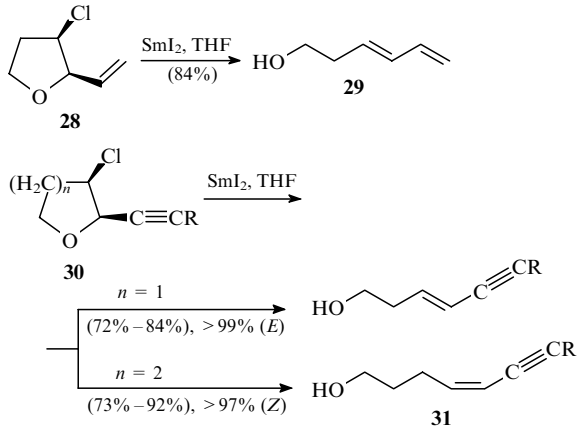


Reductive elimination of halogen atoms from 1,2,3,4-tetrahaloalkanes **25**, 1,2-dihaloalk-3-enes **26** and 1,4-dihaloalk-2-enes **27** gives 1,3-dienes in good yields. In addition to the traditional zinc,[34,35] the salts of arenetellurols were recommended.[36] In the latter case, the process can be performed readily using catalytic amount of Ar_2Te_2 that is periodically reduced by titrating the reaction mass with sodium borohydride. This method was applied to a number of linear and cyclic substrates, including those bearing additional functional groups.†

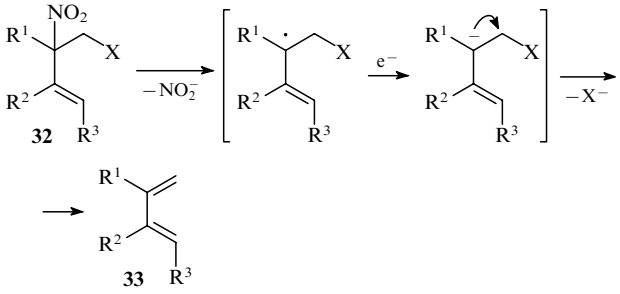


† 1,4-Dibromoalk-2-enes **27** can be prepared by treating internal[35] and, what is particularly interesting, terminal alkenes with 2 equiv. *N*-bromosuccinimide.[36] In the latter case, the bromination occurs in a stepwise mode involving allylic rearrangement. 1,2-Dibromoalk-3-enes **26** can be prepared from the corresponding diols which, in their turn, are obtainable from allylic alcohols.[25]

Reductive scission of *cis*-3-chloro-2-vinyltetrahydrofuran (**28**) with samarium iodide results in (*E*,*E*)-hexa-3,5-dien-1-ol (**29**) of > 97% geometric purity.[37] The same stereochemical result is observed in the case of 2-alkynyl-3-chlorotetrahydrofurans (**30**, $n = 1$). By contrast, their tetrahydropyran homologues (**30**, $n = 2$) in the same reaction afford the *Z*-configured enynols **31**, supposedly due to different conformational behaviour of five-membered and six-membered heterocycles.[37]



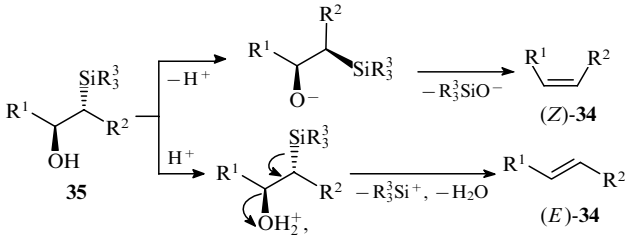
When allylic nitro compounds of the type **32** are treated with chromium(II) diacetate [$Cr(OAc)_2$ – Dipy system in dimethylformamide], their vicinal nitro- and mesyloxy (or acetoxy) groups undergo reductive elimination, which results in the formation of an additional double bond. These transformations were used to obtain conjugated dienes **33**, albeit in moderate yields.[38]



X = OMs, OAc.

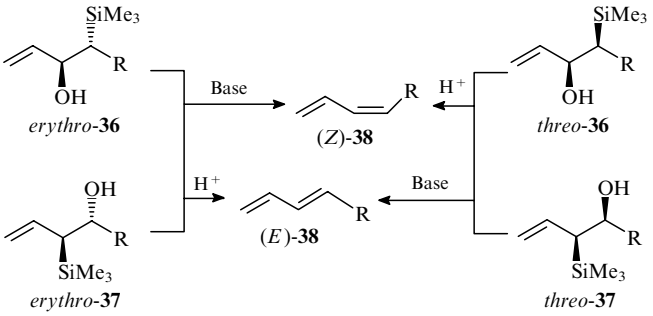
4. Stereocontrolled 1,2-elimination of R_3SiX and R_3SnX

The Peterson reaction (see a review[39]) consists in simultaneous elimination of vicinal hydroxy and silyl groups and results in the formation of a double bond. This transformation can occur both in the presence of bases (*e.g.*, Bu^{t}OK, KH) and acids (AcOH, H_2SO_4). The double bond configuration in product(s) **34** depends on the reaction conditions. When the starting compound **35** is treated with a base, the primarily formed alkoxide undergoes *syn*-elimination upon which a molecule of metal silanolate is ejected. When the process is initiated with an acid, it starts with protonation of the hydroxy group, followed by *anti*-elimination of a molecule of water, together with a silyl cation.

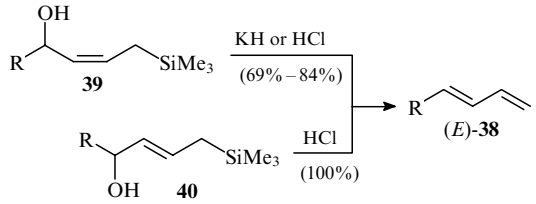


This approach can be used for the synthesis of dienes, when a double bond is already present in the starting compound. Depending on the mutual arrangement of substituents in substrates **36** and

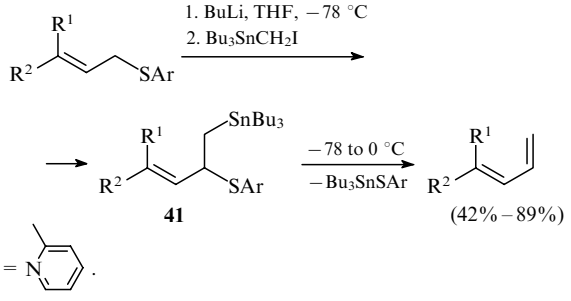
37 and on the process conditions, one obtains diene(s) **38** in the required configuration.‡



In a vinylogous version of the Peterson reaction, compounds **39** and **40** in which the allylic hydroxyl and the silyl group are located at the opposite ends of the double bond are employed as the starting substrates.[50,51] If the silyl group is attached to the terminal carbon atom (as in compounds **39** and **40**), the resulting diene **38** has always the *E*-configuration. When both the hydroxyl and the silyl group are attached to secondary carbon atoms in *erythro* relationship, the reaction affords the *E*,*E*-dienes.[52]. However, in the case of their *threo*-relationship, the resulting dienes are in the *E*,*Z*-configuration, the *Z*-bond being formed at the hydroxyl-bearing carbon atom.

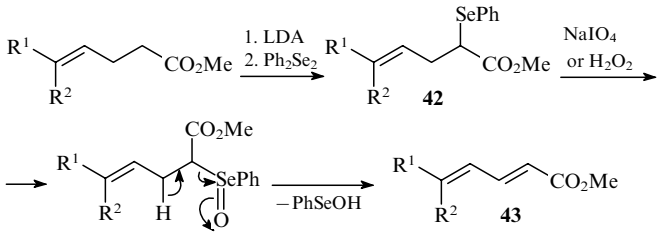


Compounds **41** containing Group IV and VI higher elements (*e.g.*, S and Sn, instead of O and Si) react similarly and spontaneously under very mild conditions; no catalyst is needed.[53]

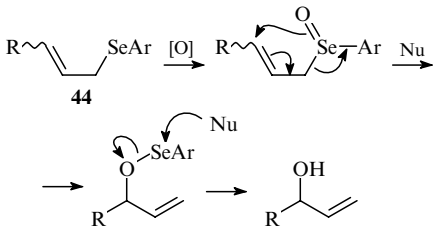


5. Oxidative 1,2-*syn*-elimination of RSeOH and RSOH

Oxidative elimination of an organoselenium fragment from aliphatic selenides is a relatively new method of alkene synthesis (see reviews [54–57]). This process involves the oxidation of a selenide to the corresponding selenoxide, which then undergoes spontaneous *syn*-elimination to give an alkene and a selenenic acid. This method has been widely used in syntheses of natural products of rather complicated structure, because there are many versatile methods for obtaining necessary organoselenium precursors (see, *inter alia*, the publications on the synthesis of α-arylseleno-γ-alkenoic acids [58–60]). Elimination of RSeOH from homoallylic selenides **42** leads to conjugated alkyl dienoates **43**.[60–65]



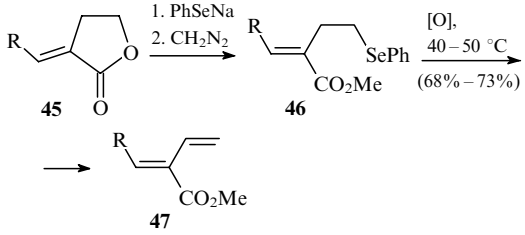
By contrast, instead of giving conjugated dienes *via* oxidative elimination, the oxidation of allylic selenides **44** mostly triggers a [2,3]-sigmatropic rearrangement that finally results in 're-arranged' allylic alcohols.[66,67]



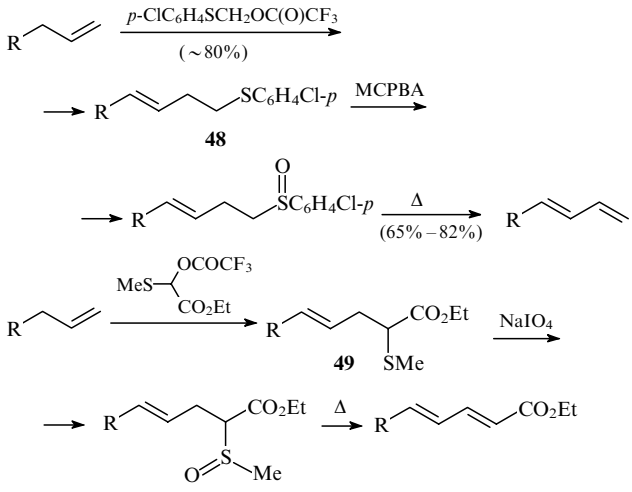
R = Alk, Ar′; Ar = *p*-$NO_2C_6H_4$.

Allylic 2,4-dinitrophenyl selenides appear to be an exclusion,[68] but even in this case, the resulting conjugated dienes are accompanied by noticeable amounts of allylic alcohols.

Due to high nucleophilicity of areneselenolates, they can open the five-membered lactone ring in compounds **45** to give selenides **46**, and subsequently conjugated dienes **47** with a functional group in the side chain.[69]



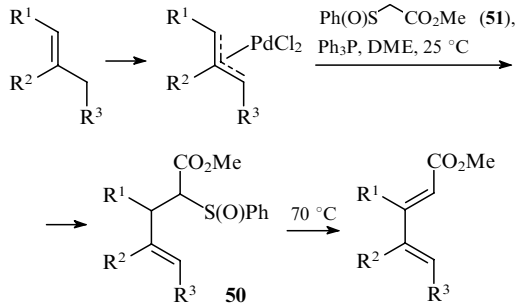
By analogy with selenoxides, aliphatic sulfoxides can undergo oxidative elimination to give alkenes, but at higher temperatures. This can be illustrated by the fragmentation of sulfoxides that were prepared by oxidising sulfides **48** and **49**.[70,71] The latter were obtained upon the addition of sulfur-containing cationoid reagents to terminal alkenes.



Elimination of a sulfoxide unit was used as the final stage in the synthesis of 2-hydroxymethylbuta-1,3-diene from 2-bromoethyl phenyl sulfide.[72]

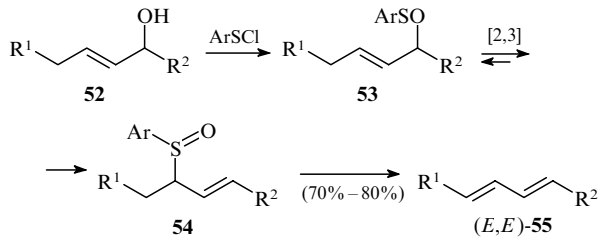
‡ Various protocols for the preparation of starting β-hydroxysilanes have been elaborated.[40–49] Particularly interesting are the reagents of the type R_3SiCH_2X (X = CO_2Alk, CN, *etc.*), which are widely used in the olefination of carbonyl compounds.[46–49]

α-Sulfinyl esters **50**, immediate precursors of alkyl alka-2,4-dienoates, are stable at room temperature. They can be readily prepared from synthon **51**, which already contains a sulfoxide grouping.[73]

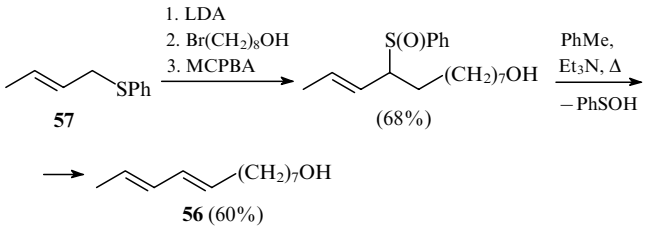


DME is 1,2-dimethoxyethane.

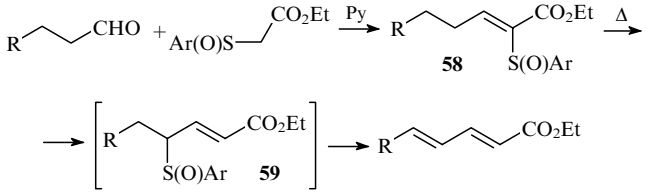
Unlike allylic selenoxides, allylic sulfoxides can be used for obtaining conjugated dienes.[66, 74] A convenient way of performing this process involves the esterification of allylic alcohols **52** with arenesulfenyl chlorides (the best results are obtained when Ar = 2,4-dinitrophenyl) followed by the rearrangement of intermediate sulfenates **53** into sulfoxides **54**; the latter then undergoing elimination to give dienes **55**.



Conjugated dienes with extended carbon chains (*e.g.*, dienic alcohol **56**) can be synthesised from suitable allylic sulfides.[75]

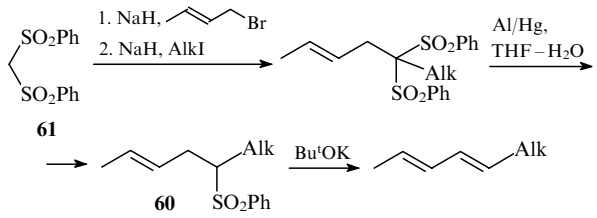


Vinyl sulfoxides of the type **58** rearrange on heating to allylic sulfoxides **59** that afford conjugated dienes upon eliminating ArSOH.[76]



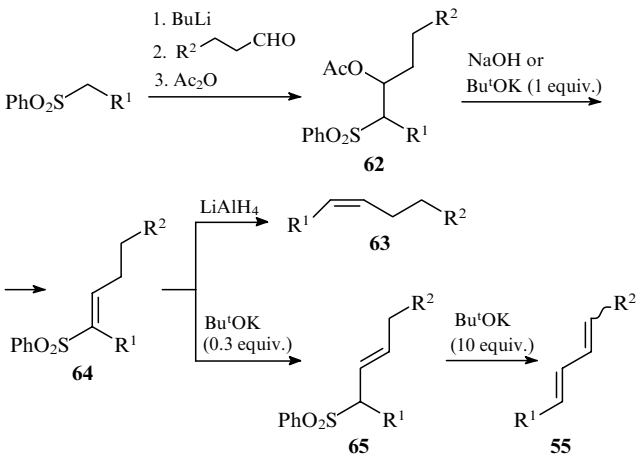
6. 1,2-Elimination of $ArSO_2H$

On treatment with bases, alkyl phenyl sulfones eject the phenylsulfinate anion to give alkenes. If the molecule of sulfone has already a double bond, this reaction leads to dienes. A synthesis of conjugated dienes from homoallylic sulfones **60** is known,[77] where the latter were obtained by sequential alkylation of bis(phenylsulfonyl)methane (**61**) first with allyl- and then with alkyl halides.

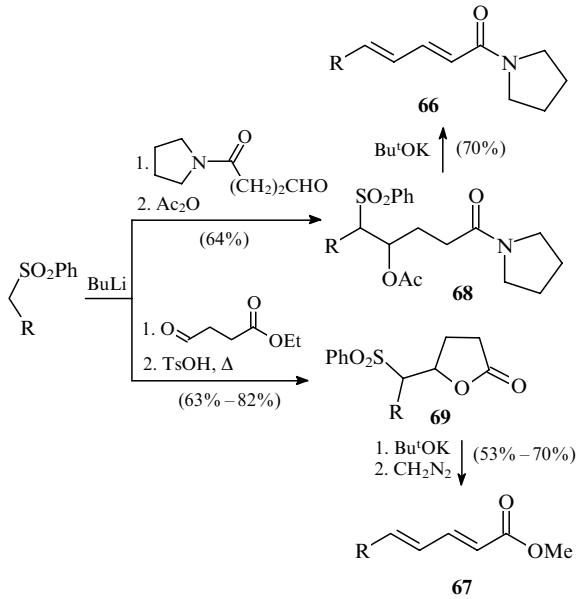


β-Acetoxysulfones **62** can be used as the precursors of alkenes **63** in the Julia method of olefination (aldol-like alkylation of an alkyl phenyl sulfone followed by acylation to give **62**, then elimination of AcOM, and reduction of the resulting vinyl sulfones **64** to give alkene **63**)[78, 79] However, when a large excess of a stronger base is used (~10 equiv.), both substituents in the acetoxy sulfone **62** undergo elimination, which gives rise to the conjugated dienes **55**.[80, 81] The dienes **55** can be obtained from the sulfones **64** either directly, or *via* intermediate allylic sulfones **65** (Scheme 2).

Scheme 2



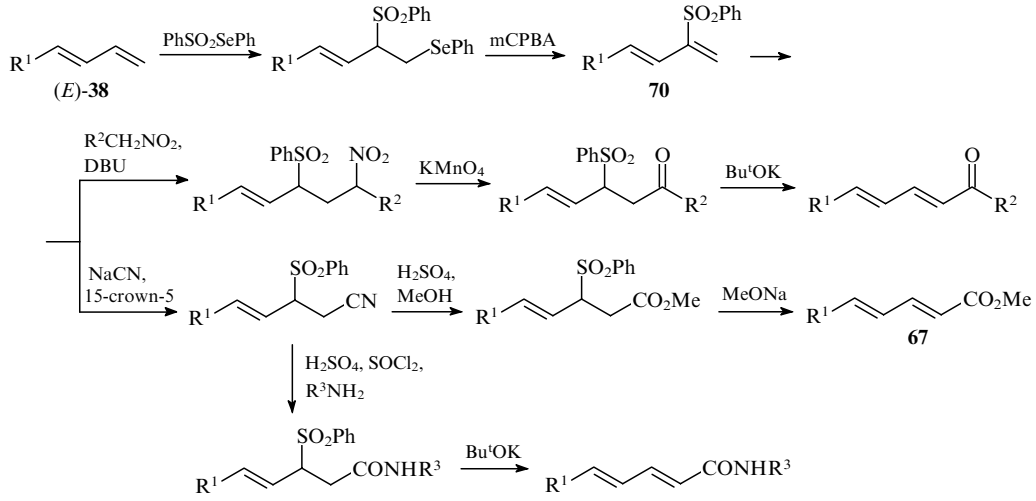
This approach is also applicable to the synthesis of amides (**66**)[82, 83] or esters (**67**)[83] of conjugated dienoic acids.



It should be noted that in the former case, there is no need to isolate the intermediate amides **68**, while in the latter case, the isolation of (1-sulfonylalkyl)butyrolactones **69** is necessary.

The terminal 1,3-dienes (*E*)-**38** are readily converted into the corresponding 2-phenylsulfonyl-1,3-dienes **70** upon treatment with $PhSO_2SePh$ (see a review[84]). The latter are strongly electrophilic, and thus are capable of adding C-nucleophiles. This is a

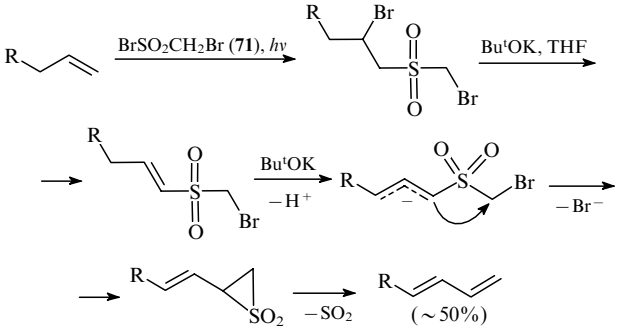
Scheme 3



convenient method for the introduction of a functionalised alkyl substituent to the 1-position of conjugated dienes (Scheme 3).[85,86]

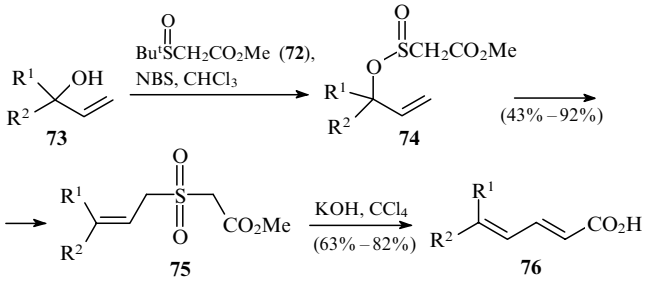
7. Fragmentation of α-halogen-substituted sulfones

The 'vinylogous' Ramberg – Bäcklund reaction (see a review [87]) is yet another example of obtaining 1,3-dienes from sulfones. From preparative standpoint, it is a C_1-homologation of alkenes with a view of introducing an additional double bond; bromomethylsulfonyl bromide (**71**), readily accessible upon bromination of 1,3,5-trithiane, is used here as a C_1 synthon.[88,89]



High regiospecificity of diene formation is observed when cyclic alkenes are used as the starting compounds. Thus the only products obtained from cycloalkenes are 3-methylenecycloalkenes, 1-methylcycloalkenes react to give 1,2-dimethylenecycloalkanes, and methylenecycloalkanes afford 1-vinylcycloalkenes.[90] In all cases, the yields of dienes are moderate. Functionally substituted alkenes have been rarely used in these reactions.

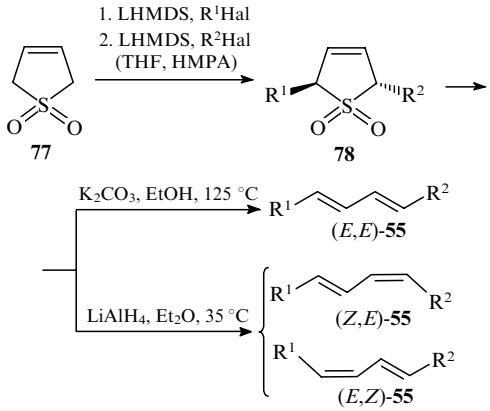
tert-Butyl methoxycarbonylmethyl sulfoxide (**72**) proved to be a convenient synthon for elongating the skeleton of allylic alcohols **73** by a C_2 moiety. The transformation takes place *via* intermediates **74** and **75** to afford alka-2,4-dienoic acids **76**.[91] Its final step is the Ramberg – Bäcklund reaction, the key intermediate of which is generated by deprotonating sulfone **76** and submitting the carbanion to α-chlorination with CCl_4 (not shown).



NBS is *N*-bromosuccinimide.

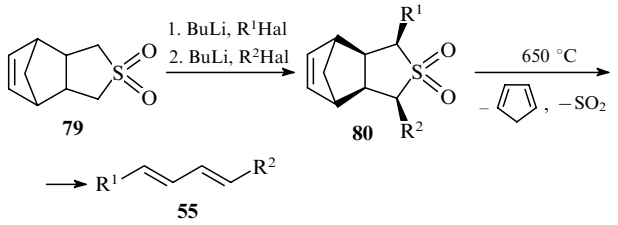
8. Cheletropic elimination

The ability of β-sulfolenes to undergo reversible fragmentation into 1,3-dienes and SO_2 (see a monograph [92]) underlies a versatile synthesis of dienes with somewhat sophisticated structure starting with successive α,α′-bis-alkylation of parental sulfolene **77**.[93,94] Depending on the procedure used to decompose the alkylated sulfolene **78**, one obtains either *E*,*E*- or *E*,*Z*-dienes. The parental sulfolene **77** acts in this method as a synthetic equivalent of 1,4-dianion of buta-1,3-diene. This strategy was employed in the synthesis of some pheromones of *Lepidoptera* that contain terminal or internal *E*,*E*-configured diene substructures.



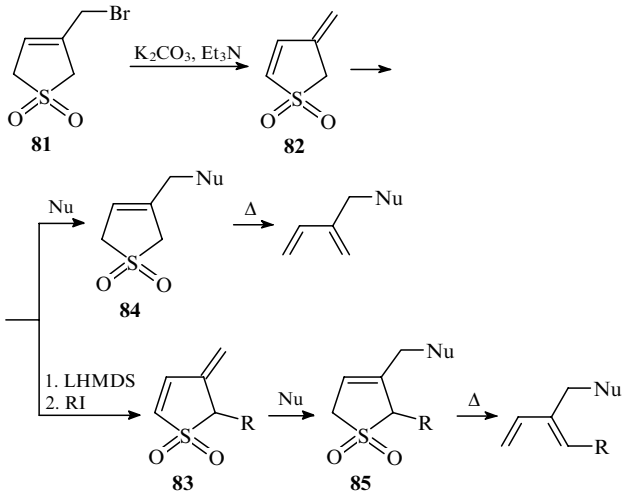
LHMDS is the lithium derivative of hexamethyldisilazane, HMPA is hexamethylphosphoramide.

For the alkylation of sulfolene-derived carbanions, it was recommended to use manganese as the counter-ion. The use of manganese counter-ion enhances the thermal stability of carbanions, so that even allylic halides with additional electrophilic groups (*e.g.*, methyl 4-bromocrotonate) [95] can be used as alkylating reagents. Another way to overcome the lability of sulfolene-derived anions is the use of its synthetic equivalent, tricyclic compound **79** (this sulfolane is prepared by cycloaddition of cyclopentadiene to 3-sulfolene). Upon vapour-phase thermolysis (650 °C), the alkylated derivatives thus formed (**80**) undergo two-step retro-fragmentation to give the *E*,*E*-configured internal dienes **55** of 91% – 95% purity.[96]

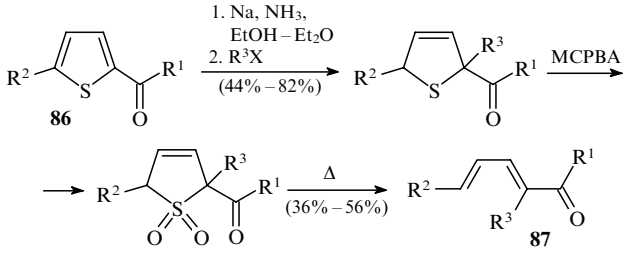


The latter approach proved useful also in the synthesis of insect pheromones.[97,98]

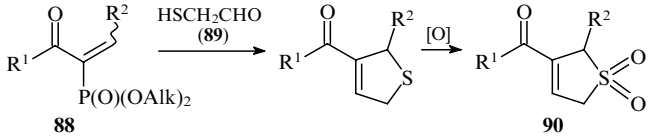
On treatment with NEt_3, 3-bromomethyl-3-sulfolene **81** is converted into 4-methylene-2-sulfolene **82**.[99] The latter, as well as its alkylated derivatives **83**, can readily enter into the Michael reaction with such nucleophiles as amines, thiols and nitroalkane-derived anions, which leads to modified β-sulfolenes **84** and **85** in up to 90% yields. Subsequent thermolysis of **84** or **85** gives rise to the branched 1,3-dienes with functionalised substituents.

