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Benzeneselenenyl Reagents in Organic Synthesis

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Abstract. An account of the most commonly used reagents for the introduction of the benzeneselenenyl (phenyl seleno) group is given. The review focuses on the various methods of its introduction as auxiliary, modifying or protective entity, and its subsequent removal, thereby often promoting other reactions as cyclizations or double bond formation. Less emphasis is laid on reactions of the phenylselenenylated intermediates with the PhSe-group left intact utilizing its stabilizing properties on charged intermediates, on reagents with a modified phenyl group, *e.g.* chiral derivatives, or on reactions not involving intermediate C–Se-bond formation.

Contents

The interim introduction of chemical entities (groups) during a complex synthesis is one of the most common principles to achieve otherwise cumbersome or impossible transformations. These entities may be devided in two categories: protective groups, which ideally render certain parts of the molecule inreactive but will not alter reactivity otherwise, and auxiliary groups which alter reactivity or selectivity. Examples of the latter category include chiral auxiliaries, umpolung strategies, or the classical alkoxycarbonyl auxiliary, *e.g.* utilizing a malonate as an acetate equivalent.

One of the most versatile groups used for auxiliary purposes is the benzeneselenenyl (phenylseleno) group (**1**) [1–6]. It can be considered *the* chemical *chameleon* – even more than the corresponding sulfur analog. In contrast to the similar sulfur derivatives with their identical variety of oxidation states, the weaker C–Se-bond (234 kJ mol^{-1}) [6], and the higher polarizability, nucleophilicity and oxidizability of selenium make the benzeneselenenyl group more useful. It may be introduced by nucleophilic, electrophilic, and – less often – by radical processes. The corresponding selenides then enable the generation, stabilization and reaction of α-

carbanions, α-radicals, and α- (and β-) carbocations. The benzeneselenenyl group can be removed by nucleophilic, electrophilic, radical, oxidative and reductive methods, thereby – if desired – generating a carbanion, radical or carbocation at its former position for further reactions. It can be used for the 'Umpolung' of functional groups, but may even become 'umgepolt' itself, *e.g.* by oxidation to a selenone. In addition its (rather limited) use as a protective group has also been reported (*vide infra*).

However, the "known toxicity of organoselenium compounds called for caution and their malodorous reputation made them double unattractive to any chemist who wanted a social life outside the laboratory" [5]. But since the development of the very facile β-*syn*-elimination of phenyl selenoxides as a reaction to generate unsaturated compounds [7, 8] the number of applications of the phenyl seleno group and substituted derivatives rised immense. More recently catalytic methods for benzene selenenyl reactions where developed which can reduce the danger of intoxication [9, 10]. However, their applicability is rather limited yet.

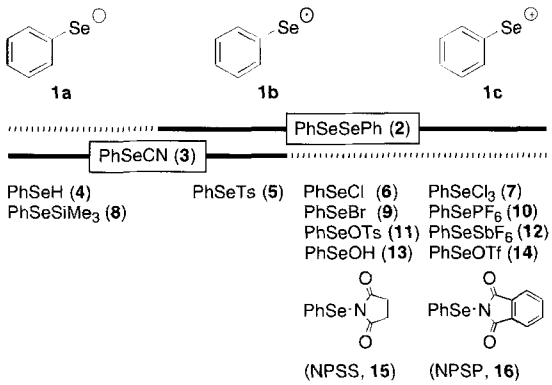
In the following we will discuss the most common reagents for the introduction of the benzeneselenenyl group and their application, followed by a very brief survey of possible transformations of the phenylselenides formed, including the removal of this auxiliary group.

Reagents [1] [11]

Most reagents for the introduction of a benzeneselenenyl group (scheme 1) are either commercially available or very easy to synthesize. The basic reagents, from which most others are obtained, are diphenyl diselenide (**2**) and phenyl selenocyanate (benzeneselenenyl cyanide, **3**). These and the resulting reagents can be devided in two main groups: electrophilic reagents, *i.e.* those attacked by (carbon) nucleophiles at selenium, and nucleophilic reagents. Benzeneselenenyl radicals are of less importance and are usually derived from the electrophilic reagents in the usual manner (hν or radical transfer reactions).

Electrophilic Benzeneselenenyl Reagents

Diphenyl diselenide (**2**) is the central reagent. Its facile preparation is well documented [12]. It can be stored indefinitely and is purified easily, the latter being a very important factor, since the benzeneselenenyl group after its removal is usually recovered in this form. Diselenide **2** is readily converted to other reagents (*vide infra*). It can be prepared by reaction of phenyl magnesium bromide or phenyllithium with elemental selenium and *in situ* oxidation of the resulting magnesium phenylselenolate[12]. Sufficiently reactive nucleophiles, *e.g.* alkyllithium reagents cleave diphenyl diselenide (**2**) but the benzeneselenenyl halides (**6**, **7**, **9**) are much better sources of electrophilic selenium [13].



Scheme 1 Benzeneselenenyl transfer reagents

Probably the most easily prepared halide is benzeneselenenyl bromide (**9**) which is obtained in nearly quantitative yield by the reaction of bromine with diphenyldiselenide (**2**) in tetrahydrofurane [14] or with phenylseleno cyanate (**3**) [15]. Benzeneselenenyl chloride (**6**) is the most frequently used reagent. It can be synthesized by treating diphenyl diselenide (**2**) with chlorine in hexane [12, 14] or with an equimolar amount of sulfuryl chloride [16, 17].

