1
Synthesis of Allenes by Isomerization Reactions

A. Stephen K. Hashmi

1.1
Introduction

Isomerization reactions are associated with a change in either the connectivity (the constitution) of the molecule or the steric arrangement of atoms or groups in the molecule. However, no change of the empirical formula is involved. Thus in isomerization reactions leading to allenes, the 1,2-diene substructure that is characteristic of this class of compounds has to be formed by one of the following reactions (Scheme 1.1):

(a) *Migration* of a non-cumulated π-bond into cumulation with a second π-bond. The non-cumulated π-bonds can either be an alkyne (Reaction A) or a conjugated or isolated diene (Reaction B). If in Reaction A the group X = H this is a prototropic *rearrangement*; another possibility would be a sigmatropic rearrangement in which X typically is a two- or three-atomic unsaturated moiety. These two cases are the most important isomerization reactions leading to allenes. Another priciple that would also fall into this category would be the rearrangement of one allene to another.

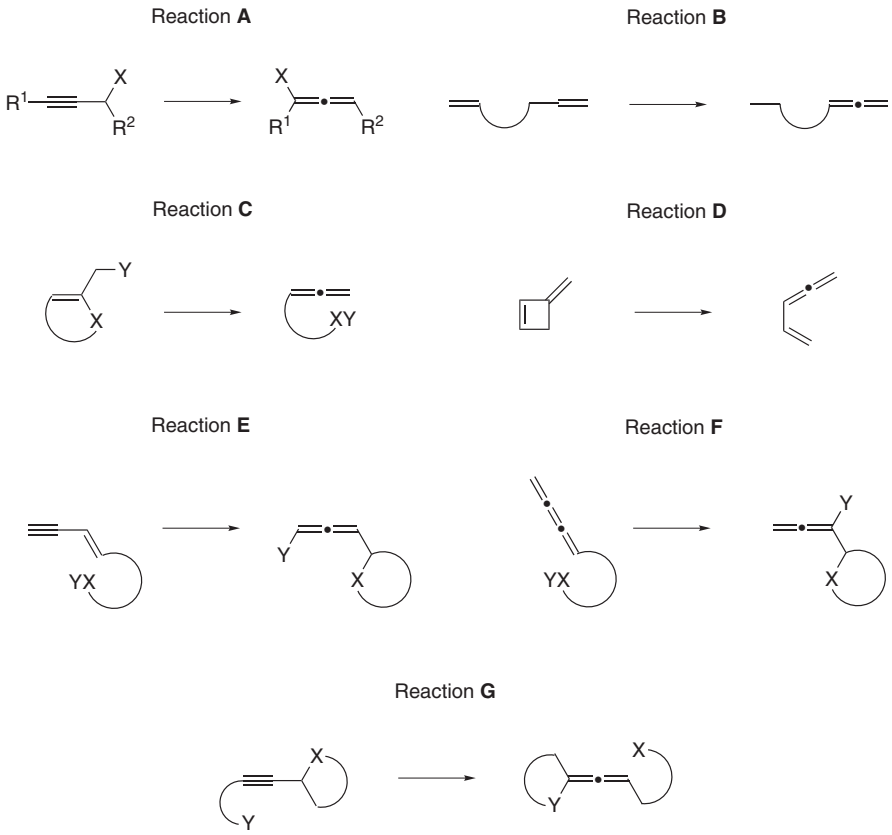
(b) Transformation of a ring (a double bond equivalent) to a π-bond by a kind of intramolecular *elimination* process (Reaction C) or an electrocyclic ring opening (Reaction D).

(c) Another option would be the *addition* of an intramolecular nucleophile to a conjugated, alkyne-containing system such as a 1,3-enyne (Reaction E) or a higher cumulene (Reaction F).

(d) A *substitution* would only fall into the category of isomerization if it is entirely intramolecular; both the attacking and the leaving group would need to remain part of the molecule. This would mean that the formation of the new bond needs to be a ring closure and the bond cleavage would be a ring opening (Reaction G).

Modern Allene Chemistry. Edited by N. Krause and A.S.K. Hashmi

ISBN: 3-527-30671-4



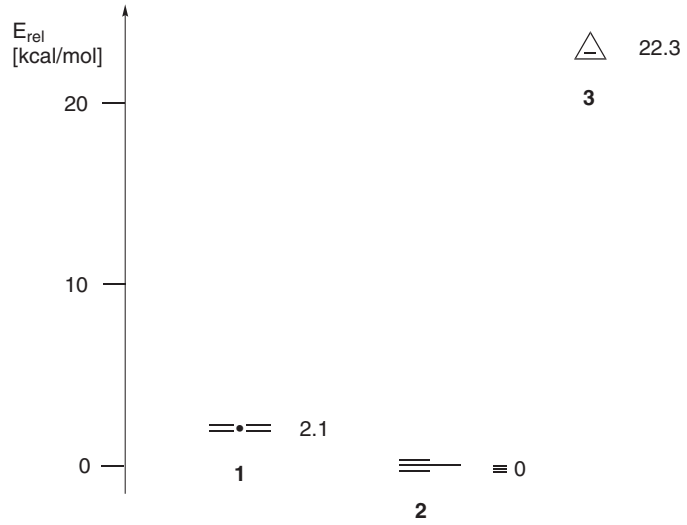
Scheme 1.1 Different conceivable Reactions A–G forming allenes by isomerization reactions.

This chapter will cover only reactions in which the isomerization to the allene starts from a stable molecule and *not* from a reactive intermediate generated in situ by reactions which are not isomerizations, such as the Doering–Moore–Skattebol reaction or free carbenes. Metallotropic rearrangements also will not be covered; many of these reactions can be found in Chapter 9. Furthermore, the allene should be the final product of the reaction and not only a transient species leading to other products (see, for example, Chapters 6 and 20).

The last review in this field was published in 1980 [1]; this chapter will focus on the new developments and applications in the past two decades, but also cite important key papers from previous work.

The isomers of the simplest allene, 1,2-propadiene **1**, are propyne **2** and cyclopropene **3** (Scheme 1.2). Their isomerization engergies have been measured and calculated [2–4]. Compound **2** is clearly the most stable isomer, **1** lies 2.1 kJ higher and **3** about 22.3 kJ. Hence in principle, if reversible, thermodynamics of an equilibrium should favor the alkyne. However, several factors can influence this in two ways, i.e. a change of the relative thermodynamic stability, for example by substituents, or a

reaction under kinetic control, for example stoichiometric deprotonation followed by kinetic protonation. For a long time different thermodynamic stability was only deduced from the ratio of the products isolated, and apart from obvious cases, where for example the relief of strain led to a clear preference in the equilibrium, a clear explanation was not possible. It was only recently that by thorough calculations the influence of the substituents on the allene was investigated [5]; for example in the synthetically important allenyl ethers and allenylamines which are thermodynamically more stable than their propargylic counterparts! The substituents are most important for the synthetic chemist because they define both the starting material and the class of allenes and thus the reactivity of the latter (see, for example, Chapters 7 and 8). Therefore, this chapter is not only ordered by the *reaction types* but these are also subdivided by the *substituents on the allenic product*.



Scheme 1.2 Isomers of the smallest allene C_3H_4 and their relative energies.

Most of the reactions are either catalytic in a reagent that initiates the isomerization, for example a base, or initiated by heating or irradiation, for example in sigmatropic rearrangements and electrocyclic ring openings. Only a small number of the reactions need a stoichiometric amount of a reagent; a typical example would be stoichiometric deprotonation with an organolithium reagent and a subsequent protonation.

As we shall see, in most of the examples smaller building blocks are synthesized by such isomerizations. The high reactivity of the allene is then utilized in further synthetic steps. However, there are also numerous reactions where complex molecules in later stages of a synthesis are synthesized by isomerizations.

1.2
Prototropic Rearrangements and Related Reactions of Alkynes

This is, as the numerous references will show, probably the most important method for the synthesis of allenes by isomerizations (Reaction A in Scheme 1.1). Examples following a different mechanism but overall delivering analogous products will also be covered in this section.

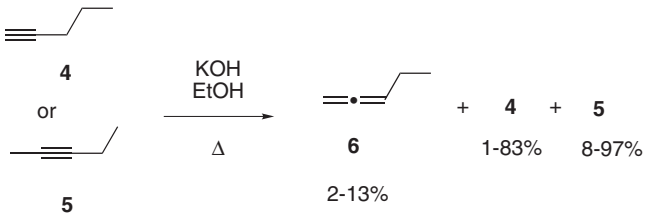
1.2.1
Hydrogen Atoms or Alkyl Groups as Substituents

In these reactions, usually an equilibrium mixture, favoring the internal alkyne, is observed. Thus it is difficult to obtain preparatively useful yields of allenes.

For the thermal isomerization of **2** to **1** [6] on the basis of kinetic data, it was suggested that at least 50% of **1** is formed via cyclopropene **3** as an intermediate [7] rather than a direct 1,3-H-shift as proposed before [8, 9]. Later theoretical calculations provided further support for that suggestion [10]. A number of other publications, some of them with basic catalysts such as sodium hydroxide, deal with this reaction [11–17]. Furthermore, **2** can be isomerized to **1** by a stoichiometric reacion with $[RuHCl(CO)(PPh_3)_3]$ and subsequent treatment with NaS_2CNMe_2 [18]. The 1,1-bisdeuterated **2** has also been investigated [19].

The next homologues are 1- and 2-butyne, where similar isomerizations have been observed [20]; a recent report describes the reaction on a basic, alkali metal-exchanged zeolite [21]. As an unexpected product, an allene was obtained in reactions with hydrogen and a samarium catalyst [16, 22].

With pentynes **4** or **5**, a similar reaction was possible with potassium hydroxide at 175 °C; here, depending on the reaction time and the temperature, between 2 and 13% of 1,2-pentadiene **6** could be obtained along with the pentynes (Scheme 1.3) [23].

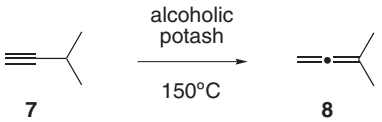


Scheme 1.3

Of further significance is the fact that *no* 1,3-pentadiene is formed! This behavior is similar to that of the butynes, where also no 1,3-butadiene was observed. Furthermore, this is in complete accordance with the proposed mechanism of the potassium 3-aminopropylamide-mediated isomerization of internal alkynes to terminal alkynes by repetitive alkyne–allene–alkyne isomerizations [24].

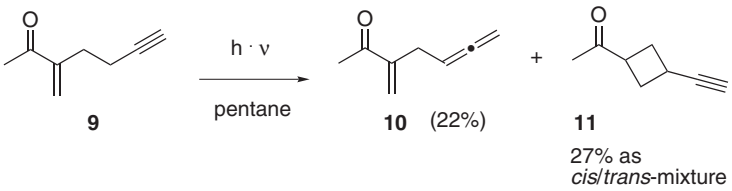
One of the papers initiating this field deals with a pentyne isomer, as early as 1888 Faworski [25] reported the isomerization of 3-methylbutyne **7** to **8** (Scheme 1.4)

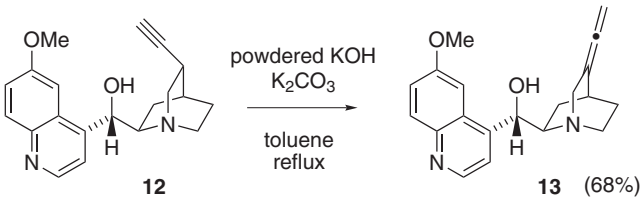
[26]. Similar reactions were conducted with ethynylcyclohexane [27, 28] and a terpene-derived alkyne [29].



Scheme 1.4

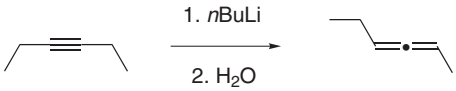
The thermal isomerization of higher terminal alkynes also delivered some allene, from 1-hexyne and 1-heptyne, for example, some 1,2-diene was formed [30]. With an α,β-unsaturated unit in the alkyne **9**, a photochemical isomerization to **10** was successful but delivered only a low yield and **11** as a significant side-product [31]. These reactions tolerate different functional groups; alcohols, ethers or, as in **12**, tertiary amines and nitriles have been used (Scheme 1.5) [32, 33].



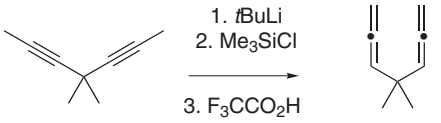


Scheme 1.5

Under basic conditions, obviously only one isomerization step takes place and thus a terminal alkyne will deliver 1,2-dienes selectively. With internal alkynes, on the other hand, selectivity can only be achieved when the alkyne is either symmetrical as in **14** [34] (Scheme 1.6) or has a tertiary center on one side as in **16** [35, 36] (Scheme 1.7). So, unlike potassium 3-aminopropylamide in 1,3-diaminopropane, where the π-bonds can migrate over a long distance by a sequence of deprotonations and reprotonations, here the stoichiometric deprotonation delivers one specific anion which is then reprotonated (in **16** after transmetalation).

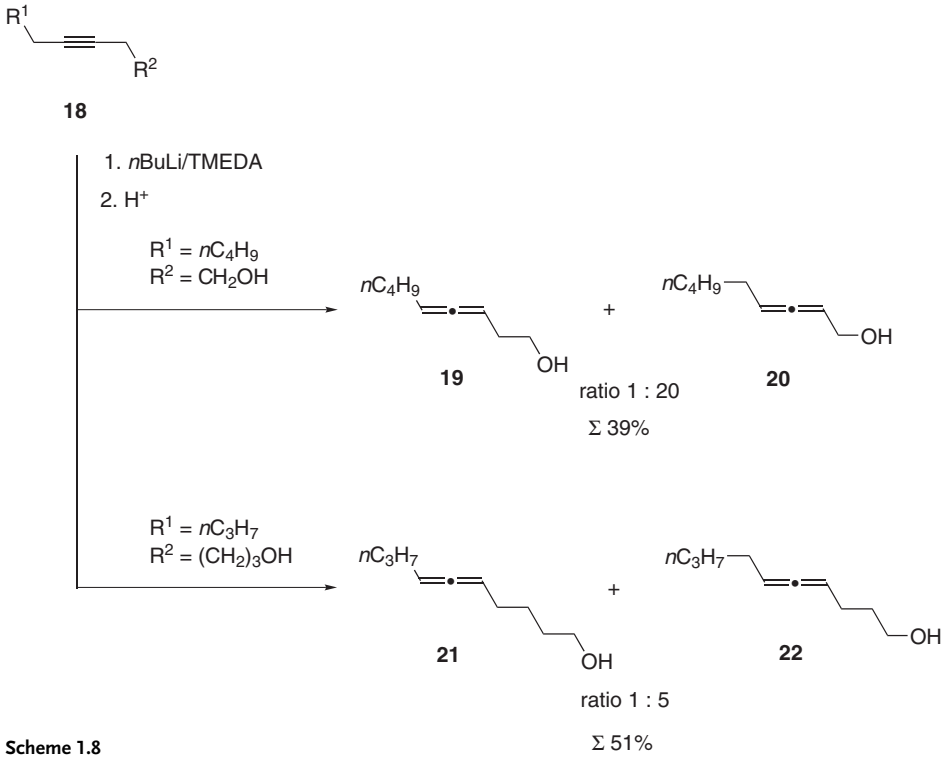


Scheme 1.6



Scheme 1.7 **16** **17** (> 27%)

On the other hand, unsymmetrical internal alkynes usually lead to two different constitutional isomers. In compounds of type **18**, selectivity in favor of **20** rather than **19** is observed (1:20) owing to the hydroxyl groups which might direct the deprotonation by directing the base to the closer propargylic methylene protons (Scheme 1.8) [37]. This chelate-like behavior, of course, becomes less significant as the tether increases; for **21** and **22** the yield is better but the selectivity is reduced to only 1:5.

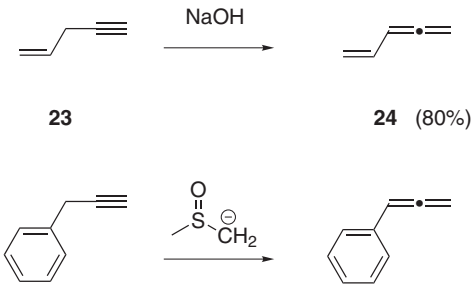


Scheme 1.8

1.2.2
Alkenyl or Aryl Groups as Substituents

The preparatively useful examples in this section can be divided into three categories.

(a) The migrating π-bond moves into conjugation with the neighboring alkene or arene. Most of these reactions follow this scheme. Here the starting material is an alkyne separated by one sp^3 center from the alkene or arene; the prototypes of these reactions leading to **24** [38, 39] and to **26** [40] have been described (Scheme 1.9).

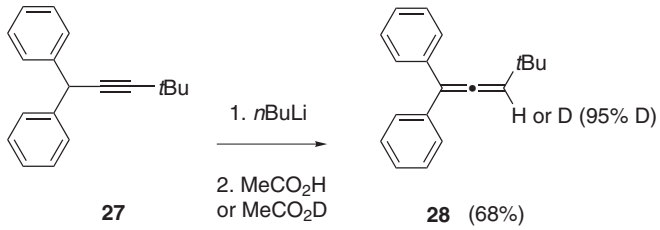


23 **24** (80%)

25 **26** (67%)

Scheme 1.9

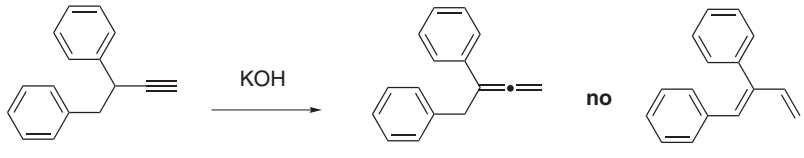
The above references, along with a number of others [41, 42], describe some more examples of substituted substrates. Even with a 1,1-diphenyl substrate **27**, a stoichiometric metalation followed by protonolyis (or deuterolyis) is necessary to obtain a good yield [43] (Scheme 1.10).



27 **28** (68%)

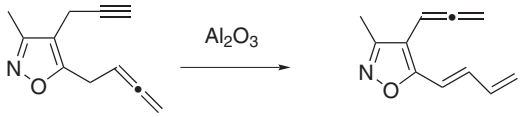
Scheme 1.10

It is notable that with substrates such as **29** still only **30** but no 1,3-diene **31**, which would bring the two aromatic rings into conjugation, is formed [44, 45] (Scheme 1.11).



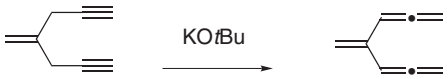
Scheme 1.11

Such a behavior cannot always be guaranteed; the heterocycle **32** with a terminal alkyne *and* an allene isomerizes both fuctional groups, the benzylic alkyne to an allene and the benzylic allene to a 1,3-diene, both now in conjugation with the heteroarene [46] (Scheme 1.12).



Scheme 1.12 **32** **33** (94%)

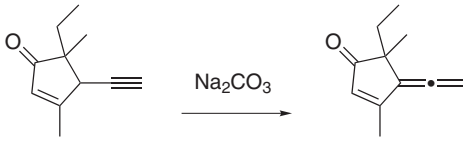
In some examples, two alkynes isomerized, leading to cross-conjugated systems such as **35** [47, 48] (Scheme 1.13).



Scheme 1.13 **34** **35** (88%)

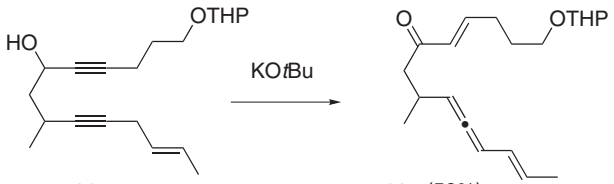
The isomerizations have also proven to be very useful in the synthesis of a series of 1,3-diarylallenes [49–55], even tolerating other functional groups such as aryl chlorides, aryl bromides [56–58] and vinyl bromides [59]. Mixed systems with an alkene on one side and an arene on the other could also be prepared [41, 60], as well as products with two olefinic substituents [61] or bisallenes [62–64].

Other functional groups tolerated in these isomerizations are ethers [65], alcohols [38, 66–69], propargylic trifluoromethyl groups [70], conjugated enones such as **36** [71] and esters [72] (Scheme 1.14).



Scheme 1.14 **36** **37** (100%)

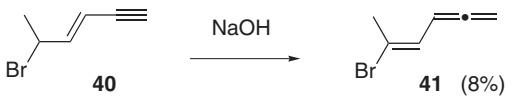
Still, occasionally the other fuctional groups react as well, for example in **38** under basic conditions the propargylic alcohol isomerizes to the α,β-unsaturated ketone [73] (Scheme 1.15), whereas in a closely related substrate from the synthesis of a subunit of compactin an allylic alcohol remains unchanged [74].