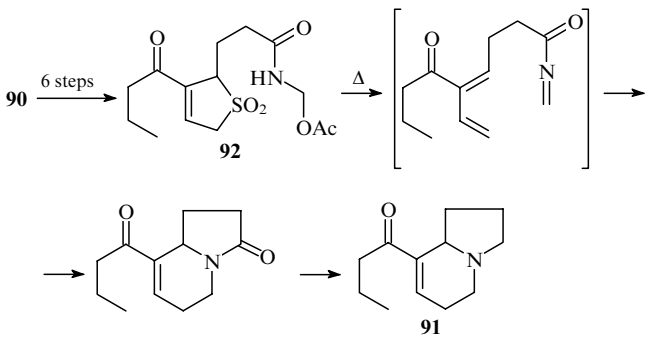


Other approaches to conjugated dienes from variously substituted and functionalised β-sulfolenes have been also reported. In one of them, readily accessible α-acylthiophenes **86** were used as the starting compounds for obtaining α-branched conjugated dienones **87** in three or four synthetic operations.[100]



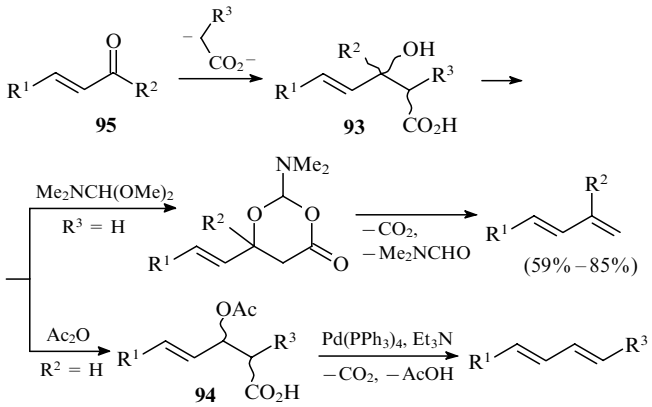
Another group of sulfolenes suitable for the synthesis of conjugated dienes can be obtained from vinylic phosphonates **88** and mercaptoacetaldehyde **89**; the synthetic protocol comprises two sequential Michael reactions followed by intramolecular Horner – Wadsworth – Emmons (HWE) reaction and oxidation.[101] It is recommendable to perform the thermolysis of sulfolenes **90** directly in the presence of electron-deficient dienophiles. This technique was employed in an elegant synthesis of compound **91**, an alkaloid of eleocanine group, from sulfolene **92**.[102]



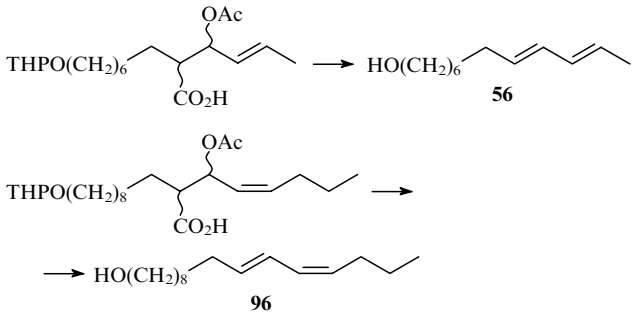


90: $R^1 = Pr^n$, $R^2 = (CH_2)_2CH=CH_2$.

β-Hydroxy acids are prone to decompose with the formation of alkenes and concomitant ejection of carboxy and hydroxy groups. If such substrates (*e.g.*, β-hydroxy acid **93**) have already a double bond, their fragmentation will give dienes. This process can be carried out by treating acids **93** either with *N*,*N*-dimethylformamide acetals [103] or with acetic anhydride.[104] Decomposition of β-acetoxy acids **94** is catalysed by palladium complexes.

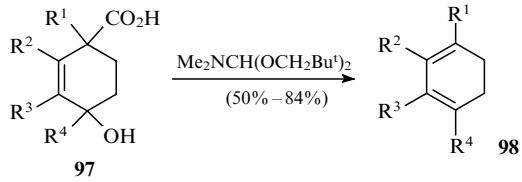


Although intermediate acetoxy acids **94** are obtained as mixtures of stereoisomers, the newly formed double bond acquires the *E*-configuration, while the double bond of the starting enal **95** ($R^2 = H$) retains its configuration in the resulting diene. These transformations were employed in stereocontrolled synthesis of the pheromones **56** and **96**.[104]



THP is tetrahydropyranyl.

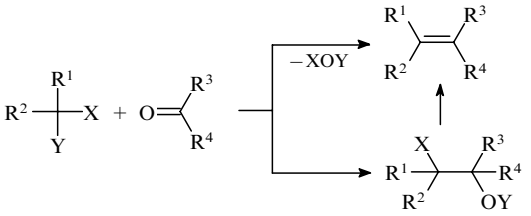
Elimination of carboxy and hydroxy groups from 4-hydroxycyclohex-2-enecarboxylic acids **97** was used in the synthesis of cyclohexadienes **98**.[105]



III. Olefination of carbonyl compounds

Olefination of a carbonyl compound means the replacement of its oxo group by the alkylidene grouping (Scheme 4).

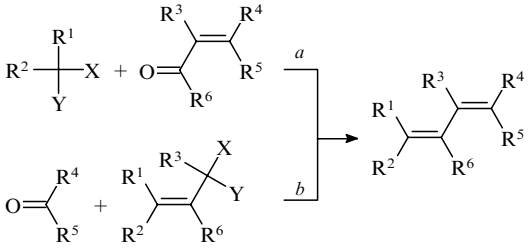
Scheme 4



The process takes place in stepwise manner and includes the addition of olefinating agent to the C=O group followed by the elimination of an X–O–Y species from the primary adduct. In some cases elimination occurs spontaneously, in others the adduct has to be isolated first, after which the second step is carried out separately. The most widely used olefination reactions are shown in Table 1.

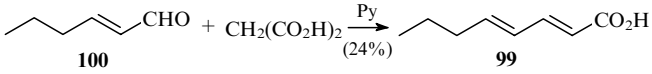
For the synthesis of conjugated dienes, it is necessary that one of the reactants should already possess a double bond. In general, two cases are possible: the double bond is present in the carbonyl compound (*a*), or the double bond belongs to the olefinating agent (*b*) (Scheme 5). Each of the cases displays its particular features depending on the chosen variant of olefination (see the corresponding subsections below). A detailed enough compendium on olefination of carbonyl compounds can be found in Larock's monograph,[10] but some of the methods cited there were used only to obtain monounsaturated compounds.

Scheme 5

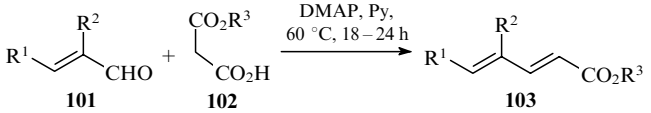


1. Condensation of CH acids with carbonyl compounds

Different variants of direct condensation of α,β-enals with active methylene compounds to give conjugated dienes are described now in all high-school textbooks. Several examples of preparation of dienoic acids are given in a review dedicated to the Knoevenagel reaction.[106] In its classical version, the highest yields (25% – 40%) are attained by heating an enal with malonic acid in pyridine [107–110] (see, *inter alia*, the preparation of octa-2,4-dienoic acid **99** from hex-2-enal **100** [109]). Instead of enal, one can use the corresponding acetal, and perform the reaction in the presence of piperidine in pyridine at 100 – 140 °C.[111] However, the yield of the dienoic acid remains about 20%.



The DMAP-catalysed condensation of enals **101** with alkyl hydrogen malonates affords dienoates **103** in good yields.[112] However, noticeable amounts of deconjugated β,γ,δ,ε-dienoates are formed when β-substituted acroleins ($R^1 \neq H$) are used in the reaction.



When the process is carried out at 140 °C in xylene in the presence of piperidine or its acetate, deconjugated *E* isomers of alk-3-enoic acids are formed as the main products.[113] The extension of this procedure to α,β-enals affords partly deconjugated alkyl dienoates **104**.[114] In total, the yield of isomeric dienes amounts to 60% if DMSO is used as the solvent (100 °C); however, a higher content of the 3*Z*,5*E*-isomer in total products is

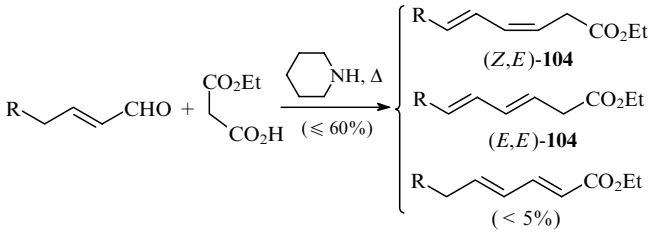


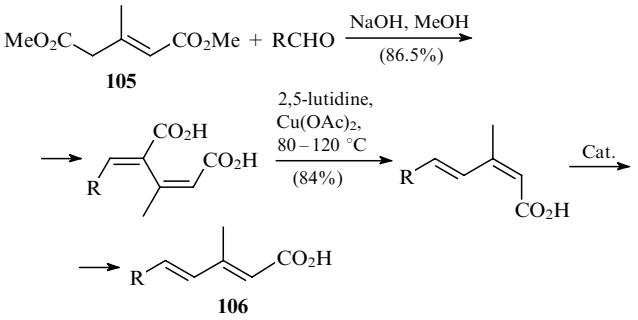
Table 1. Main types of carbonyl olefination reactions.

Olefination variant	The reagent $R^1R^2C(X)(Y)$			Comments
	X	Y	R^1 and R^2	
Aldol condensation	H	H [a]	$R^1 = CO_2R^3$, COR^3, CN	the reaction is sensitive to the nature of the carbonyl substrate
The Knoevenagel reaction	H	H [a]	$R^1 = R^2 = CO_2R^3$, CN	the reaction is characteristic of aldehydes
The Wittig reaction	$=PPh_3$		R^1 and R^2 can contain various functional groups	the reaction is sensitive to the nature of the carbonyl substrate
The Horner – Wadsworth – Emmons reaction	$P(O)(OR)_2$	H [a]	$R^1 = CO_2R^3$, COR^3, CN	the reaction is characteristic of aldehydes and less predictable with ketones
The Peterson reaction	SiR_3	H [a]	$R^1 = CO_2R^3$, CN	the reaction is applicable to nearly all types of aldehydes and ketones if they have no other reactive functional groups
The Julia – Baudin approach	SO_2Ar	H [a]	R^1 and R^2 contain no reactive functional groups	the primary adduct undergoes elimination in a separate step
The Krief reaction	SeR [b]	SeR [b]	the same	the reaction is applicable to nearly all types of aldehydes and ketones if they have no other reactive functional groups

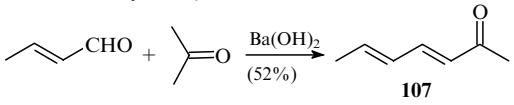
[a] Upon activation, this hydrogen atom is replaced by a positively charged counter-ion. [b] One of these RSe groups is exchanged for lithium.

attained when xylene (140 °C) is used. The unwanted 3*E*,5*E*- and 2*E*,4*E*-isomers (the content of the latter does not exceed 5%) can be removed upon converting them into inclusion complexes with urea.

Since the esters of pentenedioic (glutaconic) acid are the vinylogues of dialkyl malonates, they readily react with unsaturated aldehydes to give substituted conjugated dienes (see a review [115]). Thus the esters of 3-methylglutaconic acid (*e.g.*, **105**) were successfully employed in the synthesis of methoprene (**106**) [R = (MeO)$Me_2C(CH_2)_3CH(Me)CH_2$] as the equivalents of isoprenoid C_5 block.[116] The primarily isolated products of condensation of aldehydes with the glutaconate **105** are configurationally pure 4-carboxy-3-methylalka-(2*Z*,4*E*)-dienoic acids, which are subsequently converted into (*E*,*E*)-3-methylalka-2,4-dienoic acids **106** in several steps.

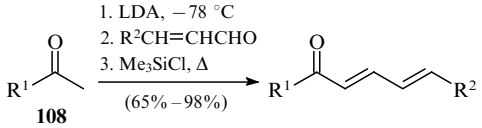


The 'classical' aldol condensation of α,β-enals with aldehydes or ketones (see a review [117]) is also used for obtaining conjugated dienes (*e.g.*, for preparing hepta-3,5-dien-2-one **107** from acetone and crotonaldehyde [118]).

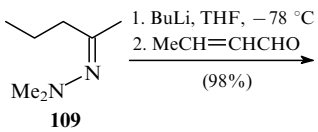


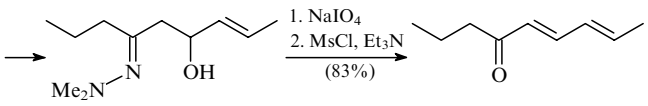
In traditional variants, hydroxides [119] or sodium sulfite [120, 121] are usually used as the bases. The yields of the products, particularly of dienals are moderate, and (quite often) even low. The yields of dienones vary over wide limits and strongly depend on the reaction conditions and on the particular nature of the reaction partners. The industrial large-scale syntheses of pseudoionone and its analogues from citral and acetone (or butan-2-one) were the objects of special research and development studies, and their conditions were duly optimised.[122]

Lately, a number of advanced procedures for directed aldol condensation have been developed. Thus high regioselectivity can be attained by using alkyl acetates or methyl ketones as the active methylene component (**108**), and lithium diisopropylamide as the base [123]. Upon treatment with LDA, ketones of the type **108** with two activated positions undergo deprotonation almost entirely at the methyl group due to the kinetic control.[124]

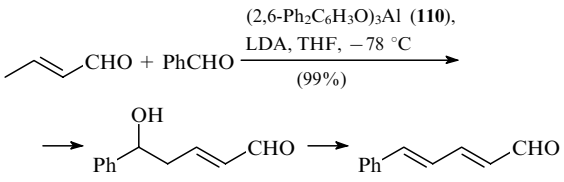


Another regioselective method of deprotonation consists in using dimethylhydrazones of asymmetric aliphatic ketones like **109**.[125]





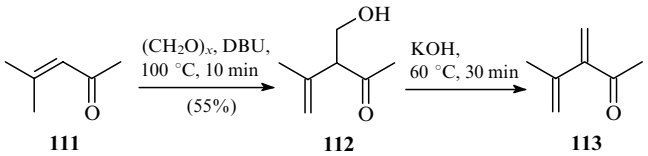
Recently [126] a conceptually new mode of aldol condensation has been developed. It consists in treating a mixture of two aldehydes, one of which is an α,β-enal, with LDA at −78 °C in the presence of aluminium tris(2,6-diphenylphenoxide) **110**. Under these conditions, α,β-enals behave exclusively as the vinylogues of the active methylene components.



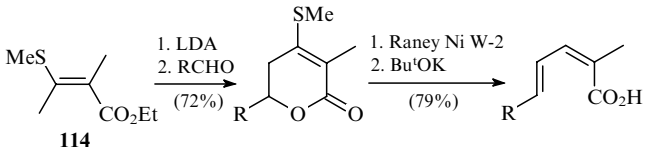
The choice of enals in this method is not confined to crotonaldehyde-like structures; higher polyenals $Me(CH=CH)_nCHO$ and conjugated enones (that react by their vinylogous anionic termini) also are suitable. Thus in 4-methylacetophenone it is the remote methyl, not the COMe group, that is activated under above conditions!

It was speculated that on mixing, the reactants form a specifically shaped conglomerate the deprotonation of which at vinylogous positions is the most favoured one. The addition of the resulting carbanion to the aldehyde component is believed to take place inside the conglomerate.

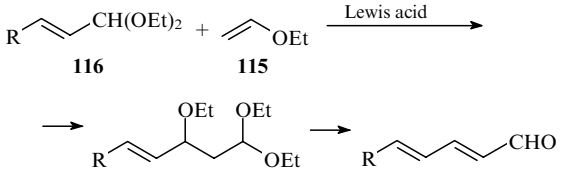
Under other conditions, the α,β-unsaturated carbonyl compounds like mesityl oxide **111** after deprotonation, add to the carbonyl substrates (electrophiles) with formation of deconjugated products, *e.g.*, **112** [127] Subsequent dehydration of the latter leads to the branched conjugated diene **113**.



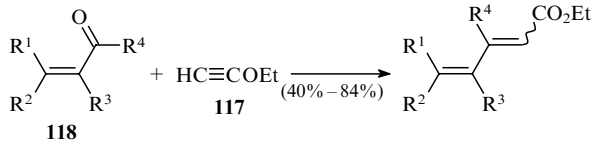
An original regio- and stereocontrolled approach to α-branched (2*Z*,4*E*)-dienoic acid relies on the use of a vinylogous synthon **114** with a methylthio group.[128]



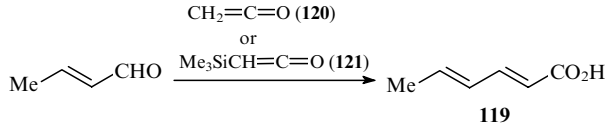
Yet another way of securing high regioselectivity in the condensation of two different carbonyl compounds is to replace conventional active methylene component by its synthetic equivalent, vinyl ether (*e.g.*, **115**). Moreover, not only aldehydes but acetals **116** can be used as carbonyl components, which operationally is more convenient. Characteristic features of this process have been thoroughly studied and discussed in a review [129] and a monograph.[130] The main shortcomings of this method are its tedious procedures and moderate yields.



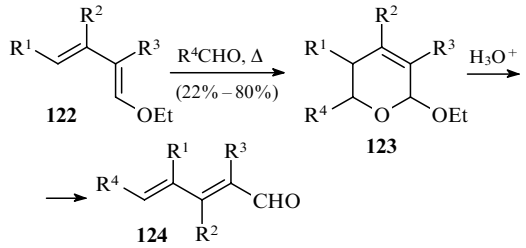
Similar results were obtained by employing ethoxyacetylene **117** instead of the active methylene component.[131–135] Using this agent, the reaction can be performed not only with aldehydes but also with ketones (**118**, $R^4 \neq H$). In this case, the overall reaction product is a mixture of stereoisomers. The process can be implemented either in the presence of $BF_3 \cdot OEt_2$, or by adding the organometallic derivative of **117** to the carbonyl component, and then by subjecting the adduct to acid hydrolysis.



Sorbic acid (**119**, fungistatic agent for food) is manufactured industrially on a multitonne scale by a process where ketene (**120**) is used as the C_2 component.[136, 137] In the laboratory practice, it can be conveniently replaced by trimetylsilyl ketene **121**.[138]



The Diels–Alder reaction of 1-alkoxybuta-1,3-dienes **122** with strongly electrophilic aldehydes leads to dihydropyran derivatives **123**, which can be subsequently transformed into dienals **124**.[139, 140] In this protocol, the compound **122** acts as a synthetic equivalent of crotonaldehyde.



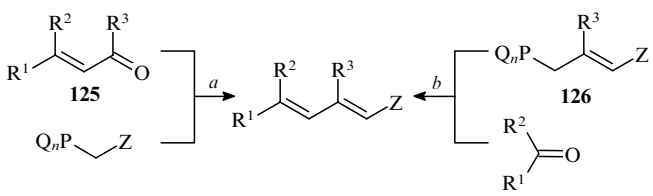
R^1, R^2, R^3 = H, Me; R^4 = H, CCl_3, CO_2Et.

2. The Wittig reaction and related processes

The Wittig reaction (in its classical or newer variants) is one of the most popular methods of olefin synthesis. Recently, its mechanistic and preparative aspects have been studied in much detail, and discussed in reviews.[141–143] In general (Scheme 6), for the construction of a conjugated diene system. it is necessary that one of the reactants, either the carbonyl compound **125** (pathway *a*) or the phosphorus-bearing compound **126** (pathway *b*) should already have a double bond in its structure.

From the standpoint of operational convenience, pathway *a* is technically simpler and thus preferable, provided that the olefinic carbonyl compound is readily accessible.

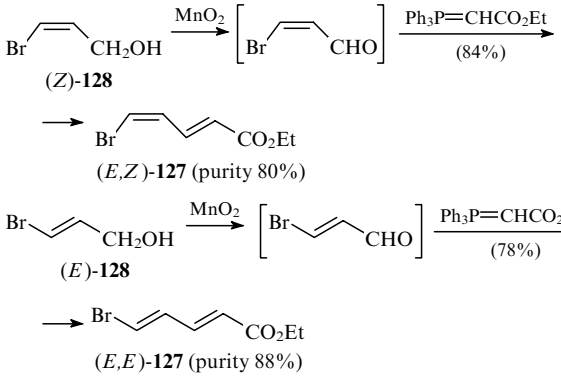
Scheme 6



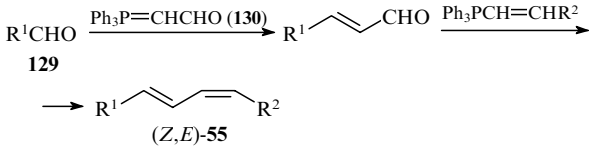
Q_nP = Ph_3P^+, $Ph_2P(O)$, $(AlkO)_2P(O)$ *etc.*; Z = Alk, Alkenyl, Ar, Het, CO_2R^4, CN, $CONR^4_2$, $C(O)R^4$ *etc.*

a. Phosphoranes

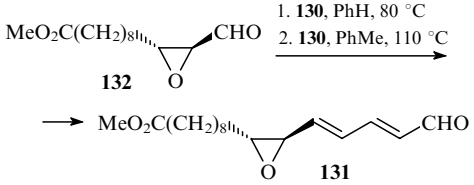
As a rule, the use of phosphoranes like $Ph_3P=CHCO_2Et$ or $Ph_3P=CHCN$ in reactions with α,β-unsaturated aldehydes is unproblematic; this is confirmed by abundant literature records. Thus a recent work describes a stereoselective *in situ* synthesis of (2*E*,4*Z*)- and (*E*,*E*)-5-bromopenta-1,3-dienoates (**127**), where the oxidation of (*Z*)- and (*E*)-3-bromoallyl alcohols was carried out in the presence of $Ph_3P=CHCO_2Et$.[144]



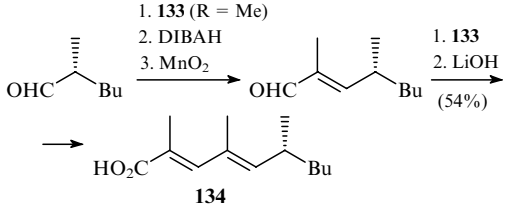
The starting α,β-enals can be obtained by elongating saturated aldehydes **129** by a C_2 fragment using 2-oxoethylidene phosphorane **130**. A stepwise process for preparing the *Z*,*E*-configured dienes **55** from alkanals **129** consisting of two sequential Wittig olefinations has been developed.[145]



The *E*,*E*-configured 5,6-*trans*-epoxyalka-2,4-dienals **131** are obtained in moderate yields by two-step elongation of *trans*-2,3-epoxyalkanals **132** with phosporane **130** first under mild, and afterwards under somewhat more drastic conditions.[146–148] Alternatively, dienal **131** can be prepared in one step using the vinylogous phosphorane $Ph_3P=CH-CH=CHCHO$.[149]



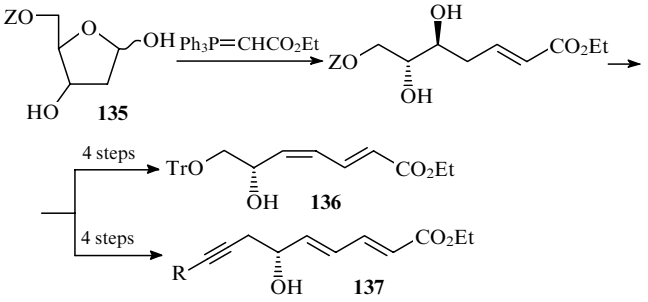
For the first stage of elongation, the phosphorane **130** can be replaced by more accessible alkoxycarbonyl-substituted phosphoranes $Ph_3P=C(CO_2Et)R$ (**133**, R = H, Alk); after that, the CO_2Et group introduced is transformed into CHO.[150] The (*E*,*E*)-dienoic acid **134** was synthesised in this way with high stereoselectivity.



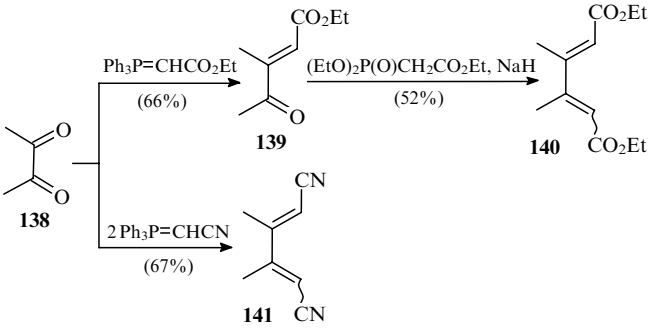
DIBAH is diisobutylaluminium hydride.

Aldol hemiacetals can be successfully used in the Wittig olefination instead of aldehydes. Thus starting from 2-deoxy-D-ribose (a naturally occuring aldol hemiacetal) or its derivatives

135, dienes **136** and **137** have been synthesised.[151, 152] Depending on the procedure employed for eliminating the 5-OH group from the intermediate dihydroxy alkenoate, the configuration of the second double bond in the target dienes can be *Z* or *E*.

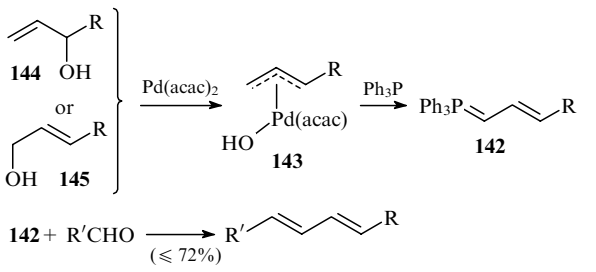


Unlike aldehydes, conjugated ketones enter reluctantly into the Wittig reactions. The α,β-enones that are not branched at the β-position sometimes enter into the Michael reaction with phosphonates of the type $(RO)_2P(O)CH_2CO_2Alk$ to give the products of 1,4-addition.[153] It is noteworthy that α-diketones **138** can react with two molecules of the above phosphonates and give conjugated dienes *via* the intermediate α,β-enone **139**.[154, 155] For the synthesis of diesters **140**, it is necessary to adopt a two-step procedure,[154] while the preparation of dinitriles **141** can be performed in one step due to the higher reactivity of the corresponding intermediate.[155]

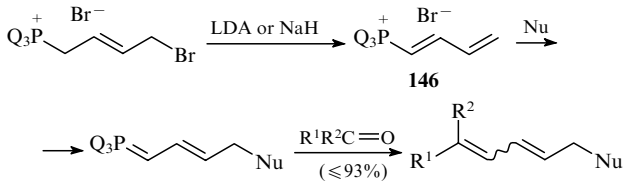


Cyclic α-diketones such as cyclobutane-1,2-dione and cyclohexane-1,2-dione also react in this way to give semicyclic dienes.

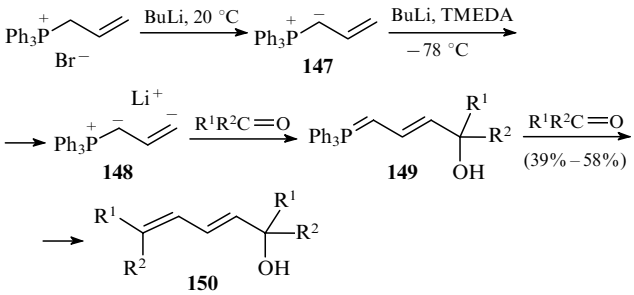
Pathway *b* of Scheme 6 looks equally attractive. The use of allylic phosphoranes **126** (Z = Alk, Ar) is justified, particularly when the precursor of the phosphonium salt, the corresponding allylic halide, is readily accessible.[156] Allylic halides of higher molecular complexity are rather difficult both to prepare and, particularly, to purify. As a consequence, roundabout approaches to allylic phosphoranes have been developed. Thus allylic phosphoranes **142** are formed *in situ* from the η^3-allylic palladium complexes **143** (prepared by heating allylic alcohols **144** or **145** in dioxane in the presence of $Pd(acac)_2$ and triphenylphosphine.[157, 158] The subsequent reaction of phosphoranes **142** with aldehydes affords conjugated dienes. This way of preparing conjugated dienes is lengthy enough and complicated by side reactions.



Another synthesis of conjugated dienes that involves indirect approach to allylic phosphoranes relies on the ability of (buta-1,3-dienyl)phosphonium compounds **146** to react with C-nucleophiles such as the dianions of β-dicarbonyl compounds or organocuprates.[159, 160]



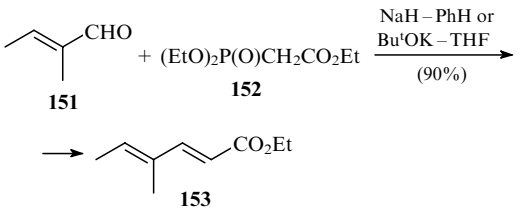
On treatment with strong bases, allyltriphenylphosphorane **147** gives metallated derivative **148**, which reacts with one molecule of a carbonyl compound as a C-nucleophile to afford the modified allylic phosphorane **149**. Then the Wittig reaction of **149** with the second molecule of aldehyde or ketone brings forth dienic alcohols **150** in moderate yields.[161]



TMEDA is *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.