The more reactive phenylselenium trichloride (**7**) is prepared by chlorination of either selenophenol (**4**), diphenyl diselenide (**2**), or benzeneselenenyl chloride (**6**) with 2 – 3 equiv. sulfuryl chloride. It is used without purification for further manipulations[18, 19]. Oxidation of diphenyl diselenide (**2**) with iodine in acetonitrile produces a reagent which is presumed to be "benzeneselenenyl iodide" [20]. It shows the same type of reactions as the other benzeneselenenyl halides but has a much higher reactivity towards *e.g.* alkenes [20]. The comproportionation reaction of phenylseleninic acid with diphenyl diselenide (**2**) leads to phenylselenenic acid "PhSeOH" (**13**) [21].

Electrophilic reagents with non-nucleophilic counter ions include benzeneselenenyl hexafluorophosphate (**10**)[22], -hexafluoroantimonate (**12**) [22], -tolylsul-

[1] *Warning*: Organoselenium compounds are usually toxic and have an unpleasant smell, which is ,however, less dramatic than that of the corresponding sulfur compounds. Though the risks are reduced by using the less volatile phenyl selenium compounds, care should be taken and a well working fume hood should be used at all times. It is advisable to recycle the phenyl selenium compounds by redox reaction to diphenyl diselenide (**2**) which is easily separated in pure form as a yellow very unpolar fraction by column chromatography.

fonate (**11**)[23], or -triflate (**14**) [24–26] which are usually prepared *in situ* from the silver salts [9]. *N*-Phenylseleno phthalimide (NPSP, **16**) and *N*-phenylseleno succinimide (NPSS, **15**) [27, 28] are either obtained by reaction of benzeneselenenyl halides with the imide anion [27, 29] or by the reversed pathway with benzene selenolate (**1a**) and the *N*-chloro imide [30]. *In situ* oxidation of diphenyl diselenide (**2**) with ammonium peroxydisulfate also generates electrophilic phenylselenium [9]. Benzene selenenyl cation (**1c**) may also be generated by single electron transfer (SET) from diphenyl diselenide (**2**) to 1,4-dicyanonaphtalene (DCN) [31, 32].

Nucleophilic Benzeneselenenyl Reagents

Benzeneselenolate (selenophenolate, **1a**) and selenophenol (**4**) can be generated directly from a phenyl metal compound (phenyl lithium or phenyl Grignard) and elemental selenium. Cleaner reagent, however, is obtained by reduction of either diphenyl diselenide (**2**) [8] or phenyl selenocyanate (**3**) [33, 34] with sodium borohydride in alcohol. The nucleophilicity of the formed anion is decreased due to complexation with borane [35]. Increased reactivity is observed if diphenyl diselenide (**2**) is reduced with lithium aluminium hydride in dioxane [36, 37]. Uncomplexed benzene selenolate (**1a**), which in some cases exhibits higher reactivity, is generated by the reduction of diphenyl diselenide (**2**) with sodium hydride [38], sodium metal [35, 39], rongalite (sodium formaldehyde sulfoxylate) [40], under phase-transfer conditions (50% NaOH, dichloromethane, triethylbenzylammonium chloride) [41] or electrochemically [42].

Benzeneselenolate (**1a**) is one of the most reactive soft nucleophiles and therefore very easily introduced into organic compounds through S_N2–type displacements or Michael type additions. It reacts with methyl iodide in methanol at room temperature seven times faster than the thiophenolate anion [43]. Trimethylsilyl phenyl selenide (**8**) is generated from benzene-selenolate (**1a**) and chlorotrimethylsilane [44].

Phenylselenocyanate (**3**) probably is the second most important basic starting material. It is synthesized by diazotation of aniline followed by treatment with sodium selenocyanate in a buffer solution containing sodium acetate [15, 45] or by reaction of benzeneselenenyl chloride (**6**) with cyanotrimethylsilane. It can be used as a (masked) nucleophilic reagent in conjunction with trialkylphosphines (*vide infra*) [46].

Benzeneselenenyl Radical Precursors

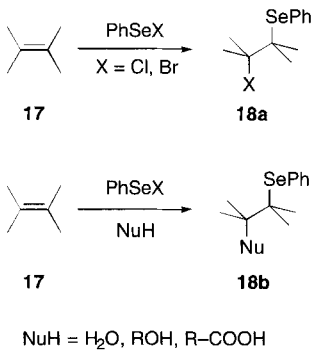
The sulfur–selenium bond of phenyl *p*-tolyl-selenosulfonate (**5**) is cleaved photolytically and a tolyl sulfonyl radical and the phenyl seleno radical (**1b**) are formed [47–49]. The latter can also be generated by photolysis or thermolysis of diphenyl diselenide (**2**) [50].

Introduction of the Phenylseleno Group

Electrophilic Reactions

Addition to Double Bonds, Selenocyclizations

The haloselenenylation of alkenes **17** with benzeneselenenyl bromide (**9**) [51] or benzeneselenenyl chloride (**6**) [17, 52–54] in aprotic solvents provides the haloselenenylation products **18a** (scheme 2). The addition proceeds exclusively in *trans*-manner due to the intervention of a selenium bridged cation (seleniranium ion) as a reaction intermediate. The ratio of *syn*-Markovnikov- *vs.* *anti*-Markovnikov-adduct can be controlled by the reaction conditions: The first are formed under thermodynamic, the latter under kinetic control [55, 56]. The overall rate law is second order; first order in both, alkene and benzeneselenenyl reagent [17]. If the reaction is carried out in alcohols, carboxylic acids or in the presence of 2–3 equiv. of water the corresponding oxyselenenylated products **18b** are obtained in high yields [51, 57–63].