Scheme 1.15 **38** **39** (50%)

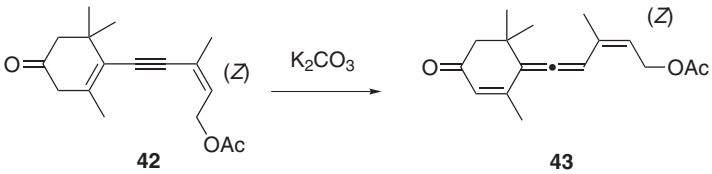
Substrate **38** also nicely displays the selectivity accompanying the neighboring alkenes or arenes: whereas with two alkyl chains on an alkyne two products would be formed, here a selective isomerization to the conjugated allene is observed.

(b) The migrating π-bond is already in conjugation to an alkene and *both* are shifted by one carbon atom during the isomerization. This 'vinylogous' case is best explained by the reaction of **40** to **41**, where – albeit in low yield due to elimination processes – even an allylic bromide delivers a vinyl bromide [75] (Scheme 1.16).



Scheme 1.16 **40** **41** (8%) (+ other products)

Similarly, the isomerization can be performed with an allylic ether [65, 76] and ketones such as **42** (with preservation of the double bond geometry!) [77] have also been reported to undergo these isomerizations (Scheme 1.17).

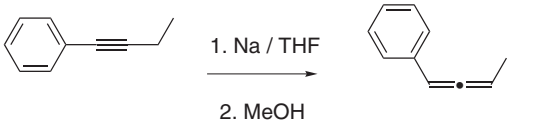


Scheme 1.17 **42** **43** (*E*) gives only (*E*)

Related steps, leading to unusual cross-conjugated systems, were discussed for the isomerization (*E*)-enediynes [78].

(c) The migrating π-bond is in conjugation with the neighboring alkene or arene and moves away. As one can imagine, this is much more difficult to achieve and therefore only a handfull of examples are found in the literature, usually providing the allene only as a side-product even in reactions with a stoichiometric amount of reagent. In the hydrocarbon series [79], **44** was reported to undergo this mode of

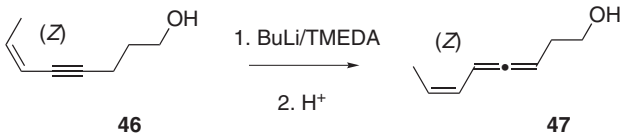
isomerization, along with a reduction, when treated with sodium or potassium [80] (Scheme 1.18).



44 **45** (up to 20%)

Scheme 1.18

Substrates with carbamate-protected [81, 82] and even free hydroxyl groups [69] reacted similarly in a deprotonation–reprotonation sequence, the latter even with retention of the *Z*-configuration of an alkene such as **46** (Scheme 1.19). The analogous (*E*)-alkene also delivers only *E*-product.



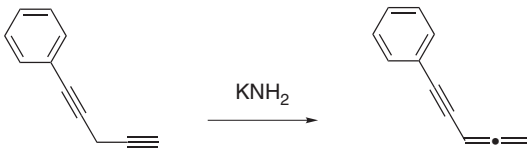
46 **47**

Scheme 1.19

An unusual approach is the isomerization of a methyl-substituted 1,2,3-butatriene to a vinylallene by stoichiometric deprotonation with *n*BuLi–TMEDA and reprotonation [83]. With an ether substituent on the butatriene a similar reaction is possible with KO*t*Bu in DMSO [84], while a phenyl-substituted butatriene reacted spontaneously in $CHCl_3$ [85].

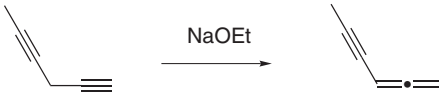
1.2.3
Alkinyl Groups as Substituents

This is a rare case; all the substrates have a skipped diyne structure, automatically raising the question of which triple bond will isomerize. In the case of the phenyl-substituted **48** it is the terminal alkyne, delivering the larger conjugated system in **49** [86] (Scheme 1.20).



Scheme 1.20 **48** **49**

Other examples reported with a terminal and an internal alkyne as in **50**, which do not like **49** have an additional possibility for conjugation, show that then the terminal alkyne isomerizes [62, 87, 88] (Scheme 1.21).



Scheme 1.21 **50** **51** (74%)

Comparable selectivities have been published for the intramolecular competition of an ester- and an alkyl-substituted alkyne [89] or a silyl- and an alkyl-substituted alkyne [90].

When the diyne is already conjugated as in 1,3-pentadiene **52**, with 4 equivalents of *n*BuLi–TMEDA, an isomerization can also be achieved [91] (Scheme 1.22). The selectivity of this process is low; starting material and 1,4-pentadiyne are also found.

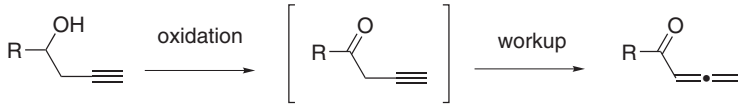
Scheme 1.22 **52** **53** (20%)

1.2.4
Carbonyl Groups as Substituents

This is a group of substrates which, along with sulfoxides, sulfones, phosphonates and related acceptors (see Sections 1.2.8 and 1.2.10), gives the most predictable results. Mild bases can be applied and this has found numerous applications in organic synthesis.

Most of the substrates for these isomerizations have a tetrahedral carbon with at least one hydrogen substituent between the carbonyl group and the alkyne. Due to the comparable high acidity of this C–H bond neighboring the carbonyl group, already a weak base such as a carbonate, a tertiary amine or aluminum oxide can deprotonate this position and a subsequent protonation at the other end of the propargyl/allenyl anion delivers the allene.

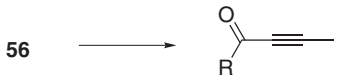
Ketones and aldehydes possess the highest α-acidity, many examples being known. In fact, it is usually very difficult to keep a terminal propargyl ketone from isomerizing to the allenyl ketone. Thus the oxidation of a homopropargylic alcohol **54**, a typical precursor, in most of these cases directly delivers the allenyl ketones **56** rather than the propargyl ketones **55** in high yields [92–109] (Scheme 1.23).



54 **55** **56**

Scheme 1.23

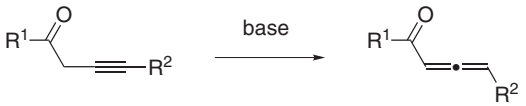
In these isomerizations, a base is not necessarily needed; for example, NMR investigation proved that oxidation under slightly acidic conditions initially indeed delivers **55**, which is stable for more than 1 week. During subsequent silica gel chromatography, which separates the acid from **55**, even with hexane–ethyl acetate on silica gel complete isomerization to **56** takes place [110]. Subsequently, more such isomerizations on silica gel were reported [111]. Studies with partially deuterated substrates prove that only the C–H bonds next to the ketone are broken during the reaction, the other propargylic C–H bonds remaining intact [112]. If the group R in **56** is strongly electron-withdrawing, even on silica gel a further isomerization to the alkynyl ketone **57** can be observed as a side reaction [110] (Scheme 1.24).



Scheme 1.24 **57**

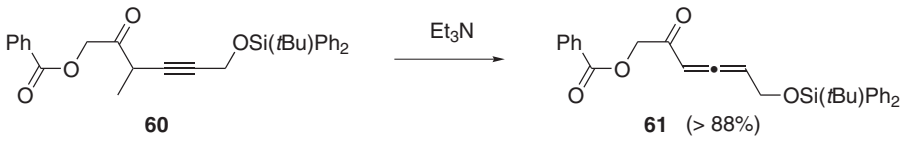
Only a distillative work-up from an acidic oxidation reaction, for example, delivers **55**, which then has to be isomerized by base to obtain **56** [113]. Similar precautions for the synthesis of **55** have been reported recently for a chromium-catalyzed oxidation [114]; here again the key is to avoid a base and even a chromatographic work-up, as already demonstrated for chromium-free Dess–Martin oxidations [110].

The whole situation changes slightly when the substrate contains a disubstituted alkyne **58** (Scheme 1.25). Then often no or only an incomplete or very slow isomerization is observed without a base. For example, a methyl substitution of the alkyne slows the reaction about 300-fold compared with the terminal alkyne [115]. However, with the base again high yields of the isomerization product **59** are obtained [116–121]. A substituent α to the carbonyl group seems to have a similar effect [122].



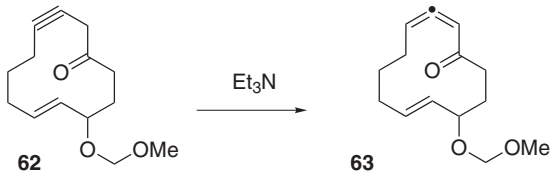
Scheme 1.25 **58** **59**

Among the most impressive applications are the reactions of the silyl- and acyl-protected diol **60** [123] (Scheme 1.26) and the 12-membered macrocyclic *E*-configured allylic ether **62** [124] (Scheme 1.27).



60 **61** (> 88%)

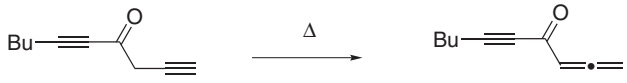
Scheme 1.26



62 63 (100%)

Scheme 1.27

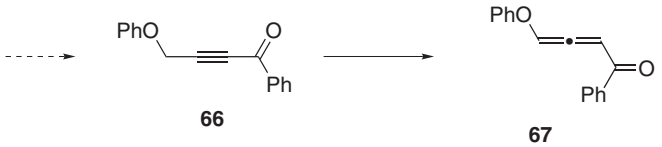
The last question still open addresses the alkynyl ketones. The reaction of **64** shows an example with a potential intramolecular competition and here it is possible to isomerize the propargyl substitutent on the ketone quantitatively without changing the 1-hexynyl substituent on the other side [125] (Scheme 1.28). From the publication it is not clear whether the isomerization is really a thermal reaction or occurs during the workup of the thermolysis reaction, for example by chromatography (compare the discussion above [110]).



64 **65** (100%)

Scheme 1.28

When alkynyl ketones are synthesized, occasionally an in situ isomerization to the allene was reported, for example in the propargylic ether **66** [126] (Scheme 1.29).

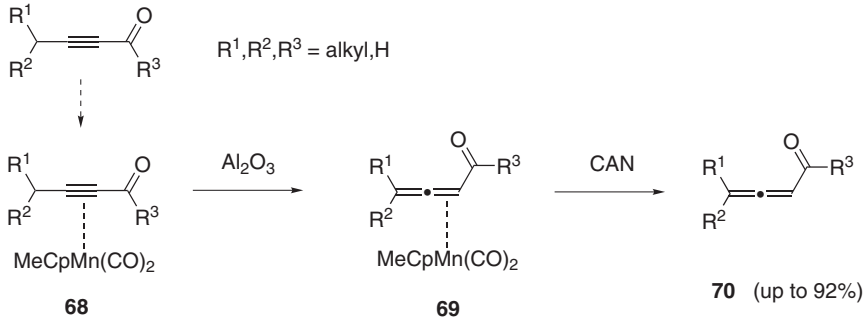


66 67

Scheme 1.29

The latter mode of reaction has even been reported to proceed in presence of silver(I) ions [127], which is not easy to understand in the context of Marshall's silver-catalyzed cycloisomerization of allenyl ketones (see Chapter 15).

An interesting sequence, again overall an isomerization, is the stoichiometric formation of the manganese complexes **68**, which, on basic alumina, isomerize to the allenyl complexes **69**; from the latter the allenes **70** can be liberated with cerium(IV) ammonium nitrate (CAN) in good yields [128] (Scheme 1.30).

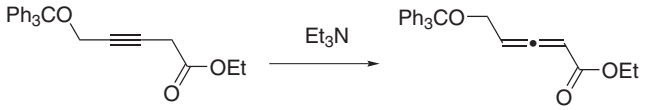


Scheme 1.30

A unique photochemical rearrangement in which an *o*-alkynylphenol is isomerized to an allenyl ketone has also been reported [129].

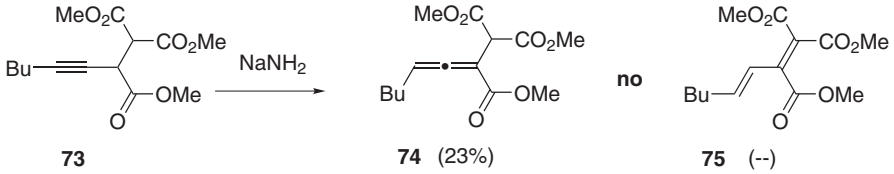
The second large class of allenes with carbonyl groups as substituents is derivatives of carboxylic acids. Overall, the same principles as with the aldehydes and ketones apply, but not as many examples are known, which might originate in part from the lower acidity of the α-hydrogen atoms of the carbonyl group compared with aldehydes and ketones.

Still, with ester groups, triethylamine is sufficient to catalyze the isomerization, as shown with the trityl-protected example **71** [130] (Scheme 1.31).



Scheme 1.31

Numerous related reactions have been published, some of them using aqueous potassium carbonate [131–135]. Again 1,3-dienes are not formed; **73** provides – apart from starting material – only **74** and no **75** [136] (Scheme 1.32).

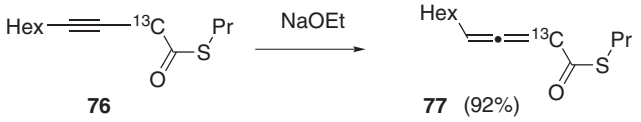


Scheme 1.32

Silyl esters have also been transformed successfully [137]; another example reports the *O*-acylation of serine with a β-alkynyl carboxylic acid anhydride accompanied by an in situ isomerization of the alkyne to the allene [138].

A number of references cover similar syntheses of allenes with carboxylic acids [131, 139–142] and amides [143] instead of carboxylic esters as electron-withdrawing

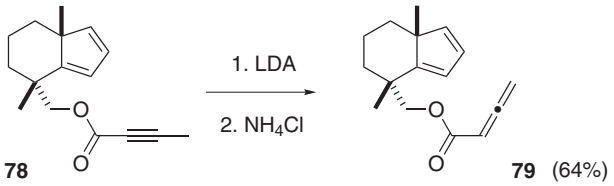
groups. A further significant example is the ^{13}C-labeled thioester **77** synthesized by isomerization for an investigation of the inactivation of β-hydroxydecanoyl thioester dehydrase [144] (Scheme 1.33). Even enyzme-catalzed isomerizations have been reported; with a hog liver isomerase, β-alkynyl thioesters deliver the corresponding allenes [144, 145].



76 **77** (92%)

Scheme 1.33

Again, the isomerization of an α-alkynyl ester to an allene requires stronger bases, in most known cases sodium amide in liquid ammonia or other strong bases [128, 147–149]. One further example is the step **78** → **79** from one of the efforts to synthesize myltaylenol [150] (Scheme 1.34).

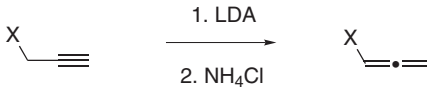


78 **79** (64%)

Scheme 1.34

1.2.5
Halogens as Substituents

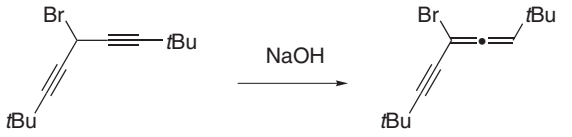
The isomerization of the smallest alkynes **80** with halogens in a propargylic position has been described for chlorine [151, 152], bromine [153] and iodine [154] (Scheme 1.35), but often might proceed by an S_N2'-type substitution rather than a prototropic rearrangement [155–159]. On the other hand, transformations such as **82** → **83** [160] or **84** → **85** [161] are clearly prototropic (Scheme 1.36). This is also true for propargylic halides such as **86** with its additional ester group assisting the prototropic isomerization [162, 163] (Scheme 1.37).



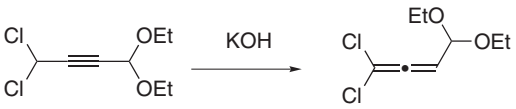
80 **81**

X = Cl,Br,I

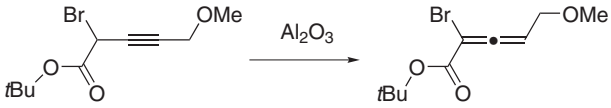
Scheme 1.35



82 **83** (65%)



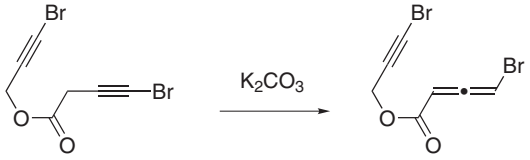
Scheme 1.36 **84** **85** (67%)



86 **87** (92%)

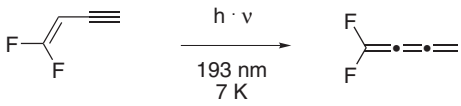
Scheme 1.37

An entirely different situation is found in alkynyl halides. Here only examples in which the rearrangement is supported by carbonyl groups [106, 164] or electron-withdrawing pentafluorophenyl groups [165] are known. As one example, the selective reaction of the alkynyl bromide next to the carbonyl group, in the presence of a second alkynyl bromide with a propargylic C–O sigma bond, is shown (**88** → **89**) [164] (Scheme 1.38).



Scheme 1.38 **88** **89**

A unique reaction is the photochemical rearrangement of **90** to the 1,1-difluorobutatriene **91** in an argon matrix at 7 K [166] (Scheme 1.39).



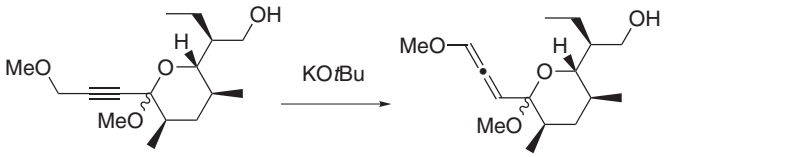
Scheme 1.39 **90** **91**

1.2.6
Oxygen as the Substituent

These allenes are very important for organic synthesis and their use is discussed in Chapter 8. For their synthesis usually a strong base is needed, typically KO*t*Bu. There are many examples; most of them cover the isomerization of a propargylic ether to the corresponding allenyl ether.

The significance of this reaction is reflected by the isomerization of the smallest representative, propargyl methyl ether, with a number of references from 1968 up to 2000 [167–175].

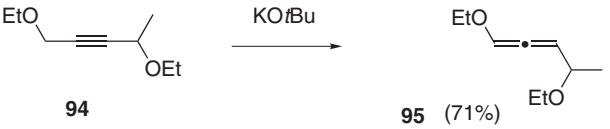
Further, a large number of examples with simple alkyl substituents [168, 171, 176–184], cyclic alkanes [185], aryl substituents [177, 186–192], olefinic substituents [78, 177, 193–196], deuterated compounds [172], thioether groups [171], ester groups [197], orthoesters [198, 199], acetals [168, 182, 200–204], silyl-protected alcohols [198, 205–211], aldehydes [212], different heterocycles [213–217], alkyl halides [218, 219] and aryl halides [192, 220–223] have been reported. A representative example is the reaction of **92**, possessing a free hydroxyl group, an acetal and a propargylic ether, to **93** [224] (Scheme 1.40).



92 **93** (49% after four more steps)

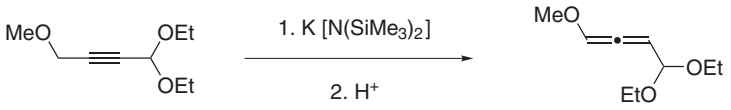
Scheme 1.40

The intramolecular competition of two propargylic alkoxy groups, one on each side of the alkyne, is interesting. In a series of substrates related to **94** [180], always the 1,2-disubstituted allene **95** (Scheme 1.41) and not a 1,1,3-trisubstituted allene is formed (see also [225, 226]). The opposite regioselectivity was described in one publication (deprotonation with *t*BuLi, then protonation), but the allenes described there proved to be labile and quickly converted to other products [227].



Scheme 1.41 **94** **95** (71%)

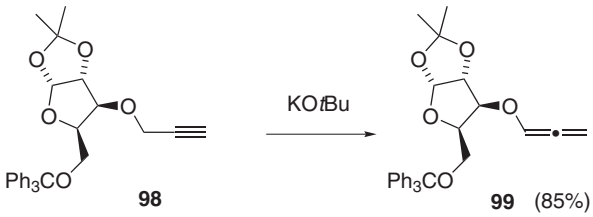
Related competitions between a propargylic ether on one side and a propargylic acetal on the other always delivered the product of an isomerization in the direction of the ether. Compound **96** with stoichiometric amounts of potassium hexamethyldisilazide serves as a recent example [228] (Scheme 1.42); other references describe the same reactivity [229–231].