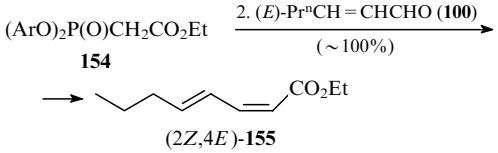
b. Phosphonates

It is profitable to replace phosphoranes by the corresponding phosphonates of the type $(EtO)_2P(O)CH_2Z$. This variant of olefination is known as the Horner – Wadsworth – Emmons reaction. Thus the olefination of tiglic aldehyde **151** with triethyl phosphonoacetate **152** affords ethyl dienoate **153** in 90% yield.[162, 163] The newly formed double bond has almost pure *E* configuration.

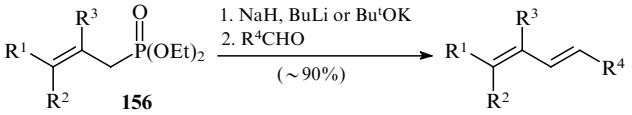


A simple procedure for implementing such a process has been proposed. It consists in mixing together and stirring an aldehyde, phosphonate **153** and concentrated aqueous K_2CO_3. The method is applicable to the synthesis of alkyl dienoates or alkadienones and provides satisfactory yields (60% – 70%).[164] Time and again, it was used in the synthesis of natural products.[4, 165, 166]

In the case of phosphonates with phenoxy groups (**154**), the stereoselectivity of olefination is reversed (with respect to the case of **152**) *i.e*, the *Z*-isomers of alk-2-enoates are produced.[167] For the reactions involving phosphonates **154**, it was recommended to use NaH, Triton B or the DBU – NaI system as the base. The reaction of hex-2-enal (**100**) with **154** afforded ethyl (2*Z*,4*E*)-octa-2,4-dienoate **155** with 97% isomeric purity.[168]



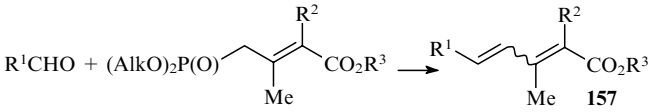
The reaction of allylic phosphonates of the type **156** with saturated aldehydes can be successfully applied to the synthesis of dienes.[169]



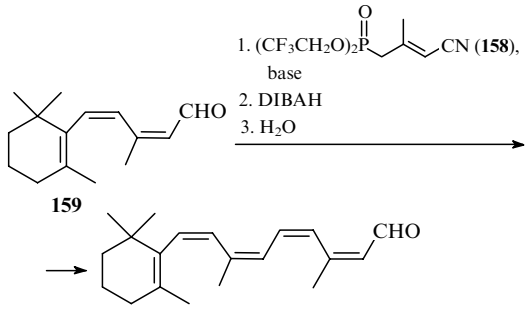
R^1, R^2, R^3 = H, Alk.

For allylic phosphonates **156** with additional functional groups (R^1 or R^2 = CO_2Alk, $CONR_2$, RCO, or CN) the HWE reaction is one of the most studied because it is widely used in the synthesis of polyenes. Such phosphonates are usually prepared by employing the Arbuzov or Michaelis–Becker reactions (see a review[142]). Recently, an interesting method for the synthesis of γ-phosphono-α,β-enones from allylic phosponates was reported.[170] Its protocol involves silylation, alkylation (if necessary) and finally acylation.

The experience accumulated since the mid-sixties suggests that the HWE reactions are sensitive to the nature of the reactants and bases used and to conditions under which they are implemented. Thus for the preparation of alkyl dienoates of the type **157**, it was recommended to use such bases as MeONa in DMF,[171] $NaNH_2$ in THF,[171] NaH in DMF,[172] and, what is particularly convenient, the systems of phase transfer catalysis: solid KOH–benzene–18-crown-6 (Cat.)[173–176] or solid KOH–benzene–$Alk_4N^+Br^-$ (Cat.).[177,178] In the latter case, 3-methylalka-2,4-dienoates **157** are formed with 90%–96% *E*,*E*-selectivity[143,178] By contrast, when the phosphonate grouping contains the 1,3,2-phospholane fragment, the reaction results in 2*Z*,4*E*-isomers (~70%–85% selectivity).[179,180]

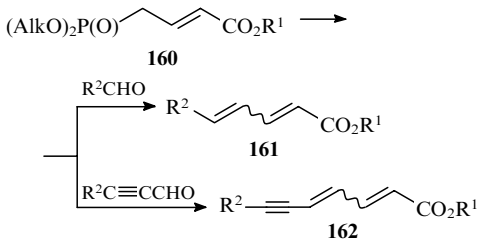


Bis(β,β,β-trifluoroethyl) esters of aliphatic phosphonic acids (Still–Gennari phosphonates) react with aldehydes to give *Z*-alkenes. The reactions of α,β-enals with bis(β,β,β-trifluoroethyl) 3-cyano-2-methylprop-2-enylphosphonate (**158**) afford the 2*Z*,4*E*-isomers of 2-methylalka-2,4-dienonitriles with high selectivity.[181] The possibility of using the phosphonate **158** for the synthesis of 1,3-dienes with *Z*-configured newly formed double bond is indicated by the reaction of (2*Z*,4*Z*)-β-ionylideneacetaldehyde (**159**) with this phosphonate.[182]



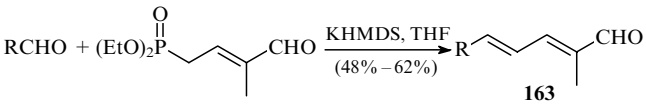
In the mixture of four stereoisomers of retinal formed in this reaction, the proportion of products with *Z*-configuration of the newly formed double bond amounts to 72%.

When non-branched phosphonocrotonates **160** are used, the yields of dienes **161** decrease (to 59% with the use of $NaNH_2$ in THF[4,166]); under conditions of phase transfer catalysis, the dienes **161** are not formed at all. However, with the use of lithium derivative of hexamethyldisalazane,[183] the dienes **161** are produced in 84% yield, whereas the use of LDA having close properties[184] provides only 27% yield. Recently, a method for the synthesis of conjugated dienes has been proposed according to which a mixture of the initial phosphonocrotonate and aldehyde is refluxed in THF in the presence of LiOH and 4 Å molecular sieves. The yield of dienes is 86%.[185] Cyclohexanones can be used successfully in place of aldehydes in this reaction.

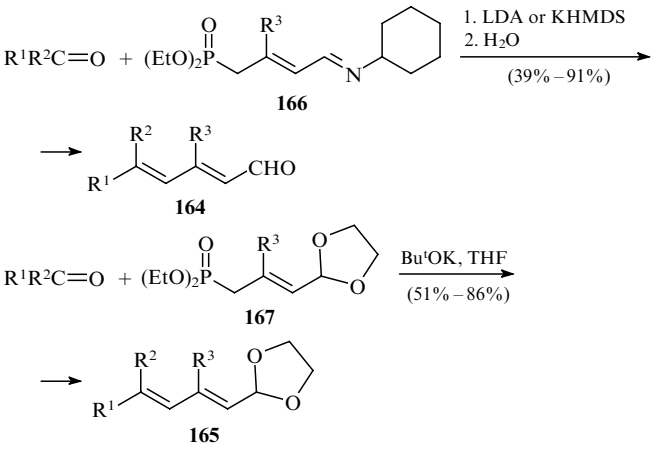


Olefination of acetylenic aldehydes by the phosphonate **160** in the presence of $NaNH_2$ in THF gives rise to the corresponding dienynoates **162** in a yield not higher than 36%.[4,186]

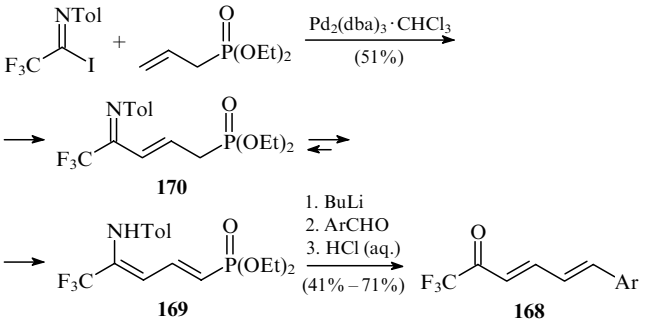
Apart from esters, dienals **163** have also been synthesised using this route.[187]



Dienic aldehydes **164** and their acetals **165** can be prepared using synthons **166** and **167** with the protected aldehyde group.[188,189]

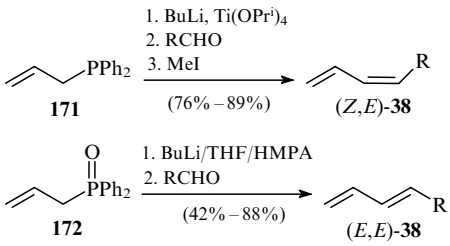


Dienyl trifluoromethyl ketones **168** are formed from dienamines **169**, tautomers of Schiff's bases **170**.[190]

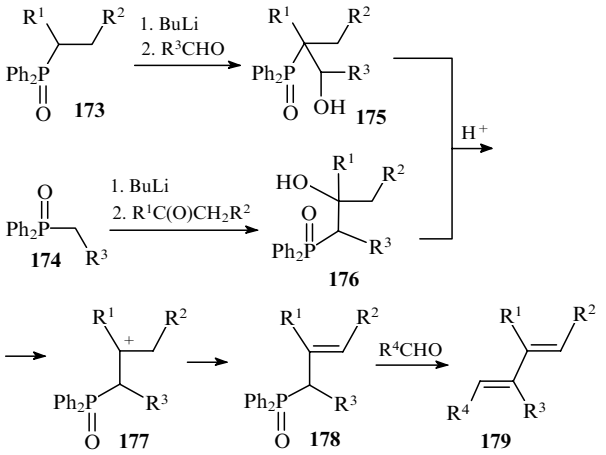


c. Allylic phosphines and phosphine oxides

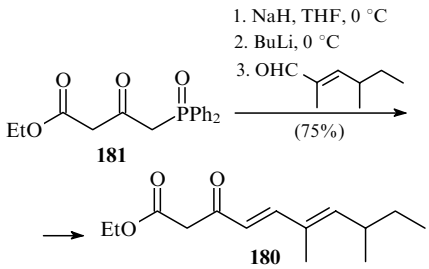
Olefination of carbonyl compounds can also be performed by means of allylic phosphines **171** and allyl phosphine oxides **172**;[191] the products **38** thus formed differ in the stereochemistry of the newly formed double bond.



Allylic phosphine oxides with more complex structures used for the synthesis of functionally substituted conjugated dienes can be prepared from simpler phosphine oxides **173** or **174**.[192] To this end, compounds **173** and **174** are made to react with aldehydes and ketones, and the reaction products **175** and **176** are subjected to dehydration. Acidic dehydration of secondary β-hydroxyphosphine oxides **175** is accompanied by the migration of the phosphorus-containing group, while dehydration of tertiary β-hydroxyphosphine oxides **176** follows the standard pathway. In both cases, tertiary carbocation **177** is formed, which is transformed, under thermodynamic control, into thermodynamically more favourable alkene **178**. Thus the same product **179** can be prepared in different ways, which makes the phosphine-oxide route more versatile.

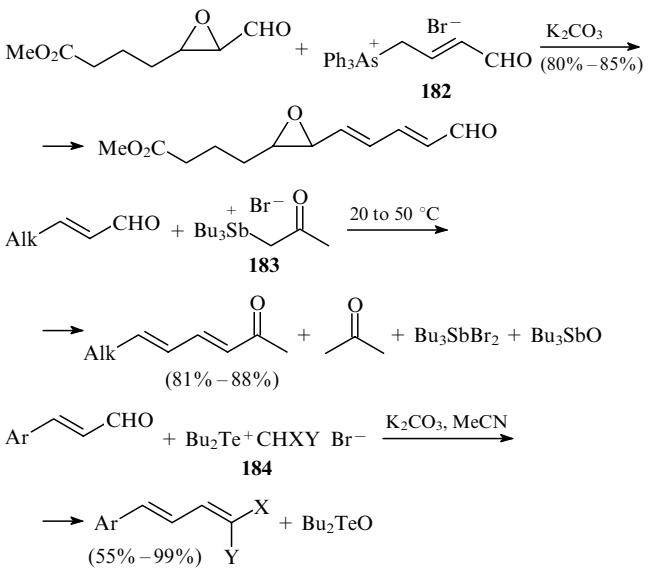


The synthesis of conjugated diene **180** containing an ethyl acetoacetate fragment as a substituent has been reported.[193] This compound was prepared using phosphine oxide **181**.



d. Related methods

In conclusion, we shall consider methods of olefination of carbonyl compounds making use of 'non-phosphorus' equivalents of the Wittig reagents based on arsenic **182**,[194,195] antimony **183**[196] and tellurium **184**.[197,198] It should be noted that in the case of complex syntheses, the use of arsonium derivatives has substantial advantages. The advantages and shortcomings involved in the use of antimony and tellurium derivatives have not been adequately elucidated.

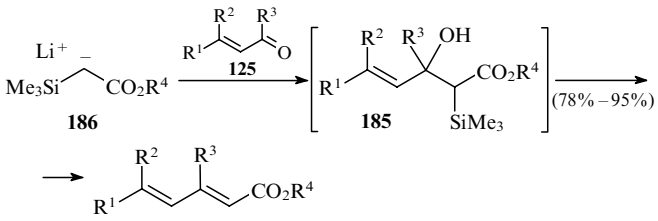


X = CN, CO_2Et; Y = H, Ph.

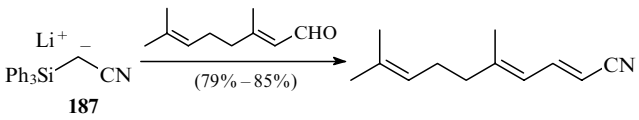
3. Miscellaneous methods of olefination of carbonyl compounds

a. The Peterson reaction

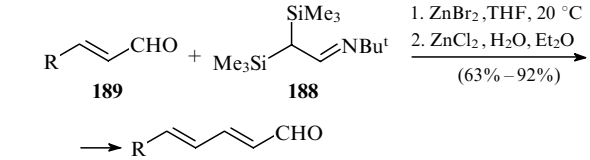
The Peterson reaction consists in elimination of vicinal silyl and hydroxy groups, resulting in the formation of a double bond (see Section II). Here, we consider the version used to olefinate α,β-unsaturated carbonyl compounds. In this technique, the starting β-hydroxy silanes **185** are formed *in situ* upon the addition of silicon-containing carbanion reagents **186** to the carbonyl compounds **125**.[46,47]



An advantage of this approach is the possibility of using not only α,β-unsaturated aldehydes but also ketones including relatively non-reactive chalcone.[48] An organosilicon reagent should contain a group exhibiting a $-M$-effect. Apart from esters **186**, the acetylene derivative $Me_3SiCH_2C{\equiv}CSiMe_3$ and the nitrile **187**[49] have also been involved in this reaction. Deprotonation is carried out by amides such as LDA; the yields are high in all cases.

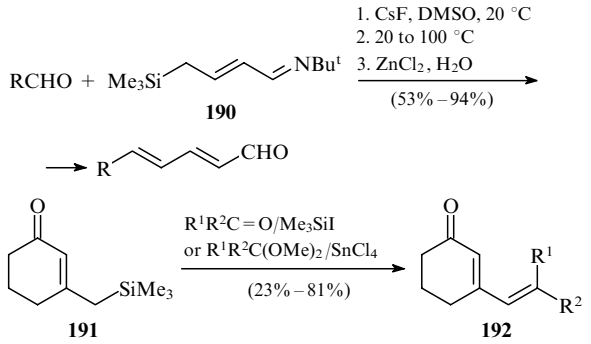


In recent years, a convenient C_2 olefinating synthon **188** has been devised; it contains two geminal silyl groups and is able to react with aldehydes **189** in the presence of Lewis acids under very mild conditions.[199]



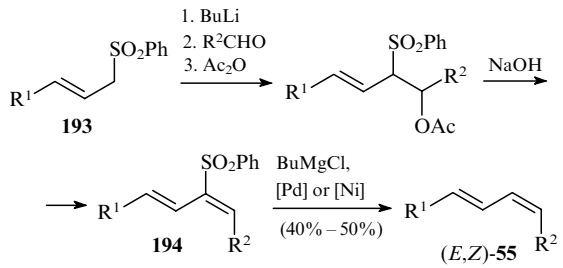
A similar vinylogous C_4 synthon with two silyl groups has not been prepared; however, C_4 olefination can be accomplished under other conditions using monosilyl reagent **190**.[200,201] The

reactions of carbonyl compounds and acetals with cyclic γ-silyl-α,β-enones **191** giving rise to dienones **192** have been described.[202]

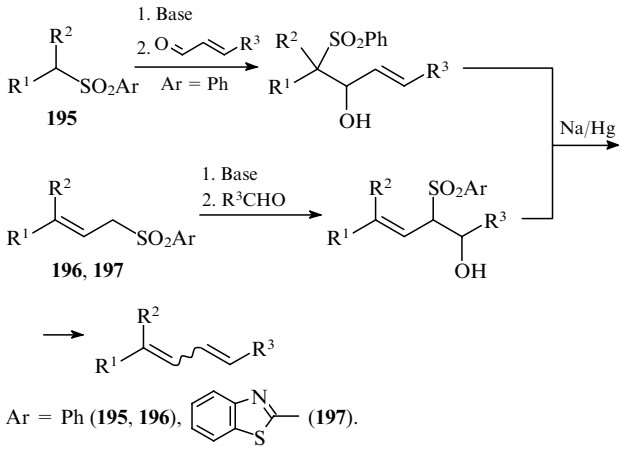


b. The Baudin – Julia method

The Julia method consists in condensation of aryl sulfones with aldehydes followed by reductive elimination of the sulfone group from unsaturated sulfone of the type **64** (see Scheme 2),[78,79] for example, on treatment with $LiAlH_4$. The involvement of unsaturated sulfones **193** in this process should furnish dienes. It has been proposed [203] to use BuMgCl for the reduction of the intermediate *Z*-olefinic sulfones **194** in the reaction catalysed by $Pd(acac)_2$ or $Ni(acac)_2$. The isomeric purity of the products **55** was 93% – 97%; however, the yields were moderate.



In another study,[204] olefination of α,β-enals with saturated sulfone of the type **195** and olefination of saturated aldehydes with allylic sulfones **196** (Ar = Ph) have been studied in substantial detail with verification of numerous factors. Elimination of vicinal sulfonyl and hydroxy groups was induced by sodium amalgam. The yields of dienes were moderate, despite the efforts made by the authors.

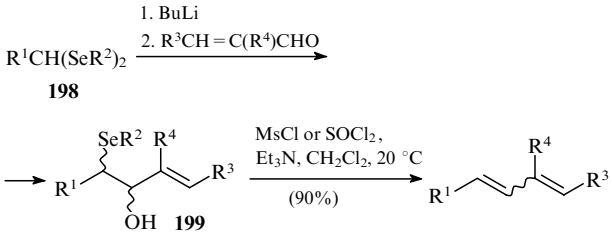


In a perfected method, the phenyl group in the sulfone **196** was replaced by various heterocyclic groups, which resulted in higher product yields, the best results being attained for the 2-benzothiazole substituent (compound **197**).[205–207] This is due to the fact that heteroatoms in the aryl group change the final steps of the olefination mechanism; this influences the product yield, which can reach 86%.

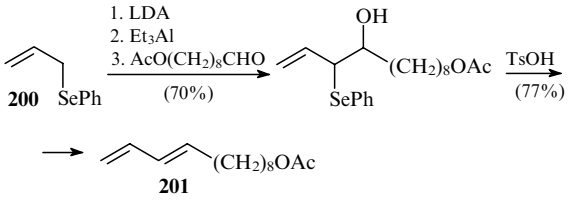
Both reactions — unsaturated sulfone + saturated aldehyde and *vice versa* — are used for the synthesis of dienes. Usually, this gives a mixture of *E,E*- and *E,Z*-isomers, their ratio being dictated by the pattern of substitution at the double bond in the reactants.

c. The Krief reaction and other olefination methods

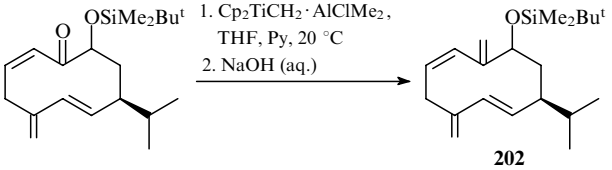
The ability of selenoacetals **198** to exchange one selenium-containing group for lithium has underlain the new Krief olefination method.[208–210] The reaction of the carbanion formed (stabilised by the remaining selenium atom) with aldehydes or ketones yields β-hydroxy alkyl selenides **199**, which readily form olefins on the subsequent treatment with acidic reagents. In the case of unsaturated aldehydes, the method results in conjugated dienes.[211,212]



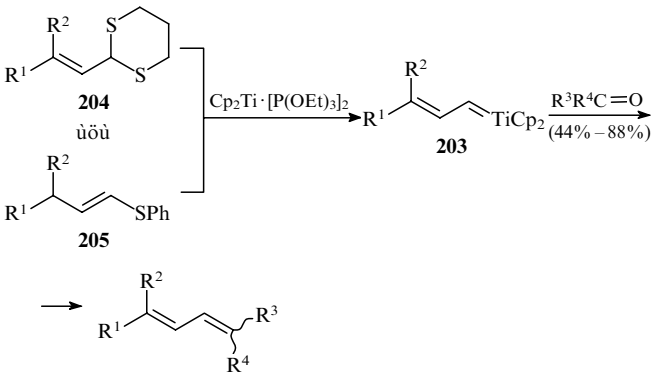
Another variant of organoselenium synthesis of dienes, namely, the reaction of a saturated aldehyde and an unsaturated selenium component, is also possible. Allyl selenides **200**, the CH acidity of which is high enough for hydrogen to be eliminated on treatment with LDA, are possible precursors of this type of selenium component. The resulting carbanion, however, exhibits ambident properties and furnishes mixtures of isomeric products in reactions with electrophiles.[213] To ensure the required regiodirectivity, the reagent is treated with Lewis acids; the ate-complex thus formed reacts with an aldehyde to give the 'normal' product **201**.



The titanium carbene complex $Cp_2Ti{=}CH_2$ (the Tebbe reagent) is an efficient methylenating agent.[214] It reacts with unsaturated carbonyl compounds giving rise to conjugated dienes including those difficult to prepare by other methods, such as **202**.[215]

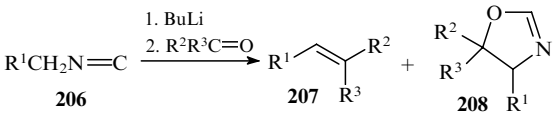


Recently, it has been shown that unsaturated analogues of the Tebbe reagent (**203**) can be prepared from α,β-enal cyclic thioacetals **204** on treatment with a titanocene(II) complex with triethyl phosphite.[216] The reactions of the carbenes **203** with aldehydes, ketones, and even esters (!) result in the formation of a new double bond. Instead of the thioacetals **204**, 1,3-diphenylthioalk-1-enes **205** (R^1 = SPh) [217] can be used in the reaction (they are produced from α,β-enals under conditions of acetalisation with monothiols). In the case of non-branched dienes ($R^2 = R^4 = H$), the proportion of *E,E*-isomer exceeds 87%.



R^3 = Alk; R^4 = H, Alk, Ar, OAlk.

Isocyanides **206** can also serve as olefinating agents;[218] however, in this case, in addition to alkenes **207**, the reaction gives substantial amounts of oxazolines **208**. This route was use to convert cinnamaldehyde into 1-phenylbuta-1,3-diene (R^1 = R^2 = H, R^3 = PhCH=CH) in 28% yield.



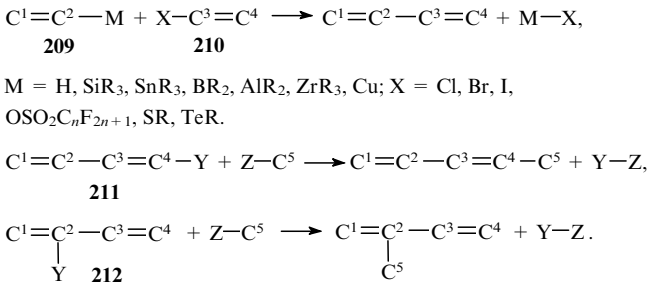
The reaction of aldehydes with diazo esters leading to α,β-unsaturated esters can also be classified as olefination. In the only known example, namely, in the reaction of cinnamaldehyde with diazo ester, the yield of the corresponding conjugated diene is 92%.[219]

IV. Organometallic reactions

1. Cross-coupling of vinylic and/or acetylenic components

Cross-coupling reactions belong to the most advanced methods for the creation of a C−C bond. The thermodynamic factor, which accounts for the occurrence of these reactions, is the formation of a favourable bond between the electropositive element M of reactant **209** and the electronegative element X of reactant **210** (Scheme 7). The reactions of the general form **209** + **210** are usually classified according to the sort of the electropositive element in the reactant **209**, the nature of which governs the mechanism of the process, although the outcome is formally the same.

Scheme 7

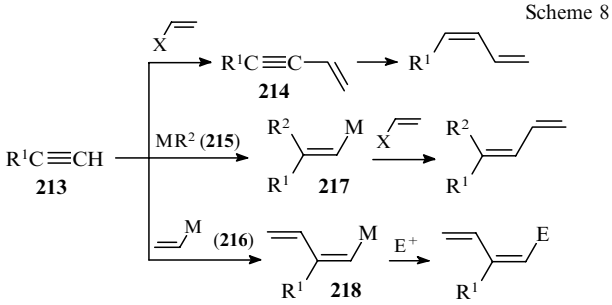


M = H, SiR_3, SnR_3, BR_2, AlR_2, ZrR_3, Cu; X = Cl, Br, I, $OSO_2C_nF_{2n+1}$, SR, TeR.

In the synthesis of carbo-substituted conjugated dienes, cross-coupling of two vinylic components giving rise to the central single bond is used most often. The replacement of the heteroatom in a preformed diene system **211** or **212** by a carbon-centred fragment is used more rarely. A fundamental feature of cross-coupling reactions is retention of the configuration of the reacting centres, which permits one to prepare, as desired, any of the possible isomers of conjugated dienes (*E*,*E*-, *E*,*Z*-, *Z*,*E*- and *Z*,*Z*-isomers).

Cross-coupling can also involve components with triple bonds such as **213**. First, they react with alkenyl reagents to give conjugated enynes **214**. Second, some organometallic reagents of the type **215** or **216** are capable of adding to triple bonds to give

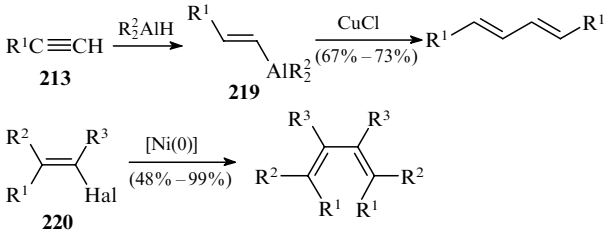
Scheme 8



new metal alkenyls, **217** or **218**, respectively. All the compounds obtained can be further converted into dienes (Scheme 8).