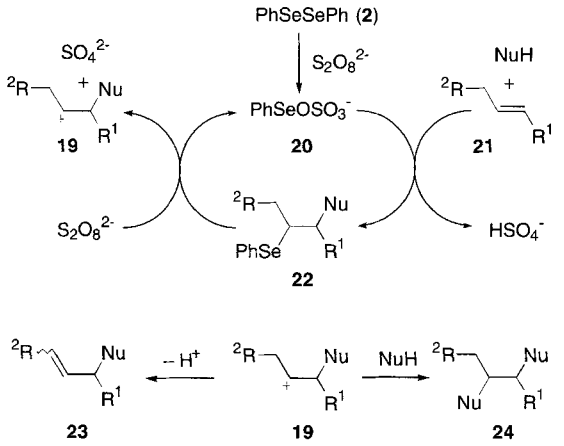


Scheme 2 Selenenylation of alkenes

Other benzeneselenenyl reagents like *N*-phenylseleno phthalimide (**16**) [27, 64] and *N,N*-dialkyl benzeneselenenyl amides [29] and other nucleophiles (NuH) react in a similar manner.

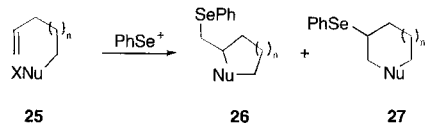
Only a catalytic amount of diphenyl diselenide (**2**) is required if the electrophilic benzene selenium species is regenerated by the reaction with ammonium peroxydisulfate (scheme 3) [9, 10]. The proposed active agent is benzeneselenenyl sulfate (**20**).

Cyclic systems (**26**, **27**) are generated if the intermediate seleniranium ion obtained from addition to alkene **25** is opened by an intramolecular nucleophile (scheme 4). Such selenocyclizations exhibit a high degree of stereo- and regioselectivity. The method has been used to synthesize lactones, cyclic ethers and thioethers, nitrogen heterocycles and carbocycles [65].



Scheme 3 Selective nucleophile addition to double bonds *via* catalytic benzeneselenenylation

Cyclization occurs at the carbon center which is most suitable to sustain a carbenium ion, but subsequent rearrangements are possible. Preferred *trans* stereochemistry of the additon was verified by X-ray analysis[65].

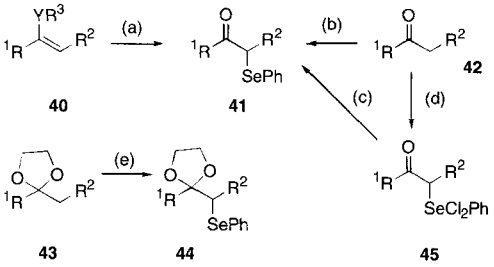


NuX = COOH, OH, SH, SAc, NHCOOEt, C=C

Scheme 4 Selenocyclization (Principle)

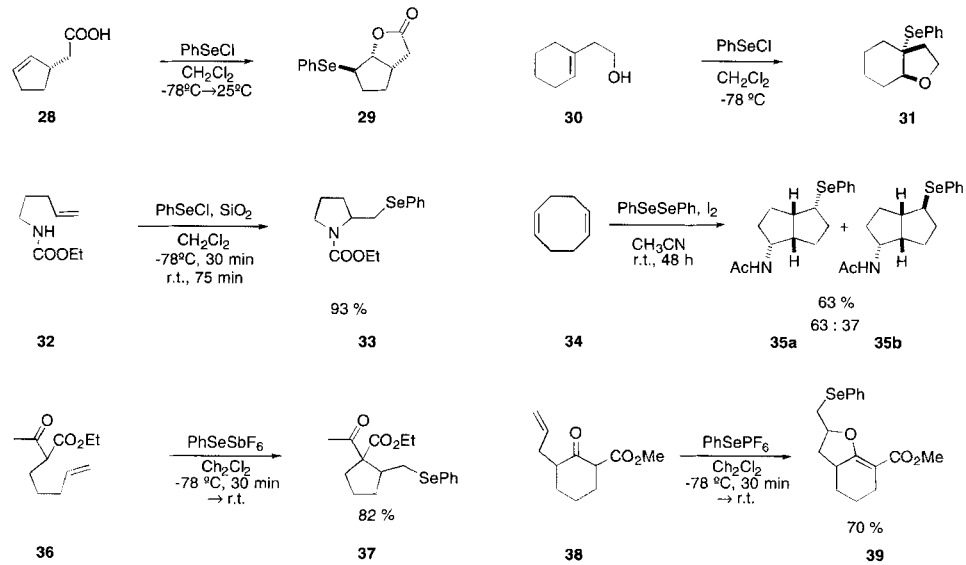
The formation of lactones from ω-unsaturated carboxylic acids (**25**, NuX = COOH; **28**) can be achieved with benzeneselenenyl chloride (**6**) at –78 °C in methylene chloride or ethyl acetate as solvent [66]. In some cases base has to be added [67]. Other reagents which have been used in phenyl selenolactonizations are *N*-phenylselenophthalimide (**16**) [27], benzeneselenenyl triflate (**14**) [25] or electrochemically generated "PhSe$^+$"-cation **1c** [68]. A variety of examples is presented in scheme 5. For the preparation of individual classes of cyclic compounds eg. lactones (**28** → **29**), ethers (**30** → **31**, **38** → **39**), amines (**32** → **33**) and carbocycles (**34** → **35**, **36** → **37**) see ref. [69].