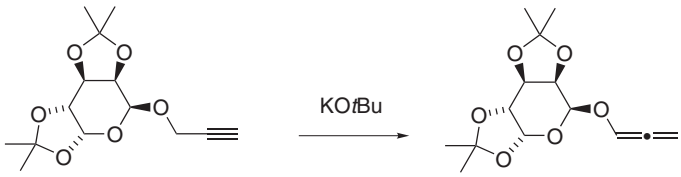
96 **97** (88%)

Scheme 1.42

The competition between a propargylic ether and a teriary propargylic amine provided an allenyl ether rather than an allenylamine [182]. The reaction was also successful with propargyl allyl ethers [232]. An additional ester group in the propargylic position is tolerated [233], and consequently the reaction also works with esters of propargylic alcohols [234–236]. In the past 4 years, several derivatives of carbohydrates were converted successfully [217, 237–241]; two examples are the isomerizations of enantiomerically pure **98** [242] and **100** [217, 243] (Scheme 1.43).



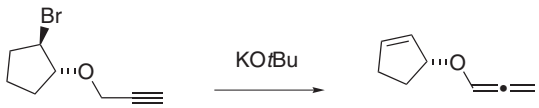
98 **99** (85%)



100 **101** (84%)

Scheme 1.43

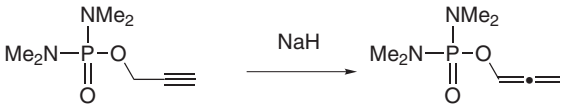
Due to the basic conditions, the reaction can be accompanied by an elimination, and then it is only locally (at the propargylic ether) an isomerization; see **102** [195] (Scheme 1.44) as one of several examples [218, 244, 245].



Scheme 1.44 **102** **103** (87%)

The combination of a silyl-migration from carbon to oxygen and a prototropic isomerization leads to allenyl silyl ethers [246].

A last and unusual substrate in this section is a propargyl ester of a phosphorus acid diamide **104** [247] (Scheme 1.45).

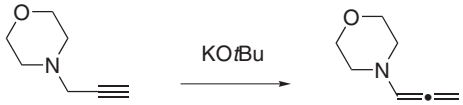


Scheme 1.45 **104** **105** (70%)

1.2.7
Nitrogen as the Substituent

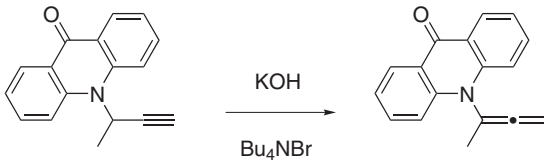
The basic principles of the previous section (oxygen substituent) can be transferred to nitrogen as the substituent. Here most of the examples use either potassium *tert*-butylate or a stoichiometric deprotonation with *n*-butyllithium followed by protonation with methanol.

A number of alkyl-substituted propargylic amines have been isomerized in that way [186, 191, 248–251], occasionally also providing alkynylamines as side-products. Compound **106** shows a recent example of a selective isomerization [252] (Scheme 1.46).



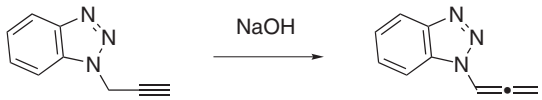
Scheme 1.46 **106** **107** (39%)

Arylamines with a propargyl group react under the same conditions [191, 253–256]; in the case of the vinylogous amide **108**, potassium hydroxide and a phase-transfer catalyst are sufficient [257] (Scheme 1.47).



Scheme 1.47 **108** **109** (65%)

In heteroaromatic compounds such as **110** [258] (Scheme 1.48), the nitrogen atom can be part of the aromatic ring [252, 259–262]. The most significant examples are found in the area of nucleobases and related heterocyclic compounds [263–271]; in **112**, for example, an alcohol group is competing with the propargylic nucleobase, and this alcohol group is probably responsible for the low yield as an isomerization



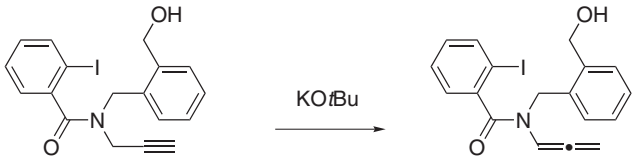
Scheme 1.48 **110** **111** (60%)

112 **113** (40%)

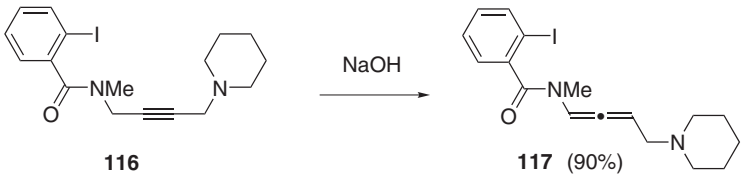
Scheme 1.49

in this direction will ultimately lead to an enone and products derived from it under the nucleophilic conditions [272, 273] (Scheme 1.49).

Amides and carbaminates are a further class of substrates [255, 274–278]. Compound **114** shows a substrate with an unprotected hydroxyl group and an aryl iodide [279] (Scheme 1.50), **116** an aryl iodide and the competition of an amide with an amine, yielding a 2.5:1 mixture of amide isomers favoring the (*Z*)-amide configuration depicted in **117** [280] (Scheme 1.51).



Scheme 1.50 **114** **115**

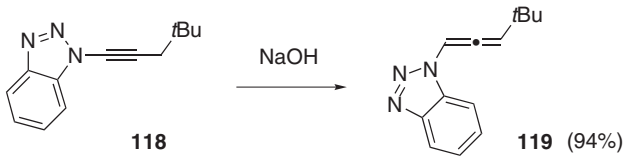


116 **117** (90%)

Scheme 1.51

Propargylated tosylamides also isomerize efficiently [221, 281]. On the other hand, rare examples are propargylated hydrazines [251], *N*-propargylated imines [282], isonitriles (must be *N*-propargylated) [283], ammonium salts [284] and azides [285].

Finally, an 'inverse' reaction, the isomerization of an alkynylbenzotriazole **118** to the corresponding allenyl compound **119**, has also been described [286] (Scheme 1.52).



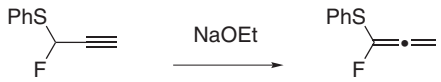
118 **119** (94%)

Scheme 1.52

1.2.8 Sulfur as the Substituent

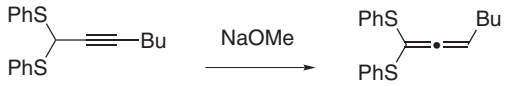
As far as propargyl thioethers are concerned, the substrates in this section follow all the principles discussed for propargyl ethers and propargylamines in the two preceding sections. For alkyl propargyl thioethers typical bases used are sodium amide in liquid ammonia, alcoholate or alkali metal hydroxide [178, 186–189, 191, 287–291], and again some derivatives of carbohydrates have been used successfully [292, 293]. If an ester group is also present in the molecule, the reaction can be accompanied by a hydrolysis to the carboxylate [294].

Among the aryl propargyl thioethers [187, 188, 191, 295–300], the fluorinated **120** is worth mentioning [301, 302] (Scheme 1.53). A few heteroaryl propargyl thioethers have also been investigated [213, 303–305].



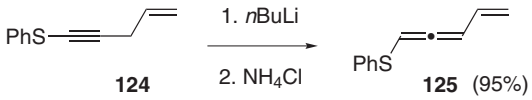
Scheme 1.53 **120** **121** (70%)

As known from the 'Umpolung' reactions, dithioacetals can be deprotonated efficiently; among others [230, 306], a recent application is **122** [307] (Scheme 1.54). Even basic aluminum oxide can catalyze these isomerizations. One older example reports the isomerization of an *S*-propargyl phosphanesulfide to the allene [308].



Scheme 1.54 **122** **123** (95%)

The 'inverse' isomerization mode, providing allenyl thioethers from alkynyl thioethers, is also known [309, 310]; for example, **124** is first deprotonated with *n*-butyllithium and then protonated with ammonium chloride [311] (Scheme 1.55).

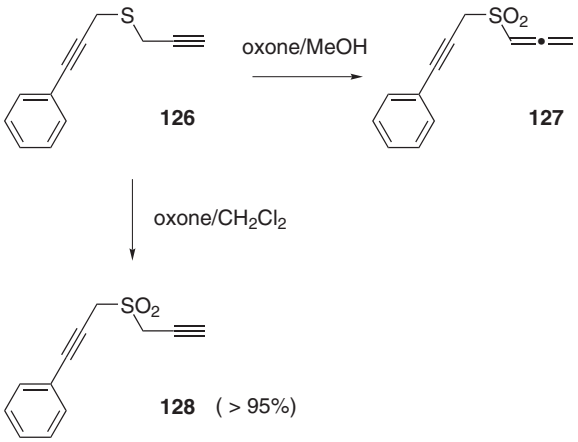


124 **125** (95%)

Scheme 1.55

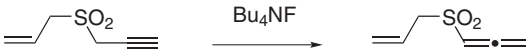
With selenium only a handfull of reactions has been published, involving both propargyl selenoethers [187, 188] and alkynyl selenoethers [312].

The reactions of the corresponding propargyl sulfoxides and sulfones now resemble the chemistry of the other acceptor-substituted derivatives such as ketones and aldehydes (see Section 1.2.4). Compared with the thioethers, here much milder bases are sufficient; apart from aluminum oxide, often triethylamine or potassium carbonate are used. Sometimes even a spontaneous isomerization takes place. The selective isomerization of one triple bond in the presence of a second triple bond in **126** [313] (Scheme 1.56) or an allyl sulfone in **129** [314] (Scheme 1.57) are just two examples out of a whole series [178, 304, 313, 315–331]. When, on the other hand, the in situ oxidation of **126** was carried out in an aprotic solvent, no isomerization at all was observed.



126 **127** **128** (> 95%)

Scheme 1.56

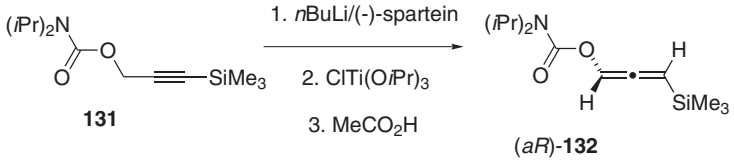


129 **130** (65%)

Scheme 1.57

1.2.9
Silyl and Stannyl Substituents

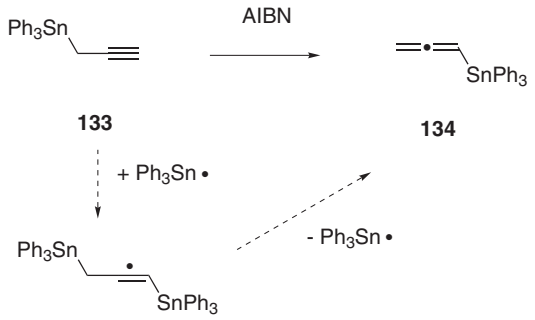
The synthesis of such compounds by prototopic rearrangement is rare; most examples use a stoichiometric deprotonation followed by reprotonation. All reactions use alkynylsilanes as substrates; there the α-effect might still influence the vinylog position, and strong bases such as *n*BuLi or LDA are needed [332–335]. Often the allene is only a side product from a reaction where an alkynyl silane is deprotonated and subjected to other electrophiles [336]. Wherease in earlier examples of a metalation with *n*BuLi, a subsequent transmetalation to zinc and a final protonolyis only traces of allene could be observed [337], the reaction of a related substrate **131** with *n*BuLi, a transmetalation to titanium and a final protonolysis delivered the allenylsilane **132** [338, 339] (Scheme 1.58). The use of sparteine as a ligand in the synthesis of **132** led to an *ee* of 88% in favor of (*aR*)-**132**.



Scheme 1.58

Deuteration studies with a silylbutatriene with KO*t*Bu in *t*BuOD provided evidence for a selective α-deprotonation [340].

For stannanes, there exists one example of a rearrangement (**133** → **134**) which at first sight resembles a prototropic rearrangement, but is in fact a radical chain reaction [341] (Scheme 1.59).



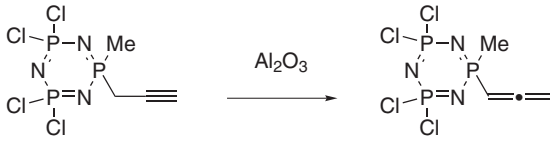
Scheme 1.59

Most of the allenes with silyl or stannyl substituents are prepared by the routes discussed in Chapter 9.

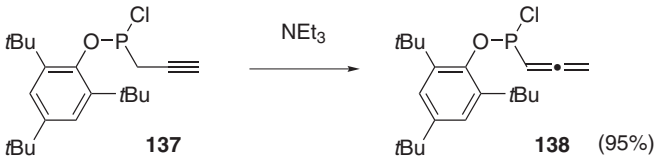
1.2.10
Phosphorus as the Substituent

The field of allenes bearing phosphorus is dominated by sigmatropic rearrangements (see Section 1.3.1). Nevertheless, some examples of prototropic rearrangements are known.

For propargyl phosphorus compounds, examples with cyclotriphosphazenes **135** [342] (Scheme 1.60), phosphinates **137** [343] (Scheme 1.61) and phosphonates **139** [344] (Scheme 1.62) have been published.



Scheme 1.60 **135** **136**

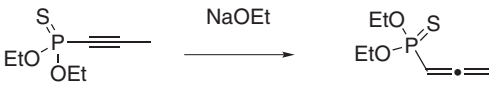


137 **138** (95%)

Scheme 1.61

Scheme 1.62 **139** **140** (40%)

The alkynyl thiophosphonate **141** allowed an isomerization with sodium ethoxide [345] (Scheme 1.63).



Scheme 1.63 **141** **142** (35%)

If one considers a TMS group to be equivalent to a proton, a recent paper describes the formation of a phosphanyl-substituted allene by a keto–enol tautomerization-like silyl migration [346].

1.2.11
Allenes from Prototropic Isomerizations of Alkynes as Reactive Intermediates

As mentioned in the Introduction, this chapter focuses on reactions that deliver allenes as the product. The principles discussed in Sections 1.2.1–1.2.9, of course, also allow the synthesis of allenes as reactive intermediates, which due to other functional groups that are present, undergo further reactions in situ. The most important examples here are base-catalyzed isomerizations to furans [347, 348] ring transfer reactions of propargylic ethers or amines [216, 349–371] and enyneallene cyclization reactions starting from propargylic sulfones [372–375] and related substrates [376, 377]. Details are discussed, for example, in Chapters 16 and 20.

1.3
Sigmatropic Rearrangements

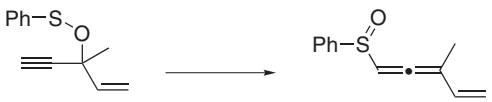
After the prototropic isomerizations, these rearrangements are the second most important synthetic methodology. In the concerted reactions a highly selective central to axial chirality transfer is possible, but this has already been exploited before the timeframe covered by this review and has been summarized [378].

1.3.1
[2,3] Sigmatropic Rearrangements

1.3.1.1 With Sulfur

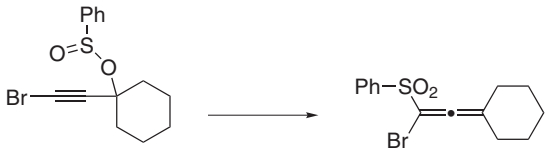
Two different types of substrates are used here, propargyl sulfenates and propargyl sulfinates. In both cases often the propargylic esters are prepared and then converted to the allenes in situ.

An example involving propargyl sulfenates is the reaction of **143** leading to the vinylallene **144** [379] (Scheme 1.64); related conversions have been reported [380] and often the propargyl sulfenates are prepared in situ and isomerize at low temperatures [381–424].



Scheme 1.64 **143** **144**

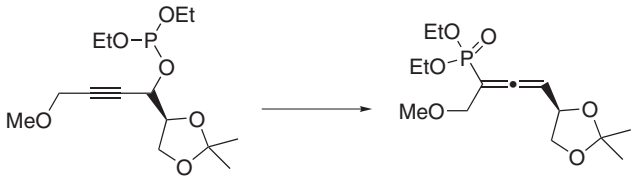
The corresponding propargyl sulfinates behave similarly. Compound **145** [425] (Scheme 1.65), demonstrating the principle with an interesting alkynyl bromide as the substrate, is just one of numerous examples [322, 380, 403, 423, 426–443].



Scheme 1.65 **145** **146** (71%)

1.3.1.2 With Phosphorus

Propargyl phosphites and derivatives thereof, in addition to phosphinates, are feasible substrates for this conversion. Here also a reaction is already observed at low temperatures. The chiral **147** delivers a mixture of diastereomers in about a 1:1 ratio [444] (Scheme 1.66).



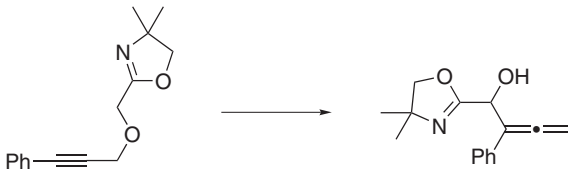
147 **148** (85%)

Scheme 1.66

Other examples cover phosphites [380, 403, 425, 445–477] and phosphinates [375, 392, 396, 423, 425, 462, 464, 471, 478–500], which have become very important in, for example, the field of enyneallenes (Chapter 20).

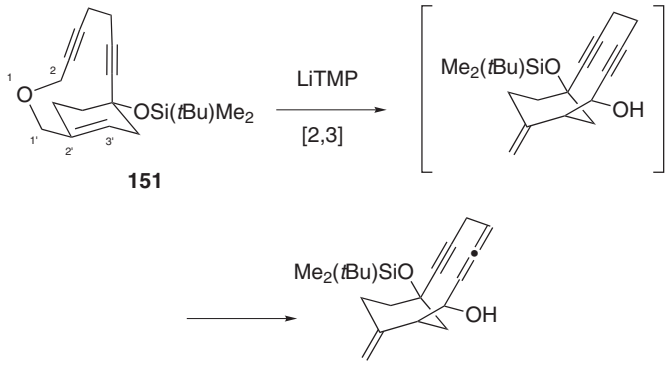
1.3.1.3 [2,3]-Wittig Rearrangement

A few isomerizations cover the Wittig rearrangement [501, 502]. Usually, anion-stabilizing groups, for example an imidate such as **149**, are used [503] (Scheme 1.67).



Scheme 1.67 **149** **150** (55%)

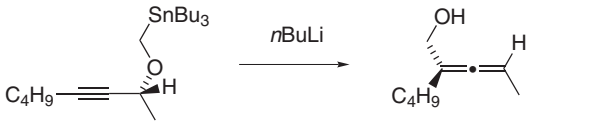
Another recent example is the formation of **152** [504] (Scheme 1.68). However, the allene unit was formed by a base-catalyzed isomerization *after* the [2,3]-Wittig rearrangement of **151**. Only one diastereomer was detected; the configuration of the allenic unit in **152** was not determined.



151 **152** (67%)

Scheme 1.68

In this context, albeit not real isomerizations, the [2,3]-Wittig rearrangements induced by a tin–lithium exchange must also be mentioned. Starting from enantiomerically pure propargylic alcohols, high *ee* values for the axial chiral allenes could be observed as shown for **153** (Scheme 1.69) [505, 506].



153 **154** (71%, 93% *ee*)

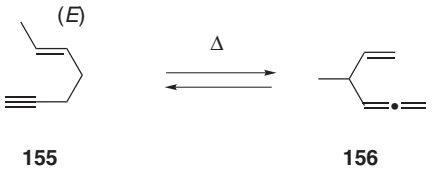
Scheme 1.69

1.3.2 [3,3]-Sigmatropic Rearrangements

This second class of sigmatropic rearrangements can again be subdivided; here we find several classical named reactions that, again with propargylic substrates, lead to allenic products.

1.3.2.1 Cope Rearrangement

There exist early examples of this transformation [507, 508], but due to the symmetric structure of the alkene part, only isotope labeling, etc., allowed the exclusion of a prototropic rearrangement. Furthermore, due to the high reaction temperatures of 340 °C and above, several different products are formed. A low-temperature version (77 K) of this reaction via the radical cation has been reported [509]. The chirality transfer has been studied and a detailed mechanistic investigation has been conducted [510]; typical experiments in that context were the reactions of substrates such as **155** and **157** (Scheme 1.70).