The reactions listed above have been thoroughly studied and discussed in numerous publications;[220–227] therefore, in this review, we present only a brief characterisation. There is a fairly detailed list of published data on each type of reaction.[10]

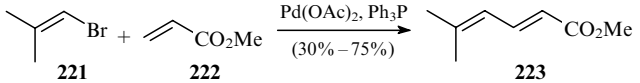
In early examples, cross-coupling has been carried out with stoichiometric amounts of organometallic reagents. The scope of these reactions is limited as they mainly permit the preparation of symmetrical compounds. This is indicated by homodimerisation of alkenylalanes **219** induced by CuCl[228] or of various alkenyl halides **220** in the presence of stoichiometric amounts of nickel complexes such as $Ni(cod)_2$ (cod is cycloocta-1,5-diene)[229] or $Ni(bipy)_n$ prepared *in situ*.[230]



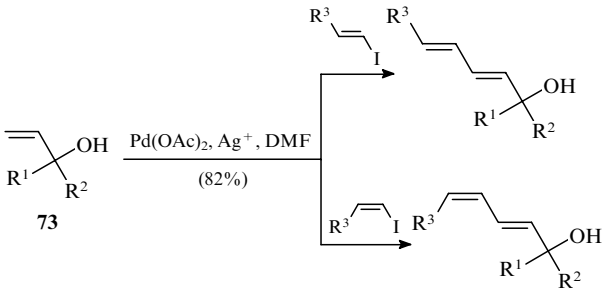
Catalytic cross-coupling protocols are much more efficient. Palladium or nickel complexes are the most popular catalysts of these processes.

a. The Heck reaction and its modifications

The coupling of α-alkenes (**209** with M = H, see reviews[220,221]) with alkenyl or aryl halides catalysed by palladium complexes is called the Heck reaction. Coupling of the vinylic components **221** and **222** affords conjugated dienes **223**.[231]

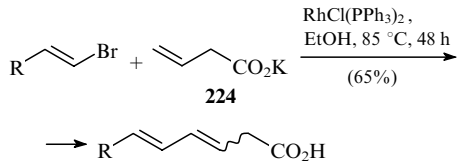


It is advantageous to perform this process in the presence of Ag salts as HHal acceptors;[232,233] in this case, the allylic alcohols **73** can also be introduced in the reaction.



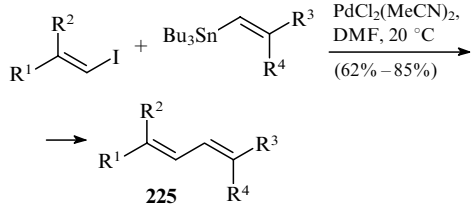
Apart from alkenyl halides, the Heck reaction can be carried out for alkenyl perfluoroalkyl sulfonates,[234,235] alkenylsilanols,[236] alkenylpentafluorosilicates[237] and alkenyl(aryl)iodonium salts.[238] Coupling of alkenyl bromides with potassium but-3-enoate (**224**), similar to the Heck reaction in the outcome but

catalysed by the rhodium complex $RhCl(PPh_3)_2$, has been described.[239]

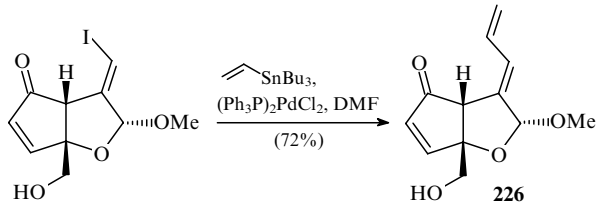


b. The Stille reaction

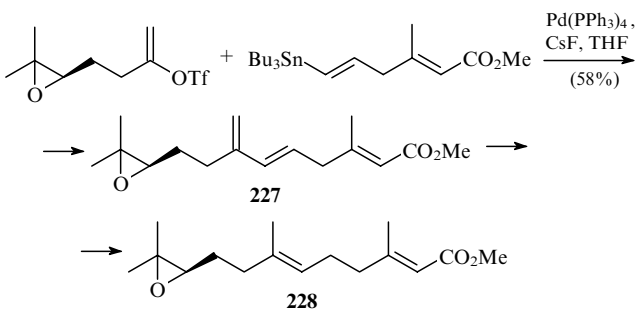
Coupling of organotin compounds with halides catalysed by palladium complexes has been called the Stille cross-coupling (**209** with M = SnR_3, see reviews [222, 223]). In addition to the synthesis of biaryls, styrenes and enynes, this reaction is also good for the synthesis of various conjugated dienes **225**.[240, 241] The reaction proceeds with full retention of the configurations of the reacting centres; the initial compounds may contain diverse substituents and the product yields are usually high.



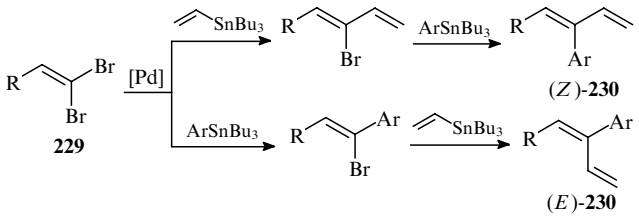
The Stille reaction has been used in the total synthesis of complex natural products, for example, didemnenones **226**, biologically active compounds generated by marine *Tunicata*.[242]



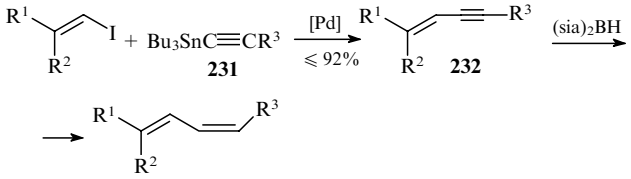
Triflates can be involved in this reaction instead of halides;[243] this has been used in the synthesis of triene **227**, the closest precursor of the C_{16} juvenile hormone (**228**).[244]



1,1-Dibromoalkenes **229** react with organotin compounds, first of all, at the bromine atom located in the *trans*-position.[245] By varying the order of addition of the alkenyltin and aryltin reagents, either *E*- or *Z*-isomers of 3-aryl-1,3-dienes **230** can be obtained as desired.



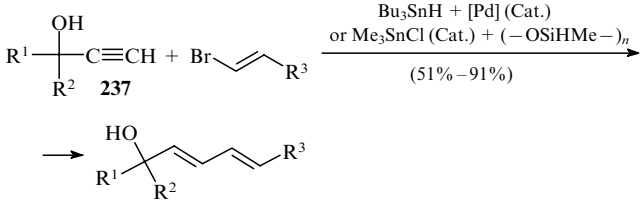
Alkynyltin derivatives **231** can also enter into the Stille cross-coupling. Conjugated enynes **232** thus formed can be reduced selectively yielding *E*,*Z*-dienes.[246]



sia is 3-methylbutan-2-yl.

Using this strategy, two pheromones **235** and **236** with similar structures but opposite configurations of the conjugated double bonds have been synthesised from the same initial alkyne **233** and alkynol **234** (Scheme 9).[246]

Direct coupling of tertiary acetylenic alcohols **237** with alkenyl bromides in the presence of stoichiometric amounts of tin hydrides seems to involve the hydrostannylation step, the overall reaction looking like the Stille cross-coupling.[247]

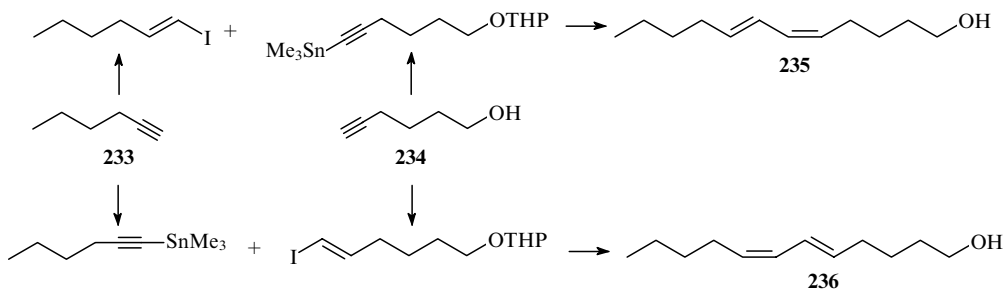


The reaction in question can also involve alkynylamines $R^1R^2C(NH_2)C{\equiv}CH$ and other sterically hindered terminal acetylenes. The same result is attained when catalytic amounts of $(Bu_3Sn)_2O$ [247] or Me_3SnCl,[248] and stoichiometric amounts of polymethylhydrosiloxanes are used instead of tin hydrides as hydride-ion donors. This modification of the Stille reaction opens up prospects for extending the scope of its application because this version implies markedly smaller proportions of tin-containing wastes.

c. The Suzuki reaction and its modifications

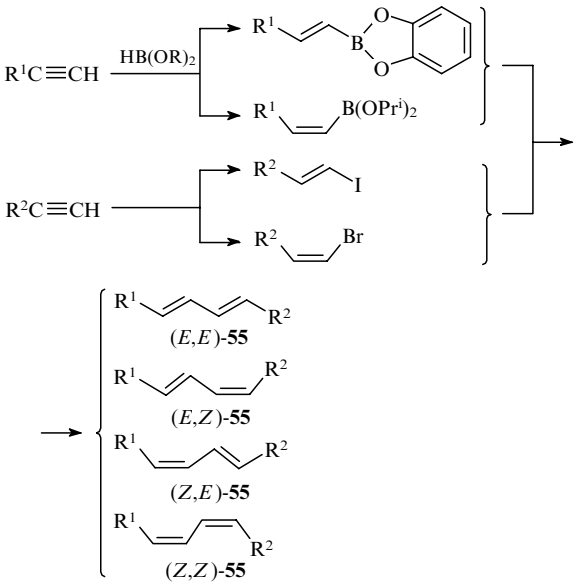
Coupling of organoboron compounds with halides or their equivalents (*e.g.*, triflates) catalysed by palladium complexes has been called the Suzuki coupling (**209** with M = BR_n, see reviews [224, 225]). Like the Stille cross-coupling, this reaction can be applied to the synthesis of various types of compound including conjugated dienes. An important feature of the process is that it

Scheme 9

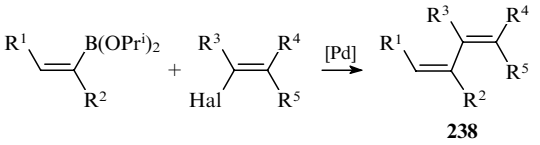


should be carried out in the presence of bases (NaOEt, NaOH, KOH, K_3PO_4, Na_2CO_3, *etc.*): coordination of the anion to the boron atom results in a higher electron density on the reaction centre, which facilitates the replacement of boron by palladium. In the case of sterically hindered alkenyl bromide, methyllithium proved to be a more suitable base.[249] The catalyst used most often is $Pd(PPh_3)_4$.

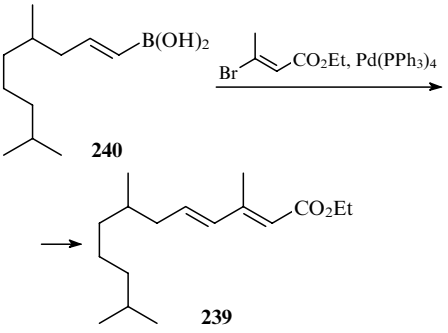
The organoboron approach is distinguished by versatility — by using specific protocols, both *E*- and *Z*-isomers of both the boron and halogen components can be prepared from terminal alkynes. The subsequent coupling in a required combination provides, at one's discretion, any isomer of the conjugated diene **55**.[222] The initial compounds can contain additional substituents and functional groups.



The Suzuki cross-coupling has been used successfully for the stereocontrolled preparation of dienes **238** with a more complex pattern of substitution including cyclic and polyfunctional compounds.[250–254]

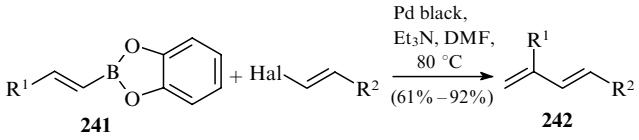


Thus this reaction has been used to prepare hydroprene (**239**) from alkenylboronic acid **240**.[255, 256]



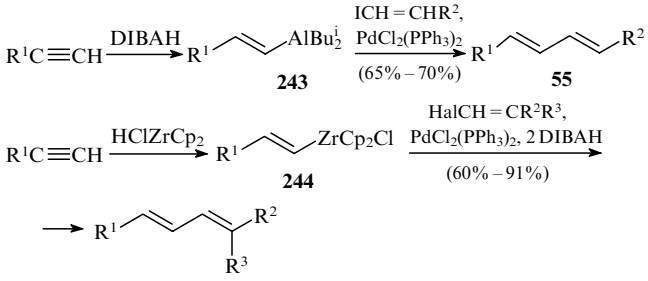
An interesting methodological expedient is to carry out this process in the aqueous acetonitrile medium.[257] The reaction was catalysed by a system comprising $Pd(OAc)_2$ and water-soluble sulfonated triphenylphosphine, $P(C_6H_4SO_3H)_3$. Both compounds subjected to coupling contained functional groups.

The nature of the base in the Suzuki cross-coupling can influence the process regioselectivity. Thus in the presence of triethylamine, catecholboranes **241** are coupled with alkenyl halides (or aryl halides) according to the 'head-to-tail' pattern giving rise to branched dienes **242**, the process regioselectivity being higher than 94%.[258]



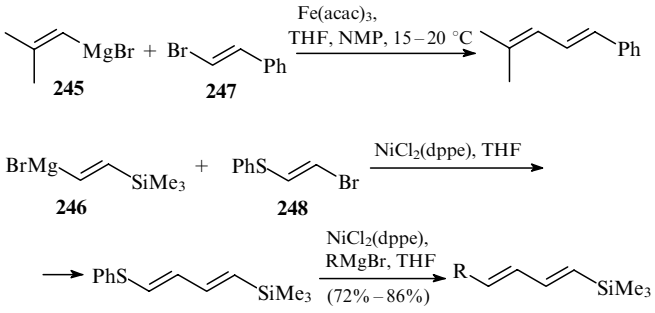
d. Other variants of cross-coupling of vinyl components

Vinyl derivatives of other elements are used somewhat less extensively in the cross-coupling reactions. The use of zinc, magnesium, aluminium and zirconium compounds for this purpose has been surveyed in a review.[224] For example, hydrometallation of terminal alkynes with R_2AlH [259, 260] or Cp_2ZrClH [261] to give the corresponding organometallic intermediates **243** and **244** followed by proper coupling resembles conceptually the Suzuki coupling discussed above.



The cross-coupling of vinylcopper reagents with alkenyl halides is also catalysed by palladium or nickel complexes. This reaction had been discovered earlier than the more convenient Stille and Suzuki reactions. Characteristic features of this process have been studied in detail by Normant and Alexakis.[9] The main work rule that ensures high yields and involvement of both alkenyl fragments of the reactants $(RCH=CH)_2CuLi$ is preliminary transmetallation of these compounds carried out by adding equivalent amounts of magnesium and zinc halides to the reaction mixture. Thus it is actually an organozinc compound that enters into the coupling reaction. Cross-coupling of neat organocopper compounds catalysed by nickel or palladium complexes gives products in a yield not exceeding 50%.

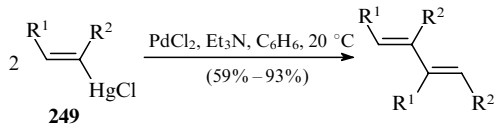
The coupling of alkenylmagnesium bromides **245** and **246** with alkenyl bromides **247** and **248** can be induced not only by palladium complexes but also by iron [262] or nickel [263, 264] complexes; in the latter case, thiolate ion can act as the leaving group.



NMP is *N*-methylpyrrolidone.

Vinyl silicon derivatives, unlike similar tin compounds, normally do not enter into the cross-coupling reaction (see reviews [265, 266]). Nevertheless, a particular type of active vinylsilanes containing fluorine atoms at silicon has been identified among them.[267–269] Vinyl iodides and triflates were used as electrophiles; $(\eta^3\text{-}C_3H_5)PdCl_2$ was found to be the best catalyst. The process was carried out in THF at 60 °C in the presence of Bu_4NF.

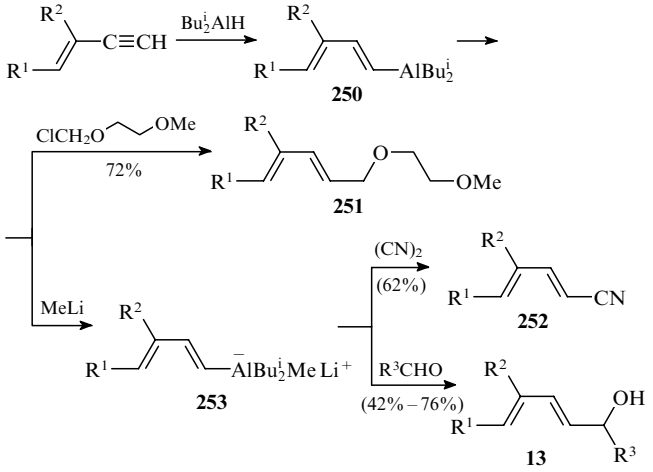
Dimerisation of alkenylmercury reagents **249** follows the 'head-to-tail' pattern.[270]



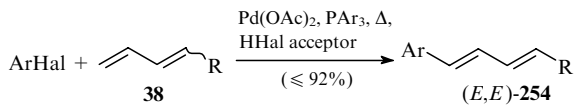
249

e. Cross-coupling of diene and saturated components

This reaction is used more rarely. Two general cases are known, one with the diene component acting as the nucleophile and the saturated one being the electrophile and *vice versa*. Dienylalane **250** reacts with methoxyethoxymethyl chloride (MEMCl) to give the expected ether **251**.[271] The compound **250** does not react properly with aldehydes and cyanogen; however, the target dienonitriles **252** and dienic alcohols **13** can be prepared from the corresponding ate-complex **253**.[271, 272]

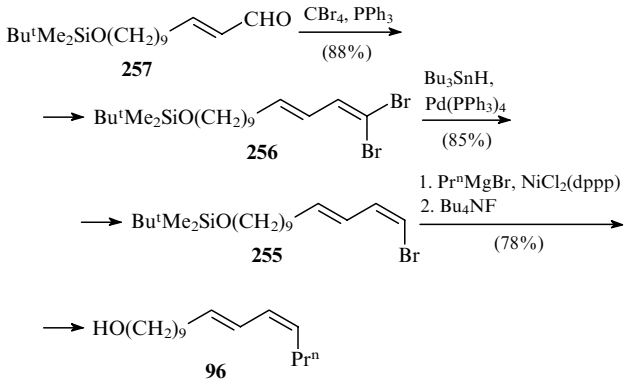


Yet another example of using a 'nucleophilic' diene component is the Heck arylation of the terminal conjugated dienes **38**.[273, 274] The process is carried out in the presence of HHal acceptors such as amines [273] and silver or thallium acetates,[274] the *E*,*E*-isomer of diene **254** being formed predominantly irrespective of the configuration of the initial compound **38**.

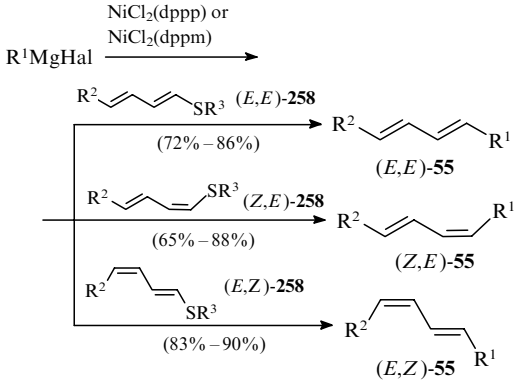


38 (*E*,*E*)-**254**

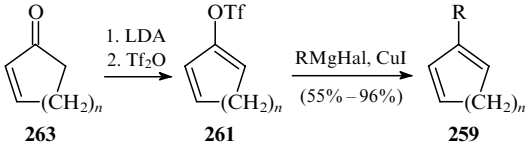
An original synthesis of bombykol **96** can serve as an example of cross-coupling with 'electrophilic' diene component **255** (easily prepared from dibromide **256** formed upon bromination of unsaturated aldehyde **257**) and a 'nucleophilic' saturated component.[275] In this case, the bond configuration at the reaction centre is not violated. This strategy was verified using numerous examples, the yields of *Z*,*E*-dienes ranging from 58% to 85%.[275]



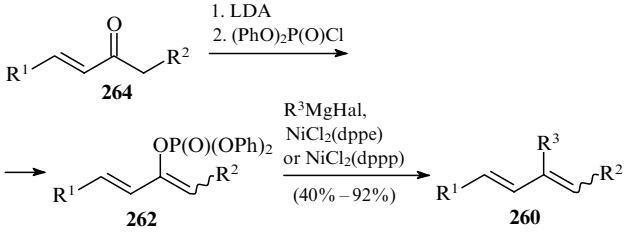
Some examples of using dienyl sulfides **258** (R^3 = Ph, Bu^t) in these reactions are documented;[45, 263, 276] in this case, the thiolate ion is the leaving group (the *tert*-butyl substituent is preferred [45]). The configuration of the products **55** remains the same as in the initial sulfides **258**.



The cross-coupling strategy makes it possible to substitute a nucleofugal group at the 2-position of the diene system; this results in branched derivatives **259** and **260**. Dienol triflates **261** or phosphates **262**, which are easily prepared from the corresponding α,β-enones **263** or **264**, can serve as convenient substrates for this purpose. The cyclic dienol triflates **261** react with the Grignard reagents in the presence of catalytic amounts of CuI,[277] while the acyclic phosphates **262** react in the presence of complex nickel catalysts.[278] The dienes **260** are formed as mixture of geometric isomers. The phosphate strategy is suitable also for the synthesis of cyclic dienes **259**.

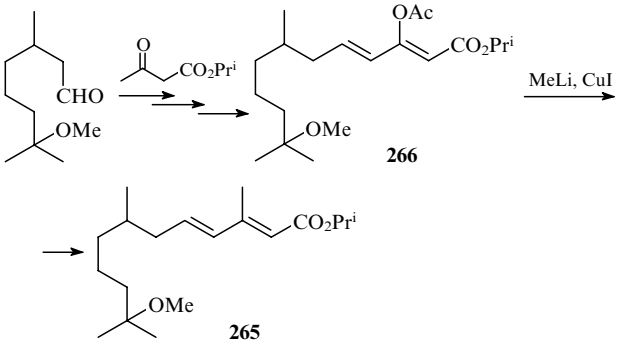


263 **261** **259**



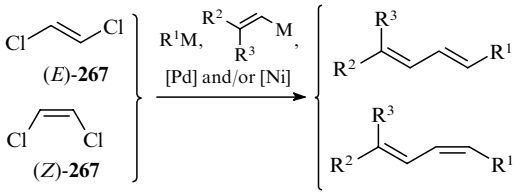
262 **260**

This technique has been used to introduce a methyl group during the synthesis of methoprene (**265**) according to the $C_{10} + C_4 + C_1$ pattern; the substitution of the methyl group for the OAc group in compound **266** occurred with complete retention of the initial configuration.[279]



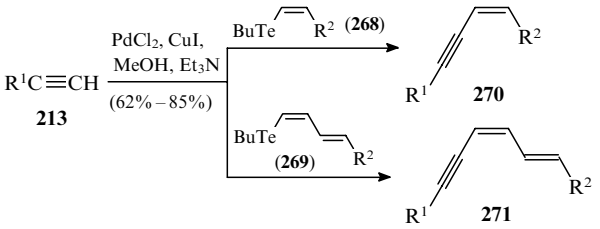
f. Cross-coupling involving 1,2-dihaloethenes

The (*E*)- and (*Z*)-isomers of 1,2-dichloroethene (**267**) can serve as convenient and inexpensive synthons for the preparation of conjugated dienes (as well as styrenes, enynes and so forth) (see a review [280]). By varying the conditions and catalysts, it is possible to perform consecutive coupling of these compounds, first, with a saturated and then, a vinylic component (or *vice versa*),[281] resulting in the formation of the target dienes in high yields and with high isomeric purity. It is of interest that 1,2-dibromoethene is much less effective in this type of process.[280]

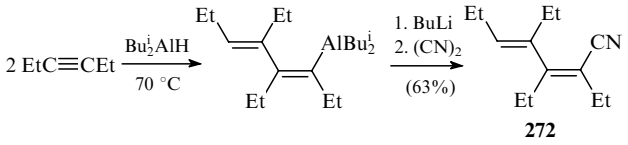


g. Synthesis of 1,3-dienes from alkynes and allenes

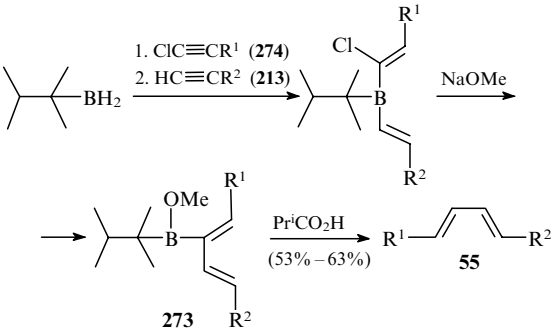
As noted above, alkynes can be used in the cross-coupling instead of alkenes. The reactions of terminal alkynes or their metallated derivatives with alkenyl halides (the Sonogashira reaction, see a review,[282] and transformation of **213** into **214** in general Scheme 8) yield conjugated enynes, which can be reduced to dienes (the reduction techniques are described in Section VII). In addition to alkenyl halides, these reactions can be carried out for alkenyl- (**268**) and dienyl tellurides **269**; these afford conjugated enynes **270** and dienynes **271**, respectively.[283]



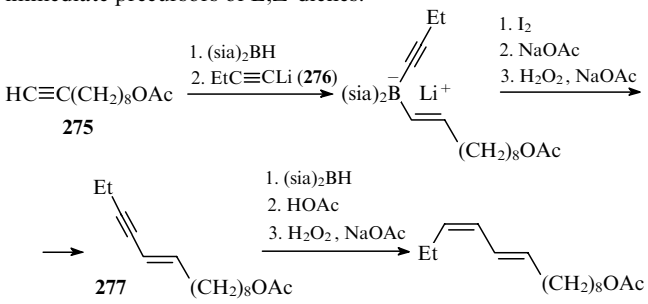
The addition of metal hydrides or organometallic reagents to the triple bond is stereospecific (*cis*-1,2-addition), which permits the preparation of pure isomers. Of relatively early studies, one should note the synthesis of dienonitrile **272** on the basis of hydroalumination of hex-3-yne.[272]



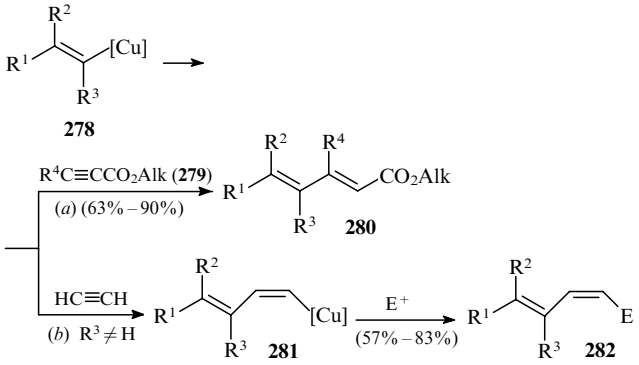
Hydroboration of alkynes resulting in alkenylboranes is the obligatory first stage of the Suzuki cross-coupling (see above). However, other methods of transformation of alkenylboranes **273** into the conjugated dienes **55** are also known, for example, successive hydroborations of chloroalkyne **274** and the alkyne **213** followed by the borotropic rearrangement.[284]



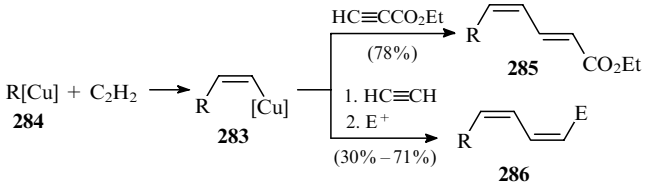
Yet another organoboron method consists in sequential chemoselective coupling of two alkynes (**275** and **276**, the latter as the lithium derivative), which gives conjugated enynes **277**, the immediate precursors of *E*,*Z*-dienes.[285, 286]



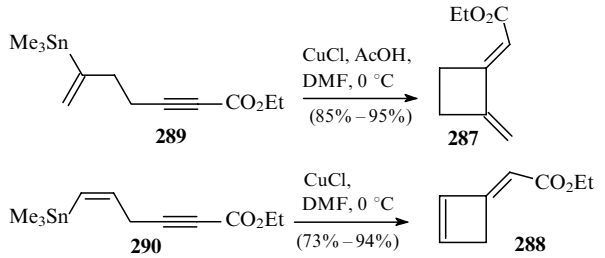
The addition of the cuprate reagents at the triple bond has been studied most comprehensively (see reviews [9, 287]). In early studies,[288, 289] cuprate reagents **278** have been prepared from the corresponding vinyllithium derivatives; their subsequent *syn*-addition to the triple bond in alk-2-ynoates **279** furnished dienoates **280** (pathway *a*). The stereochemical outcome of the reaction is important: the new double bond always has the *E*-configuration and the initial configuration of the vinylcuprate reagent does not change.