α–Phenylseleno Carbonyl Compounds



Scheme 6 Formation of α–phenylseleno carbonyl compounds and -acetals[(a) PhSeX (b) Lewis acid catalysis, PhSeX, (c) thiourea, (d) $PhSeCl_3$ // (e) PhSeCl//X, Y, R: see text]

Most commonly, electrophilic benzeneselenenyl transfer reagents are used in the α-benzeneselenenylation of carbonyl compounds to form α-phenylseleno carbonyl compounds **41** (scheme 6). Almost all methods require enol derivatives **40** such as enol ethers (YR^3 = OR) [70, 71], silyl enol ethers (YR^3 = $OSiMe_3$) [72], enol acetates (YR^3 = O_2CCH_3) [14, 73], enamines (YR^3 = NR_2) [74], or lithium enolates (YR^3 = OLi) [14, 75, 76] as nucleophiles. The direct formation of the α-



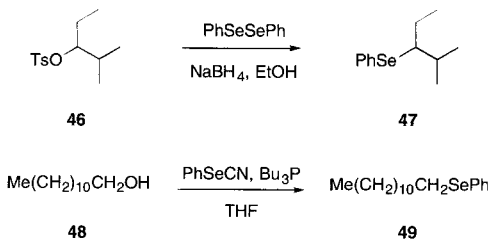
Scheme 5 Selenocyclizations (Examples)

phenylseleno derivatives **41** from carbonyl compounds **42** can be accomplished by reaction with benzene-selenenyl chloride (**6**) in ethyl acetate at room temperature [16] or by electrophilic phenylselenium (**1c**) generated from diphenyl diselenide (**2**) *in situ* either by SeO_2-oxidation [77] or electrochemically [78]. The reaction of aldehydes (**41**, R^1=H) with benzeneselenenyl chloride (**6**) requires heat or acid catalysis [79, 80]. Aldehydes (**41**, R^1=H) also can be α-phenylselenenylated with the rather unstable morpholino benzeneselenenyl amines [81–83] or benzeneselenenyl dimethylamine [84]. The direct transformation of acetals **43** to α-phenylselenoacetals **44** can be achieved by reaction with benzeneselenenyl chloride (**6**) in dichloromethane [70]. A very simple, recently developed method is the reaction of either aldehydes or ketones with phenylselenium trichloride (**7**) in acetonitrile at room temperature [18, 19]. The primarily formed dichloro adduct **45** is reduced *in situ* with thiourea to yield the desired α-phenylseleno carbonyl compound **41**.

Nucleophilic Reactions

Alkylselenides, S_N2–Cleavage of Esters

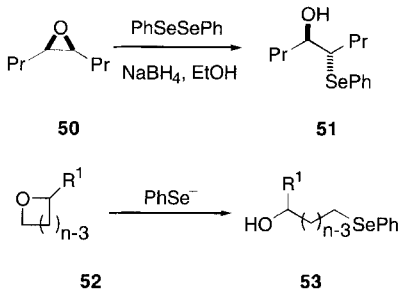
Simple organic selenides are obtained from an alcoholic solution of the benzenselenolate anion (**1a**) by addition of alkyl or benzyl halides [39, 41, 45, 85–88] or alkyl tosylates (cf. scheme 7, **46** → **47**) [39, 40, 89–91].



Scheme 7 Preparation of Alkyl phenylselenides

Primary and secondary alcohols **48** can be converted directly to alkyl selenides with phenylselenocyanate (**3**) [34, 90] or *N*-phenylselenophthalimide (**16**) [92] in the presence of tributylphosphine (scheme 7, **48** → **49**). Another direct conversion of alcohols to the corresponding phenyl selenides utilizes benzeneselenol (**4**) in the presence of zinc chloride [93].

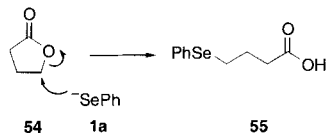
The use of epoxides (**50**) as electrophiles leads to β-hydroxy alkylselenides (**51**) [8, 40, 94]. Larger cyclic ethers can be cleaved with selenide obtained from the reduction of diphenyl diselenide (**2**) with lithium aluminium hydride in dioxane (scheme 8). Subsequent addition of oxetanes (**52**, n = 4) gives γ–phenyl selenenyl alcohols (**53**, n =4). Increased reaction temperature



Scheme 8 Ringopening of cyclic ethers with phenylselenide anion

and time allows cleavage of tetrahydrofuranes (**52**, n = 5) to δ-phenyl selenenyl alcohols (**53**, n = 5). The similar reaction of a cyclic acetal gave an acyclic monoseleno acetal as the sole product [36, 37].

Table 1 "Anomalous" nucleophilic cleavage of lactone **54**: carboxylate as leaving group.