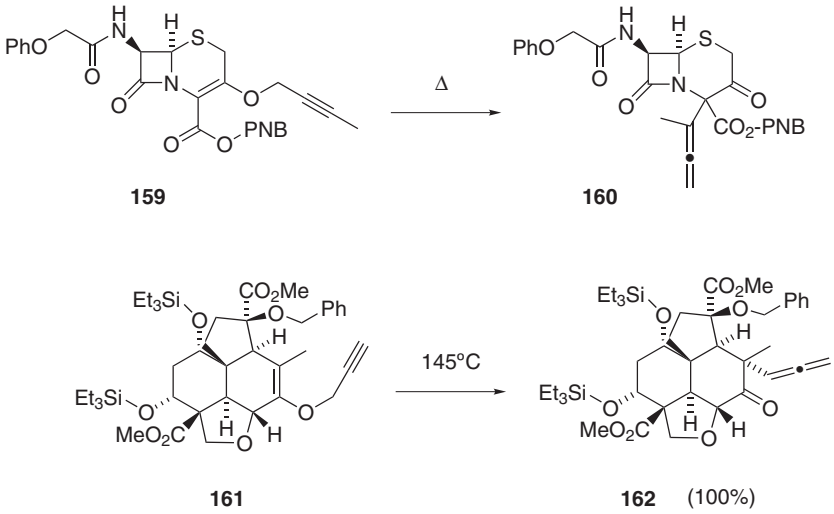
(*R*,*E*)-**157** (*R*,*E*)-**158**

Scheme 1.70

Thermodynamic and kinetic data for Cope rearrangements leading to allenes have been measured [511]. For preparatively useful yields the equilibrium can be shifted to the allene, for example by the classical use of allylic alcohols leading to carbonyl compounds [512].

1.3.2.2 **Claisen Rearrangement**

The Claisen rearrangement of propargyl vinyl ethers directly delivers the allene; no equilibrium is observed. This reaction was also successful with complex substrates; in order to show this, of numerous examples [375, 513–536], the compounds **159** [537] and **161** [538] are depicted (Scheme 1.71).

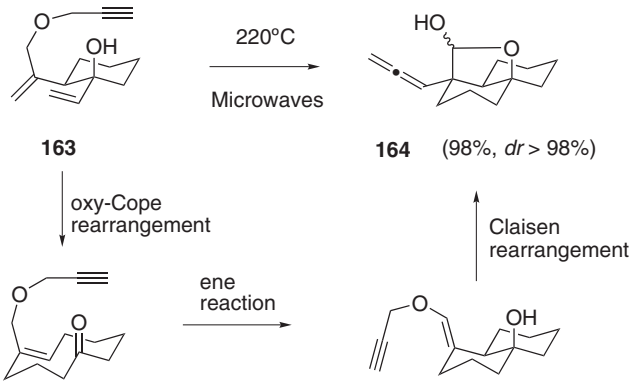


159 **160**

161 **162** (100%)

Scheme 1.71

A remarkable example is the combination of three pericyclic reactions for the synthesis of decalin frameworks with quaternary centers by a tandem oxy-Cope–ene–Claisen reaction shown in **163** [539] (Scheme 1.72).



Scheme 1.72

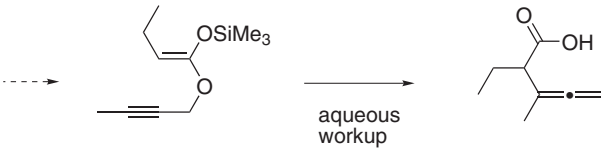
In many of the reactions the allenes are only intermediates in such tandem sequences [540–542] or the starting materials generated in situ [543–545].

Thio- [546] and even iodonio-Claisen rearrangements are known [547].

In arylpropargylamines with two *ortho*- and a *para*-substituent, by protonation a charge-induced sequence of a [3,3]-sigmatropic aza-Claisen rearrangement (with inversion of the propargyl system to the allene) and a subsequent [1,2]-shift (without inversion of the allene) can be observed [548]. 1-Propargyloxy-λ^5-phosphorin derivatives undergo comparable isomerizations; the thermodynamic driving force is the formation of the phosphane oxide [549]. However, the reaction probably does not follow a concerted mechanism, otherwise after the equivalent of a *para*-Claisen-rearrangement not an allene but an alkyne should be generated from the propargyl reactant.

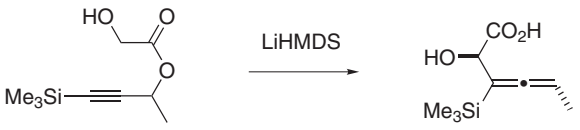
1.3.2.3 **Keteneacetals, Esterenolates and Orthoesters**

Reactions proceeding via propargyl keteneacetals such as **165** [550] (Scheme 1.73) also generate allenes by isomerization reactions.



Scheme 1.73 **165** **166** (53%)

Often these intermediates are generated in situ from orthoesters and propargylic alcohols [551] or propargyl esters such as **167** (Scheme 1.74) [552].



167 **168** (88%)

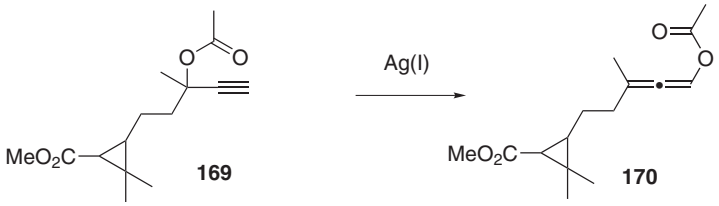
dr 95 : 5 in favor of the depicted diastereomer

Scheme 1.74

Other examples are based on the classical one-pot procedure starting from an orthoester, a catalytic amount of acid and a propargylic alcohol [553–558]. Esterenolates react similarly [559, 560].

1.3.2.4 **Esters**

The [3,3]-sigmatropic rearrangement of propargyl esters [234, 561] is usually an equilibrium reaction; for example steric repulsion can help to deliver mainly the allene [562] and faster reaction kinetics are observed with silver(I) and copper(I) catalysts [562–571] (see cyclopropane **169** in Scheme 1.75) [572], and recently also rhodium(I) catalysts [573].

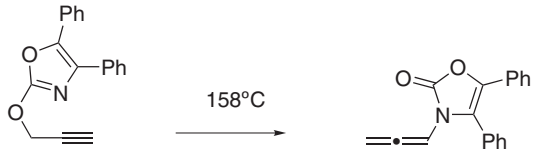


169 **170**

Scheme 1.75

1.3.2.5 **Acetimidates**

In analogy with the propargyl esters, propargyl acetimidates can be used, and then the equilibrium clearly lies on the side of the allene [574, 575]. Often the acetimidate is a substructure of a heterocycle such as **171** (Scheme 1.76) [576] or related compounds [577, 578].

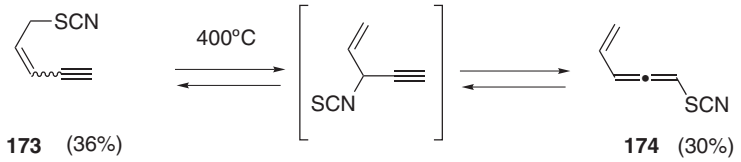


Scheme 1.76 **171** **172** (90%)

A thioimidate substructure was reported to react analogously with good yields [579].

1.3.2.6 Other Substrates

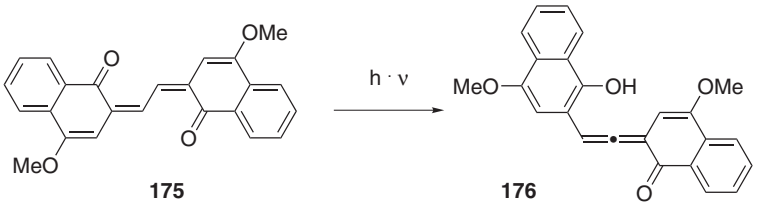
Several other propargylic substrates have successfully undergone [3,3]-sigmatropic rearrangements. Examples are thiocyanates to isothiocyanates [580], the opposite conversion [581] and the equilibrium between such species as exemplified by **173** (Scheme 1.77) [582], cyanates to isocyanates [582] and the formation of isoselenocyanates [583] and azides [584].



Scheme 1.77

1.4 Rearrangements of Other Systems with at Least Two π-Bonds

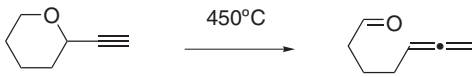
These reactions would fall into the category Reaction B in Scheme 1.1. Thermodynamically such an isomerization should be strongly disfavored and indeed the only example seems to be the conversion of **175** to **176** under photochemical conditions [129] (Scheme 1.78). There a significant amount of energy is put into the system and the aromatization also helps.



Scheme 1.78

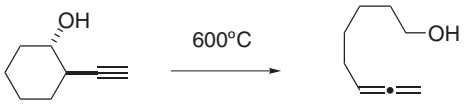
1.5 Retro-ene Reactions

While there seem to exist only a few examples for Reaction C in Scheme 1.1 [585], which mostly are photochemical [586–595], these retro-ene reactions can be considered as the purely intramolecular case of a substitution described in Reaction G. The thermolysis of **177** delivers **178** by such a retro-ene reaction [596] (Scheme 1.79).



Scheme 1.79 **177** **178**

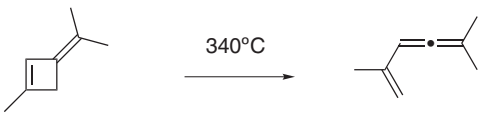
A C–C bond cleavage instead of C–O bond cleavage in the examples above was reported for the vacuum pyrolysis of **179** [597] (Scheme 1.80).



Scheme 1.80 **179** **180** (71%)

1.6 Electrocyclic Ring Openings

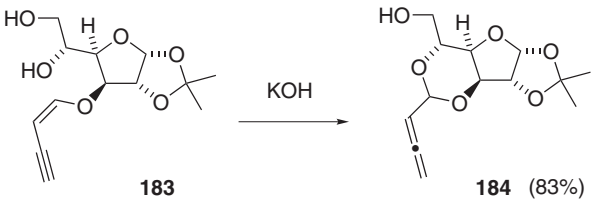
This is Reaction D in Scheme 1.1. The reaction gives preparatively useful yields of **182** from the substituted **181** [598] (Scheme 1.81). On the other hand, a vinylallene often is only a transient species [599]. Further references cover the inverse reaction, the ring closure of the unsubstituted vinylallene [600] and the equilibrium of related substrates [601–605].



Scheme 1.81 **181** **182** (55%)

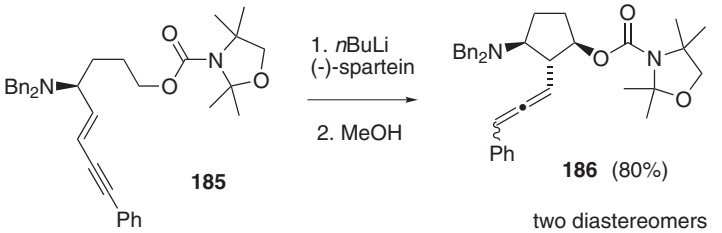
1.7 Intramolecular Conjugate Additions

Some examples of Reaction E in Scheme 1.1 are known. A 1,3-enyne, **183**, will deliver the allene **184** [606] (Scheme 1.82). A related reaction of **185** was also successful [607] (Scheme 1.83).



183 **184** (83%)

Scheme 1.82



185 **186** (80%)

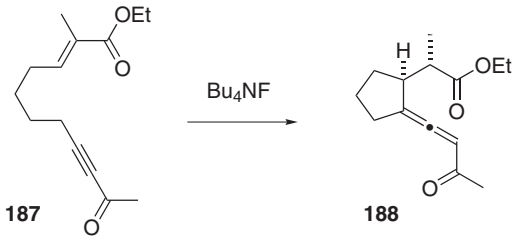
two diastereomers
dr 70 : 30

Scheme 1.83

It seems that there exist no examples of Reaction F in Scheme 1.1.

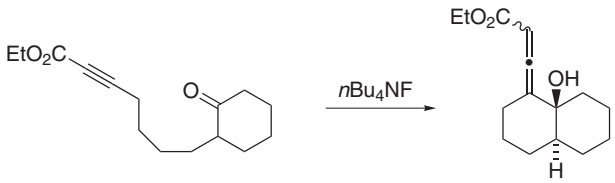
1.8
Complex Reactions and Rearrangements

A combination of a deprotonation with an intramolecular Michael addition/isomerization is found in the conversion of **187** to **188** [608] (Scheme 1.84). The analogous intramolecular addition to a carbonyl group leads to **190** [609] (Scheme 1.85).



187 **188**

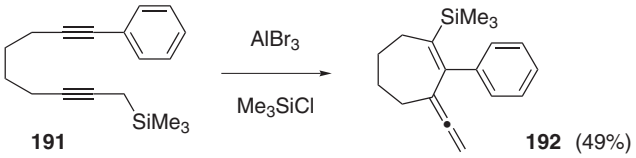
Scheme 1.84



189 **190** (87%)

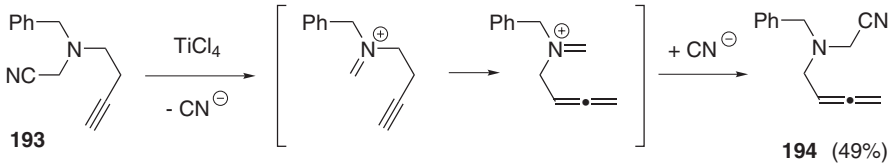
Scheme 1.85

The migration of a silyl group in **191** instead of a proton is possible with $HfCl_4$ or $AlBr_3$ as a catalyst [610] (Scheme 1.86).



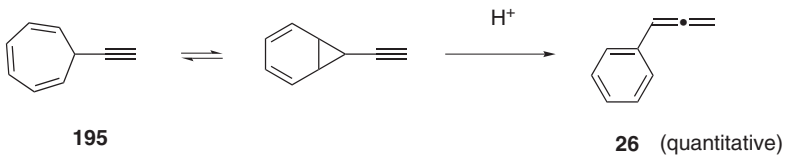
Scheme 1.86

The combination of a $TiCl_4$-catalyzed formation of an iminium salt from **193**, a subsequent [3,3]-sigmatropic rearrangement followed by a return of the cyanaide provided **194** (Scheme 1.87) [611].



Scheme 1.87

Ethynylcycloheptatriene **195** when treated with acid isomerizes to phenylallene **26** [612] (Scheme 1.88).



Scheme 1.88

1.9 Conclusion

Isomerization reactions are an excellent method for the synthesis of allenes. Depending on the method, numerous functional groups are tolerated, hence these reactions match the demands of modern synthesis. In the other chapters of this book we will encounter these reactions again, embedded in a wider chemical context. Not the preparation of the allene but its use in organic synthesis and the benefits of its high reactivity will then be the major focus.

References

[1] W. E. Huntsman, in *The Chemistry of Ketenes, Allenes and Related Compounds, Part 2*, S. Patai (Ed.), Wiley: Chichester, 1980, pp. 521–667.

[2] L. Radom, W. A. Lathan, W. J. Hehre, J. A. Pople, *J. Am. Chem. Soc.* **1971**, *93*, 5339–5342.

[3] R. Kakkar, R. Garg, P. Chadha, *Theochem* **2002**, *617*, 141–147.

[4] R. Kakkar, *Int. J. Quantum Chem.* **2003**, *94*, 93–104.

[5] V. B. Kobychev, N. M. Vikovskaya, N. S. Klyba, B. A. Trofimov, *Russ. Chem. Bull.* **2002**, *51*, 774–782.

[6] J. M. Slobodin, *J. Allg. Chem. (Russ.)* **1936**, *6*, 1806–1814 (citation according to *Chem. Zentralbl.* **1937**, *I*, 4491).

[7] H. Hopf, H. Priebe, R. Walsh, *J. Am. Chem. Soc.* **1980**, *102*, 1210–1212.

[8] A. Lifshitz, M. Frenklach, A. Burcat, *J. Phys. Chem.* **1975**, *79*, 1148–1152.

[9] J. N. Bradley, K. O. West, *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 967–971.

[10] N. Honjou, J. Pacansky, M. Yoshimine, *J. Am. Chem. Soc.* **1984**, *106*, 5361–5363.

[11] J. B. Harkness, G. B. Kistiakowsky, W. H. Mears, *J. Chem. Phys.* **1937**, *5*, 682–694.

[12] R. C. Lord, P. Venkateswarlu, *J. Chem. Phys.* **1952**, *20*, 1237–1247.

[13] J. F. Cordes, H. Guenzler, *Chem. Ber.* **1959**, *92*, 1055–1062.

[14] B. Agre, A. M. Taber, V. V. Beregovykh, F. D. Klebanova, N. V. Nekrasov, N. V. Sobolev, I. V. Kalechits, *Pharm. Chem. J. (Engl. Transl.)* **1983**, *17*, 221–225; *Khim. Farm. Zh.* **1983**, *17*, 333–336.

[15] H. Imamura, A. Ohmura, S. Tsuchiya, *Chem. Lett.* **1984**, 203–204.

[16] H. Imamura, K. Kitajima, S. Tsuchiya, *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 1647–1654.

[17] S. G. Davis, C. K. Law, H. Wang, *J. Phys. Chem. A* **1999**, *103*, 5889–5899.

[18] A. F. Hill, C. T. Ho, J. D. E. T. Wilton-Ely, *J. Chem. Soc., Chem. Commun.* **1997**, 2207–2208.

[19] W. E. Shuler, W. H. Fletcher, *J. Mol. Spectrosc.* **1957**, *1*, 95–106.

[20] J. M. Slobodin, *Zh. Obshch. Khim.* **1937**, *7*, 2376–2380; *Chem. Zentralbl. II* **1938**, *109*, 1559–1560.

[21] J.-C. Lavalley, J. Lamotte, A. Travert, J. Czyzniewska, M. Ziolek, *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 331–335.

[22] H. Imamura, K. Kitajima, S. Tsuchiya, *Chem. Lett.* **1988**, 249–250.

[23] T. L. Jacobs, R. Akawie, R. G. Cooper, *J. Am. Chem. Soc.* **1951**, *73*, 1273–1276.

[24] K. S. Takai, in *Encyclopedia of Reagents for Organic Synthesis*, L.A. Paquette (Ed.), Vol. 6, Wiley: Chichester, pp. 4185–4187.

[25] A. E. Faworski, *J. Prakt. Chem.* **1888**, *37*, 382–395.

[26] J. M. Slobodin, *Zh. Obshch. Khim.* **1934**, *4*, 778–782; *Chem. Zentralbl. II* **1935**, *106*, 1335–1335.

[27] W. Jegorowa, *Zh. Russ. Fiz.-Khim. O-va* **1911**, *43*, 1116–1124; *Chem. Zentralbl. I* **1912**, *83*, 1010–1010.

[28] A. I. Chirko, K. I. Ivanov, I. G. Tishchenko, *J. Org. Chem. USSR (Engl.Transl.)* **1975**, *11*, 2091–2095; *Zh. Org. Khim.* **1975**, *11*, 2058–2062.

[29] J. W. Wheeler, R. H. Chung, Y. N. Vaishnav, C. C. Shroff, *J. Org. Chem.* **1969**, *34*, 545–549.

[30] C. D. Hurd, R. E. Christ, *J. Am. Chem. Soc.* **1937**, *59*, 2161–2165.

[31] R. A. Cormier, W. L. Schreiber, W. C. Agosta, *J. Am. Chem. Soc.* **1973**, *95*, 4873–4884.

[32] W. M. Braje, J. Frackenpohl, O. Schrake, R. Wartchow, W. Beil, H. M. R. Hoffmann, *Helv. Chim. Acta* **2000**, *83*, 777–792.

[33] M. V. Baker, D. H. Brown, B. W. Skelton, A. H. White, *Aust. J. Chem.* **2000**, *53*, 791–798.

[34] J. Klein, J. Y. Becker, *Tetrahedron* **1972**, *28*, 5385–5392.

[35] W. R. Roth, U. Kowalczik, G. Maier, H. P. Reisenauer, R. Sustmann, W. Müller, *Angew. Chem.* **1987**, *99*, 1330–1331; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1285–1287.

[36] G. G. Bargamov, E. M. Kagramanova, M. D. Bagramova, *Russ. Chem. Bull.* **1998**, *47*, 656–658; *Izv. Akad. Nauk Ser. Khim.* **1998**, *47*, 677–680.

[37] M. Enomoto, T. Katsuki, M. Yamaguchi, *Tetrahedron Lett.* **1986**, *27*, 4599–4600.

[38] M. Bertrand, *C. R. Hebd. Seances Acad. Sci.* **1958**, *247*, 824–827.

[39] J. Grimaldi, M. Bertrand, *Bull. Soc. Chim. Fr.* **1971**, 947–957.

[40] A. Medlik-Balan, J. Klein, *Tetrahedron* **1980**, *36*, 299–304.

[41] J. Klein, S. Brenner, *Tetrahedron* **1970**, *26*, 5807–5819.

[42] E. T. Bogoradovskii, V. L. Maksimov, T. P. Zubova, *Russ. J. Gen. Chem.* **1993**, *63*, 665–666; *Zh. Obshch. Khim.* **1993**, *63*, 954–955.