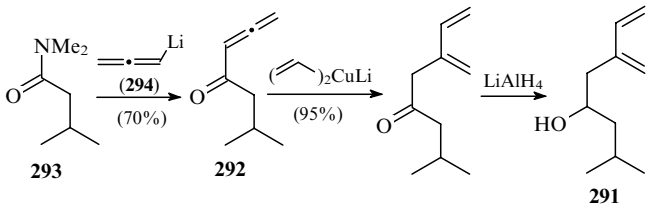
The development of methods for the addition of cuprate reagents to a non-activated triple bond has markedly extended the scope of the synthesis of dienes.[287, 290] Starting from different vinylcuprates **278** ($R^3 \neq H$) and acetylene (pathway *b*), one can obtain diene intermediates **281**, which then react with C-electrophiles (AlkI, CO_2, $PhSCH_2NEt_2$). This affords dienes **282** in which the double bond is *Z*-configured. Simple vinylcuprates **283** are formed from alkylcuprates **284** and acetylene; according to the stereochemistry of this process, this vinylcuprate has a *cis*-configuration.[291 – 293] By varying the natures of the second, acetylenic component and the final electrophile, one can obtain products **285** and **286** with a desired configuration of the second double bond.



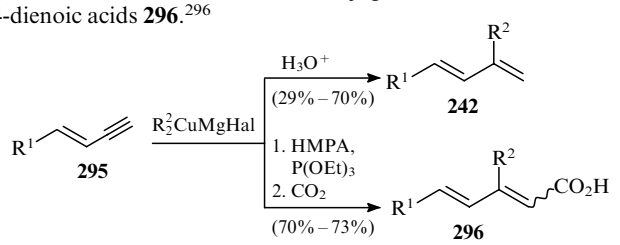
Recently, the organocuprate method has been successfully used for the preparation of dienes of the cyclobutane series of type **287** and **288** using an intramolecular reaction.[294] Fairly stable organotin substrates **289** and **290**, which underwent transmetallation under the reaction conditions, served as the precursors of active species.



The ability of cuprate reagents to add to the double bond of α,β-enones has been used for the formation of the conjugated diene system in the synthesis of ipsenol **291**. The α-allenyl ketone **292** needed for this purpose was prepared from amide **293** and allene **294**.[295]



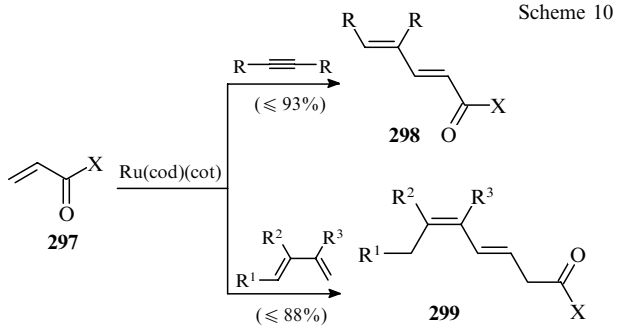
The addition of alkylcuprate reagents at the triple bond of enynes **295** results in the branched conjugated dienes **242** or alka-2,4-dienoic acids **296**.[296]



h. Coupling of alkene and alkyne components using ruthenium catalysts

The last decade was marked by enhanced interest in the catalysts based on ruthenium complexes (see a review [297]) which catalyse other types of transformation than palladium, which has become a routine material. These processes include coupling of activated alkenes **297** with alkynes (Scheme 10). This reaction catalysed by the Ru(cod)(cot) complex (cot is cycloocta-1,3,5,7-tetraene) and resulting in conjugated dienes **298** is a stereospecific addition of a terminal alkene to the triple bond.[298] The product yield depends dramatically on the nature of the substituents: in the case of acrylates (X = OAlk), good results were obtained only with diphenylacetylene (R = Ph); on passing to acrylamides (X = NMe_2), the range of possible acetylenic components is broader.

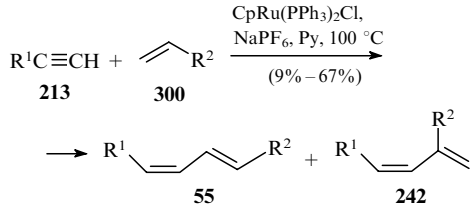
Scheme 10



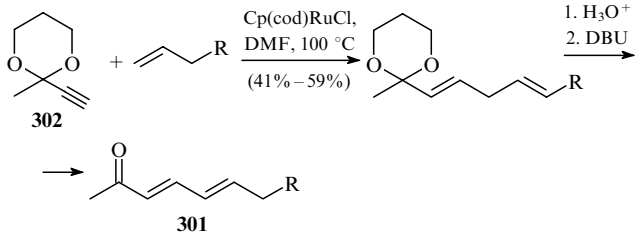
X = OAlk, Alk, $NAlk_2$.

Instead of alkynes, diene hydrocarbons can also been used in this reaction;[299] in this case, incompletely conjugated dienyl carbonyl compounds **299** are formed as the reaction products. This reaction is also sensitive to the type of substitution at the double bonds of the reactants and can result in isomer mixtures.

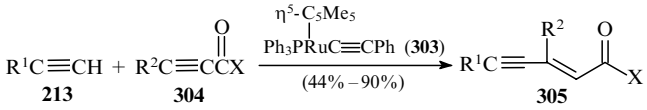
Coupling of terminal non-activated alkynes **213** with non-activated alkenes **300** takes place on prolonged refluxing in pyridine in the presence of $CpRu(PPh_3)_2Cl$ and $NaPF_6$.[300] The newly formed double bond in the diene **55** always has the *Z*-configuration, the process being accompanied by the formation of noticeable amounts (up to 13%) of non-linear isomers of **242**.



The reactions of alkynes with alkenes catalysed by another ruthenium catalyst, Cp(cod)RuCl, result in 1,4-dienes.[301] This method is suitable for the preparation of conjugated dienones **301** only in the case where the initial acetylene derivative **302** contains a latent carbonyl group. This facilitates isomerisation of the 1,4-diene system to a conjugated one.

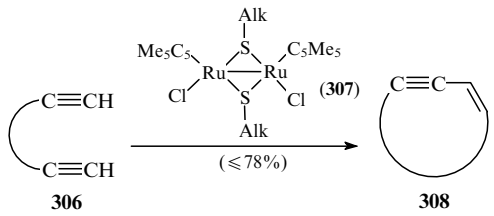


Coupling of two different acetylene derivatives **213** and **304** catalysed by the complex **303**, which gives enynes **305** (potential precursors of dienes), proceeds strictly stereospecifically.[302, 303]



C_5Me_5 is pentamethylcyclopentadienyl.

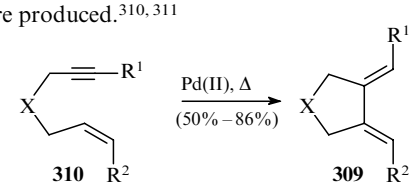
Intramolecular cyclisation of diterminal diacetylenes of the general type **306** with a relatively long linking chain (which can contain functional groups and even a ferrocene residue) induced by ruthenium complex **307** is accompanied by the formation of enynes of the macrocyclic series **308** (see Ref. 304).



i. Syntheses of exocyclic dienes

In conclusion, mention should be made of several intramolecular cross-coupling reactions of the same type, resulting in five-membered vicinally substituted carbo- or heterocyclic compounds **309**. Of these, cyclisation of 1,6-enynes of the general type **310** has been studied most comprehensively. When catalysed by palladium complexes,[305 – 308] this reaction proceeds smoothly in most cases if the vinyl group of the initial enyne **310** does not contain a substituent (R^2 = H). A single example has been reported [309] where this reaction occurred smoothly in the presence of a substituent in this group, namely, $R^2 = CH_2OR^3$. However, in most cases, mixtures of isomers having the same carbon skeleton

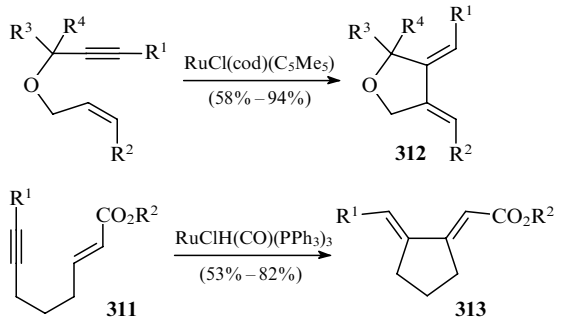
of the type **309** and differing in the position of the double bonds are produced.[310, 311]



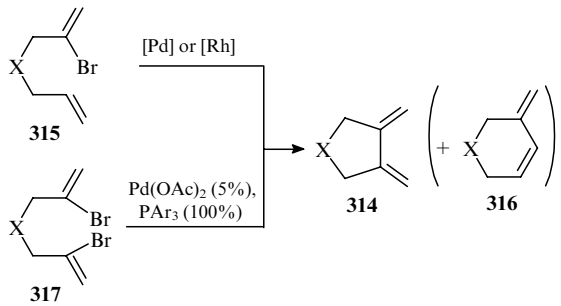
X = CMe_2, $C(CO_2Me)SO_2Ph$, $C(CO_2Me)_2$, NR.

In some cases, this approach can be used to prepare six-membered rings but with some limitations regarding the type of substitution in the initial compounds.[312, 313] Similar regularities have been found for the same transformation catalysed by nickel complexes immobilised on phosphinylated polystyrene.[313]

Ruthenium complexes, for example, $RuCl(cod)(C_5Me_5)$ and $RuClH(CO)(PPh_3)$, are capable of inducing cyclisation of allyl propargyl ethers[314] and derivatives of alk-2-en-7-ynoic acids **311**[315] the products of which are dienes **312** and **313**, respectively. Reactions catalysed by ruthenium complexes are much less sensitive to the nature of substituents than the same reactions catalysed by palladium complexes.

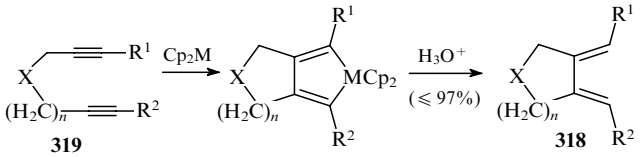


The preparation of vicinal di-*exo*-methylene compounds **314** by intramolecular cyclisation of bromides **315** (process of the Heck reaction type) has been described.[308, 316] The reaction takes place smoothly in the presence of the $Pd(OAc)_2 - PPh_3$ catalytic system[308] or the $RhCl(PPh_3)_4$ catalyst,[316] whereas with the $Pd(PPh_3)_4$ catalyst, the six-membered isomer **316** is the major product.[316] Intramolecular coupling of dibromides **317** affords the dimethylene isomer **314** as the only product; according to the balance, a stoichiometric amount of a reducing agent [Ph_3P or $(p\text{-}MeOC_6H_4)_3P$] is required.[317]



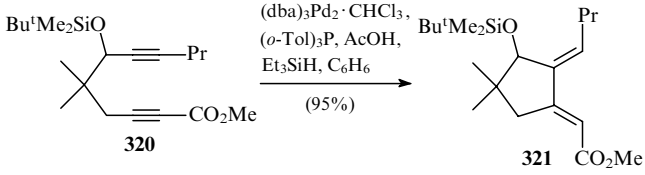
X = $PhCH_2N$, $C(CO_2Et)_2$, $C(COMe)_2$.

1,2-Dialkylidene-substituted cyclic compounds **318** can also be prepared from diacetylene derivatives **319**; this requires participation of a reducing reagent. In one of the procedures, cyclisation is induced by titanocene (Cp_2Ti)[318] or zirconocene (Cp_2Zr) generated *in situ*.[319] In most cases, the use of zirconium is more advantageous than titanium:[320] in the synthesis of four-, five-, six- and seven-membered rings, good yields are obtained even in the case of bulky R^1 and R^2 substituents. However, when $R^1 = R^2 = OEt$, it is necessary to use the titanium reagent.



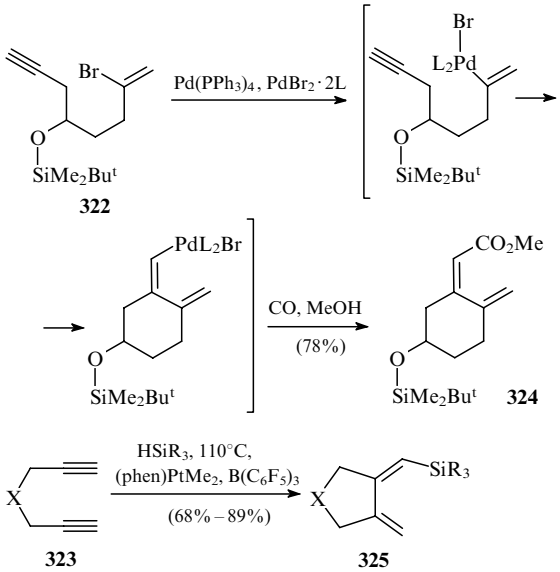
X = CH_2, O; $n = 0-3$; M = Ti, Zr.

The transformation of 1,6-diynes, for example, **320**, into the corresponding exocyclic diene **321** can be carried out with participation of the $(dba)_3Pd_2 \cdot CHCl_3$ palladium catalyst and the Et_3SiH reducing agent (stoichiometric amounts).[321]



In the case of other substrates of this chemical type, the yields vary in the range of 34% – 95%.

Two cases of cyclisation of compounds **322** and **323** followed by functionalisation are known.[322, 323] The functional groups being introduced occupy the *Z*-position in products **324** and **325**, which is related to the mechanism of intramolecular *syn*-carbometallation at the cyclisation stage.



X = $C(CO_2Me)_2$, $C(CH_2OR^1)_2$, $[C(CO_2Et)_2]_2$.

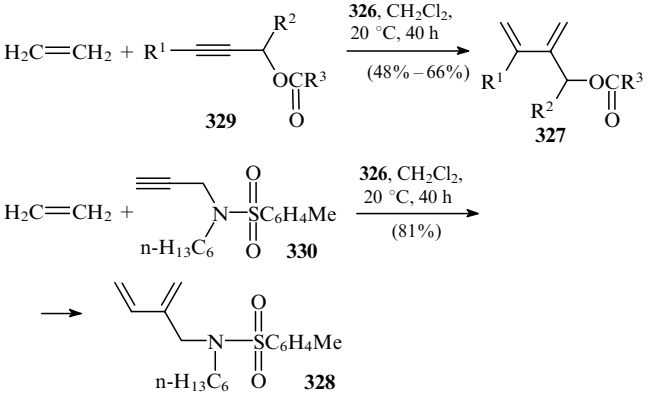
2. Miscellaneous reactions catalysed by organometallic compounds

The reactions considered in this Section are difficult to classify on the basis of a particular feature. Most of them have been discovered in the current decade and it is obvious that these investigations are at the stage of accumulation of facts. Nevertheless, it can be noted that the interest of researchers tends towards reactions catalysed by ruthenium complexes. These complexes are active in transformations differing from those catalysed by Pd and Ni complexes. Some of them (cross-coupling of alkenes and alkynes) were described in the preceding Section.

a. Alkene – alkyne metathesis

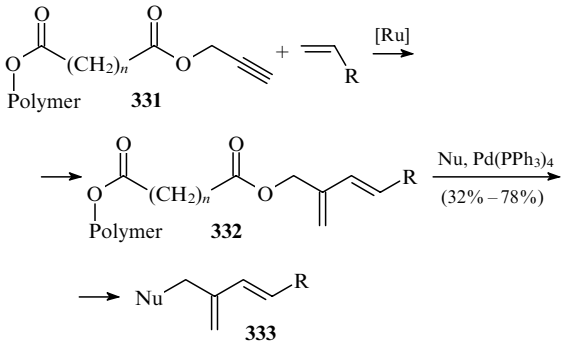
Ruthenium carbenoid complexes catalyse an interesting coupling reaction of alkenes with alkynes during which the reactants undergo metathesis to give branched conjugated dienes.[324, 325] One of these complexes, $Cl_2(Cy_3P)_2Ru{=}CHPh$ (**326**, Cy is cyclohexyl), the so-called Grubbs catalyst II, has now become com-

mercially available and has been tested in reactions of ethylene with numerous acetylene derivatives of various structures. Unfortunately, only for dienes of the type **327** and **328**, have preparative yields been attained; esters of propargyl alcohols **329** and *N*-tosylpropargylamines **330** served as the precursors of these products. However, even in these cases, reactions did not proceed to completion, which is in line with the concept of reversibility of metathesis.

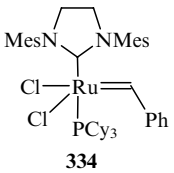


By conducting reactions under a pressure of ethylene (~4 atm), one can shift the equilibrium towards the products (for esters of type **329** with the terminal triple bond, $R^1 = H$, the yields increased to 92%);[326] however, upon further increase in the ethylene pressure, the reactions were retarded due to the degenerate ethylene–ethylene metathesis.[326, 327]

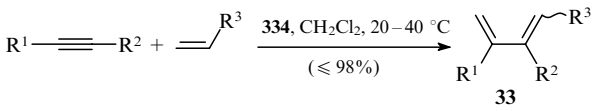
The problem of separation of the initial and final compounds, the polarities of which are close, should also be mentioned. An ingenious solution of this problem has been proposed.[328] The researchers suggested that the initial propargyl alcohol be immobilised on a polymeric support through a linker of an ester structure **331**.[328] In this case, after metathesis, the immobilised product has already the allyl carboxylate structure **332**. The subsequent reaction of the compound **332** with nucleophiles catalysed by palladium complexes results in diene product **333**, which passes to the solution, while the unreacted propargyl derivative **331** remains on the support.



Stable imidazolidinylruthenium complex **334**, obtained recently

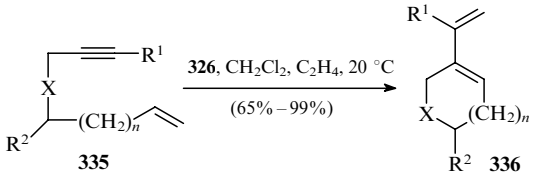


exhibits in many cases a much higher efficiency than the Grubbs catalyst II.[329] In particular, with the assistance of this complex, metathesis can be carried out for alkenes and alkynes characterised by a substantially broader spectrum of functionalisation and substitution [330] (*cf.* data of Refs 325 and 327).



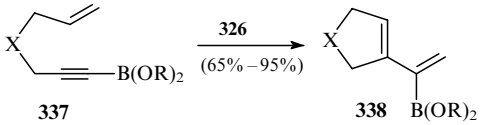
R^1 = $Ph_3CO(CH_2)_2$, Me_3Si, Cy, CO_2Bu^t, CH_2OAc, $CH_2OSiR^4_3$;
R^2 = H, Alk, CH_2OAc; R^3 = CH_2SiMe_3, $CH_2OSiR^4_3$, CH_2CO_2Bn.

The intramolecular alkene–alkyne metathesis of enynes **335**, discovered previously, is much less sensitive to the chemical type of the initial compounds than the intermolecular process because it is accompanied by the formation of favourable cyclic systems **336**.[331, 332] The product yields are very high, except for the case of terminal alkynes ($R^1 = H$). Later, the problem of low yields from terminal alkynes has been unexpectedly solved: it was found that this process should be carried out under an atmosphere of ethylene.[333] Ethylene does not formally participate in the reaction but it favours catalyst transfer in the form of the carbene $Ru=CH_2$.



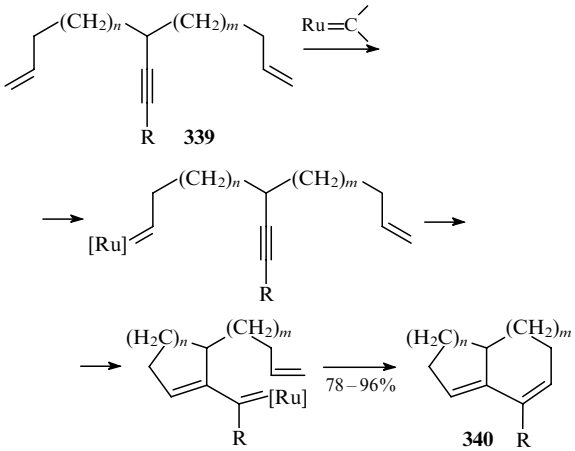
X = O, NR^3, $C(CO_2Et)_2$; R^1 = Me, CH_2OAc, $CH_2OSiMe_2Bu^t$, CO_2Me, H; R^2 = H, Ph; n = 0–2.

A study [334] demonstrating the possibility of involvement of alkynylboronic acids **337** in intramolecular metathesis deserves attention. Under the action of Ru catalyst **326**, they are smoothly converted into boryl-substituted dienes **338**, potential substrates for the Suzuki cross-coupling.[334]

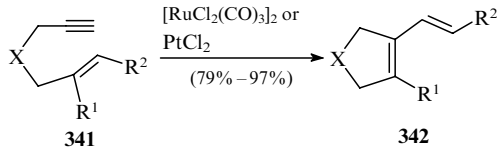


X = CH_2, $(CH_2)_2$, O, TsN, OCH_2O, $C(CO_2Et)_2$.

It is of interest that compounds **339** with an appropriate mutual arrangement of the two double bonds and one triple bond undergo double metathesis catalysed by $Cl_2(Cy_3P)_2Ru=CHCH=CPh_2$ (Grubbs catalyst I) to give bicyclic 1,3-diene structures of the general type **340** (n = 1, 2; m = 0–2).[335] The nature of the substituent R at the triple bond plays a crucial role: high product yields were obtained for R = H, Alk, Ph, CO_2Me, whereas for R = Br, I, Me_3Si or Bu_3Sn, cyclisation did not proceed. When tungsten-based catalysts of metathesis are used, cyclisation of the same substrates involves two double bonds and is accompanied by the ejection of a lower alkene without participation of the acetylene fragment.

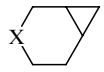


1,6-Enynes **341** are converted in the presence of $[RuCl_2(CO)_3]_2$ to give diene product **342**. The process fits formally the concept of the intramolecular alkene–alkyne metathesis considered above. Nevertheless, the researchers [336] suggest a different reaction mechanism.



341 **342**

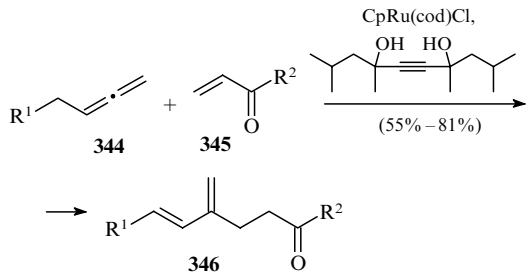
With $PtCl_2$ catalysis, enynes of the type **341** containing electron-withdrawing groups or a cyclic enyne fragment (with a medium or large ring) are also converted into formal metathesis products **342**).[337] Otherwise, they tend to form cyclopropane derivatives **343**.



343

b. Synthesis of 1,3-dienes from allene derivatives

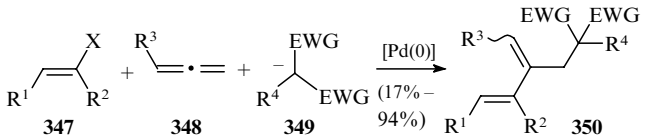
Ruthenium complexes catalyse an unusual addition of allenes **344** to activated alkenes **345** giving rise to 1,3-disubstituted conjugated dienes **346**.[338] To activate the catalyst, alkynols are used, the best results being attained with 2,4,7,9-tetramethyldec-5-yne-4,7-diol.



344 **345** **346**

The presence of a nitrile, ester or amide substituent in the side chain of the allene does not influence the course of the reaction. Regarding allene alcohols, a limitation has been found in the study of the mechanism — the number of carbon atoms between the allene system and the hydroxy group should not equal three or four; otherwise, oxygen-containing heterocyclic compounds are formed.[339]

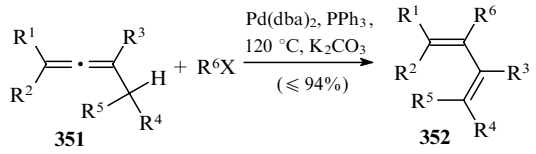
Palladium complexes can catalyse not only cross-coupling of vinylic components but also other types of reaction resulting in conjugated dienes. A series of studies dealing with coupling of vinylic (**347**), allene (**348**) and CH-acidic (**349**) components,[340–344] resulting in branched functionalised dienes of the type **350**, has been reported. Various combinations of three components differing in the nature of the substituents and functional groups have been tested. Thus the vinylic component can be either linear or incorporated in a carbo- or heterocyclic system; the leaving group can be represented by either bromide or triflate. Among C-nucleophiles, Schiff's base $Ph_2C{=}NCH_2{-}\ CO_2Me$ has been studied, apart from the standard β-dicarbonyl compounds. The yields vary over broad limits and can reach 94%.



347 **348** **349** **350**

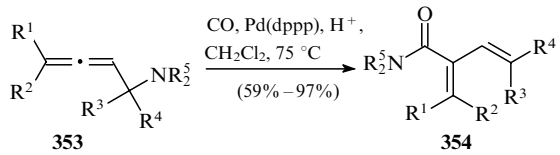
EWG is electron-withdrawing group.

Allene hydrocarbons **351** containing an allylic α-hydrogen atom undergo a $Pd(dba)_2$-catalysed reaction with aryl and alkenyl halides and triflates [345] to give conjugated diene compounds **352**. The highest yields (60% – 94%) were obtained in the case of aryl bromides and iodides.



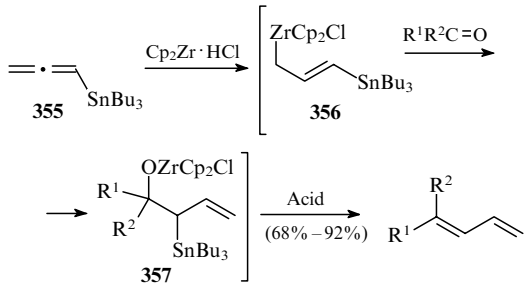
351 **352**

Carbonylation of allenylmethylamines **353** is directed at the allylic position, to the central atom of the allene system. The allylic rearrangement affords conjugated dienes **354** with the amino-carbonyl function at the 2-position.[346]



353 **354**

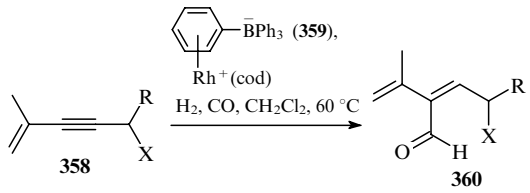
Hydrozirconation of allenylstannane (**355**) yields intermediate **356**, the reaction of which with aldehydes or ketones is accompanied by the allylic rearrangement [347] (the same outcome is provided by the reaction of aldehydes with pinacol 1-trimethylsilylprop-1-ene-3-boronate [43,44]). Decomposition of adduct **357** is accompanied by the formation of conjugated dienes, the proportion of *E*,*E*-isomer being more than 93% in the case of aldehydes (R^2 = H).[347]



355 **356** **357**

c. Synthesis of 1,3-dienes on the basis of alkynes

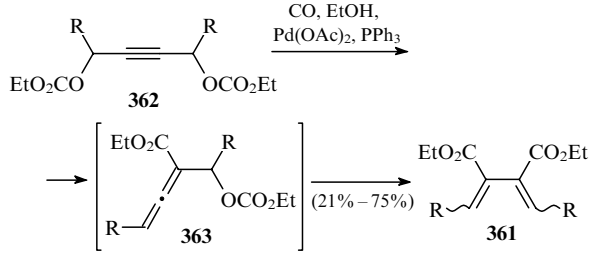
Hydroformylation of conjugated enynes **358** in the presence of rhodium complex **359** gives branched dienic aldehydes **360**.[348] A minor admixture of monounsaturated aldehyde is also formed.



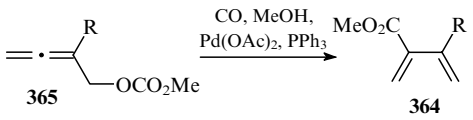
358 **360**

X = H, OAc, OMe.

Diethyl dienedioates **361** are produced upon carbonylation of alkyne-α,α′-diol dicarbonates **362**.[349] The reaction occurs through the intermediate formation of allene derivative **363**. The possibility of preparing dienoates **364** from the corresponding α-allenyl carbonates **365** was also demonstrated.

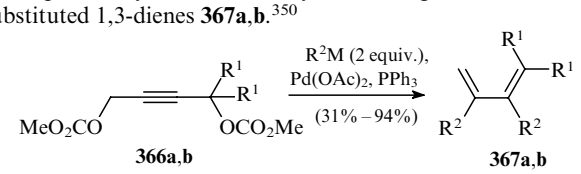


362 **363** **361**



365 **364**

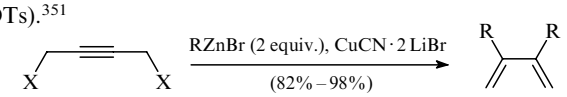
The reaction of propargyl dicarbonates **366a**,**b** with organoboron or -tin compounds catalysed by palladium complexes is accompanied by the double allylic rearrangement, resulting in substituted 1,3-dienes **367a**,**b**.[350]



366a,**b** **367a**,**b**

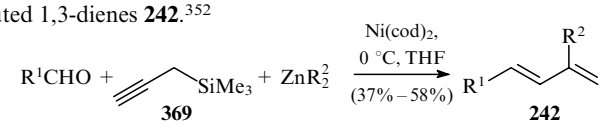
R^1 = H (**a**), Me (**b**); R^2M = $NaBPh_4$, $ArB(OH)_2$, $HetB(OH)_2$, $HetSnBu_3$, $PhC{\equiv}CSnBu_3$.