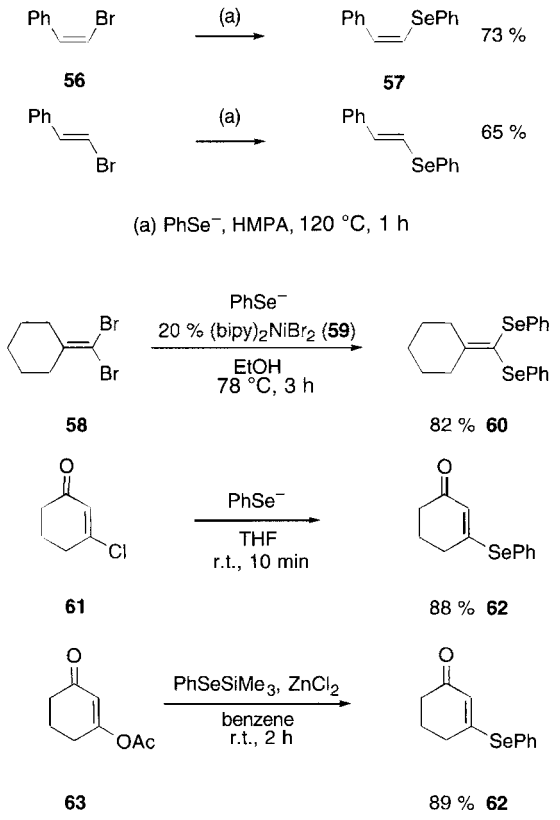


Conditions	Yield of **55**
$(PhSe)_2$, $NaBH_4$, THF/EtOH	0 %
$(PhSe)_2$, Na°, THF/HMPA	85 %
PhSeH, NaH, THF/HMPA	85 %

Since the benzene selenolate anion (**1a**) is a very potent nucleophile [43], it can be used for the "atypical" nucleophilic cleavage of esters and lactones (table 1, **54** → **55**). As a soft nucleophile it shows preference for the attack at the alkoxy carbon (soft–soft interaction) rather than at the carbonyl carbon atom (soft–hard interaction) of an ester. For the S_N2-type cleavage of esters or lactones uncomplexed benzene selenolate anion (**1a**) is required [95, 96]. It can be generated by the reduction of diphenyl diselenide (**2**) with sodium hydride [38] or sodium metal [35, 39]. The decreased nucleophilicity of benzene selenolate (**1a**) complexed with Lewis acid, *e.g.* generated by the method of Sharpless (Ethanol, $NaBH_4$) [8, 16], makes it inert for the reaction with esters.

Alkenylselenides

Benzene selenolate (**1a**) reacts with vinyl halides **56** (scheme 9) to give phenyl vinyl selenides **57** with retention of the configuration [85]. In the presence of nickel(II) catalyst **59** even less reactive vinyl halides react and α,α-dihaloalkenes like **58** can be transformed to the diphenylseleno keteneacetals **60** [97].



Scheme 9 Preparation of vinyl selenides *via* nucleophilic processes

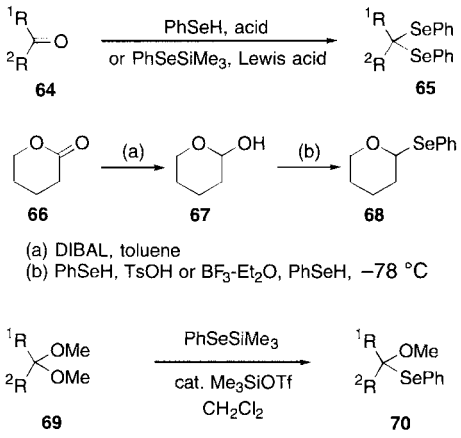
Treatment of β-halo-α,β-unsaturated ketones like **61** with benzene selenolate (**1a**) gives β-phenylseleno enones, *e.g.* **62** [98], which can also be prepared by reaction of trimethylsilyl phenyl selenide (**8**) with enol acetates of 1,3-diketones **63** under Lewis acid catalysis [99].

Reactions at Carbonyl Groups and Michael Additions

Selenoacetals **65** (scheme 10) can be obtained from diphenyl diselenide (**2**) with diazoalkanes [100] and from the reaction of benzene selenolate (**1a**) with diiodomethane or with carbonyl compounds **64** under Lewis acid catalysis (usually with zinc chloride) [100].

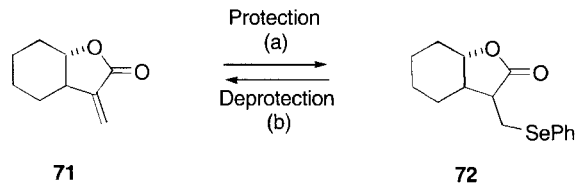
The reaction of trimethylsilyl phenyl selenide (**8**) with carbonyl compounds under $AlCl_3$-catalysis is carried out under mild conditions forming the desired selenoacetals **65** in up to 90% yield [100]. α-Phenylseleno ethers (**68** and **70**) are obtained either by replacing the anomeric oxygen substituent in hemiacetals like compound **67** [101] or by reaction of dimethyl acetals (**69**) with trimethylsilyl phenyl selenide (**8**) [102].

The benzene selenolate anion (**1a**) also undergoes conjugate addition to α,β-unsaturated carbonyl compounds, *e.g.* to methylene lactone **71** to give selenide **72** (scheme 11) [103]. Due to the facile and perfectly regioselective oxidative β-phenylselenoxide elimination

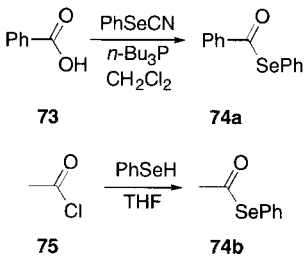


Scheme 10 Formation of phenylseleno (hemi) acetals

the unsaturation is easily regenerated by oxidizing reagents. Thus the benzeneselenenyl group can be used to protect labile Michael systems. Electrochemically formed benzene selenolate anions (**1a**) also add to unsaturated esters and ketones in conjugate fashion [42].