[43] M. G. Steinmetz, R. T. Mayes, *J. Am. Chem. Soc.* **1985**, *107*, 2111–2121.

[44] T. Ando, N. Tokura, *Bull. Chem. Soc. Jpn.* **1957**, *30*, 259–263.

[45] T. Ando, N. Tokura, *Bull. Chem. Soc. Jpn.* **1958**, *31*, 351–355.

[46] D. T. Manning, H. A. Coleman, *J. Org. Chem.* **1969**, *34*, 3248–3252.

[47] F. Lehrich, H. Hopf, *Tetrahedron Lett.* **1987**, *28*, 2697–2700.

[48] W. R. Roth, R. Langer, M. Bartmann, B. Stevermann, G. Maier, H. P. Reisenauer, R. Sustmann, W. Müller, *Angew. Chem.* **1987**, *99*, 271–272; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 256–258.

[49] T. L. Jacobs, D. Dankner, *J. Org. Chem.* **1957**, *22*, 1424–1427.

[50] T. L. Jacobs, D. Dankner, S. Singer, *Tetrahedron* **1964**, *20*, 2177–2180.

[51] H. A. Staab, H.-A. Kurmeier, *Chem. Ber.* **1968**, *101*, 2697–2708.

[52] E. J. Moriconi, J. F. Kelly, *J. Org. Chem.* **1968**, *33*, 3036–3046.

[53] A. I. Chirko, I. G. Tishchenko, S. G. Stepin, K. I. Ivanov, *J. Org. Chem. USSR (Engl. Transl.)* **1973**, *9*, 1709–1711; *Zh. Org. Khim.* **1973**, *9*, 1687–1690.

[54] A. J. G. van Rossum, R. J. F. Nivard, *J. Chem. Soc., Perkin Trans. 2* **1976**, 1322–1326.

[55] M. W. Klett, R. P. Johnson, *J. Am. Chem. Soc.* **1985**, *107*, 3963–3971.

[56] T. L. Jacobs, S. Singer, *J. Org. Chem.* **1952**, *17*, 475–481.

[57] A. J. Brattesani, E. Maverick, O. J. Muscio, T. L. Jacobs, *J. Org. Chem.* **1992**, *57*, 7346–7349.

[58] M. Oku, S. Arai, K. Katayama, T. Shioiri, *Synlett* **2000**, 493–494.

[59] N. A. Porter, D. J. Hogenkamp, F. F. Khouri, *J. Am. Chem. Soc.* **1990**, *112*, 2402–2407.

[60] W. R. Roth, T. Bastigkeit, *Liebigs Ann. Org. Bioorg. Chem.* **1996**, 2171–2184.

[61] U. Moedlhammer, H. Hopf, *Angew. Chem.* **1975**, *87*, 492–493; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 501–502.

[62] H. Hopf, *Chem. Ber.* **1971**, *104*, 3087–3095.

[63] G. Eglington, R. A. Raphael, J. A. Zabhiewicz, *J. Chem. Soc. C* **1969**, 469–473.

[64] C. M. Bowes, D. F. Montecalvo, F. Sondheimer, *Tetrahedron Lett.* **1973**, 3181–3184.

[65] J. P. Dulcere, V. Agati, J. Rodriguez, *J. Chem. Soc., Chem. Commun.* **1993**, 1038–1039.

[66] W. Oroshnik, G. Karmas, A. D. Mebane, *J. Am. Chem. Soc.* **1952**, *74*, 3807–3813.

[67] W. Oroshnik, A. D. Mebane, G. Karmas, *J. Am. Chem. Soc.* **1953**, *75*, 1050–1058.

[68] M. L. Roumestant, J. P. Dulcère, J. Gore, *Bull. Soc. Chim. Fr.* **1974**, 1124–1128.

[69] S. J. Kim, J. K. Cha, *Tetrahedron Lett.* **1988**, *29*, 5613–5616.

[70] Y. I. Porfir'eva, V. A. Konotopov, A. A. Petrov, *J. Org. Chem. USSR (Engl. Transl.)* **1969**, *5*, 1860–1869; *Zh. Org. Khim.* **1969**, *5*, 1914–1923.

[71] A. Doutheau, J. Gore, M. Malacria, *Tetrahedron* **1977**, *33*, 2393–2398.

[72] K. Yoshida, P. A. Grieco, *Chem. Lett.* **1985**, 155–158.

[73] E. A. Deutsch, B. B. Snider, *Tetrahedron Lett.* **1983**, *24*, 3701–3704.

[74] E. A. Deutsch, B. B. Snider, *J. Org. Chem.* **1982**, *47*, 2682–2684.

[75] A. Doutheau, J. Gore, *Bull. Soc. Chim. Fr.* **1976**, 1189–1194.

[76] P. A. A. Klusener, H. Hommes, J. C. Hanekamp, A. C. H. T. M. van der Kerk, L. Brandsma, *J. Organomet. Chem.* **1991**, *409*, 67–81.

[77] S. R. Abrams, B. V. Milborrow, *Phytochemistry* **1991**, *30*, 3189–3195.

[78] W. R. Roth, H. Hopf, C. Horn, *Chem. Ber.* **1994**, *127*, 1781–1796.

[79] A. I. Chirko, K. I. Ivanov, I. G. Tishchenko, T. I. Girko, *J. Org. Chem. USSR (Engl. Transl.)* **1974**, *10*, 2057–2060; *Zh. Org. Khim.* **1974**, *10*, 2040–2044.

[80] J. L. Derocque, F.-B. Sundermann, *J. Org. Chem.* **1974**, *39*, 1736–1744.

[81] M. Oestreich, R. Fröhlich, D. Hoppe, *Tetrahedron Lett.* **1998**, *39*, 1745–1748.

[82] M. Oestreich, R. Fröhlich, D. Hoppe, *J. Org. Chem.* **1999**, *64*, 8616–8626.

[83] A. Maercker, H. Wunderlich, U. Girreser, *Eur. J. Org. Chem.* **1998**, 793–798.

[84] H. A. Selling, J. A. Rompes, P. P. Montijn, S. Hoff, J. H. van Boom, L. Brandsma, J. F. Arens, *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 119–130.

[85] I. Saito, Y. Kazuhiro, R. Nagata, E. Murahashi, *Tetrahedron Lett.* **1990**, *31*, 7469–7472.

[86] N. M. Libman, T. L. Dmitrieva, S. G. Kuznetsov, A. A. Andreev, *J. Org. Chem. USSR (Engl. Transl.)* **1980**, *16*, 231–241; *Zh. Org. Khim.* **1980**, *16*, 261–273.

[87] W. J. Gensler, J. Casella, Jr, *J. Am. Chem. Soc.* **1958**, *80*, 1376–1380.

[88] W. J. Gensler, A. Whitehead, *J. Org. Chem.* **1973**, *38*, 3843–3848.

[89] R. J. Bushby, G. H. Whitham, *J. Chem. Soc. B* **1970**, 563–569.

[90] V. I. Mel'nikova, K. K. Pivnitskii, *J. Org. Chem. USSR (Engl. Transl.)* **1990**, *26*, 64–67; *Zh. Org. Khim.* **1990**, *26*, 78–82.

[91] T. L. Chwang, R. West, *J. Am. Chem. Soc.* **1973**, *95*, 3324–3330.

[92] M. Bertrand, *C. R. Hebd. Seances Acad. Sci.* **1957**, *244*, 1790–1791.

[93] M. Bertrand, J. Le Gras, *Bull. Soc. Chim. Fr.* **1962**, 2136–2140.

[94] M. Bertrand, J. Le Gras, *C. R. Hebd. Seances Acad. Sci.* **1962**, *255*, 1305–1307.

[95] J. Le Gras, *C. R. Hebd. Seances Acad. Sci. Ser. C* **1966**, *263*, 1460–1463.

[96] T. M. Penning, *Steroids* **1982**, *39*, 301–311.

[97] V. Balasubramanian, I. R. McDermott, C. H. Robinson, *Steroids* **1982**, *40*, 109–119.

[98] A. D. Baxter, T. Javed, B. J. Wakefield, J. Hollerton, R. F. Newton, S. M. Roberts, *J. Chem. Soc., Perkin Trans.1* **1985**, 1803–1806.

[99] K. G. Bowers, J. Mann, E. B. Walsh, O. W. Howarth, *J. Chem. Soc., Perkin Trans.1* **1987**, 1657–1666.

[100] G. Dana, E. Touboul, M. Mellot-Srour, *Tetrahedron* **1992**, *48*, 1617–1626.

[101] J. A. Marshall, G. S. Bartley, *J. Org. Chem.* **1994**, *59*, 7169–7171.

[102] J. Wang, P. J. De Clercq, *Tetrahedron Lett.* **1996**, *37*, 3395–3398.

[103] Y.-J. Chen, C.-Y. Wang, W.-Y. Lin, *Tetrahedron* **1996**, *52*, 13181–13188.

[104] A. S. K. Hashmi, T. L. Ruppert, T. Knöfel, J. W. Bats, *J. Org. Chem.* **1997**, *62*, 7295–7304.

[105] A. S. K. Hashmi, L. Schwarz, *Chem. Ber./ Recl.* **1997**, *130*, 1449–1456.

[106] A. S. K. Hashmi, J.-H. Choi, J. W. Bats, *J. Prakt. Chem./Chem.-Ztg.* **1999**, *341*, 342–357.

[107] C. Mukai, E. Kasamatsu, T. Ohyama, M. Hanaoka, *J. Chem. Soc., Perkin Trans. 1* **2000**, 737–744.

[108] Y. Ding, X. Huang, *Synth. Commun.* **2001**, 31, 449–454.

[109] A. S. K. Hashmi, L. Schwarz, M. Bolte, *Eur. J. Org. Chem.* **2004**, 1923–1935.

[110] A. S. K. Hashmi, J. W. Bats, J.-H. Choi, L. Schwarz, *Tetrahedron Lett.* **1998**, *39*, 7491–7496.

[111] N. Chinkov, N. Morlender-Vais, I. Marek, *Tetrahedron Lett.* **2002**, *43*, 6009–6010.

[112] R. J. Highet, D. F. Covey, C. H. Robinson, *J. Org. Chem.* **1980**, *45*, 3286–3289.

[113] W. D. Huntsman, T.-K. Yin, *J. Org. Chem.* **1983**, *48*, 3813–3814.

[114] L. Schmieder-van de Vondervoort, S. Bouttemy, J. M. Padron, J. Le Bras, J. Muzart, P. L. Alsters, *Synlett* **2002**, 243–246.

[115] R. W. Spencer, T. F. Tam, E. Thomas, V. J. Robinson, A. Krantz, *J. Am. Chem. Soc.* **1986**, *108*, 5589–5597.

[116] L. Crombie, A. G. Jacklin, *J. Chem. Soc.* **1955**, 1740–1748.

[117] D. Ma, Y. Yu, X. Lu, *J. Org. Chem.* **1989**, *54*, 1105–1109.

[118] J. A. Marshall, E. D. Robinson, *J. Org. Chem.* **1990**, *55*, 3450–3451.

[119] J. A. Marshall, X.-j. Wang, *J. Org. Chem.* **1992**, *57*, 3387–3396.

[120] T. Harada, T. Katsuhira, A. Osada, K. Iwazaki, K. Maejima, A. Oku, *J. Am. Chem. Soc.* **1996**, *118*, 11377–11390.

[121] M. S. F. Jie, K. Lie, M. M. L. Lau, *Chem. Phys. Lipids* **1999**, *101*, 237–242.

[122] R. C. Larock, M.-S. Chow, S. J. Smith, *J. Org. Chem.* **1986**, *51*, 2623–2624.

[123] J. A. Marshall, J. Liao, *J. Org. Chem.* **1998**, *63*, 5962–5970.

[124] J. A. Marshall, X.-j. Wang, *J. Org. Chem.* **1991**, *56*, 6264–6266.

[125] G. Majetich, Y. Zhang, G. Dreyer, *Tetrahedron Lett.* **1993**, *34*, 449–452.

[126] A. K. Filippova, G. S. Lyashenko, I. D. Kalikhman, V. Y. Vitkovskii, G. G. Naumova, N. S. Vyazankin, *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.)* **1983**, *32*, 861–863; *Izv. Akad. Nauk SSSR Ser. Khim.* **1983**, 950–953.

[127] A. A. Shchegolev, V. A. Smit, S. A. Khurshudyan, V. A. Chertkov, V. F. Kucherov, *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.)* **1977**, *26*, 1001–1006; *Izv. Akad. Nauk SSSR Ser. Khim.* **1977**, 1093–1099.

[128] M. Franck-Neumann, F. Brion, *Angew. Chem.* **1979**, *91*, 736–737; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 688–689.

[129] H. Laatsch, A. J. Schmidt, A. Kral, N. Heine, G. Haucke, *Indian J. Chem. Sect. B* **1997**, *6*, 476–484.

[130] T. Yasokouchi, K. Kanematsu, *Tetrahedron Lett.* **1989**, *30*, 6559–6562.

[131] G. Eglinton, E. R. H. Jones, G. H. Mansfield, M. C. Whiting, *J. Chem. Soc.* **1954**, 3197–3200.

[132] E. A. Shapiro, I. E. Dolgii, O. M. Nefedov, *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.)* **1980**, *29*, 1493–1499; *Izv. Akad. Nauk SSSR Ser. Khim.* **1980**, *9*, 2096–2102.

[133] B. B. Snider, D. K. Spindell, *J. Org. Chem.* **1980**, *45*, 5017–5020.

[134] M. E. Jung, M. Node, R. W. Pfluger, M. A. Lyster, J. A. Lowe, *J. Org. Chem.* **1982**, *47*, 1150–1152.

[135] M. E. Jung, J. A. Lowe III, M. A. Lyster, M. Node, R. W. Pfluger, R. W. Brown, *Tetrahedron* **1984**, *40*, 4751–4766.

[136] M. Kato, M. Kageyama, R. Tanaka, K. Kuwahara, A. Yoshikoshi, *J. Org. Chem.* **1975**, *40*, 1932–1941.

[137] T. R. R. Pettus, R. H. Schlessinger, *Synth. Commun.* **2002**, *32*, 3019–3026.

[138] B. Lachance, R. L. Salvador, D. Z. Simon, *Eur. J. Med. Chem. Chim. Ther.* **1987**, *22*, 179–186.

[139] E. R. H. Jones, B. L. Shaw, M. C. Whiting, *J. Chem. Soc.* **1954**, 3212–3217.

[140] G. H.. Mansfield, M. C. Whiting, *J. Chem. Soc.* **1956**, 4761–4764.

[141] L. Crombie, P. A. Jenkins, D. A. Mitchard, *J. Chem. Soc., Perkin Trans. 1* **1975**, 1081–1090.

[142] A. C. Oehlschlager, E. Czyzewska, R. Aksela, H. D. Pierce, *Can. J. Chem.* **1986**, *64*, 1407–1413.

[143] G. Himbert, D. Fink, *J. Prakt. Chem./ Chem.-Ztg.* **1996**, *338*, 355–362.

[144] J. M. Schwab, C.-K. Ho, W.-B. Li, C. A. Townsend, G. M. Salituro, *J. Am. Chem. Soc.* **1986**, *108*, 5309–5316.

[145] F. M. Miesowicz, K. E. Bloch, *Biochem. Biophys. Res. Commun.* **1975**, *65*, 331–335.

[146] F. M. Miesowicz, K. Bloch, *J. Biol. Chem.* **1979**, *254*, 5868–5877.

[147] J. C. Craig, M. Moyle, *Proc. Chem. Soc.* **1962**, 283–284.

[148] M. P. Cooke, *J. Org. Chem.* **1993**, *58*, 6833–6837.

[149] J. Cousseau, P. Albert, *Bull. Soc. Chim. Fr.* **1986**, 910–915.

[150] S. Doye, T. Hotopp, R. Wartchow, E. Winterfeldt, *Chem. Eur. J.* **1998**, *4*, 1480–1488.

[151] T. L. Jacobs, J. R. McClenon, O. J. Muscio, Jr, *J. Am. Chem. Soc.* **1969**, *91*, 6038–6041.

[152] S. S. Kumaran, K. P. Lim, J. V. Michael, J. L. Tilson, A. Suslensky, A. Lifshitz, *Isr. J. Chem.* **1996**, *36*, 223–232.

[153] Y.-W. Wu, M.-L. Hwang, W.-L. Hsu, F.-H. Fang, *J. Chin. Chem. Soc. (Taipei)* **1998**, *45*, 307–312.

[154] C. S. L. Baker, P. D. Landor, S. R. Landor, A. N. Patel, *J. Chem. Soc.* **1965**, 4348–4354.

[155] T. L. Jacobs, W. F. Brill, *J. Am. Chem. Soc.* **1953**, *75*, 1314–1317.

[156] G. Fontaine, C. André, C. Jolivet, P. Maitte, *Bull. Soc. Chim. Fr.* **1963**, 1444–1448.

[157] M. Gaudemar, *C. R. Hebd. Seances Acad. Sci.* **1964**, *258*, 4803–4804.

[158] L. Brandsma, H. D. Verkruijsse, *Synth. Commun.* **1991**, *21*, 69–72.

[159] B. Koenig, B. Eilers, *Synth. Commun.* **1997**, *10*, 1685–1688.

[160] H. Hauptmann, *Tetrahedron Lett.* **1974**, 3593–3596.

[161] K. N. Shavrin, I. V. Krylova, I. B. Shvedova, G. P. Okonnishnikova, I. E. Dolgy, O. M. Nefedov, *J. Chem. Soc., Perkin Trans. 2* **1991**, 1875–1882.

[162] N. F. Osborne, *J. Chem. Soc., Perkin Trans. 1* **1982**, 1429–1434.

[163] M.Verny, R. Vessière, *Bull. Soc. Chim. Fr.* **1967**, 2210–2216.

[164] M. V. Mavrov, V. F. Kucherov, *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl.Transl.)* **1972**, *21*, 1706–1711; *Izv. Akad. Nauk SSSR Ser. Khim.* **1972**, *21*, 1763–1769.

[165] E. T. Bogoradovskii, V. L. Maksimov, *Russ.J. Gen. Chem.* **1994**, *64*, 1103–1104; *Zh. Obshch. Khim.* **1994**, *64*, 1226–1227.

[166] C. Koetting, W. Sander, M. Senzlober, *Chem. Eur. J.* **1998**, *4*, 2360–2365.

[167] J. Hine, L. G. Mahone, C. L. Liotta, *J. Org. Chem.* **1967**, *32*, 2600–2609.

[168] S. Hoff, L. Brandsma, J. F. Arens, *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 916–924.

[169] F. J. Weiberth, S. S. Hall, *J. Org. Chem.* **1985**, *50*, 5308–5314.

[170] F. Ameer, S. E. Drewes, M. W. Drewes, G. H. P. Roos, M. C. Watson, *J. Chem. Soc., Perkin Trans. 1* **1988**, 1425–1430.

[171] M. A. Tius, J.-B. Ousset, D. P. Astrab, A. H. Fauq, S. Trehan, *Tetrahedron Lett.* **1989**, **30**, 923–924.

[172] S. V. Eroshchenko, L. M. Sinegovskaya, O. A. Tarasova, Y. L. Frolov, B. A. Trofimov, I. S. Ignatyev, *Spectrochim. Acta, Part A* **1990**, *46*, 1505–1512.

[173] R. Zimmer, *Synthesis* **1993**, 165–178.

[174] Y. Fall, G. Gomez, C. Fernandez, *Tetrahedron Lett.* **1999**, *40*, 8307–8308.

[175] A. Rosowsky, J. E. Wright, C. M. Vaidya, R. A. Forsch, H. Bader, *J. Med. Chem.* **2000**, *43*, 1620–1634.

[176] S. Hoff, L. Brandsma, J. F. Arens, *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 609–619.

[177] A. S. Atavin, V. I. Lavrov, O. N. Sidrova, B. A. Trominov, *J. Org. Chem. USSR (Engl. Transl.)* **1971**, *7*, 227–231; *Zh. Org. Khim.* **1971**, *7*, 235–240.

[178] S. Braverman, Y. Duar, S. Segev, *Tetrahedron Lett.* **1976**, 3181–3184.

[179] B. Cazes, S. Julia, *Bull. Soc. Chim. Fr.* **1977**, 931–935.

[180] P. E. van Rijn, R.H. Everhardus, J. van der Ven, L. Brandsma, *Recl. J. R. Neth. Chem. Soc.* **1981**, *100*, 372–375.

[181] H. D. Verkruijsse, W. Verboom, P. E. van Rijn, L. Brandsma, *J. Organomet. Chem.* **1982**, *232*, C1–C4.

[182] A.-L. Gustavsson, T. Liljefors, B. S. Hansson, *J. Chem. Ecol.* **1995**, *21*, 815–832.