A reaction with a similar outcome giving rise to similar dienes consists in the interaction of organotin compounds of various structures with α,α′-disubstituted acetylenes **368** (X = Cl, OTs).[351]



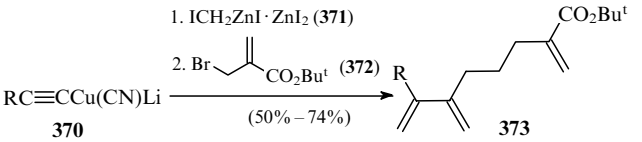
368

In the presence of $Ni(cod)_2$, propargylsilane **369** reacts with aldehydes and organozinc compounds to give the 2,4-disubstituted 1,3-dienes **242**.[352]

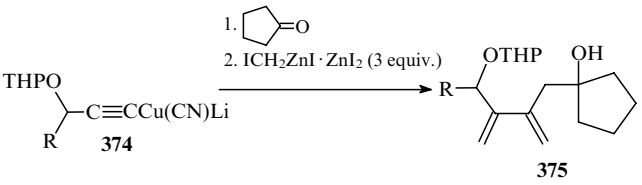


369 **242**

Complex cyanocuprates **370** derived from terminal alkynes add 4 moles of iodomethylzinc iodide (**371**). The subsequent treatment of the addition product with electrophilic reagent **372** furnishes conjugated 2,3-disubstituted diene **373**.[353] The reaction includes the stages of insertion of a carbenoid and two allylic rearrangements. In the case where the cyanocuprate complex **374** contains a fragment of sterically hindered ether and the process is initially carried out in the presence of an electrophile (cyclopentanone), three moles of the reagent **371** are added. This route was used to prepare diene **375**.

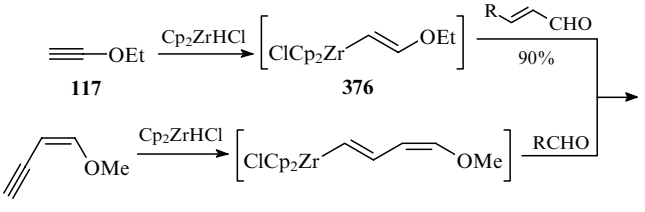


370 **373**

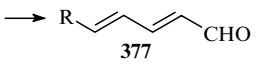


374 **375**

Hydrozirconation of ethoxyacetylene (**117**) and treatment of the resulting zirconium intermediate **376** with α,β-enals affords dienals **377** in a preparative yield.[354] The same products can be obtained using the same reactions but starting from 1-methoxybut-1-en-3-yne and a saturated aldehyde.

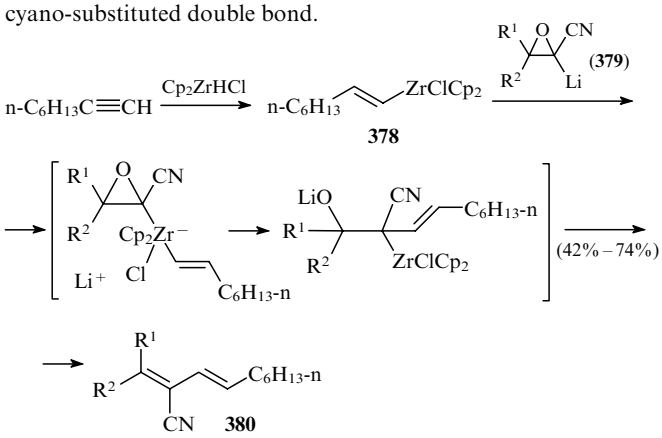


117 **376**



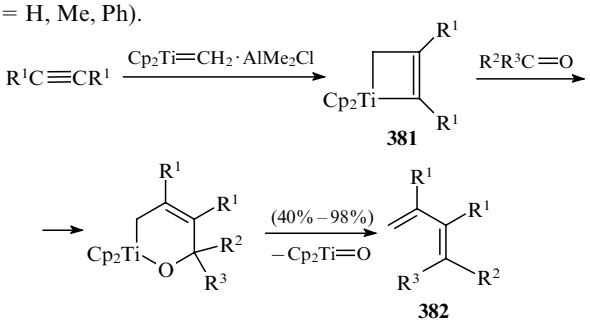
377

Alkenylzirconium compound **378** reacts with lithiated epoxy nitriles **379** to yield nitriles **380**.[355] If pure epoxy nitrile isomers are used, the reaction still gives a mixture of geometric isomers at the cyano-substituted double bond.



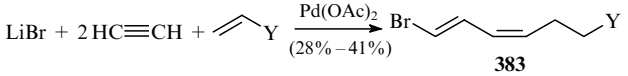
378 **380**

The reaction of disubstituted acetylenes with the carbene derivative of titanocene (the Tebbe reagent) results in a [2 + 2]-addition product, substituted titanacyclobutene **381**.[356] The subsequent regioselective reaction of **381** with carbonyl compounds gives conjugated dienes **382**. In the case of dimethyl- or diethylacetylene (R^1 = Me, Et), various aldehydes and ketones can be used, whereas in the case of tolan (R^1 = Ph), the range of carbonyl compounds is limited to reactive aldehydes (R^2 = H; R^3 = H, Me, Ph).



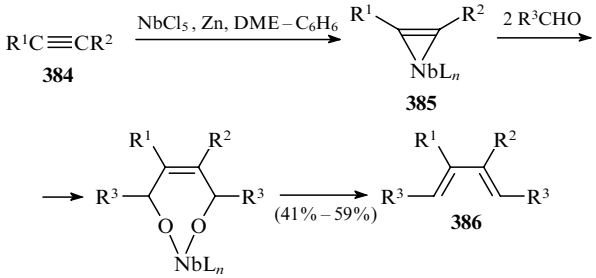
381 **382**

A curious process of acetylene dimerisation in the presence of electron-deficient alkenes makes it possible to prepare bifunctional *Z*,*E*-dienes **383**.[357] Acrolein (Y = CHO), vinyl ketones (Y = COR), nitroethylene (Y = NO_2) and β-substituted crotonaldehyde were tested in this reaction. In the latter case, the product yield was not more than 3%.



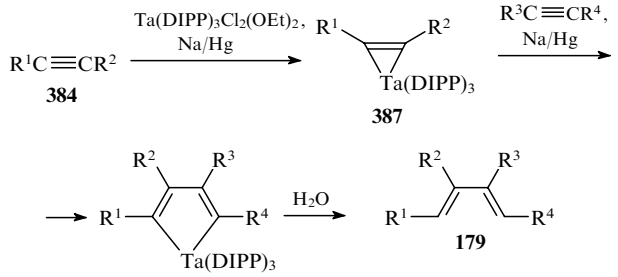
383

The reactions of disubstituted alkynes **384** with niobium pentachloride under reductive conditions gives intermediate **385**, containing the niobiacyclopropene fragment, able to add two equivalents of aldehydes.[358] Finally, conjugated dienes **386** with identical substituents at the ends of the system are produced.



384 **385** **386**

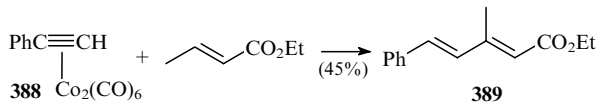
Similar tantalum compounds **387** add a second acetylene molecule; after hydrolysis, the conjugated diene **179** is liberated.[359] The scope and limitations of this method have not been adequately studied.



384 **387** **179**

DIPP is 2,6-diisopropylphenoxide.

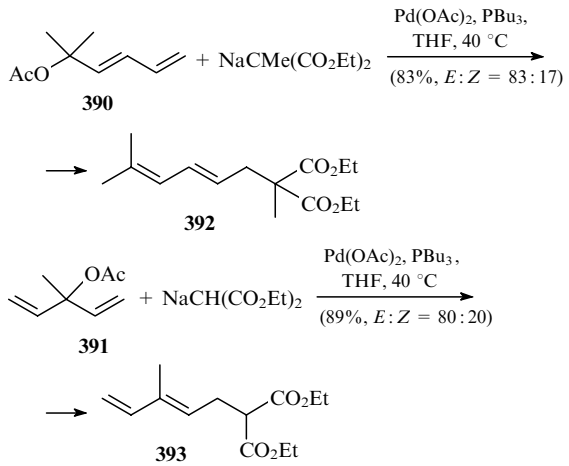
The reactions of hexacarbonyldicobalt complexes of alkynes **388** with activated alkenes afford conjugated dienes **389** in moderate yields.[360]



388 **389**

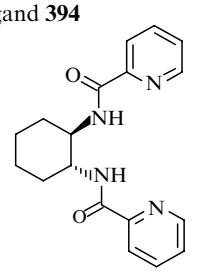
d. Syntheses of conjugated dienes from other dienes

Allylic acetates **390** and **391** react with malonate anions in the presence of palladium catalysts to give products **392** and **393** with a diene system.[361, 362] To ensure the maximum regio- and stereoselectivity, the process should be carried out in the presence of tributylphosphine. When triphenylphosphine is used, the regioselectivity substantially decreases. For example, the transformation of the acetate **391** gives, in addition to the product **393**, 40% of the product of nucleophile addition at the central carbon atom.



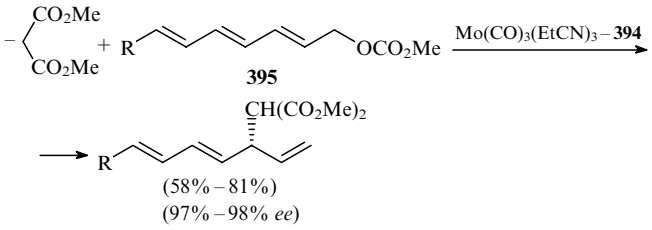
390 **392** **391** **393**

The reaction of allylic carbonates with the dimethyl malonate carbanion catalysed by the $Mo(CO)_3(EtCN)_3$ system with chiral ligand **394**



394

is accompanied by allylic rearrangement producing optically active homoconjugated compounds.[363] When triene carbonates **395** are used, the conjugated diene system is retained in the product and is connected to the chiral carbon atom.

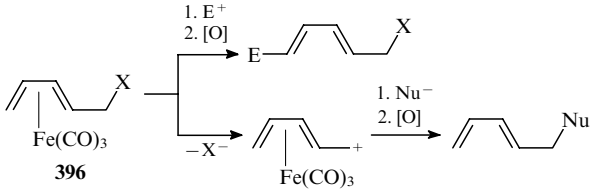


395

The reaction of dienes with electron-deficient alkenes (see Scheme 10)[299] catalysed by ruthenium complexes should also be attributed to this type of reaction.

e. Reactions of iron diene complexes

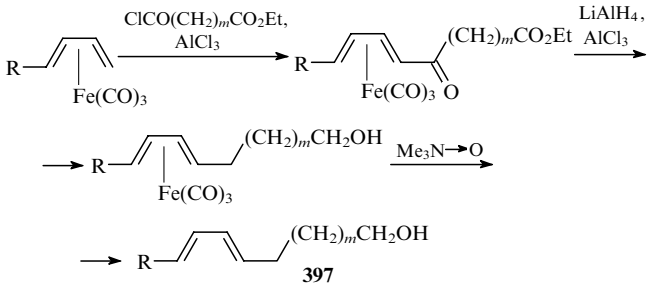
Conjugated dienes form stable complexes **396** with tricarbonyliron (see a review[364]). The electron-donating properties of $Fe(CO)_3$ facilitate the addition of electrophilic reagents at the termini of the diene system and contribute to the stabilisation of the allylic carbocation; this enables introduction of nucleophilic reagents into this position.



396

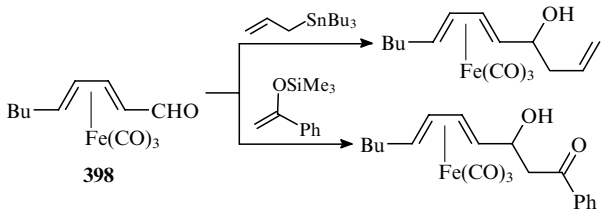
It has been proposed to use this type of complexation as a temporary protection of a diene system. The diene regeneration from the complex takes place on treatment with mild oxidants, for example, $(NH_4)_2Ce(NO_3)_6$ or *N*-oxides.

The following examples demonstrate the successfulness of using this strategy in fine organic synthesis. Complexes of terminal dienes can easily be converted into functional derivatives **397** some of which are insect pheromones.[365]



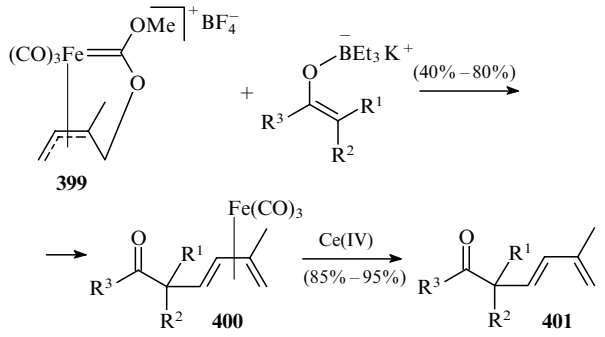
397

The complex of conjugated dienal **398** can react with some C-nucleophiles at the aldehyde group without a catalyst.[366]

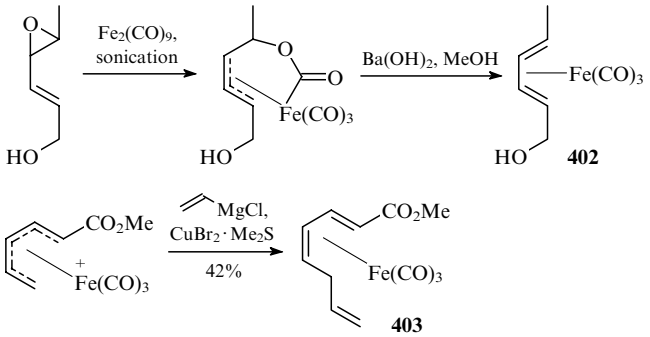


398

The reaction of π-allylcarbene cationic complex of tricarbonyliron **399** with boron ate-complexes of enolates yields η^4-complex derived from conjugated diene **400**.[367] Decomposition of the complex **400** on treatment with Ce(IV) gives rise to diene **401** containing an oxo group in the β-position.

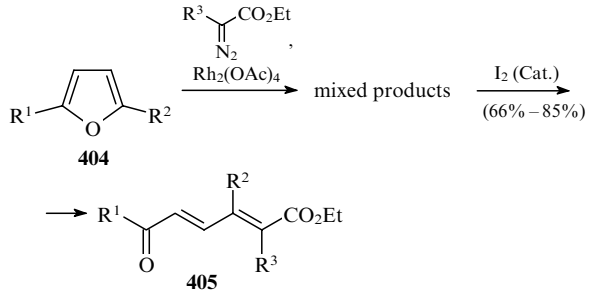


Mention should be made of recent publications [368, 369] describing the synthesis of functional derivatives of diene tricarbonyliron complexes **402** [368] and **403**.[369]

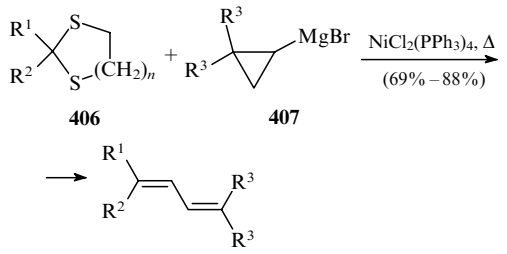


f. Miscellaneous organometallic reactions

The reaction of furans **404** with diazo esters in the presence of $Rh_2(OAc)_4$ affords a product mixture containing, among other compounds, oxodienoate **405**.[370] On treatment with catalytic amounts of iodine, this mixture can be converted into the pure diene (*E*,*E*)-**405** (or a mixture of *E*,*E*- and *E*,*Z*-isomers if $R^2 \neq H$).



Cyclic thioacetals **406** react with cyclopropyl Grignard reagents **407** in the presence of catalytic amounts of $NiCl_2(PPh_3)_2$ on refluxing in benzene or toluene to give dienes.[371] If the type of substitution in the three-membered ring differs from that in **407**, the reaction gives a mixture of isomers.

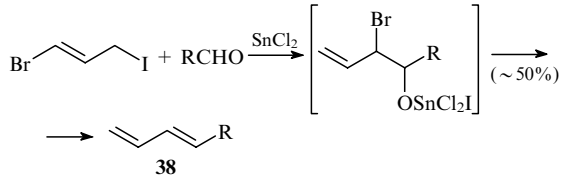


V. The synthon approach to conjugated dienes

Many reactions considered above could have been placed in this Section because versatile reagents can simultaneously be regarded as synthons if they contain fragments incorporated in the product molecule. Below we consider 'synthon syntheses' not included in the preceding Sections. They are arranged according to the type of fragment introduced in the final conjugated diene.

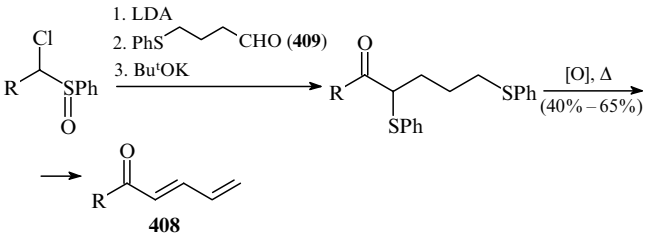
1. The $=CH-CH=CH_2$ (C_3) synthons

The widely known allylic Wittig reagents and their analogues are equivalent to the $=CH-CH=CH_2$ synthon. This type of reagents also includes 1-bromo-3-iodopropene.[372] The reaction of this compound with aldehydes on treatment with tin(II) chloride is accompanied by allylic rearrangement and gives terminal 1,3-dienes **38** in moderate yields.

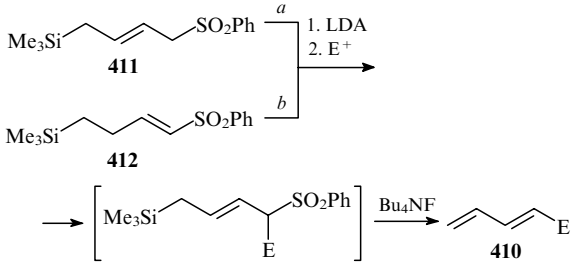


2. The $-CH=CH-CH=CH_2$ (C_4) synthons

In a known four-step procedure for the preparation of butadienyl ketones **408**, 4-phenylthiobutanal (**409**) is used as the source of the diene fragment for 'dienylation' of α-chlorosulfoxides.[373]



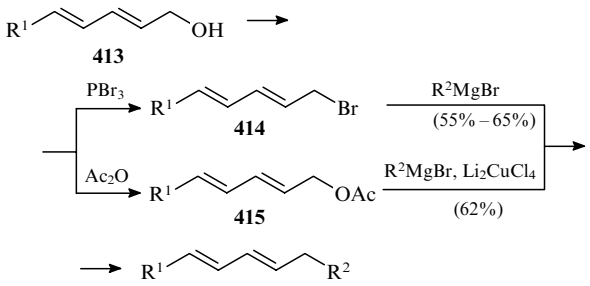
A broader range of compounds of type **410** can be prepared on the basis of 1-phenylsulfo-4-trimethylsilylbut-2-ene (**411**) (pathway *a*).[374] The same products are formed when a more readily available isomer, 1-phenylsulfo-4-trimethylsilylbut-1-ene (**412**) is used instead (pathway *b*).[375]



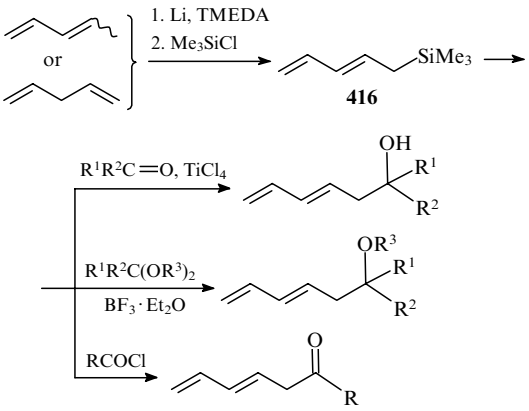
E = Alk, RC(O), , R_3Si, R_3Ge.

3. The $-CH_2-CH=CH-CH=CH_2$ (C_5) synthons and their homologues

The readily available 2,4-dienes of the general formula **413** containing a functional group (for example, a hydroxy group) at the 1-position can serve as the sources of these synthons. The corresponding allyl bromide **414** or acetate **415** acts as an electrophile when treated with Grignard reagents.[376, 377]

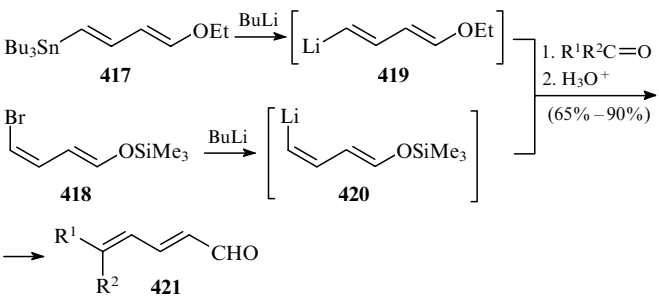


The reaction of pentadiene isomers with lithium followed by treatment with trimethylchlorosilane yields only one product, 1-trimethylsilylpenta-2,4-diene (**416**).[378, 379] This compound reacts with C-electrophiles of various types.

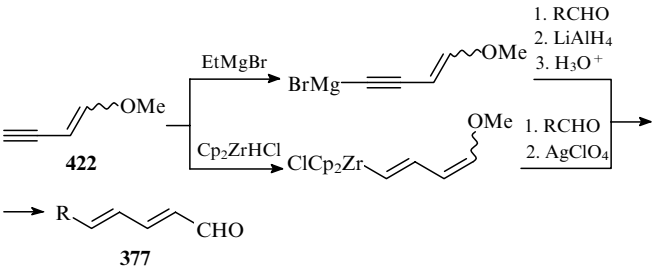


4. The =CH–CH=CH–CHO (C_4) synthons

Many compounds considered in Section III can be considered among the reagents capable of serving as sources of these synthons. Nevertheless, other versatile reagents for such 'dienylation' also do exist. For example, 1,4-heterodisubstituted butadienes **417** or **418** can be easily converted into organolithium derivatives **419** or **420**, which are much more reactive towards aldehydes and ketones than the Wittig–Horner reagents. Final hydrolysis gives rise to dienals **421**, formed predominantly as the *E*,*E*-isomers [380–382] (almost 100% for R^2 = H).

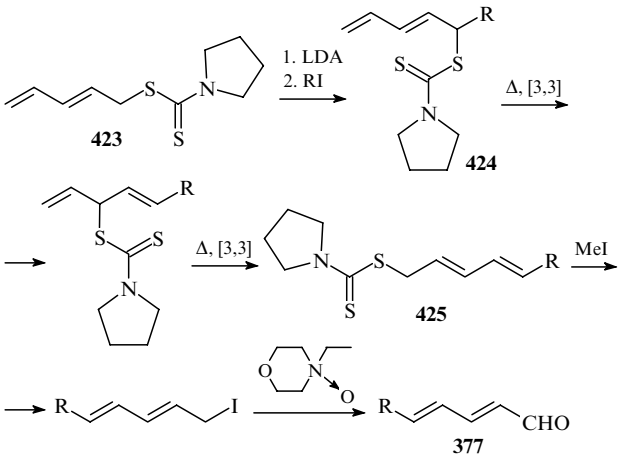


The dienals **377** can also be prepared using 1-methoxybut-1-en-3-yne (**422**) or its homologues.[354, 383, 384]

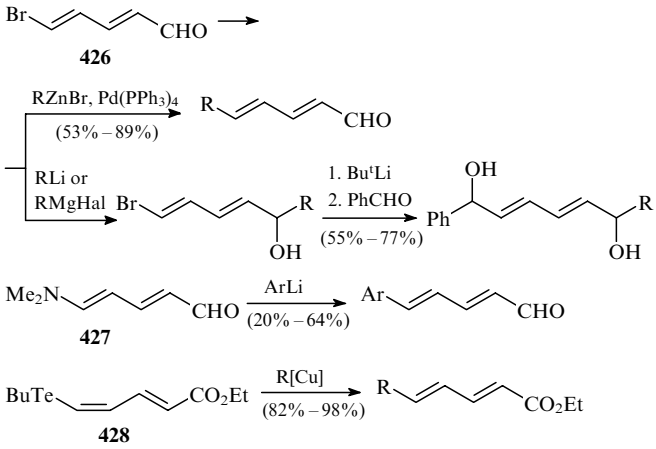


5. The –CH=CH–CH=CHCHO and –CH=CH–CH=CHCO$_2$R (C_5) synthons

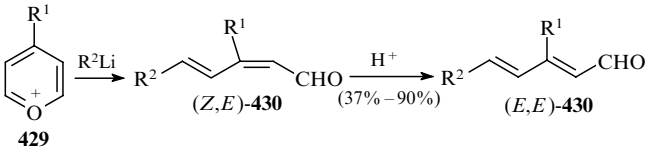
Reagent **423**, equivalent to a nucleophilic synthon of the given type, belongs to the class of thiol thiocarbamates. The products of its α-alkylation (**424**) undergo two [3,3]-heterosigmatropic rearrangements giving ultimately linear dienes **425**,[385] which are precursors of the dienals **377**.



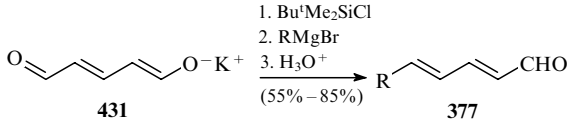
However, the most widely used synthons of this type are electrophilic reagents such as 5-bromopenta-2,4-dienal (**426**),[386, 387] 5-dimethylaminopenta-2,4-dienal (**427**)[388] and ethyl 5-(butyltelluro)penta-2,4-dienoate (**428**).[389] Substitution of alkyl groups for the electronegative elements (Br, NMe_2 and BuTe) in these compounds is accomplished by means of organometallic reagents.



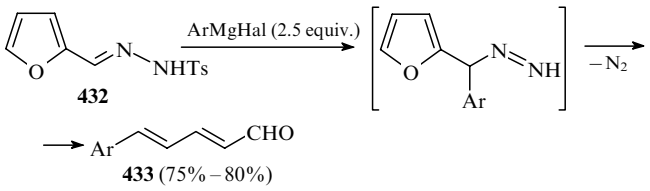
Yet another source of the synthons in question is represented by pyrylium salts **429**.[390, 391] The (*Z*,*E*)-alkadienals **430** formed initially in their alkylation are easily transformed into the *E*,*E*-isomers.



A similar role is played by the potassium derivative of glutacondialdehyde (**431**), which can be easily converted into the dienal **377** upon protection of one of the functional groups, treatment with a Grignard reagent and acid hydrolysis.[392]

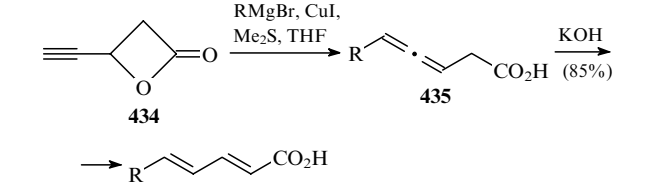


Furfural tosylhydrazone (**432**) can serve as a convenient synthon for the preparation of various 5-arylpenta-2,4-dienals **433**.[393]

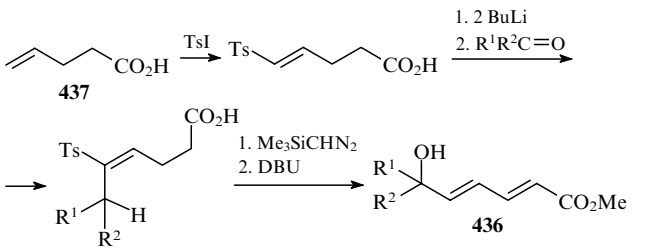


When made to react with alkylmagnesium halides, the same furfural **432** furnishes other products, namely, furan derivatives.