Scheme 11 Protection of Michael substrates and oxidative β-deselenenylation of carbonyl compounds [(a) PhSeSePh, $NaBH_4$, THF (b) H_2O_2, cat. AcOH, THF]



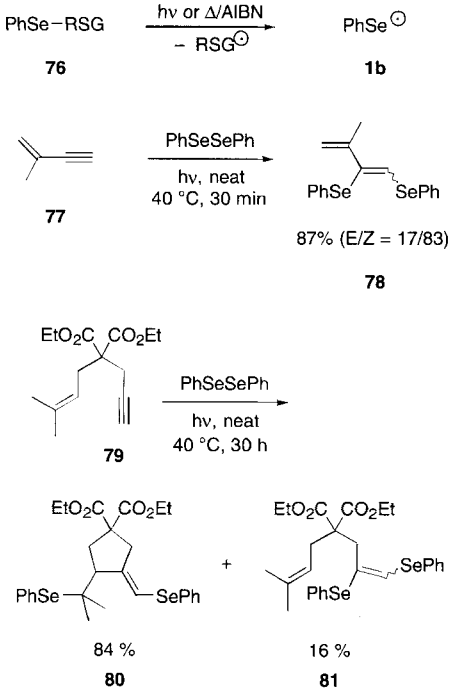
Scheme 12 Syntheses of selenoesters

Selenoesters (*e.g.* **74**, scheme 12) are useful precursors for acyl radicals (v. i.). They are obtained by the reaction of carboxylic acids **73** with phenylseleno cyanate (**3**) in the presence of tributylphosphine [92, 104–106]. Acyl halides **75** readily react with benzeneselenol (**4**) to give the corresponding selenoesters **74** [107].

Benzeneselenenyl Radical Additions

Benzeneselenenyl radicals (**1b**, scheme 13) are generated by photolysis or thermolysis in the presence of an

initiator from precursors **76**, most commonly diphenyl diselenide (**2**) [50] or phenylseleno sulfonates **5** [49]. They add in 1,2-manner to olefins [108], allenes [109], and acetylenes (*e.g.* **77**) [110–112], the latter preferentially resulting in the *Z*-1,2-diselenenylalkenes (cf. **78**). Acetylenes with a tethered carbon–carbon double bond at a suitable distance for radical cyclizations lead to carbocycles, preferentially cyclopentane derivatives, such as **80**, obtained from enyne **79** [113, 114]. The addition of benzene selenol (**4**) to acetylenes is considered to proceed *via* a radical mechanism, too [113, 115].

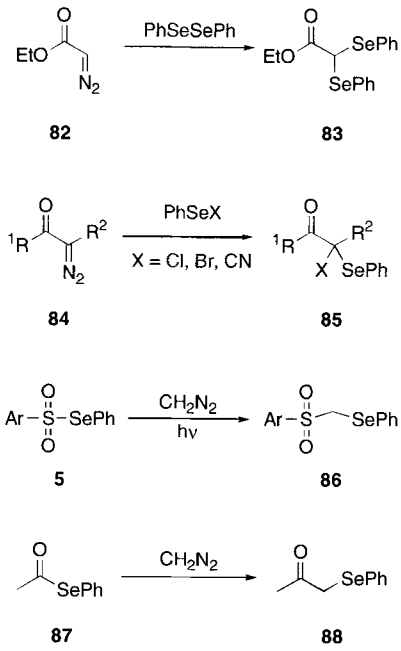


Scheme 13 Generation and addition reactions of phenylselenenyl radicals (RSG = radical stabilizing group, *e.g.* benzeneselenenyl, tosyl)

Carbene Type Reactions

Diazo compounds undergo insertion reactions into Se–Se- (**82** → **83**; scheme 14) [116, 117], Se–X- (X = Cl, Br; **84** → **85**)[118–124], Se–SO_2Ar- (**5** → **86**) [48] and Se–C-bonds (**87** → **88**) [125].

The majority of these processes occur *via* ionic mechanisms [125] although a free radical mechanism [48] is proposed for the reaction of phenylselenosulphonate (**5**). Diazoacetate insertions into alkyl selenides catalyzed by asymmetric rhodium or copper complexes have been reported as well [126].

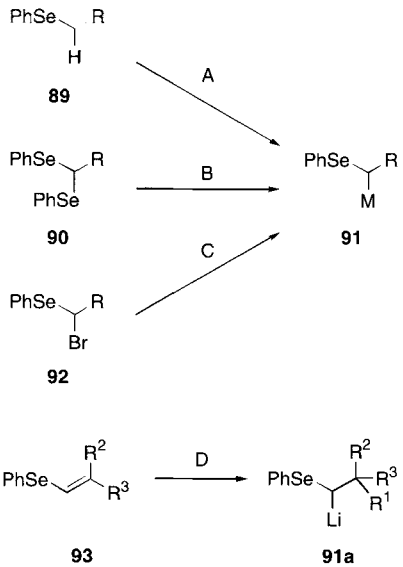


Scheme 14 Insertion of diazo compounds into Se–X bonds

Generation of α-Phenylselenium Stabilized Reactive Intermediates

α-Phenylseleno Carbanions

α-Phenylseleno carbanions [127] are stabilized by the overlap of non-occupied *4d*°-orbitals of selenium with the sp^3-orbital of the α-carbon atom carrying the negative charge.