[183] H. Hu, D. Smith, R. E. Cramer, M. A. Tius, *J. Am. Chem. Soc.* **1999**, *121*, 9895–9896.

[184] A. J. Bartlett, T. Laird, W. D. Ollis, *J. Chem. Soc., Chem. Commun.* **1974**, 496–497.

[185] P. Kocienski, R. Whitby, *Synthesis* **1991**, 1029–1038.

[186] H. Normant, R. Mantione, *C. R. Hebd. Seances Acad. Sci.* **1964**, *259*, 1635–1637.

[187] G. Pourcelot, *C. R. Hebd. Seances Acad. Sci.* **1965**, *260*, 2847–2850.

[188] G. Pourcelot, P. Cadiot, *Bull. Soc. Chim. Fr.* **1966**, 3016–3024.

[189] R. Mantione, *Bull. Soc. Chim. Fr.* **1969**, 4514–4522.

[190] N. Šarcevic, J. Zsindely, H. Schmid, *Helv. Chim. Acta* **1973**, *56*, 1457–1476.

[191] G. Pourcelot, P. Cadiot, C. Georgoulis, *Tetrahedron* **1982**, *38*, 2123–2128.

[192] F. M. Moghaddam, R. Emami, *Synth. Commun.* **1997**, *27*, 4073–4078.

[193] J. P. C. M. van Dongen, A. J. De Jong, H. A. Selling, P. P. Montijn, J. H. van Boom, L. Brandsma, *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 1077–1081.

[194] K. Hayakawa, S. Ohsuki, K. Kanematsu, *Tetrahedron Lett.* **1986**, *27*, 947–950.

[195] J.-P. Dulcere, J. Crandall, R. Faure, M. Santelli, V. Agati, M. N. Mihoubi, *J. Org. Chem.* **1993**, *58*, 5702–5708.

[196] P. J. Parsons, P. Thomson, A. Taylor, T. Sparks, *Org. Lett.* **2000**, *2*, 571–572.

[197] A. T. Bottini, J. G. Maroski, V. Dev, *J. Org. Chem.* **1973**, *38*, 1767–1769.

[198] B. Capon, A. K. Siddhanta, C. Zucco, *J. Org. Chem.* **1985**, *50*, 3580–3584.

[199] M. A. Tius, H. Hu, J. K. Kawakami, J. Busch-Petersen, *J. Org. Chem.* **1998**, *63*, 5971–5976.

[200] T. Ishikawa, T. Mizuta, K. Hagiwara, T. Aikawa, T. Kudo, S. Saito, *J. Org. Chem.* **2003**, *68*, 3702–3705.

[201] P. E. Harrington, T. Murai, C. Chu, M. A. Tius, *J. Am. Chem. Soc.* **2002**, *124*, 10091–10100.

[202] L. Brandsma, N. A. Nedolya, B. A. Trofimov, *Russ. Chem. Bull.* **2000**, *49*, 1634–1636; *Izv. Akad. Nauk Ser. Khim.* **2000**, *49*, 1645–1647.

[203] H. J. Reich, M. J. Kelly, R. E. Olson, R. C. Holtan, *Tetrahedron* **1983**, *39*, 949–960.

[204] E. R. H. Jones, P. R. Leeming, W. A. Remers, *J. Chem. Soc.* **1960**, 2257–2263.

[205] R. W. Hoffmann, B. Kemper, R. Metternich, T. Lehmeier, *Liebigs Ann. Chem.* **1985**, 2246–2260.

[206] I. Kadota, M. Kawada, V. Gevorgyan, Y. Yamamoto, *J. Org. Chem.* **1997**, *62*, 7439–7446.

[207] M. A. Tius, H. Hu, *Tetrahedron Lett.* **1998**, *39*, 5937–5940.

[208] A. Kaur, G. Kaur, S. Trehan, *Indian J. Chem. Sect. B* **1998**, *37*, 1048–1050.

[209] I. A. Stergiades, M. A. Tius, *J. Org. Chem.* **1999**, *64*, 7547–7551.

[210] S. Kamijo, Y. Yamamoto, *Tetrahedron Lett.* **1999**, *40*, 1747–1750.

[211] K. Sakaguchi, M. Fujita, H. Suzuki, M. Higashino, Y. Ohfune, *Tetrahedron Lett.* **2000**, *41*, 6589–6592.

[212] A. Padwa, M. Meske, Z. Ni, *Tetrahedron* **1995**, *51*, 89–106.

[213] M. Spada, R. S. Klein, B. A. Otter, *J. Heterocycl. Chem.* **1989**, 1851–1857.

[214] T.-L. Ho, M.-H. Chang, *J. Chem. Soc., Perkin Trans. 1* **1999**, 2479–2482.

[215] T.-L. Ho, M. H. Chang, *Tetrahedron Lett.* **1994**, *35*, 4819–4822.

[216] H.-J. Wu, S.-H. Lin, C.-C. Lin, *Heterocycles* **1994**, *38*, 1507–1518.

[217] P. Rochet, J.-M. Vatèle, J. Goré, *Synthesis* **1994**, 795–799.

[218] J. P. Dulcere, M. N. Mihoubi, J. Rodriguez, *J. Chem. Soc., Chem. Commun.* **1988**, 237–239.

[219] J.-P. Dulcère, M. N. Mihoubi, J. Rodriguez, *J. Org. Chem.* **1993**, *58*, 5709–5716.

[220] J. Castro, A. Moyano, M. A. Pericas, A. Riera, A. E. Greene, *J. Org. Chem.* **1996**, *61*, 9016–9020.

[221] R. Grigg, J. M. Sansano, *Tetrahedron* **1996**, *52*, 13441–13454.

[222] R. Grigg, J. M. Sansano, V. Santhakumar, V. Sridharan, R. Thangavelanthum, M. Thornton-Pett, D. Wilson, *Tetrahedron* **1997**, *53*, 11803–11826.

[223] T. Ghoshi, T. Sada, H. Fujimoto, C. Nagayama, E. Sugino, S. Hibino, *J. Org. Chem.* **1997**, *62*, 2535–2543.

[224] P. J. Kocienski, R. C. D. Brown, A. Pommier, M. Procter, B. Schmidt, *J. Chem. Soc., Perkin Trans. 1* **1998**, 9–40.

[225] R. Mantione, *Bull. Soc. Chim. Fr.* **1969**, 4523–4527.

[226] J. A. Marshall, E. D. Robinson, J. Lebreton, *J. Org. Chem.* **1990**, *55*, 227–239.

[227] R. Whitby, P. Kocienski, *Tetrahedron Lett.* **1987**, *28*, 3619–3622.

[228] F. Le Strat, J. Maddaluno, *Tetrahedron Lett.* **2000**, *41*, 5367–5372.

[229] R. Mantione, M. L. Martin, G. J. Martin, H. Normant, *Bull. Soc. Chim. Fr.* **1967**, 2912–2918.

[230] G. A. Wildschut, J. H. van Boom, L. Brandsma, J. F. Arens, *Recl. Trav. Chim. Pays-Bas* **1968**, **87**, 1447–1452.

[231] M. V. Mavrov, *J. Org. Chem. USSR (Engl. Transl.)* **1983**, *19*, 626–632; *Zh. Org. Khim.* **1983**, *19*, 710–717.

[232] D. Goeppel, I. Muenster, R. Brueckner, *Tetrahedron* **1994**, *50*, 3687–3708.

[233] M. J. Sleeman, G. V. Meehan, *Tetrahedron Lett.* **1989**, *30*, 3345–3348.

[234] M. Verny, R. Vessière, *Bull. Soc. Chim. Fr.* **1969**, 1729–1737.

[235] D. Hoppe, C. Gonschorrek, *Tetrahedron Lett.* **1987**, *28*, 785–788.

[236] P. A. Jacobi, J. I. Kravitz, *Tetrahedron Lett.* **1988**, *29*, 6873–6876.

[237] T. Arnold, B. Orschel, H.-U. Reissig, *Angew. Chem.* **1992**, *104*, 1084–1086; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1033–1035.

[238] P. Rochet, J.-M. Vetèle, J. Goré, *Synlett* **1993**, 105–107.

[239] P. Harrington, M. A. Tius, *Org. Lett.* **2000**, *2*, 2447–2450.

[240] R. Lysek, P. Kajewski, Z. Urbanczyk-Lipkowska, B. Furman, Z. Kaluza, L. Kozerski, M. Chmielewski, *J. Chem. Soc., Perkin Trans. 2* **2000**, 61–67.

[241] A. Hausherr, B. Orschel, S. Scherer, H.-U. Reissig, *Synthesis* **2001**, 1377–1385.

[242] R. Lysek, B. Furman, Z. Kaluza, J. Frelek, K. Suwinska, Z. Urbanczyk-Lipkowska, M. Chmielewski, *Tetrahedron: Asymmetry* **2000**, *11*, 3131–3150.

[243] H. B. Mereyala, S. R. Gurrala, S. K. Mohan, *Tetrahedron* **1999**, *55*, 11331–11342.

[244] O. A. Tarasova, B. A. Trofimov, A. V. Afonin, L. M. Sinegovskaya, N. A. Kalinina, S. V. Amosova, *J. Org. Chem. USSR (Engl. Transl.)* **1991**, *27*, 1018–1025; *Zh. Org. Khim.* **1991**, *27*, 1172–1180.

[245] J. P. Dulcère, V. Agati, R. Faure, *J. Chem. Soc., Chem. Commun.* **1993**, 270–271.

[246] I. Kuwajima, M. Kato, *Tetrahedron Lett.* **1980**, 623–626.

[247] G. Sturtz, J. P. Paugam, B. Corbel, *Synthesis* **1974**, 730–732.

[248] W. G. Galesloot, M. J. A. de Bie, L. Brandsma, J. F. Arens, *Recl. Trav. Chim. Pays-Bas* **1970**, *89*, 575–587.

[249] J. C. Craig, N. N. Ekwuribe, *Tetrahedron Lett.* **1980**, *21*, 2587–2590.

[250] M. F. Shostakovskii, B. U. Minbaev, L. P. Krasnomolova, *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.)* **1980**, *29*, 102–105; *Izv. Akad. Nauk SSSR Ser. Khim.* **1980**, 117–121.

[251] H. D. Verkruijsse, H. J. T. Bos, L. J. de Noten, L. Brandsma, *Recl. J. R. Neth. Chem. Soc.* **1981**, *100*, 244–246.

[252] G. Broggini, L. Bruche, G. Zecchi, T. Pilati, *J. Chem. Soc., Perkin Trans.1* **1990**, 533–539.

[253] J.-L. Dumont, W. Chodkiewicz, P. Cadiot, *Bull. Soc. Chim. Fr.* **1967**, 1197–1203.

[254] G. Broggini, G. Molteni, G. Zecchi, *J. Chem. Res. (M)* **1993**, 1263–1278.

[255] L.-L. Wei, J. A. Mulder, H. Xiong, C. A. Zificsak, C. J. Douglas, R. P. Hsung, *Tetrahedron* **2001**, *57*, 459–466.

[256] G. Broggini, G. Zecchi, *J. Chem. Soc., Perkin Trans. 1* **1991**, 1843–1846.

[257] J. Reisch, R. A. Salehi-Artimani, *J. Heterocycl. Chem.* **1989**, 1803–1806.

[258] A. R. Katritzky, J. Li, M. F. Gordeev, *J. Org. Chem.* **1993**, *58*, 3038–3041.

[259] H. Galons, I. Bergerat, C. Combet Farnoux, M. Miocque, *Synthesis* **1982**, 1103–1105.

[260] A. Padwa, T. Caruso, S. Nahm, A. Rodriguez, *J. Am. Chem. Soc.* **1982**, *104*, 2865–2871.

[261] B. Lupo, G. Tarrago, *Synth. Commun.* **1982**, *12*, 381–394.

[262] T. Choshi, T. Sada, H. Fujimoto, C. N. Nagayama, E. Sugano, Shibino, *Tetrahedron Lett.* **1996**, *37*, 2593–2596.

[263] S. Phadtare, J. Zemlicka, *J. Org. Chem.* **1989**, *54*, 3675–3679.

[264] S. Radl, L. Kovarova, J. Holubek, *Collect. Czech. Chem. Commun.* **1991**, *56*, 439–448.

[265] S. Radl, L. Kovarova, *Collect. Czech. Chem. Commun.* **1991**, *56*, 2413–2419.

[266] S. Phadtare, D. Kessel, T. H. Corbett, H. D. Renis, B. A. Court, J. Zemlicka, *J. Med. Chem.* **1991**, *34*, 421–429.

[267] C. Simons, S. Chokekijchai, H. Mitsuya, J. Zemlicka, *Nucleosides Nucleotides* **1994**, *13*, 1779–1790.

[268] B. C. N. M. Jones, J. V. Silverton, C. Simons, S. Megati, H. Nishimura, Y. Maeda, H. Mitsuya, J. Zemlicka, *J. Med. Chem.* **1995**, *38*, 1397–1405.

[269] L. Kovacs, G. Kiss, P. Benke, G. Pócsfalvi, *Acta Chem. Scand.* **1996**, *50*, 466–468.

[270] W. E. Lindsell, C. Murray, P. N. Preston, T. A. J. Woodman, *Tetrahedron* **2000**, *56*, 1233–1246.

[271] Bogentoft, Ö. Ericsson, P. Stenberg, B. Paniel, *Tetrahedron Lett.* **1969**, 4745–4748.

[272] S. Phadtare, J. Zemlicka, *J. Am. Chem. Soc.* **1989**, *111*, 5925–5931.

[273] S. Hayashi, S. Phadtare, J. Zemlicka, M. Matsukura, H. Mitsuya, S. Broder, *Proc. Natl. Acad. Sci. USA* **1988**, *85*, 6127–6131.

[274] M. Noguchi, H. Okada, M. Watanabe, K. Okuda, O. Nakamura, *Tetrahedron* **1996**, *52*, 6581–6590.

[275] L.-L. Wei, H. Xiong, C. J. Douglas, R. P. Hsung, *Tetrahedron Lett.* **1999**, *40*, 6903–6908.

[276] P. Fretwell, R. Grigg, J. M. Sansano, V. Sridharan, S. Sukirthalingam, D. Wilson, J. Redpath, *Tetrahedron* **2000**, *56*, 7525–7540.

[277] F. Le Strat, J. Maddaluno, *Org. Lett.* **2002**, *4*, 2791–2794.

[278] J. Huang, H. Xiong, R. P. Hsung, C. Rameshkumar, J. A. Mulder, T. P. Grebe, *Org. Lett.* **2002**, *4*, 2417–2420.

[279] R. Grigg, I. Koeppen, M. Rasparini, V. Sridharan, *J. Chem. Soc., Chem. Commun.* **2001**, 964–965.

[280] R. Grigg, V. Loganathan, V. Sridharan, P. Stevenson, S. Sukirthalingam, T. Worakun, *Tetrahedron* **1996**, *52*, 11479–11502.

[281] S. S. Kinderman, J. H. van Maarseveen, H. E. Schoemaker, H. Hiemstra, F. P. J. T. Rutjes, *Org. Lett.* **2001**, *3*, 2045–2048.

[282] S.-F. Chen, P. S. Mariano, *Tetrahedron Lett.* **1985**, *26*, 47–50.

[283] J. W. Zwikker, R. W. Stephany, *Synth. Commun.* **1973**, *3*, 19–23.

[284] T. Laird, W. D. Ollis, *J. Chem. Soc., Chem. Commun.* **1972**, 557–559.

[285] K. Banert, *Chem. Ber.* **1989**, *122*, 1963–1967.

[286] A. R. Katritzky, S. Zhang, A. H. M. Hussein, Y. Fang, P. J. Steel, *J. Org. Chem.* **2001**, *66*, 5606–5612.

[287] L. Brandsma, H. E. Wijers, J. F. Arens, *Recl. Trav. Chim. Pays-Bas* **1963**, *82*, 1040–1046.

[288] A. Schaap, L. Brandsma, J. F. Arens, *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 393–398.

[289] Y. S. P. Cheng, E. Dominguez, P. J. Garratt, S. B. Neoh, *Tetrahedron Lett.* **1978**, 691–694.

[290] S.-K. Yeo, M. Shiro, K. Kanematsu, *J. Org. Chem.* **1994**, *59*, 1621–1632.

[291] N. Waizumi, T. Itoh, T. Fukuyama, *Tetrahedron Lett.* **1998**, *39*, 6015–6018.

[292] G. Guillerm, D. Guillerm, C. Witkowski-Vandenplas, *Nucleosides Nucleotides* **2001**, *20*, 685–688.

[293] G. Guillerm, D. Guillerm, C. Vandenplas-Witkowski, H. Rogniaux, N. Carte, E. Leize, A. van Dorsselaer, E. de Clercq, C. Lambert, *J. Med. Chem.* **2001**, *44*, 2743–2752.

[294] M. Yamamoto, H. Munakata, M. Z. Hussein, S. Kohmoto, K. Yamada, *J. Chem. Res. (M)* **1990**, 0279–0296.

[295] H. Takeshita, K. Uchida, H. Mametsuka, *Heterocycles* **1983**, *20*, 1709–1712.

[296] E. Arlandini, M. Ballabio, L. D. Prada, L. M. Rossi, P. Trimarco, *J. Chem. Res. (M)* **1983**, 1575–1585.

[297] G. Broggini, G. Molteni, G. Zecchi, *J. Chem. Res. (M)* **1993**, 2649–2662.

[298] N. G. Kundu, B. Nandi, *Synlett.* **2001**, 415–417.

[299] B. Nandi, N. G. Kundu, *J. Chem. Soc., Perkin Trans. 1* **2001**, 1649–1655.

[300] A. Ogawa, K. Sakagami, A. Shima, H. Suzuki, S. Komiya, Y. Katano, O. Mitsunobu, *Tetrahedron Lett.* **2002**, *43*, 6387–6390.

[301] S. M. Riyadh, H. Ishii, T. Fuchigami, *Tetrahedron Lett.* **2001**, *42*, 3009–3012.

[302] S. M. Riyadh, H. Ishii, T. Fuchigami, *Tetrahedron* **2002**, *58*, 5877–5884.

[303] V. P. Upadhyaya, V. R. Srinivasan, *Indian J. Chem. Sect. B* **1981**, *20*, 161–162.

[304] T. Benneche, K. Undheim, *Acta Chem. Scand., Ser. B* **1983**, *37*, 115–120.

[305] M. M. Krayushkin, M. A. Kalik, E. Y. Zvezdina, *Russ. Chem. Bl.* **1993**, *42*, 488–490; *Izv. Akad. Nauk SSSR Ser. Khim.* **1993**, 532–534.

[306] N. H. Andersen, A. D. Denniston, D. A. McCrae, *J. Org. Chem.* **1982**, *47*, 1145–1146.

[307] C. C. Fortes, C. F. D. Garrote, *Synth. Commun.* **1997**, *27*, 3917–3941.

[308] A. N. Pudovik, N. G. Khusainova, *J. Gen. Chem. USSR (Engl. Transl.)* **1969**, *39*, 1384; *Zh. Obshch. Khim.* **1969**, *39*, 1417.

[309] J. H. Van Boom, L. Brandsma, J. F. Arens, *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 97–122.

[310] R. R. Kostikov, G. S. Varakin, A. P. Molchanov, K. A. Ogloblin, *Russ. J. Org. Chem.* **1996**, 31–35; *Zh. Org. Khim.* **1996**, *32*, 39–43.

[311] S. Florio, L. Ronzini, E. Epifani, R. Sgarra, *Tetrahedron* **1993**, *49*, 10413–10420.

[312] H. J. Reich, S. K. Shah, P. M. Gold, R. E. Olson, *J. Am. Chem. Soc.* **1981**, *103*, 3112–3120.

[313] X.-P. Cao, T.-L. Chan, H.-F. Chow, *Tetrahedron Lett.* **1996**, *37*, 1049–1052.

[314] L. Bouchez, P. Vogel, *Synthesis* **2002**, 225–231.

[315] S. T. McDowell, C. J. M. Stirling, *J. Chem. Soc. B* **1967**, 351–355.

[316] W. E. Truce, L. D. Markley, *J. Org. Chem.* **1970**, *35*, 3275–3281.

[317] F. G. Bordwell, T. G. Mecca, *J. Am. Chem. Soc.* **1972**, *94*, 5829–5837.

[318] S. Bradamante, P. Del Buttero, S. Maiorana, *J. Chem. Soc., Perkin Trans.1* **1973**, 612–615.

[319] K. Koosha, J. Berlan, M.-L. Capmau, W. Chodkiewicz, *Bull. Soc. Chim. Fr.* **1975**, 1284–1290.

[320] M. Hanack, F. W. Massa, *Tetrahedron Lett.* **1981**, *22*, 557–558.

[321] A. J. Guildford, R. W. Turner, *J. Chem. Soc., Chem. Commun.* **1983**, 466–467.