3-Ethynyl-β-propiolactone (**434**) reacts with organomagnesium compounds in the presence of copper(I) salts to give allenic acids **435**, which can be isomerised to dienoic acids.[394]

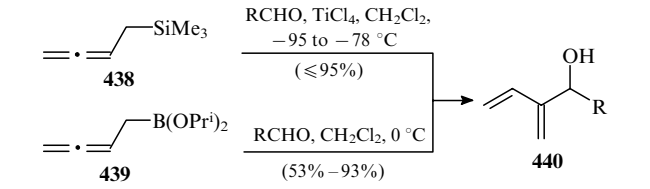


Finally, a three-step procedure for the synthesis of methyl 6-hydroxyalka-2,4-dienoates **436** has been developed; in this method, pent-4-enoic acid (**437**) serves as the source of the diene fragment.[395]

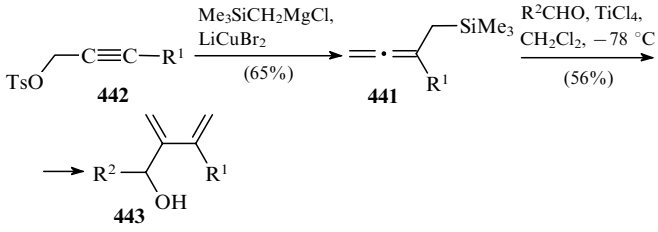


6. The $-C(=CH_2)-CH=CH_2$ (C_4) synthons

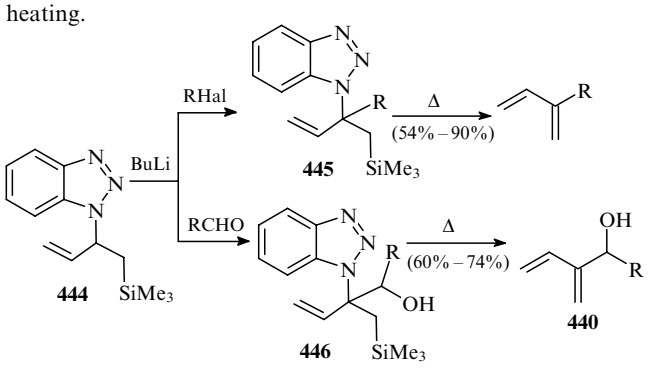
The synthon approach has been implemented successfully for the preparation of branched 1,3-dienes with functional substituents at the 2-position. One approach is based on the allylic rearrangement of allylsilanes and allylboranes in the reactions with carbonyl compounds. α-Allene derivatives **438** and **439**, similar to the allylic derivatives of silanes and boranes, react with carbonyl compounds at the *sp*-hybridised carbon atom yielding branched compounds **440**, which contain a conjugated diene fragment.[396, 397] In the case of the silyl derivative **438**, not only aldehydes but also acetals can be used, resulting in the corresponding ethers. The effect of a chiral group present in the electrophilic reagent was studied; after removal of this group, the resulting secondary dienic alcohols had *ee* values of up to 96%.



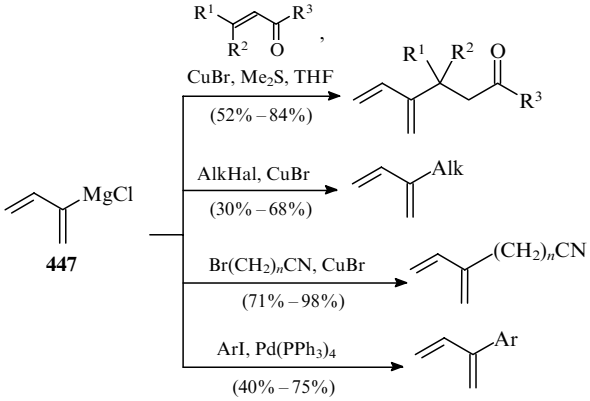
Branched allene silanes **441**, which can be easily prepared from acetylene derivatives **442**, behave in a similar way. They can be used to prepare 2,3-disubstituted butadienes **443**.[398]



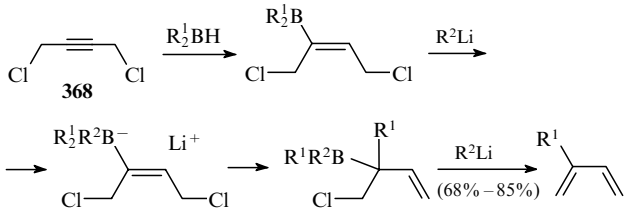
Great synthetic capabilities are provided by the butene derivative **444**, containing benzotriazole and trimethylsilyl vicinal groups.[399] After introduction of a desired fragment, the vicinal groups from the structures **445** and **446** can be eliminated by heating.



The Grignard reagent **447**, prepared from 2-chlorobuta-1,3-diene (chloroprene), can react with a number of electrophilic reagents, namely, α,β-unsaturated carbonyl compounds,[400] alkyl halides[400, 401] (including various bromoalkanonitriles[401]) and aryl iodides.[402] This is a very simple and versatile approach to the synthesis of 2-substituted 1,3-dienes. In the absence of copper salts, the Grignard reagent **447** can add to ketones; however, this gives about 25% of the rearranged allene-type product.[403]



2-Substituted butadienes with a bulky substituent R^1 can be prepared from 1,4-dichlorobut-2-yne (**368**) using hydroboration.[404] The mechanism of this reaction has been studied in detail.[405]

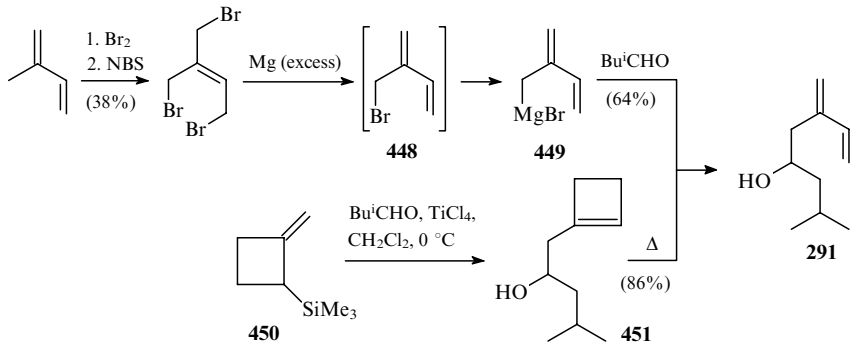


7. The $-CH_2-C(=CH_2)-CH=CH_2$ (C_5) synthons

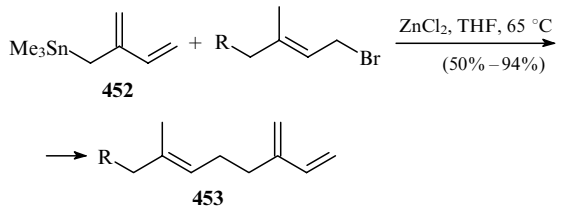
α-Bromoisoprene (**448**) and organometallic derivatives prepared from it are typical examples of the title synthons. A convenient method has been proposed for the preparation of the corresponding Grignard reagent **449** in two simple steps without isolation of the bromoisoprene **448**.[34] The reaction of the Grignard reagent **449** with isovaleraldehyde results in ipsenol (**291**) (Scheme 11). 1-Methylene-2-(trimethylsilyl)cyclobutane (**450**) can be used instead of the Grignard reagent **449**; the compound **450** reacts with aldehydes with the allylic rearrangement to give a cyclobutene derivative **451**.[406] Pyrolysis of this product furnishes the same diene derivative **291**.

Organotin compound **452** with an isoprene fragment reacts with allylic bromides in the presence of Lewis acids giving rise to

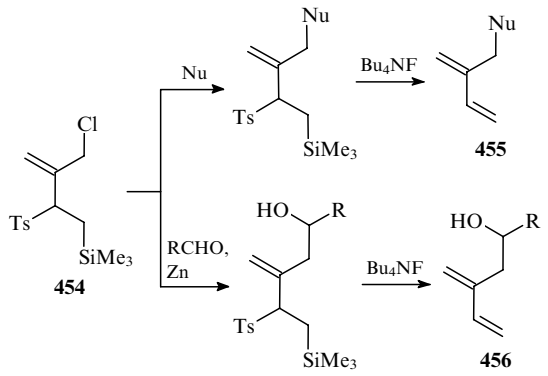
Scheme 11



branched 1,3-dienes.[407] This method was tested in the synthesis of the corresponding terpenes **453** — myrcene (R = H) and β-farnesene (R = $Me_2C=CHCH_2$).



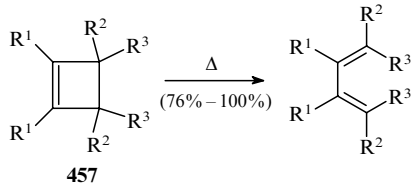
In compound **454**, the allylic chloromethyl group can serve as both an electrophilic and a nucleophilic centre, depending on the reaction conditions.[408] The tosyl and trimethylsilyl vicinal substituents act as a latent double bond, resulting in the vinyl fragment in the final products **455** and **456**.



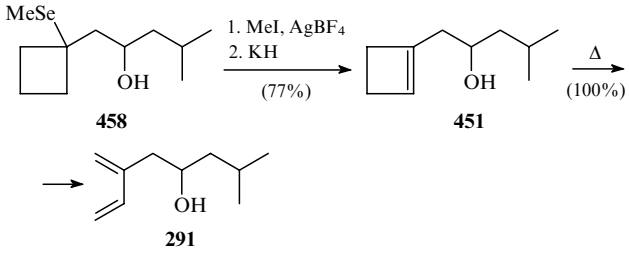
VI. Electrocyclic reactions

1. Thermolysis of cyclobutenes

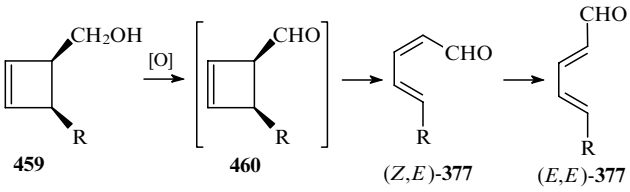
Two electrocyclic reactions resulting directly in conjugated dienes are known, namely, thermal disrotatory closure of conjugated hexatrienes accompanied by the formation of cyclohexadienes and conrotatory opening of cyclobutenes to give conjugated dienes, occurring at high temperatures. The use of the former reaction for preparative purposes is limited; some publications dealing with this topic are cited in a monograph.[10] The latter reaction has found a more extensive synthetic application. Depending on the nature of substituents in the initial compound, the process can be performed either by heating cyclobutene derivatives having the general formula **457**[409,410] or by passing them through a heated Vigreux column at a reduced pressure.[411]



This method has been used in elegant syntheses of ipsenol **291**;[406,412] in one of them, the initial cyclobutene derivative **451** was prepared from the corresponding selenide **458**.



Unlike primary alcohols **459**, 3-formylcyclobutenes **460** undergo ring opening even at low temperatures.[413] The low-temperature Swern oxidation of the alcohol **459** affords the expected *Z*,*E*-isomer **377** (conrotatory ring opening), which is readily transformed into the *E*,*E*-isomer when allowed to stand. Oxidation of the cyclobutenol **459** with pyridinium chlorochromate at room temperature directly affords (*E*,*E*)-**377**.

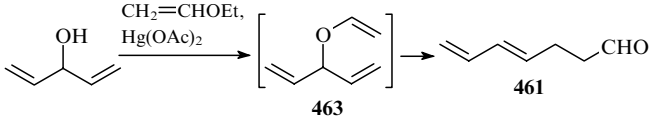


Other electrocyclic reactions are suitable for the synthesis of conjugated dienes only in those cases where the compounds under study contain additional double bonds or functional groups capable of being readily detached to give a double bond.

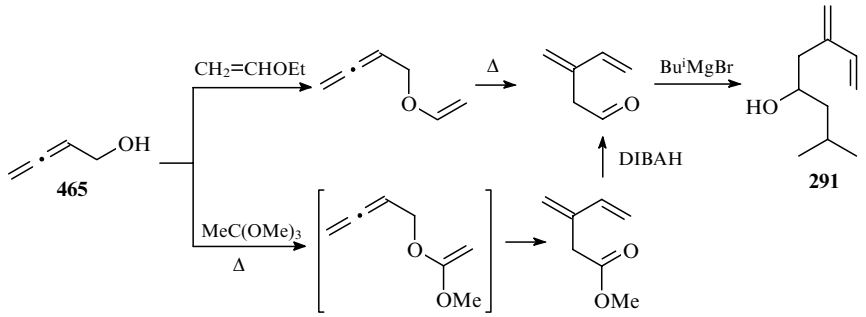
2. Sigmatropic [3,3]-rearrangements

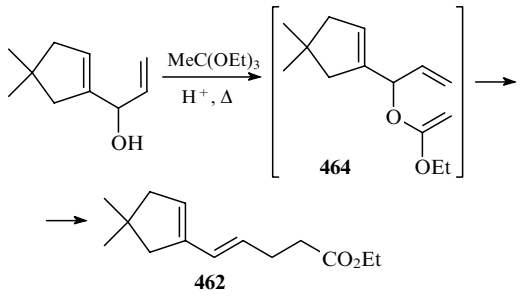
Sigmatropic [3,3]-rearrangements have been often used for the preparation of conjugated dienes; the variant used most often is the Claisen rearrangement consisting in the thermal transformation of vinyl allyl ethers into Δ^4-unsaturated functional derivatives (see a review [414]).

An example is provided by the syntheses of diene derivatives **461** and **462** by the Claisen rearrangement of vinyl ethers of divinylmethanols **463** and **464**, respectively.[415–417] In the latter case, triethyl orthoacetate serves as an equivalent of the vinyl ether.



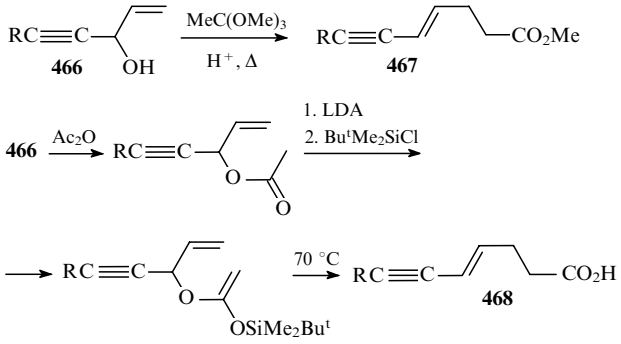
Scheme 12



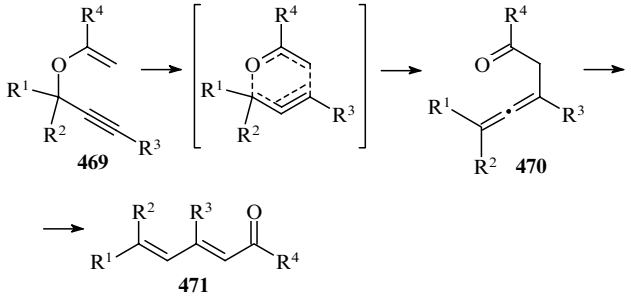


A similar reaction involving buta-2,3-dien-1-ol **465** results in branched conjugated dienes; this was employed in two equivalent syntheses of ipsenol **291** (Scheme 12).[418, 419]

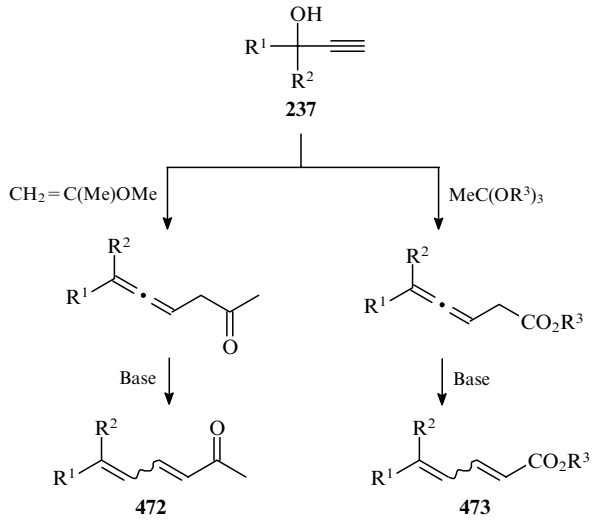
Vinylalkynylmethanols **466** can be used to prepare conjugated enynoates **467** and enynoic acids **468**, which are the closest precursors of dienes.[420, 421]



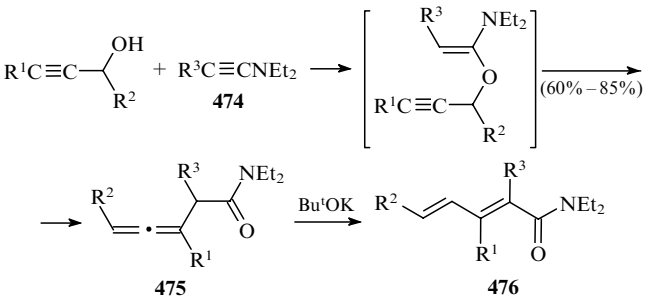
The Claisen rearrangement of propargyl vinyl ethers with the general formula **469** gives rise to β-oxoallene derivatives **470**, which readily isomerise into conjugated diene derivatives **471**. This process became exceptionally important after it had proved to be useful for the synthesis of vitamins A and E and some valuable terpenoids.



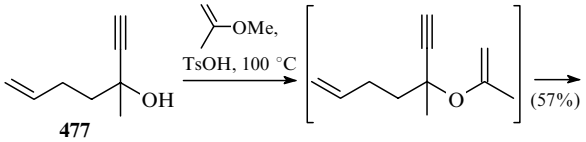
In many cases, there is no need to synthesise these propargyl vinyl ethers because they are formed *in situ* under the reaction conditions from the corresponding propargyl alcohols **237**. Initially, this was attained by either pyrolysis of their acetoacetates or heating with ethyl acetoacetate or diethyl malonate (the product yields were moderate in this case).[422–424] Later, these reactions were substantially updated; more precisely, isopropenyl methyl ether was taken instead of ethyl acetoacetate [425] and orthoesters of carboxylic acids were used in place of diethyl malonate.[426–428] The yields of products **472** and **473** depend markedly on the pattern of substitution in the initial compounds, being very high under favourable circumstances.

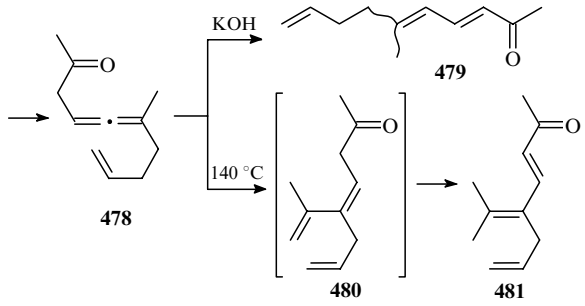


The reaction of propargyl alcohol with ynamine **474** occurs in a similar way, giving rise to *N*,*N*-diethylamides of allenic **475** and dienoic **476** acids.[429]

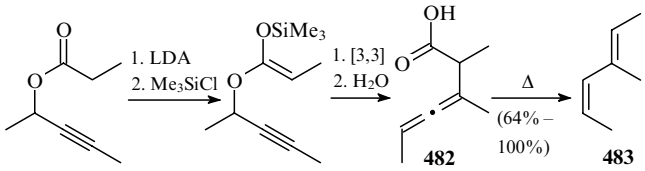


Acetylenic alcohol **477** containing a butenyl fragment reacts with isopropenyl methyl ether to give allene ketone **478**. On treatment with an alkali, this product isomerises in a conventional way to give ketone **479** with a diene fragment.[430] However, on prolonged heating, the ketone **478** can undergo one more [3,3]-sigmatropic rearrangement accompanied by the formation of intermediate **480** and, further, the conjugated dienone **481**.

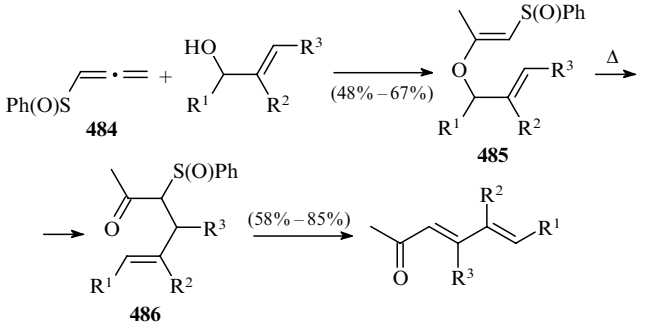




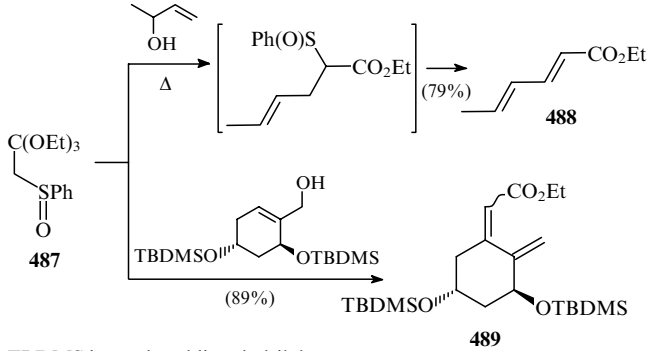
β-Allene acids obtained from ethers of propargyl alcohols upon [3,3]-sigmatropic rearrangement can also be used in another synthesis of dienes; decarboxylation of allene acid **482** is accompanied by the migration of the β,γ-double bond, resulting in the formation of conjugated 3-methylhexa-2,4-diene (**483**).[431]



The Claisen rearrangement can also involve allyl vinyl ethers of a more complicated structure. Thus allenyl phenyl sulfoxide **484** reacts with allyl alcohol derivatives to give adduct **485** with a suitable mutual arrangement of the double bonds.[432] The driving force of the rearrangement is transformation of the β-alkoxyvinyl sulfoxide fragment into the α-sulfinyl ketone fragment. Conjugated diene is formed in the subsequent thermal elimination of the sulfoxide group from compound **486**.

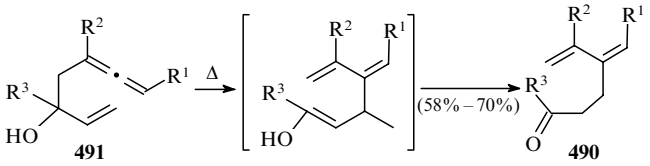


α-Phenylsulfinyl-Δ^4-unsaturated derivatives can be synthesised from allylic alcohols using yet another reagent, *viz*., triethyl phenylsulfinylacetate (**487**). Elimination of the sulfoxide group occurs simultaneously with the sigmatropic rearrangement.[433] This method allows one-step synthesis of not only linear (**488**) but also exocyclic (**489**) conjugated dienes.

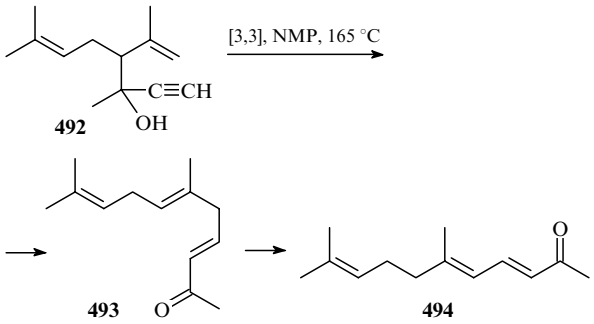


TBDMS is *tert*-butyldimethylsilyl.

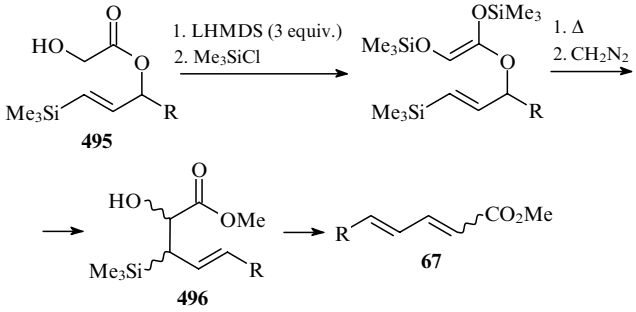
Branched dienes of the type **490** are produced in the allene version of the oxy-Cope rearrangement of alcohols **491**.[434, 435]



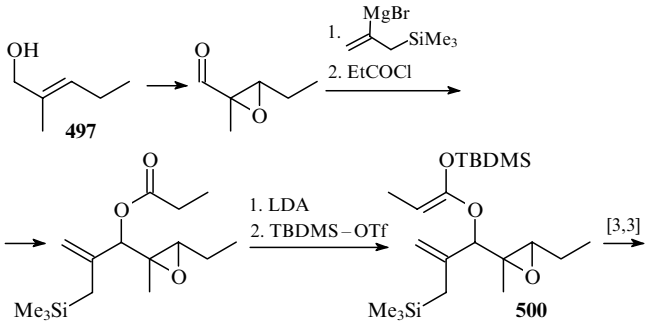
The oxy-Cope [3,3]-rearrangement of 1,5-enyn-4-ols **492** results initially in a compound with incompletely conjugated α,β,δ,ε-dienone fragment (**493**), which can be subsequently isomerised to give compound **494** with a conjugated α,β,γ,δ-dienone fragment.[436] It is convenient to combine isomerisation with the rearrangement by adding inorganic halogen compounds (HCl, HBr, I_2, NH_4Br) to the reaction mixture.[437] The method is applicable for the synthesis of pseudoionone.

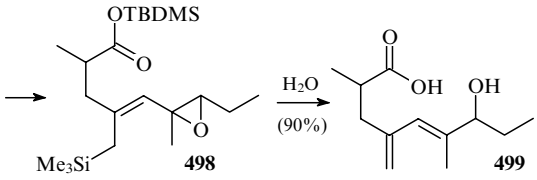


The hydroxy and trimethylsilyl vicinal groups can serve as a source of the double bond (the Peterson reaction). If the molecule of the initial compound **495** is constructed in such a way that, after rearrangement, these substituents in the product **496** occur in the required positions, this may provide a route to the conjugated dienes **67**.[438] The initial compounds **496** were resolved into individual *erythro*- and *threo*-diastereomers, which were convrted into individual *E*,*E*- and *Z*,*E*-isomers of the dienoates **67** by varying the elimination method.



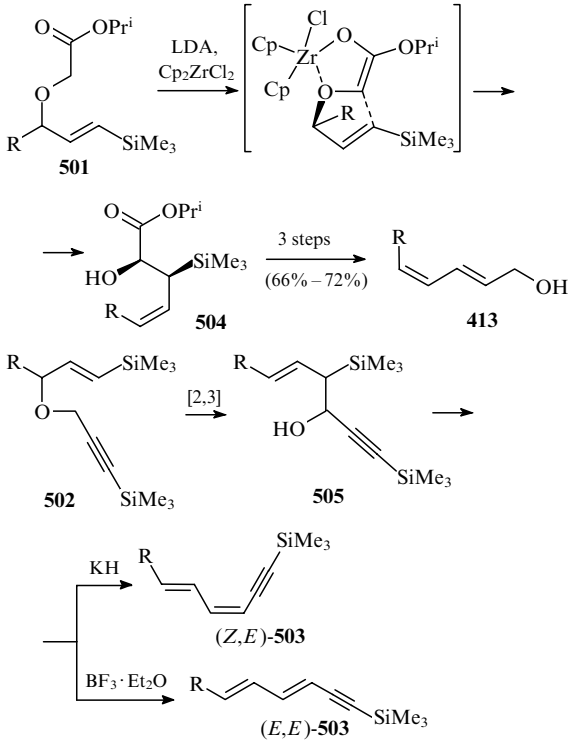
Compound **498**, which contains a trimethylsilyl group and an epoxide ring on different sides of the double bond, is unstable and is easily converted into hydroxy acid **499** with a diene fragment. The compound **498** is formed in the [3,3]-sigmatropic rearrangement of the precursor **500**,[439] which is, in turn, prepared from 2-methylpent-2-enol (**497**).





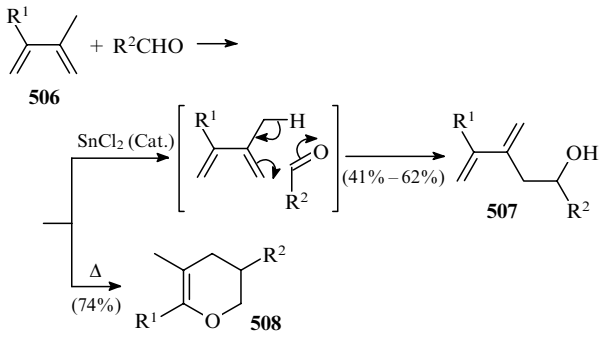
3. The Wittig sigmatropic [2,3]-rearrangement

The Wittig rearrangement of carbanions derived from compounds **501** and **502** has also been used to synthesise conjugated dienes of the type **413** and **503**.[440, 441] In both cases, the second double bond was formed upon elimination of the silyl and hydroxy groups from the corresponding alcohols **504** and **505** (the Peterson reaction); in the former case, zirconium served as the counter-cation to ensure the required configuration of alcohol **504** (*cf.* data of Ref. 442).