Scheme 15 Preparation of α-phenylseleno carbanions (Method A: Deprotonation; B: Se/Li-Exchange; C: Halogen/Metal-Exchange; D: Alkyllithium addition)

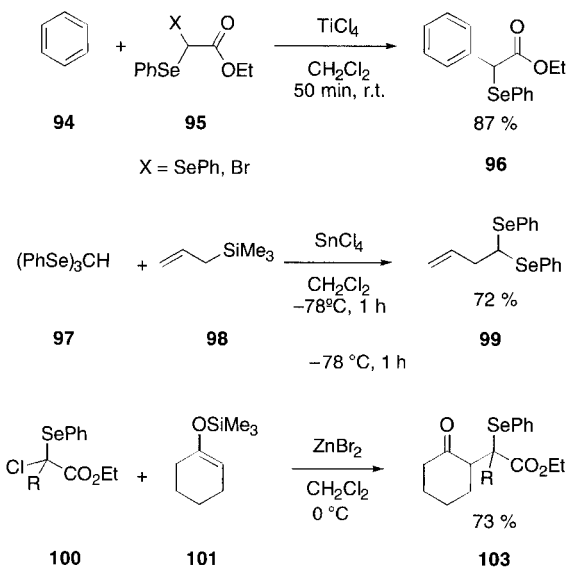
α-Phenylseleno "carbanions" can be generated from selenoacetals **90** by selenium lithium exchange resulting in the formation of the corresponding α-lithiated phenyl seleno compounds (**91**, M = Li, Method B) [40, 128–136] or by deprotonation of phenyl selenides **89**

or phenyl selenoxides with sodium or lithium diisopropylamide (Method A) [86, 137–145]. A new method utilizes halogen metal exchange from the readily available α-halo selenides **92** (see *e.g.* **84** → **85**) under Reformatsky-conditions (Method C) [146] or the additon of alkyllithium compounds to vinyl selenides **93** (Method D) [147, 148].

α-Phenylseleno alkyllithium compounds **91** (M = Li) are configurationally labile and undergo fast racemization [149, 150]. The Grignard reagents **91** (M = MgBr) obtained by transmetallation with magnesium bromide exhibit a higher configurational stability [151]. Diastereomeric complexes are formed with chiral diamines as ligands. The diastereomeric ratio could be determined by ^{77}Se NMR [152, 153].

α-Phenylseleno Carbocations

Selenium stabilizes α-carbenium ions [154, 155] even in the presence of otherwise destabilizing groups. The carbocations can be generated by Lewis acid assisted abstraction of an α-halogenide or another α-phenylselenide (scheme 16), *e.g.* from the easily available α-halo-α-benzeneselenenyl fatty acid esters **95** (cf. **85**) [156].



94 **95** **96** **97** **98** **99** **100** **101** **103**

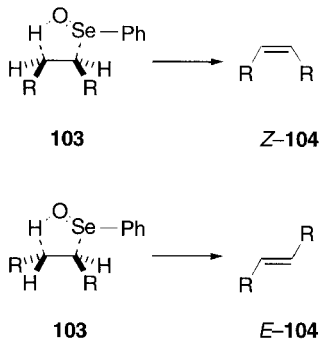
Scheme 16 Generation and reactions of selenium stabilized carbocations

The cations may be used for the reaction with any kind of suitable nucleophile. A variety of reactions is presented in scheme 16. Common carbon nucleophiles include aromatic compounds (Friedels Craft type reactions) like the reaction of benzene (**94**) with selenohaloester **95** to give phenyl acetate **96** (cf. **129** for further transformations) [156], allylsilanes (**97/98** → **99**) [157] or silyl enol ethers which can be converted to functionalized 1,4-diketo compounds (**100/101** → **103**) [154, 158].

Manipulations and Removal of Benzeneselenenyl Groups

Oxidation and Selenoxide Elimination (Double Bond Generation)

Transformation of phenyl selenides into phenyl selenoxides can be achieved by a great variety of oxidants. The resulting phenyl selenoxides **103** undergo facile thermal *syn*-elimination of phenylseleninic acid to give unsaturated compounds **104** which usually have, in noncyclic systems, *trans*-configuration which can be understood as a consequence of steric repulsions in the transition states (cf. scheme 17) [159].