[322] S. E. Denmark, M. A. Harmata, K. S. White, *J. Org. Chem.* **1987**, *52*, 4031–4042.

[323] K. C. Nicolaou, S. Wendeborn, P. Maligres, K. Isshiki, N. Zein, G. Ellestad, *Angew. Chem.* **1991**, *103*, 462–464; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 418–420.

[324] T. Matsuoka, T. Hasegawa, K. Harano, T. Hisano, *Heterocycles* **1992**, *33*, 179–188.

[325] J. R. Williams, J. C. Boehm, *Bioorg. Med. Chem. Lett.* **1992**, *2*, 933–936.

[326] K. Toshima, K. Ohta, A. Ohtsuka, S. Matsumura, M. Nakata, *J. Chem. Soc., Chem. Commun.* **1993**, 1406–1407.

[327] G. Broggini, G. Molteni, G. Zecchi, *J. Org. Chem.* **1994**, *59*, 8271–8274.

[328] J. R. Williams, J. C. Boehm, *Steroids* **1995**, *60*, 699–708.

[329] W.-M. Dai, C. W. Chow, L. Zhou, A. Ishii, C. W. Lau, Q. Li, W. Hamaguchi, S.-i. Nishimoto, *Bioorg. Med. Chem. Lett.* **1999**, *9*, 2789–2794.

[330] L. Brandsma, N. A. Chernysheva, B. A. Trofimov, *Phosphorus Sulfur Silicon Relat. Elem.* **2000**, *159*, 143–148.

[331] S. Braverman, Y. Zafrani, H. E. Gottlieb, *Tetrahedron* **2001**, *57*, 9177–9186.

[332] R. West, P. C. Jones, *J. Am. Chem. Soc.* **1969**, *91*, 6156–6161.

[333] R. Mantione, Y. Leroux, *J. Organomet. Chem.* **1971**, *31*, 5–15.

[334] M. Ishikawa, H. Sugisawa, L. Fabry, M. Kumada, *J. Organomet. Chem.* **1978**, *161*, 299–311.

[335] P. E. Peterson, B. L. Jensen, *Tetrahedron Lett.* **1984**, *25*, 5711–5714.

[336] D. Clark, D. A. Travis, *Bioorg. Med. Chem.* **2001**, *9*, 2857–2862.

[337] G. Courtemanche, J.-F. Normant, *Tetrahedron Lett.* **1991**, *32*, 5317–5320.

[338] C. Schultz-Fademrecht, B. Wibbeling, R. Froehlich, D. Hoppe, *Org. Lett.* **2001**, *3*, 1221–1224.

[339] S. Dreller, M. Drybusch, D. Hoppe, *Synlett* **1991**, 397–400.

[340] P. J. Stang, M. R. White, *J. Am. Chem. Soc.* **1981**, *103*, 5429–5433.

[341] G. A. Russell, L. L. Herold, *J. Org. Chem.* **1985**, *50*, 1037–1040.

[342] H. R. Allcock, P. J. Harris, R. A. Nissan, *J. Am. Chem. Soc.* **1981**, *103*, 2256–2261.

[343] H. Lang, U. Lay, M. Leise, L. Zsolnai, *Z. Naturforsch., Teil B* **1993**, *48*, 27–36.

[344] A. J. Zapata, Y. Gu, G. B. Hammond, *J. Org. Chem.* **2000**, *65*, 227–234.

[345] A. N. Pudovik, E. M. Faizullin, *J. Gen. Chem. USSR (Engl. Transl.)* **1968**, *38*, 1857; *Zh. Obshch. Khim.* **1968**, *38*, 1908.

[346] M. Reisser, A. Maier, G. Maas, *Synlett* **2002**, 1459–1462.

[347] J. A. Marshall, W. J. DuBay, *J. Org. Chem.* **1993**, *58*, 3435–3443.

[348] J. A. Marshall, W. J. DuBay, *J. Org. Chem.* **1994**, *59*, 1703–1708.

[349] K. Hayakawa, M. Yodo, S. Ohsuki, K. Kanematsu, *J. Am. Chem. Soc.* **1984**, *106*, 6735–6740.

[350] K. Hayakawa, Y. Yamaguchi, K. Kanematsu, *Tetrahedron Lett.* **1985**, **26**, 2689–2692.

[351] K. Hayakawa, S. Ohsuki, K. Kanematsu, *Tetrahedron Lett.* **1986**, *27*, 4205–4208.

[352] Y. Yamaguchi, K. Hayakawa, K. Kanematsu, *J. Chem. Soc., Chem. Commun.* **1987**, 515–516.

[353] Y. Yamaguchi, H. Yamada, K. Hayakawa, K. Kanematsu, *J. Org. Chem.* **1987**, *52*, 2040–2046.

[354] K. Hayakawa, F. Nagatsugi, K. Kanematsu, *J. Org. Chem.* **1988**, *53*, 860–863.

[355] Y. Yamaguchi, N. Tatsuta, K. Hayakawa, K. Kanematsu, *J. Chem. Soc., Chem. Commun.* **1989**, 470–472.

[356] K. Hayakawa, K. Aso, M. Shiro, K. Kanematsu, *J. Am. Chem. Soc.* **1989**, *111*, 5312–5320.

[357] S. Nagashima, K. Kanematsu, *Tetrahedron: Asymmetry* **1990**, *1*, 743–749.

[358] K. Kanematsu, S. Soejima, G. Wang, *Tetrahedron Lett.* **1991**, *32*, 4761–4764.

[359] K. Kanematsu, M. Tsuruoka, Y. Takaoka, T. Sasaki, *Heterocycles* **1991**, *32*, 859–862.

[360] K. Kanematsu, S. Soejima, *Heterocycles* **1991**, *32*, 1483–1486.

[361] C. C. Lin, L.-H. Chen, H.-J. Wu, *J. Chin. Chem. Soc.* **1991**, *38*, 613–617.

[362] K. Kanematsu, A. Nishizaki, Y. Sato, M. Shiro, *Tetrahedron Lett.* **1992**, *33*, 4967–4970.

[363] H.-J. Wu, W.-D. Shao, F.-H. Ying, *Tetrahedron Lett.* **1994**, *35*, 729–732.

[364] Y. Baba, T. Sakamoto, K. Kanematsu, *Tetrahedron Lett.* **1994**, *35*, 5677–5680.

[365] H.-J. Wu, F.-H. Ying, W.-D. Shao, *J. Org. Chem.* **1995**, *60*, 6168–6172.

[366] M. Lee, H. Moritomo, K. Kanematsu, *Tetrahedron* **1996**, *52*, 8169–8180.

[367] H.-J. Wu, C.-H. Yen, C.-T. Chuang, *Tetrahedron Lett.* **1996**, *37*, 7395–7398.

[368] S.-H. Tsai, W.-S. Chung, H.-J. Wu, *J. Chin. Chem. Soc.* **1996**, *43*, 281–288.

[369] C. O. Kappe, S. S. Murphree, A. Padwa, *Tetrahedron* **1997**, *53*, 14179–14233.

[370] H.-J. Wu, C.-H. Yen, C.-T. Chuang, *J. Org. Chem.* **1998**, *63*, 5064–5070.

[371] C.-T. Chuang, C.-H. Yen, H.-J. Wu, *J. Chin. Chem. Soc.* **1998**, *45*, 789–797.

[372] Y. Sakai, Y. Bando, K. Shishido, M. Shibuya, *Tetrahedron Lett.* **1992**, *33*, 957–960.

[373] M.-J. Wu, C.-F. Lin, J.-S. Wu, H.-T. Chen, *Tetrahedron Lett.* **1994**, *35*, 1879–1882.

[374] W.-M. Dai, K. C. Fong, H. Danjo, S.-i. Nishimoto, *Angew. Chem.* **1996**, *108*, 821–822; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 779–781.

[375] J. W. Grissom, D. Klingberg, D. Huang, B. J. Slattery, *J. Org. Chem.* **1997**, *62*, 603–626.

[376] K. Toshima, K. Ohta, T. Ohtake, K. Tatsuta, *Tetrahedron Lett.* **1991**, *32*, 391–394.

[377] H. Li, H.-R. Zhang, J. L. Petersen, K. K. Wang, *J. Org. Chem.* **2001**, *66*, 6662–6668.

[378] C. J. Elsevier, in *Houben–Weyl Stereoselective Synthesis*, G. Helmchen, R. W. Hoffmann, J. Mulzer, E. Schaumann (Eds), Thieme: Stuttgart, 1996, pp. 537–566.

[379] V. Ch. Christov, I. K. Ivanov, *Phosphorus Sulfur Silicon Relat. Elem.* **2002**, *177*, 2445–2454.

[380] V. Ch. Christov, B. Prodanov, R. Nikolova, *Phosphorus Sulfur Silicon Relat. Elem.* **2000**, *166*, 275–282.

[381] A. J. Bridges, J. W. Fischer, *J. Chem. Soc., Chem. Commun.* **1982**, 665–666.

[382] I. Cutting, P. J. Parsons, *Tetrahedron Lett.* **1983**, *24*, 4463–4464.

[383] E. M. G. A. van Kruchten, A. Haces, W. H. Okamura, *Tetrahedron Lett.* **1983**, *24*, 3939–3942.

[384] G. Zomer, H. Wynberg, N. M. Drayer, *Steroids* **1984**, *44*, 293–300.

[385] J. D. Buynak, M. N. Rao, R. Y. Chandrasekaran, E. Haley, P. de Meester, S. C. Chu, *Tetrahedron Lett.* **1985**, *26*, 5001–5004.

[386] W. H. Okamura, G.-Y. Shen, R. Tapia, *J. Am. Chem. Soc.* **1986**, *108*, 5018–5019.

[387] H.-J. Altenbach, H. Soicke, *Tetrahedron Lett.* **1986**, *27*, 1561–1562.

[388] S. W. Djuric', M. Miyano, M. Clare, R. M. Rydzewski, *Tetrahedron Lett.* **1987**, *28*, 299–302.

[389] S. R. Abrams, A. C. Shaw, *J. Org. Chem.* **1987**, *52*, 1835–1839.

[390] G. Pairaudeau, P. J. Parsons, J. M. Underwood, *J. Chem. Soc., Chem. Commun.* **1987**, 1718–1720.

[391] M. Ceruti, F. Viola, G. Grosa, G. Balliano, L. Delprino, L. Cattel, *J. Chem. Res. (M)* **1988**, 0239–0260.

[392] R. A. Gibbs, K. Bartels, R. W. K. Lee, W. H. Okamura, *J. Am. Chem. Soc.* **1989**, *111*, 3717–3725.

[393] R. Nagata, H. Yamanaka, E. Murahashi, I. Saito, *Tetrahedron Lett.* **1990**, *31*, 2907–2910.

[394] E. Block, D. Putman, *J. Am. Chem. Soc.* **1990**, *112*, 4072–4074.

[395] A. Padwa, W. H. Bullock, B. H. Norman, J. Perumattam, *J. Org. Chem.* **1991**, *56*, 4252–4259.

[396] J. K. Crandall, T. A. Ayers, *Tetrahedron Lett.* **1991**, *32*, 3659–3662.

[397] A. S. Craig, A. W. Norman, W. H. Okamura, *J. Org. Chem.* **1992**, *57*, 4374–4380.

[398] M. Gray, P. J. Parsons, A. P. Neary, *Synlett* **1992**, 597–598.

[399] J. B. Baudin, S. A. Julia, R. Lorne, *Bull. Soc. Chim. Fr.* **1992**, 440–456.

[400] Z. Ni, X. Wang, A. Rodriguez, A. Padwa, *Tetrahedron Lett.* **1992**, *33*, 7303–7306.

[401] M. Gray, P. J. Parsons, A. P. Neary, *Synlett* **1993**, 281–282.

[402] X. Wang, Z. Ni, X. Lu, A. Hollis, H. Banks, *J. Org. Chem.* **1993**, *58*, 5377–5385.

[403] S. Braverman, Z. Lior, *Tetrahedron Lett.* **1994**, *35*, 6725–6728.

[404] X. Wang, J. Donovalova, A. Hollis, D. Johnson, A. Rodriguez, G. D. Kennedy, G. Krishnan, H. Banks, *J. Heterocycl. Chem.* **1994**, *31*, 871–876.

[405] M. Harmata, C. B. Gamlath, C. L. Barnes, D. E. Jones, *J. Org. Chem.* **1995**, *60*, 5077–5092.

[406] A. Padwa, H. Lipka, S. H. Watterson, *Tetrahedron Lett.* **1995**, *36*, 4521–4524.

[407] A. Padwa, M. Meska, S. S. Murphree, S. H. Watterson, Z. Ni, *J. Am. Chem. Soc.* **1995**, *117*, 7071–7080.

[408] M. Taing, H. W. Moore, *J. Org. Chem.* **1996**, *61*, 329–340.

[409] C. Bintz-Giudicelli, D. Uguen, *Tetrahedron Lett.* **1997**, *38*, 2973–2976.

[410] N. Edwards, J. A. Macritchie, P. J. Parsons, M. G. B. Drew, A. W. Jahans, *Tetrahedron* **1997**, *53*, 12651–12660.

[411] K. Banert, W. Fendel, J. Schlott, *Angew. Chem.* **1998**, *110*, 3488–3491; *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3289–3292.

[412] N. Edwards, J. A. Macritchie, P. J. Parsons, *Tetrahedron Lett.* **1998**, *39*, 3605–3608.

[413] C. P. Raj, N. A. Dhas, M. Cherkinski, A. Gedanken, S. Braverman, *Tetrahedron Lett.* **1998**, 39, 5413–5416.

[414] C. P. Raj, S. Braverman, *Synth. Commun.* **1999**, *29*, 2629–2638.

[415] J. R. Bull, R. S. Gordon, R. Hunter, *Synlett* **1999**, 599–601.

[416] J. R. Bull, R. Gordon, R. Hunter, *J. Chem. Soc., Perkin Trans. 1* **2000**, 3129–3139.

[417] S. Braverman, E. V. K. S. Kumar, M. Cherkinsky, M. Sprecher, I. Goldberg, *Tetrahedron Lett.* **2000**, *41*, 6923–6928.

[418] C. Mukai, H. Yamashita, M. Hanaoka, *Org. Lett.* **2001**, *3*, 3385–3388.

[419] c. Mukai, I. Nomura, K. Yamanishi, M. Hanaoka, *Org. Lett.* **2002**, *4*, 1755–1758.

[420] S. Ma, H. Ren, Q. Wei, *J. Am. Chem. Soc.* **2003**, *125*, 4817–4830.

[421] C. Mukai, I. Nomura, S. Kitagaki, *J. Org. Chem.* **2003**, *68*, 1376–1385.

[422] C. Mukai, R. Ukon, N. Kuroda, *Tetrahedron Lett.* **2003**, *44*, 1583–1586.

[423] R. W. Saalfrank, U. Bauer, K. Hilbig, A. Welch, *Chem. Ber.* **1993**, *126*, 823–836.

[424] M. E. Maier, *Eur. J. Org. Chem.* **2000**, 3945–3948.

[425] R. W. Saalfrank, A. Welch, M. Haubner, U. Bauer, *Liebigs Ann. Org. Bioorg. Chem.* **1996**, 171–182.

[426] G. Smith, C. J. M. Stirling, *J. Chem. Soc. C* **1971**, 1530–1535.

[427] L. Horner, V. Binder, *Liebigs Ann. Chem.* **1972**, *757*, 33–68.

[428] S. Braverman, H. Mechoulam, *Tetrahedron* **1974**, *30*, 3883–3890.

[429] L. A. van Dijck, B. J. Laschenwerden, J. G. C. M. Vermeer, *Recl. Trav. Chim. Pays-Bas* **1977**, *96*, 200–206.

[430] M. Cinquini, S. Colonna, F. Cozzi, *J. Chem. Soc., Perkin Trans. 1* **1978**, 247–249.

[431] H. J. Altenbach, H. Soicke, *Liebigs Ann. Chem.* **1982**, 1096–1104.

[432] E. M. G. A. van Kruchten, W. H. Okamura, *Tetrahedron Lett.* **1982**, 1019–1022.

[433] S. Braverman, Y. Duar, *J. Am. Chem. Soc.* **1983**, *105*, 1061–1063.

[434] S. E. Denmark, M. A. Harmata, *Tetrahedron Lett.* **1984**, *25*, 1543–1546.

[435] M. Harmata, C. B. Gamlath, C. L. Barnes, *Tetrahedron Lett.* **1990**, *31*, 5981–5984.

[436] Y. Tamaru, K. Nagao, T. Bando, Z.-i. Yoshida, *J. Org. Chem.* **1990**, *55*, 1823–1829.

[437] M. Conrads, J. Mattay, *Synthesis* **1991**, 11–14.

[438] J.-B. Baudin, S. Julia, *Bull. Soc. Chim. Fr.* **1995**, *132*, 196–214.

[439] J. B. van der Linden, P. F. T. M. van Asten, S. Braverman, B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas* **1995**, *114*, 51–60.

[440] K. Hiroi, F. Kato, H. Nakasato, *Chem. Lett.* **1998**, 553–554.

[441] K. Hiroi, F. Kato, *Tetrahedron* **2001**, *57*, 1543–1550.

[442] S. Braverman, T. Pechenick, Y. Zafrani, *Tetrahedron Lett.* **2001**, *42*, 1391–1394.

[443] H.-J. Gais, M. van Gumpel, Markus M. Schleusner, G. Raabe, J. Runsink, C. Vermeeren, *Eur. J. Org. Chem.* **2001**, 4275–4304.

[444] V. K. Brel, *Synthesis* **2001**, 1539–1545.

[445] V. Mark, *Tetrahedron Lett.* **1962**, 281–285.

[446] A. N. Pudovik, I. M. Aladzheva, L. N. Yakovenko, *J. Gen. Chem. USSR (Engl. Transl.)* **1965**, *35*, 1214–1220; *Zh. Obshch. Khim.* **1965**, *35*, 1210–1217.

[447] M. Huché, P. Cresson, *Bull. Chem. Soc. Fr.* **1975**, 800–804.

[448] R. S. Macomber, E. R. Kennedy, *J. Org. Chem.* **1976**, *41*, 3191–3197.

[449] W. Welter, A. Hartmann, M. Regitz, *Chem. Ber.* **1978**, *111*, 3068–3085.

[450] H.-J. Altenbach, R. Korff, *Tetrahedron Lett.* **1981**, *22*, 5175–5178.

[451] V. K. Brel', B. I. Ionin, A. A. Petrov, *J. Gen. Chem. USSR (Engl. Transl.)* **1982**, *52*, 709–716; *Zh. Obshch. Khim.* **1982**, *52*, 816–825.

[452] T. N. Belyaeva, A. V. Dogadina, B. I. Ionin, A. Petrov, *J. Gen. Chem. USSR (Engl. Transl.)* **1982**, *52*, 1267–1268; *Zh. Obshch. Khim.* **1982**, *52*, 1432–1433.

[453] H. Collet, P. Calas, A. Commeyras, *J. Chem. Soc., Chem. Commun.* **1984**, 1152–1153.

[454] R. S. Macomber, T. C. Hemling, *J. Am. Chem. Soc.* **1986**, *108*, 343–344.

[455] D. O. Spry, A. R. Bhala, *Heterocycles* **1986**, *24*, 1799–1806.

[456] I. Morita, S.-i. Tada, K. Kunimoto, M. Tsuda, M. Kise, K. Kimura, *Chem. Pharm. Bull.* **1987**, *35*, 3898–3904.

[457] S. E. Denmark, J. E. Marlin, *J. Org. Chem.* **1987**, *52*, 5742–5745.

[458] D. H. Beach, F. Chen, M. T. Cushion, R. S. Macomber, G. A. Krudy, M. A. Wyder, E. S. Kaneshiro, *Antimicrob. Agents Chemother.* **1997**, *41*, 162–168.

[459] B. W. Metcalf, C. L. Wright, J. P. Burkhart, J. O. Johnston, *J. Am. Chem. Soc.* **1981**, *103*, 3221–3222.

[460] H. Faraj, A. Aumelas, M. Claire, A. Rondot, G. Auzou, *Steroids* **1991**, *56*, 558–561.

[461] K. S. Akerfeldt, P. A. Bartlett, *J. Org. Chem.* **1991**, *56*, 7133–7144.

[462] S. E. Denmark, J. E. Marlin, *J. Org. Chem.* **1991**, *56*, 1003–1013.

[463] M. Muller, A. Mann, M. Taddei, *Tetrahedron Lett.* **1993**, *34*, 3289–3290.

[464] B.-z. Cai, G. M. Blackburn, *Synth. Commun.* **1997**, 3943–3950.