4. Ene reaction

Ene reactions take place between the dienes **506** and reactive aldehydes and afford dienic alcohols **507**.[443] The formation of the compounds **507**, however, can be explained in terms of the Prins reaction mechanism, which is known to be accelerated by acids. On heating without a catalyst, the above-mentioned reactants enter into a [4 + 2]-cycloaddition reaction giving rise to dihydropyrans **508**.



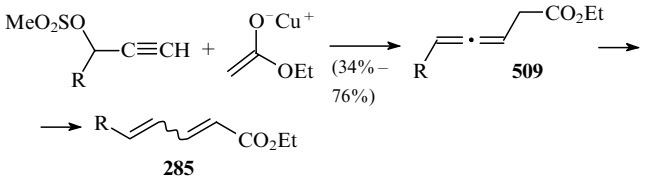
R^1 = H, Me; R^2 = CCl_3, CO_2Bu.

VII. Methods based on migration or reduction of multiple bonds

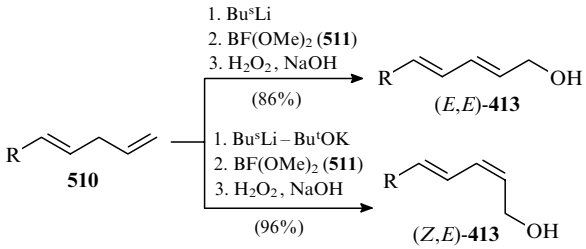
The strategy for the synthesis of dienes making use of migration and reduction is attractive because a conjugated diene system is formed at the final stage of the synthesis in a molecule which already has the required carbon skeleton and functional groups in the required positions.

1. The migration of multiple bonds

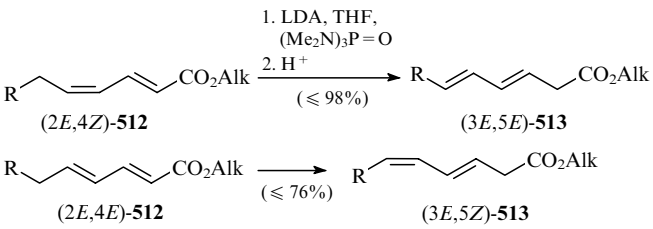
On treatment with bases or some transition metal complexes, non-conjugated dienes are converted into thermodnamically more favourable conjugated isomers. Generally, this reaction is not regioselective, therefore, it has a preparative value for hydrocarbon substrates only in a few cases, for example, in the synthesis of cycloocta-1,3-diene by heating cycloocta-1,5-diene in DMSO in the presence of potassium *tert*-butoxide.[444] However, the situation changes dramatically if the molecule contains a carbonyl group; in this case, the migration of multiple bonds results in an individual product. Examples of isomerisation of 2,5-dien-1-ones and β-allene ketones and esters into 2,4-diene derivatives are considered in Section VI. An organocopper route to the dienes **285** from β-allene esters **509** is also known. Unfortunately, this route is suitable only in the case where sulfonates of secondary acetylenic alcohols and ethyl acetate enolate are used as the initial compounds.[445]



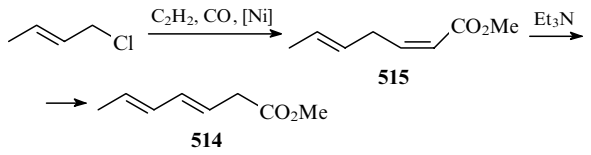
On treatment with strong bases, homoconjugated 1,4-dienes **510** form a delocalised carbanion, which is attacked regioselectively by specific reagents, for example, $BF(OMe)_2$ (**511**).[446] The subsequent treatment of these products with hydrogen peroxide yields primary conjugated dienic alcohols (*E*,*E*)-**413** or (*Z*,*E*)-**413**. Depending on the configuration of the Δ^4-double bond in the initial 1,4-diene **510** and the type of base, definite stereoisomers **413** are produced.



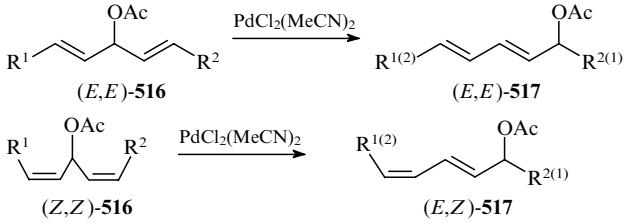
The diene system of alka-2,4-dienoates **512** can be deconjugated from the carbonyl group by treatment with LDA in THF in the presence of HMPTA[162, 447] or *N*,*N*′-dimethyl-*N*,*N*′-(1,3-propylene)urea (DMPU).[163] It is of interest that the dienes (2*E*,4*Z*)-**512** are converted into (3*E*,5*E*)-**513**, while (2*E*,4*E*)-**512** are converted into (3*E*,5*Z*)-**513**.[447]



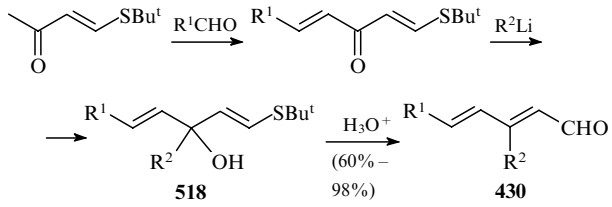
Thus methyl hepta-3,5-dienoate (**514**) can be prepared from incompletely conjugated dienoate **515** on prolonged keeping (12 h) in the presence of Et_3N.[448]



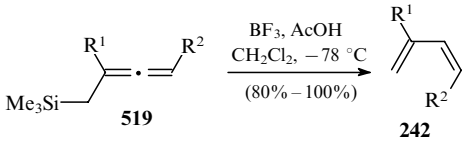
Divinylmethanols and their derivatives are readily isomerised on treatment with acidic reagents to give conjugated diene derivatives. For example, the allylic rearrangement of dialkenylmethyl acetates **516** catalysed by palladium complexes takes place with retention of the configuration of one double bond.[449] It is evident that in the case of non-symmetrical substrates ($R^1 \neq R^2$), the reaction gives rise to a mixture of regioisomers **517**.



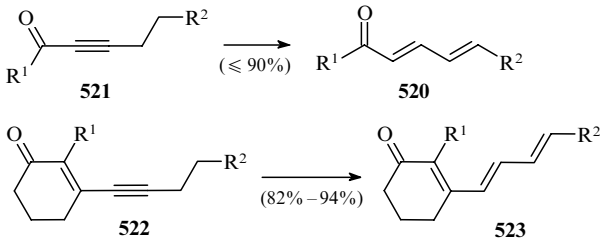
The regiodirectivity of this type of rearrangement can be controlled by introducing a heteroatom into the β-position of one of the vicinal groups. For example, readily available thio derivatives **518** can be smoothly converted into dienals **430**.[450]



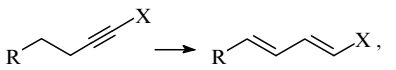
The rearrangement of α-silylallenes **519** into dienes **242** is also regioselective and, in some cases, stereoselective.[451]



In the last decade, an absolutely new method for the synthesis of conjugated diene derivatives **520** was discovered; this is isomerisation of alkynes **521**, in which the triple bond is located close to an electron-withdrawing group. In the first publication, it was noted that this isomerisation is induced by various palladium catalysts.[452] Similar results have been obtained with ruthenium or iridium complexes,[453, 454] which have also proved suitable for isomerisation of cyclohexene derivatives **522** into the corresponding trienes **523**.



Later, it has been found that the crucial role in the isomerisation is played by the phosphine ligands contained in the catalysts. Indeed, prolonged refluxing of various activated alkynes in toluene in the presence of triphenylphosphine alone also furnishes the diene isomers of type **520** in very good yields.[455] Later, factors influencing the reaction route have been studied in detail

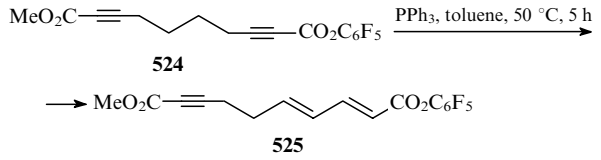


and recommendations for methods have been given. The data are summarised in Table 2. For isomerisation of less reactive amides of alk-2-ynoic acids (X = $C(O)NR_2$) to take place, the process should be carried out at higher temperatures (refluxing in xylene) in the presence of acetic acid. Conversely, more reactive acetylenic ketones [X = C(O)Alk and C(O)Ar] are isomerised even at room temperature on treatment with Ph_3P. For a similar transformation of esters (X = CO_2R) and *N*,*N*-dialkylamides [X = $C(O)NR_2$], tributylphosphine was found to be the reagent of choice.[456]

Table 2. Isomerisation of acetylene derivatives into conjugated dienes.

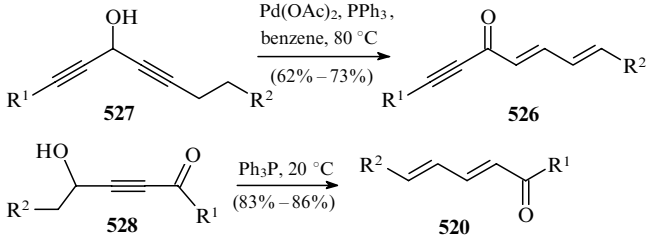
X	R	Catalyst	Reaction conditions		Yields (%)	Ref.
			T /°C	*t* /h		
$C(O)Bu^t$	Me	$Pd(OAc)_2$, Ph_3P	100	22	73	452
C(O)Cy	H	$Pd(OAc)_2$, dppb	100	21	73	452
C(O)Ph	Et	$Pd(OAc)_2$, dppb	100	0.75	82	452
CO_2Bn	Me	Ph_3P	110	6	75	455
C(O)Ph	Et	Ph_3P	80	4	83	455
C(O)NHPh	Me	Ph_3P, AcOH	140	14	84	455
C(O)Me	C_5H_{11}	Ph_3P	25	34	84	456
CO_2Me	Et	Ph_3P	25	35	0	456
CO_2Me	Et	Bu_3P	110	24	82	456
CO_2All	Me	Bu_3P	25	48	80	456
C(O)N(All)Bn	Me	Bu_3P	110	24	60	456
$CO_2C_6F_5$	Bu	Ph_3P	50	5	96	457, 458
$CO_2C_6F_5$	$HC \equiv C(CH_2)_2$	Ph_3P	50	5	76	457, 458
$(CF_2)_8Cl$	Me	Ph_3P	110	24	0	459
$(CF_2)_8Cl$	Me	$Pd(dba)_2$, Ph_3P, AcOH	110	12	82	459
$(CF_2)_4Cl$	Me	$Pd(dba)_2$, Ph_3P, AcOH	110	12	75	459
CF_3	$(CH_2)_5OH$	$Pd(dba)_2$, Ph_3P, AcOH	110	12	85	459

However, pentafluorophenyl esters (X = $CO_2C_6F_5$), which exhibit strong electron-withdrawing properties, can be isomerised under milder conditions, namely, at 50 °C and in the presence of Ph_3P; if the molecule contains other acetylenic groups, they remain intact.[457, 458] In this connection, an interesting example is the selective transformation of diacetylene **524** into dienyne **525**.

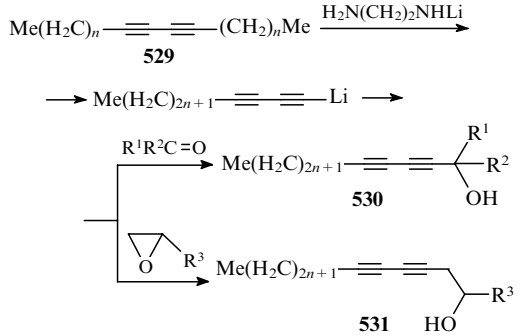


Among acetylene derivatives able to undergo isomerisation, 'non-carbonyl' polyfluoroalkyl compounds proved to be an interesting type of substrates [459] (see Table 2). The transformation of these compounds into dienes requires the presence of palladium catalysts and acetic acid, apart from phosphines.

Two processes, similar at the first glance, are known to form a diene system (for example, in compounds **526** and **520**) from dialkynylmethanols **527**[460] and α-oxo-α′-hydroxyacetylenes **528**.[461] Nevertheless, for balance, the former reaction requires involvement of an oxidising agent, while the latter, of a reducing agent.

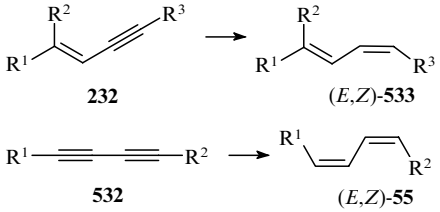


On treatment with superbases, for example, lithium aminoethylamide, internal alkynes are transformed into terminal isomers. It has been shown recently that this process can also be applied successfully to diacetylenes **529**. Since terminal diynes are unstable, it has been suggested that the lithium derivatives formed initially should be quenched immediately with electrophilic reagents; this provides a pathway to diacetylenic alcohols **530** and **531**, which are potential precursors of the corresponding conjugated dienes.[462–464]



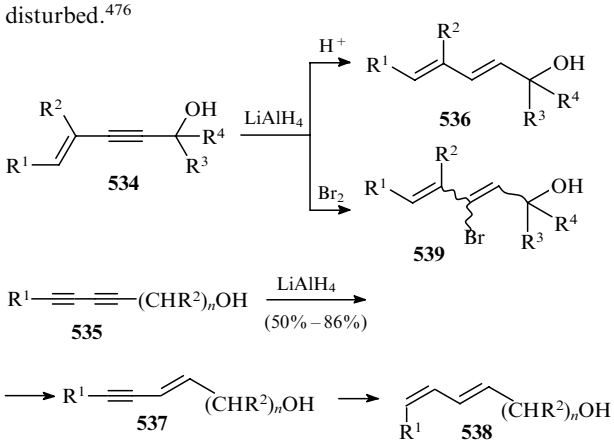
2. Partial reduction of a triple bond in enynes and 1,3-diynes

Incomplete reduction of the conjugated enynes **232** and diynes **532** to the dienes **533** and **55** has been considered comprehensively in the literature;[8, 10, 12] therefore, only the basic principles are discussed here. The transformation of a triple bond into a *Z*-double bond in these systems is accomplished using the same techniques as employed for monoacetylenes. Hydrogenation in the presence of Lindlar-type catalysts ensures, in principle, the required transformation (see, for example, Ref. 465); however, the presence of the second, conjugated bond activates the substrate molecule, resulting in a lower selectivity. Better results are obtained when hydrogen carriers are used; for this purpose, the substrate is refluxed in ethanol-containing solvents with activated zinc.[466–468]



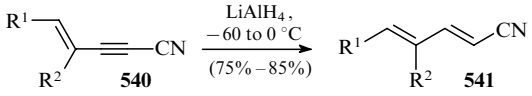
However, hydroboration of the triple bond followed by protolysis of the resulting vinylborane has won the greatest recognition. The hydroborating reagent of choice is di(*sec*-isoamyl)borane $(sia)_2BH$, which is reactive, under the reaction conditions, only towards triple bonds but does not affect double bonds. This method was used to transform enynes and diacetylenes into insect pheromones containing a conjugated diene system in which either one or both double bonds have *Z*-configuration.[246, 420, 469]

Unfortunately, known methods of reduction of alkynes into *E*-alkenes (sodium in liquid ammonia, $LiAlH_4$ with heating) are inapplicable to the reduction of enynes and diynes, because in this case reactions give complex mixtures of products. Exceptions are enynic alcohol **534**[26, 470–472] and diynic alcohol **535** (*n* = 0, 1),[473–475] which are hydrogenated to dienic **536** and enynic **537** alcohols, respectively. In the compound **535**, the triple bond closest to the hydroxy group is reduced fairly smoothly to the *E*-double bond on treatment with $LiAlH_4$ in ether or THF. Hydrogenation products, namely, conjugated *E*-enynic alcohols **537**, can further be converted into *E*,*Z*-dienic alcohols **538**.[475] In the case of propargyl compounds, the desired effect is also attained by transforming the alcohol into alcoholate with the subsequent addition of DIBAH, the reduction taking place within the ate-complex formed.[473] It is noteworthy that careful bromination of the reaction mixture carried out instead of the final hydrolysis in the reduction of the enynic alcohols **534** results in bromo-containing dienic alcohols **539** being formed as the major products; in this case, the configuration of double bonds is disturbed.[476]



n = 0, 1.

Enynonitriles **540** can undergo similar reduction, the cyano group in products **541** being stable against lithium aluminium hydride under the reaction conditions.[477]

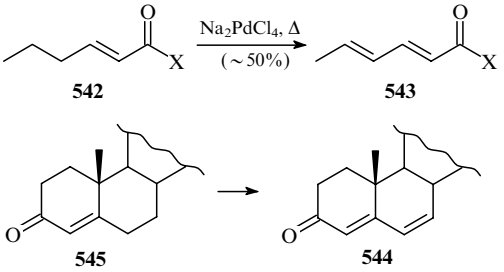


VIII. Miscellaneous methods

The methods discussed in this Section could be assigned, if desired, to one or another type of reactions considered in the preceding Sections. However, these examples are usually single

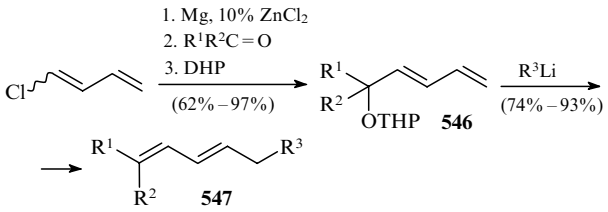
and have substantial differences from the typical processes; therefore, we consider them separately.

The introduction of double bonds by elimination of vicinal hydrogen atoms finds only limited use. The high-temperature catalytic dehydrogenation occurs selectively only in the preparation of simple dienes, for example, butadiene from butane and butenes or isoprene from isopentane. Of more complex examples, one should note the transformation of α,β-unsaturated oxo compounds **542** (X = Ph, OEt) into the corresponding dienes **543** on treatment with stoichiometric amounts of Na_2PdCl_4 as an oxidant.[478] The yields are moderate in all cases. This method has been used to prepare steroidal dienones with fragment **544** from the corresponding enones **545**.



542 **543** **545** **544**

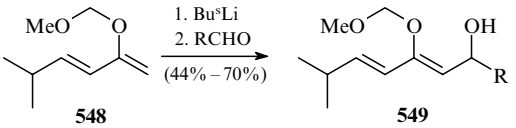
The tetrahydropyranyl derivatives of α-dienic alcohols **546** can react with a number of C-, N-, Si- or Sn-nucleophiles giving rise to dienes **547** with a different arrangement of double bonds.[479] The methoxymethyl derivatives react in a similar way; however, the reaction stereoselectivity is lower.



546 **547**

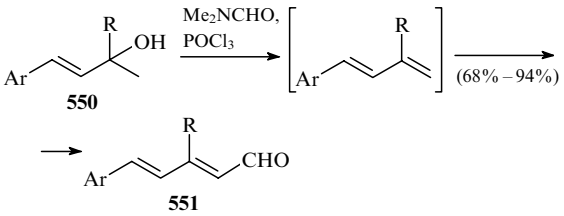
DHP is dihydropyran; R^3 = Alk, NEt_2, $SiMe_2Ph$, $SnMe_3$.

The methoxymethyl ether of the enol **548** can be introduced, after lithiation, into reactions with aldehydes.[480] The resulting dienes **549** contain an oxygen function at the diene system. The presence of this function is necessary for this reaction to take place (chelate control).



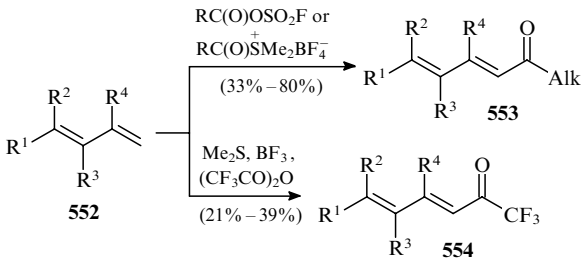
548 **549**

The tertiary analogues of cinnamic alcohols **550** are dehydrated under reaction conditions and the resulting diene is formylated giving rise to dienals **551**.[481]



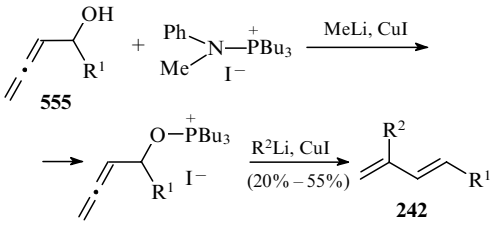
550 **551**

Direct acylation of conjugated dienes **552** has remained problematic until recently. However, development of reactive cationoid reagents has enabled the synthesis of dienones **553** and **554** in reasonable yields.[482–484]



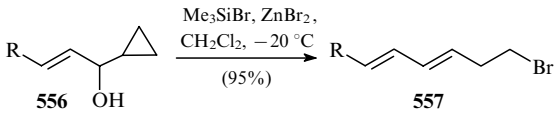
552 **553** **554**

The use of α-allenyl alcohols **555** in the synthesis of alkenes according to the Murahashi method affords the conjugated dienes **242**.[485]



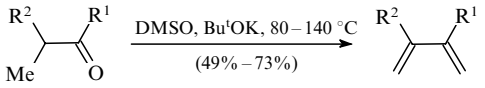
555 **242**

The carbocationic rearrangement of cyclopropylalcohols can proceed smoothly under appropriate conditions to yield homoallyl derivatives. In the case of cyclopropyl(alkenyl)methanols **556**, conjugated diene system **557** is produced.[486–488]



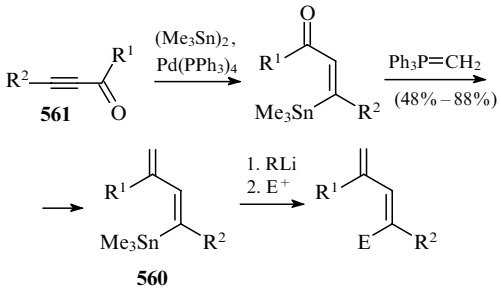
556 **557**

A very simple method for the synthesis of dienes consists in heating of aliphatic α-branched ketones **558** in DMSO with potassium *tert*-butoxide,[489] DMSO serving as the source of a new carbon atom in the molecule of product **559**. Unfortunately, in many instances, these reactions give mixtures of isomers.



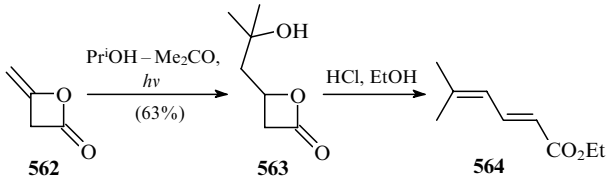
558 **559**

A two-step method for the preparation of dienylstannanes **560** from acetylenic carbonyl compounds **561** is documented.[490] Transmetallation provides a nucleophilic diene equivalent.



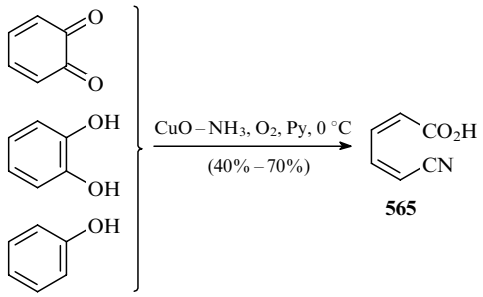
561 **560**

Diketene **562** exposed to UV radiation in a mixture of propan-2-ol and acetone gives adduct **563**, which is a convenient precursor of conjugated dienoate **564**.[491]



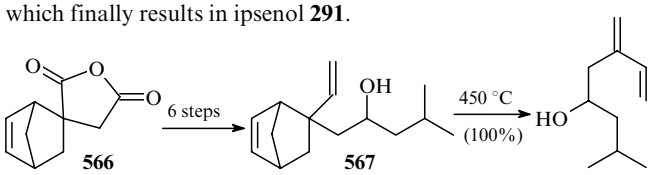
562 **563** **564**

Oxidation of *o*-quinone, pyrocatechol or phenol with ammoniacal copper oxide in pyridine results in *cis,cis*-muconic acid mononitrile (**565**).[492] In the case of substituted compounds, for example, 4-*tert*-butyl-*o*-quinone, a mixture of regioisomers is formed.



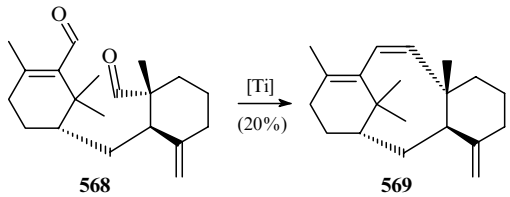
565

The adduct **566** of itaconic anhydride with cyclopentadiene was converted into compound **567**. Pyrolysis of this compound liberates the methylene group, which had initially been protected; this group is found to be conjugated with a new vinyl group,[493] which finally results in ipsenol **291**.



566 **567** **291**

The coupling of two carbonyl compounds by means of the McMurry titanium reagent results in alkenes; if one compound is unsaturated, the expected product is a diene. Thus intramolecular cyclisation of dialdehyde **568** results in diterpene hydrocarbon **569** difficult to prepare by other methods.[494]



568 **569**

IX. Conclusion

One cannot but note the great diversity of the methods for synthesis of conjugated dienes considered in this review. Nevertheless, despite the wide range of choice, when selecting the method of synthesis of a target object, a researcher would be guided, first of all, by its reliability and simplicity as well as the availability and cost of initial compounds and, strange though it may seem, by the reputation and popularity of the method. Table 3 presents a comparative analysis of the methods considered. It is fairly difficult to evaluate the true 'rating' of each of them because this requires analysis of a different type of literature, namely, the use of these methods in target-directed syntheses of intricate structures in which they are often used only as an episode in a multistep protocol. The more reliable the method, the less the attention researchers draw to it! The popularity of a method can be judged to some extent by the presence of reviews devoted to it, or (less reliably) by mentions of this method in textbooks.

When methods' reputations are equivalent, when planning the synthesis, one should analyse first of all the possibility of performing the task on the basis of standard reactions, *viz*., elimination (the formation of double bonds with a preformed carbon skeleton), olefination of carbonyl compounds (the $C_1 + C_3$ pattern of diene formation with formation of a double bond) and, more rarely, cross-coupling (the $C_2 + C_2$ pattern of diene formation with the formation of the central single bond, or the C_4 + substituent pattern). Each of these general approaches has its own limitations. In particular, alkenyl halides and alkenyl derivatives of elements used in cross-coupling are rather expensive and their synthesis requires high skills. This and other reasons stimulate the search for new, different reactions which would provide an absolutely untrivial approach to the synthesis of conjugated dienes. The progress achieved in the alkene – alkyne metathesis over the last three years can serve as an example. This method, as well as new organometallic reactions, undoubtedly hold great promise because it requires rather simple initial compounds and commercially available metal complex catalysts.

Table 3. Brief characterisation of the most important methods for the preparation of conjugated dienes (from the bibliography of this review).

Reactions	Stereohemical outcome	Features	The range of yields (%)	The number of references (of these, reviews)
Elimination	depends on the method and the substrate	effective methods are expensive	36 – 97	92 (8)
Reduction of enynes and diynes	good for the synthesis of *Z*-isomers, poorer for *E*-isomers	inexpensive method	50 – 86	15
Olefination of carbonyl compounds				118 (9)
condensation	high for linear *E*-dienes	used for the synthesis of α-functionalised dienes	24 – 98	35 (6)
Wittig reactions	depends on the method and the substrate but is controllable	adjustment of details for a particular synthesis is often required	27 – 98	58 (3)
other reactions	depends on the method and the substrate	more reliable than the Wittig olefination	23 – 94	25
Cross-coupling	very high; determined by the reactant structure	high cost of the reactants	30 – 93	104 (16)
Miscellaneous organometallic reactions	depends on the method and the substrate	some procedures are very effective	21 – 99	48 (1)
Electrocyclic reactions	high	industrially feasible	25 – 90	35 (3)
Miscellaneous methods	depends on the method and the substrate	–	20 – 95	75

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