[465] J. M. Cox, T. R. Hawkes, P. Bellini, R. M. Ellis, R. Barrett, J. J. Swanborough, S. E. Russel, P. A. Walker, N. J. Barns, A. J. Knee, T. Lewis, P. R. Davies, *Pestic. Sci.* **1997**, *50*, 297–311.

[466] V. K. Brel, *Synthesis* **1998**, 710–712.

[467] D. D. Enchev, *Phosphorus Sulfur Silicon Relat. Elem.* **1998**, *134*, 187–192.

[468] D. D. Enchev, M. Kirilov, *Phosphorus Sulfur Silicon Relat. Elem.* **1998**, *134*, 193–198.

[469] V. K. Brel, *Synthesis* **1999**, 463–466.

[470] V. K. Brel, *Synth. Commun.* **1999**, *29*, 3869–3880.

[471] R. W. Saalfrank, M. Haubner, C. Deutscher, W. Bauer, *Eur. J. Org. Chem.* **1999**, 2367–2372.

[472] V. Ch. Christov, B. Prodanov, R. Nikolova, *Phosphorus Sulfur Silicon Relat. Elem.* **2000**, *166*, 275–282.

[473] D. D. Enchev, *Phosphorus Sulfur Silicon Relat. Elem.* **2000**, *165*, 243–248.

[474] D. D. Enchev, *Phosphorus Sulfur Silicon Relat. Elem.* **2000**, *165*, 273–284.

[475] V. K. Brel, *Synthesis* **2002**, 1829–1832.

[476] C.-F. Xu, Y.-X. Liu, W.-H. Wang, R.-Z. Cao, L.-Z. Liu, *Heteroat. Chem.* **2002**, *13*, 633–637.

[477] V. K. Brel, P. J. Stang, *Eur. J. Org. Chem.* **2003**, 224–229.

[478] A. Sevin, W. Chodkiewicz, *Tetrahedron Lett.* **1967**, 2975–2980.

[479] A. Sevin, W. Chodkiewicz, *Bull. Chem. Soc. Fr.* **1969**, 4016–4022.

[480] R. Nagata, H. Yamanaka, E. Okazaki, I. Saito, *Tetrahedron Lett.* **1989**, *30*, 4995–4998.

[481] J. A. Palenzuela, H. Y. Elnagar, W. H. Okamura, *J. Am. Chem. Soc.* **1989**, *111*, 1770–1773.

[482] K. C. Nicolaou, P. Maligres, J. Shin, E. de Leon, D. Rideout, *J. Am. Chem. Soc.* **1990**, *112*, 7825–7826.

[483] M. L. Curtin, W. H. Okamura, *J. Org. Chem.* **1990**, *55*, 5278–5287.

[484] J. W. Grissom, B. Slattery, *Tetrahedron Lett.* **1994**, *35*, 5137–5140.

[485] M. Schmittel, M. Strittmatter, S. Kiau, *Tetrahedron Lett.* **1995**, *36*, 4975–4978.

[486] J. W. Grissom, D. Huang, *Angew. Chem.* **1995**, *107*, 2196–2198; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2037–2039.

[487] M. Schmittel, S. Kiau, T. Siebert, M. Strittmatter, *Tetrahedron Lett.* **1996**, *37*, 7691–7694.

[488] M. Schmittel, M. Strittmatter, K. Vollmann, S. Kiau, *Tetrahedron Lett.* **1996**, *37*, 999–1002.

[489] C. Darcel, C. Bruneau, P. H. Dixneuf, *Synthesis* **1996**, 711–714.

[490] K. Pravia, R. White, R. Fodda, D. F. Maynard, *J. Org. Chem.* **1996**, *61*, 6031–6032.

[491] M. Schmittel, M. Keller, S. Kiau, M. Strittmatter, *Chem. Eur. J.* **1997**, *3*, 807–816.

[492] M. Schmittel, J.-P. Steffen, I. Bohn, *Heterocycl. Commun.* **1997**, *3*, 443–447.

[493] C. Santelli-Eouvier, L. Toupet, M. Santelli, *J. Org. Chem.* **1997**, *62*, 9039–9047.

[494] M. Schmittel, S. Kiau, *Liebigs Ann./Recl.* **1997**, 733–736.

[495] O. de Frutos, A. M. Echavarren, *Tetrahedron Lett.* **1997**, *38*, 7941–7942.

[496] M. Schmittel, J.-P. Steffen, D. Auer, M. Maywald, *Tetrahedron Lett.* **1997**, *38*, 6177–6180.

[497] A. R. de Lera, A. Castro, A. Torrado, S. Lopez, *Tetrahedron Lett.* **1998**, *39*, 4575–4578.

[498] B. Iglesias, A. Torrado, A. R. de Lera, S. Lopez, *J. Org. Chem.* **2000**, *65*, 2696–2705.

[499] M. Schmittel, J.-P. Steffen, M. Maywald, B. Engels, H. Helten, P. Musch, *J. Chem. Soc., Perkin Trans. 2* **2001**, 1331–1339.

[500] M. Schmittel, M. Maywald, *J. Chem. Soc., Chem. Commun.* **2001**, 155–156.

[501] M. Huche, P. Cresson, *Tetrahedron Lett.* **1975**, 367–368.

[502] J. A. Marshall, X.-j. Wang, *J. Org. Chem.* **1991**, *56*, 960–969.

[503] S. Florio, C. Granito, G. Ingrosso, L. Troisi, *Eur. J. Org. Chem.* **2002**, 3465–3472.

[504] T. Skrydstrup, H. Audrain, G. Ulibarri, D. S. Grierson, *Tetrahedron Lett.* **1992**, *33*, 4563–4566.

[505] J. A. Marshall, E. D. Robinson, A. Zapata, *J. Org. Chem.* **1989**, *54*, 5854–5855.

[506] J. A. Marshall, X.-J. Wang, *J. Org. Chem.* **1990**, *55*, 2995–2996.

[507] D. K. Black, S. R. Landor, *J. Chem. Soc.* **1965**, 6784–6788.

[508] W. D. Huntsman, J. A. De Boer, M. H. Woosley, *J. Am. Chem. Soc.* **1966**, *88*, 5846–5850.

[509] S. Dai, R. S. Pappas, G.-F. Chen, Q.-X. Guo, J. T. Wang, F. Williams, *J. Am. Chem. Soc.* **1989**, *111*, 8759–8761.

[510] K. A. Owens, J. A. Berson, *J. Am. Chem. Soc.* **1990**, *112*, 5973–5985.

[511] W. R. Roth, F. Bauer, K. Braun, R. Offerhaus, *Angew. Chem.* **1989**, *101*, 1092–1094.

[512] N. Manisse, J. C. Pommelet, J. Chuche, *Bull. Soc. Chim. Fr.* **1972**, 2422–2429.

[513] D. K. Black, S. R. Landor, *J. Chem. Soc.* **1965**, 6784–6788.

[514] P. Cresson, M. Atlani, *C. R. Hebd. Seances Acad. Sci. Ser. C* **1967**, *265*, 942–944.

[515] J. Grimaldi, M. Malacria, M. Bertrand, *Bull. Soc. Chim. Fr.* **1975**, 1720–1724.

[516] J. M. Reuter, R. G. Salomon, *Tetrahedron Lett.* **1978**, 3199–3202.

[517] P. T. Lansbury, A. K. Serelis, J. E. Hengeveld, D. G. Hangauer, *Tetrahedron* **1980**, *36*, 2701–2710.

[518] G. Brooke, E. I. Wallis, *J. Fluorine Chem.* **1982**, *20*, 173–186.

[519] M. R. Banks, J. M. Barker, P. R. Huddleston, *J. Chem. Res. (M)* **1984**, 0369–0389.

[520] G. Brooke, J. R. Cooperwaite, *J. Chem. Soc., Perkin Trans. 1* **1985**, 2643–2650.

[521] Y. M. Dangyan, M. R. Tirakyan, G. A. Panosyan, S. O. Badanyan, *J. Gen. Chem. USSR (Engl. Transl.)* **1986**, *56*, 1344–1346; *Zh. Obshch. Khim.* **1986**, *56*, 1517–1520.

[522] J. Fischer, C. Kilpert, U. Klein, W. Steglich, *Tetrahedron* **1986**, *42*, 2063–2074.

[523] G. A. Tolstikov, S. A. Ismailov, M. S. Miftakhov, *J. Org. Chem. USSR (Engl. Transl.)* **1989**, *25*, 1414–1415; *Zh. Obshch. Khim.* **1989**, *25*, 1566–1567.

[524] J. Barluenga, F. Aznar, M. Bayod, J. M. Alvarez, *Tetrahedron Lett.* **1989**, *30*, 5919–5922.

[525] S. E. Denmark, M. A. Harmata, K. S. White, *J. Am. Chem. Soc.* **1989**, *111*, 8878–8891.

[526] M. E. Jung, C. N. Zimmerman, *J. Am. Chem. Soc.* **1991**, *113*, 7813–7814.

[527] H. Yoshida, Y. Takahashi, H. Kinoshita, S. Ukishima, T. Ogata, K. Matsumoto, *Bull. Chem. Soc. Jpn.* **1991**, *64*, 3565–3570.

[528] G. L'abbe, S. Emmers, W. Dehaen, L. K. Dyall, *J. Chem. Soc., Perkin Trans. 1* **1994**, 2553–2558.

[529] J. W. Grissom, D. Huang, *J. Org. Chem.* **1994**, *59*, 5114–5116.

[530] G.-q. Shi, W.-l. Cai, *J. Org. Chem.* **1995**, *60*, 6289–6295.

[531] R. R. Akhmetvaleev, L. R. Imaeva, T. A. Belogaeva, M. S. Miftakhov, *Russ. Chem. Bull.* **1997**, *46*, 1963–1964; *Izv. Akad. Nauk Ser. Khim.* **1997**, 2067–2068.

[532] H. Hopf, J. Wolff, *Eur. J. Org. Chem.* **2001**, 4009–4030.

[533] J. A. Cooper, C. M. Olivares, G. Sandford, *J. Org. Chem.* **2001**, *66*, 4887–4891.

[534] T. Durand-Reville, L. B. Gobbi, B. L. Gray, S. Ley, J. S. Scott, *Org. Lett.* **2002**, *4*, 3847–3850.

[535] C. Agami, F. Couty, G. Evano, *Eur. J. Org. Chem.* **2002**, 29–38.

[536] W. Peng, S. Zhu, *Tetrahedron* **2003**, *59*, 4641–4650.

[537] D. O. Spry, A. R. Bhala, *Heterocycles* **1986**, *24*, 1653–1661.

[538] S. V. Ley, C. E. Gutteridge, A. R. Pape, C. D. Spilling, C. Zumbrunn, *Synlett* **1999**, 1295–1297.

[539] L. Barriault, I. Denissova, *Org. Lett.* **2002**, *4*, 1371–1374.

[540] B. J. Newhouse, J. Bordner, D. J. Augeri, C. S. Litts, E. F. Kleinman, *J. Org. Chem.* **1992**, *57*, 6991–6995.

[541] K. I. Booker-Milburn, M. Fedouloff, S. J. Paknoham, J. B. Strachan, J. L. Melville, M. Voyle, *Tetrahedron Lett.* **2000**, *41*, 4657–4661.

[542] K. C. Majumdar, S. K. Ghosh, *Tetrahedron Lett.* **2002**, *43*, 2111–2113.

[543] J. L. Wood, G. A. Moniz, *Org. Lett.* **1999**, *1*, 371–374.

[544] D. Desmaele, N. Champion, *Tetrahedron Lett.* **1992**, *33*, 4447–4450.

[545] M. J. Begley, M. Landlow, G. Pattenden, *J. Chem. Soc., Perkin Trans. 1* **1988**, 1095–1106.

[546] K. Hartke, T. Gillmann, *Liebigs Ann. Chem.* **1986**, 1718–1727.

[547] M. Ochiai, T. Ito, Y. Takaoka, Y. Masaki, *J. Am. Chem. Soc.* **1991**, *113*, 1319–1323.

[548] D. Barmettler, H.-J. Hansen, *Helv. Chim. Acta* **1990**, *73*, 1515–1573.

[549] K. Dimroth, O. Schaffer, G. Weiershaeuser, *Chem. Ber.* **1981**, *114*, 1752–1766.

[550] Y. Aoki, I. Kuwajima, *Tetrahedron Lett.* **1990**, *51*, 7457–7460.

[551] M. A. Henderson, C. H. Heathcock, *J. Org. Chem.* **1988**, *53*, 4736–4745.

[552] T. Fujisawa, E. Maehata, H. Kohama, T. Sato, *Chem. Lett.* **1985**, 1457–1458.

[553] J. J. Chilot, A. Doutheau, J. Gore, *Bull. Soc. Chim. Fr.* **1984**, 307–316.

[554] Y. Hanzawa, K. Kawagoe, A. Yamada, Y. Kobayashi, *Tetrahedron Lett.* **1985**, *26*, 219–222.

[555] T. Hudlicky, L. D. Kwart, M. H. Tiedje, B. C. Ranu, R. P. Short, J. O. Frazier, H. L. Rigby, *Synthesis* **1986**, 716–727.

[556] S. Pyo, J. F. Skowron, III, J. K. Cha, *Tetrahedron Lett.* **1992**, *33*, 4703–4706.

[557] A. Srikrishna, S. Nagaraju, P. Kondaiah, *Tetrahedron* **1995**, *51*, 1809–1816.

[558] G. Lai, W. K. Anderson, *Synth. Commun.* **1995**, *25*, 4087–4091.

[559] A. L. Castelhano, S. Horne, G. J. Taylor, R. Billedeau, A. Krantz, *Tetrahedron* **1988**, *44*, 5451–5166.

[560] J. E. Baldwin, J. A. Walker, *J. Chem. Soc., Chem. Commun.* **1973**, 117–118.

[561] B. Bowden, R. C. Cookson, H. A. Davis, *J. Chem. Soc., Perkin Trans. 1* **1973**, 2634–2637.

[562] P. D. Landor, S. R. Landor, *J. Chem. Soc.* **1956**, 1015–1019.

[563] G. Saucy, R. Marbet, H. Lindlar, O. Isler, *Helv. Chim. Acta* **1959**, *42*, 1945–1955.

[564] M. Julia, S. Julia, B. Stalla-Bourdillou, C. Descoins, *Bull. Soc. Chim. Fr.* **1964**, 2533–2541.

[565] M. Apparu, R. Glenat, *C. R. Hebd. Seances Acad. Sci. Ser. C* **1967**, *265*, 400–402.

[566] H. Schlossarczyk, W. Sieber, M. Hesse, H. J. Hansen, H. Schmid, *Helv. Chim. Acta* **1973**, *56*, 875–944.

[567] K. H. Schulte-Elte, H. Strickler, F. Gautschi, W. Pickenhagen, M. Gadola, J. Limacher, B. L. Müller, F. Wuffli, G. Ohloff, *Liebigs Ann. Chem.* **1975**, 484–508.

[568] D. G. Oelberg, M. D. Schiavelli, *J. Org. Chem.* **1977**, *42*, 1804–1806.

[569] R. C. Cookson, M. C. Cramp, P. J. Parsons, *J. Chem. Soc., Chem. Commun.* **1980**, 197–198.

[570] R. E. Banks, A. J. Miller, J. M. Nunn, P. Stanley, T. J. R. Weakley, Z. Ullah, *J. Chem. Soc., Perkin Trans. 1* **1981**, 1096–1102.

[571] D. M. Hollinshead, S. C. Howell, S. V. Ley, M. Mahon, N. M. Ratcliffe, P. A. Worthington, *J. Chem. Soc., Perkin Trans. 1* **1983**, 1579–1589.

[572] A. K. Chopra, B. P. S. Khambay, H. Madden,G. P. Moss, B. C. L. Weedon, *J. Chem. Res. (M)* **1989**, 1612–1631.

[573] K. Miki, K. Ohe, S. Uemura, *Tetrahedron Lett.* **2003**, *44*, 2019–2022.

[574] L. E. Overman, C. K. Marlowe, L. A. Clizbe, *Tetrahedron Lett.* **1979**, 599–600.

[575] L. E. Overman, L. A. Clizbe, R. L. Freerks, C. K. Marlowe, *J. Am. Chem. Soc.* **1981**, *103*, 2807–2815.

[576] A. Padwa, L. A. Cohen, *J. Org. Chem.* **1984**, *49*, 399–406.

[577] K. Banert, S. Groth, *Angew. Chem.* **1992**, *104*, 865–867; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 866–868.

[578] D. Ranganathan, R. Rathi, K. Kesavan, W. P. Singh, *Tetrahedron* **1986**, *42*, 4873–4878.

[579] D. K. Bates, M. Xia, M. Aho, H. Mueller, R. R. Raghavan, *Heterocycles* **1999**, *51*, 475–480.

[580] K. Banert, S. Groth, H. Hückstädt, J. Lehmann, J. Schlott, K. Vrobel, *Synthesis* **2002**, 1423–1433.

[581] K. Banert, M. Hagedorn, A. Müller, *Eur. J. Org. Chem.* **2001**, 1089–1103.

[582] K. Banert, *Liebigs Ann./Recl.* **1997**, 2005–2018.

[583] K. Banert, C. Toth, *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1627–1629.

[584] K. Banert, M. Hagedorn, *Angew. Chem.* **1989**, *101*, 1710–1711; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1675–1676.

[585] R. Gericke, I. Lues, *Tetrahedron Lett.* **1992**, *33*, 1871–1874.

[586] K. H. Schulte-Elte, G. Ohloff, *Helv. Chim. Acta* **1971**, *45*, 370–397.

[587] H. Heimgartner, L. Ulrich, H.-J. Hansen, H. Schmid, *Helv. Chim. Acta* **1971**, *54*, 2313–2354.

[588] W. Sieber, *Helv. Chim. Acta* **1972**, *55*, 3005–3026.

[589] H. Heimgartner, J. Zsindely, H.-J. Hansen, H. Schmid, *Helv. Chim. Acta* **1973**, *56*, 2924–2945.

[590] P. Courtot, R. Rumin, *Tetrahedron* **1976**, *32*, 441–446.

[591] J. Oren, B. Fuchs, *J. Am. Chem. Soc.* **1986**, *108*, 4881–4887.

[592] K. Ebata, T. Matsuo, T. Inoue, Y. Otsuka, C. Kabuto, A. Sekiguchi, H. Sakurai, *Chem. Lett.* **1996**, 1053–1054.

[593] E. S. Johnson, G. J. Balaich, I. P. Rothwell, *J. Am. Chem. Soc.* **1997**, *119*, 7685–7693.

[594] M. Abe, W. Adam, W. M. Nau, *J. Am. Chem. Soc.* **1998**, *120*, 11304–11310.

[595] S. Delbaere, G. Vermeersch, *Tetrahedron Lett.* **2003**, *44*, 259–262.

[596] A. Viola, J. J. Collins, *J. Chem. Soc., Chem. Commun.* **1980**, 1247–1248.

[597] H. Hopf, R. Kirsch, *Angew. Chem.* **1985**, *97*, 796–797; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 783–784.

[598] F. T. Bond, *J. Org. Chem.* **1966**, *31*, 3057–3058.

[599] J. E. Ezcurra, C. Pham, H. W. Moore, *J. Org. Chem.* **1992**, *57*, 4787–4789.

[600] E. Gil-Av, J. Herling, *Tetrahedron Lett.* **1967**, 1–4.

[601] D. J. Pasto, W. Kong, *J. Org. Chem.* **1989**, *54*, 4028–4033.

[602] M. Regitz, *Bull. Soc. Chim. Belg.* **1992**, *101*, 359–380.

[603] W. Klop, L. Brandsma, *J. Chem. Soc., Chem. Commun.* **1983**, 988–989.

[604] W. Huang, D. Fang, K. Temple, T. T. Tidwell, *J. Am. Chem. Soc.* **1997**, *119*, 2832–2838.

[605] W. Huang, T. T. Tidwell, *Synthesis* **2000**, 457–470.

[606] C. Auge, S. David, A. Lubineau, *J. Chem. Soc., Chem. Commun.* **1980**, 568–569.

[607] M. Oesterich, D. Hoppe, *Tetrahedron Lett.* **1999**, *40*, 1881–1884.

[608] C. Kuroda, Y. Kimura, H. Nogami, *J. Chem. Res. (M)* **1998**, 822–843.

[609] F. Wendling, M. Miesch, *Org. Lett.* **2001**, 2689–2692.

[610] E. Yoshikawa, M. Kasahara, N. Asao, Y. Yamamoto, *Tetrahedron Lett.* **2000**, *41*, 4499–4502.

[611] T.-K. Yang, S.-M. Hung, D.-S. Lee, A.-W. Hong, C.-C. Cheng, *Tetrahedron Lett.* **1989**, *30*, 4973–4976.

[612] T. Kitagawa, J. Kamada, S. Minegishi, K. Takeuchi, *Org. Lett.* **2000**, *2*, 3011–3013.