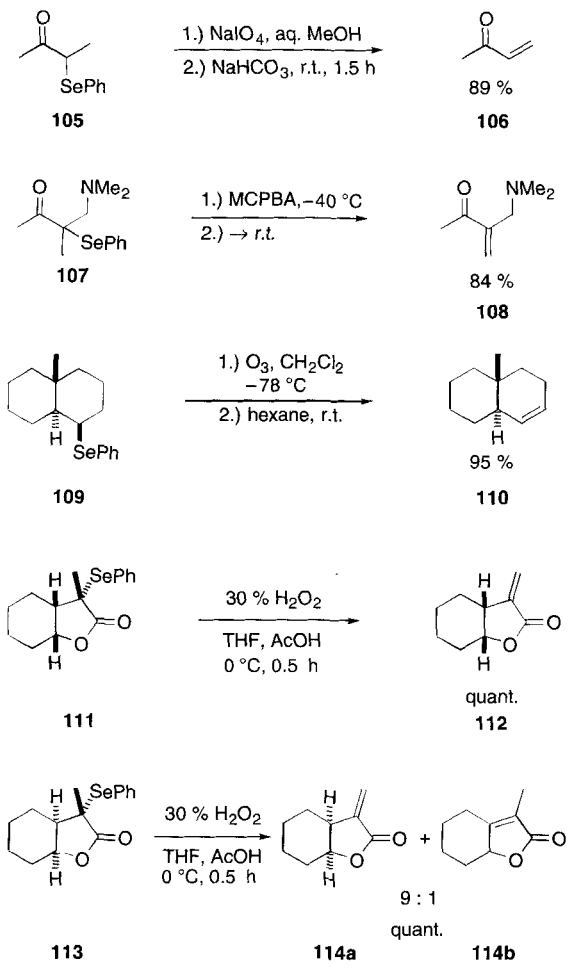


103 *Z*-**104** **103** *E*-**104**

Scheme 17 Diastereoselective alkene formation *via syn* selenoxide elimination

If hydrogens in both, the β and β'–position are available, a regioisomeric mixture of alkenes is formed, in which the least substituted one usually prevails [89]. In cyclic systems the regioselectivity and – if possible – geometry of double bound formation is determined by conformational effects of the ring (cf. scheme 18: **109** → **110**) [75]. In five or six membered rings an endocyclic double bound is formed preferentially (*e.g.* **112** from **111**; **114a** vs. **114b** from **113**) [75]. C-H-Acidic-, allylic- or propargylic protons are more easily removed than benzylic, methyl, methylene, or methine hydrogens, usually in this order [75, 89]. The removal of hydrogen in β-hetero-substituted phenylselenoxides selectively occurs away from the heteroatom to form the corresponding allylic derivatives (*e.g.* **107** → **108**)[6].

Common reagents for the oxidation of phenyl selenides to phenyl selenoxides are sodium periodate (cf. **105** → **106**) [14, 16, 74, 75, 160], peracids (*meta*-chloro perbenzoic acid or peracetic acid) [14, 16, 29, 74, 137], ozone [7, 14, 160], or hydrogen peroxide [51, 89, 137, 160, 161] (scheme 18).



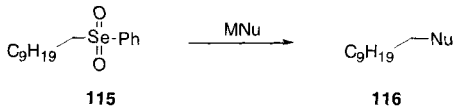
Scheme 18 Regioselectivity in selenoxide eliminations

An excess of oxidizing agent is not required usually [2]), but in case of a sluggish fragmentation reaction it can aid to remove the resulting benzeneselenenic acid (benzeneselenenyl hydroxide, PhSeOH, **13**) by converting it to benzeneseleninic acid (PhSe(O)OH). Possible side reactions of the elimination are the re-addition of the elimination product (PhSeOH) to the freshly formed olefin to give β-hydroxy phenylselenides, or the formation of epoxides with perbenzeneseleninic acid formed by overoxidation of benzeneseleninic acid [6, 162]. To avoid such problems either a slight excess of oxidizing agent in the presence of a base to neutralize the resulting benzenselenic acids may be used [163, 164], or *t*-butyl hydroperoxide on alumina [165, 166]. Better results are sometimes obtained with 2-nitrophenylselenenyl derivatives [16, 51].

Full Oxidation and Phenylselenone Substitution

Phenyl selenones are thermally more stable than phenyl selenoxides and can be prepared by oxidation of the phenyl selenides using up to 5 equivalents of peroxycarboxylic acids[167–169], potassium permanganate [167], hydrogen peroxide in the presence of seleninic acid [170], or potassium hydrogen persulfate [171].

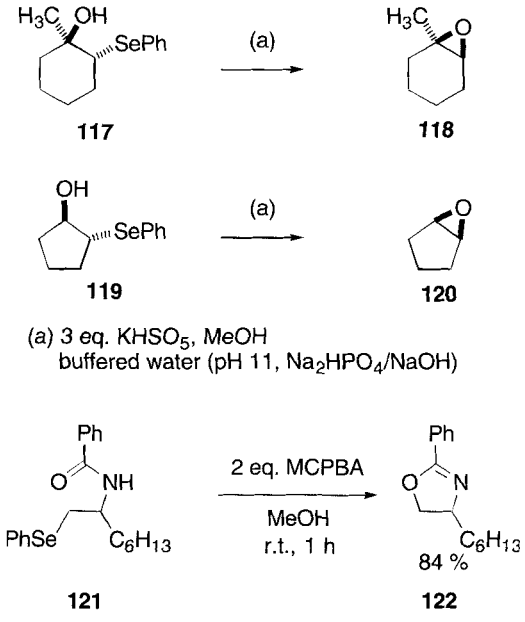
Table 2 Some nucleophilic substitution reactions of decyl-phenyl-selenone



115 116

(eq.)	MNu	Conditions	Yield (%)
2.0	NaI	Acetone, 20 °C, 1 h	97
5.0	NaN_3	DME/H_2O, 20 °C, 0.7 h	93
1.1	PhSNa	EtOH, 20 °C, 0.5 h	94
xs	H_2O	DMF, 80 °C, 1.25 h	95

Phenyl selenones are excellent leaving groups and substitutions can be achieved with all common nucleophiles (table 2) [99, 170, 172–179]. Intramolecular versions of the reaction yield the corresponding (heterocyclic) compounds, *e.g.* epoxides **118** and **120** from **117** and **119** respectively, or – in a less common reaction – 4,5-dihydrooxazol **122** from selenoamide **121** (cf. scheme 19).

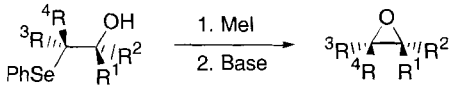


Scheme 19 Heterocycles from intramolecular selenone substitution reactions

[2]) An excess also may result in oxidation to selenones which have a different reactivity.

Selenonium Ion Formation (Ternerization) and Substitution

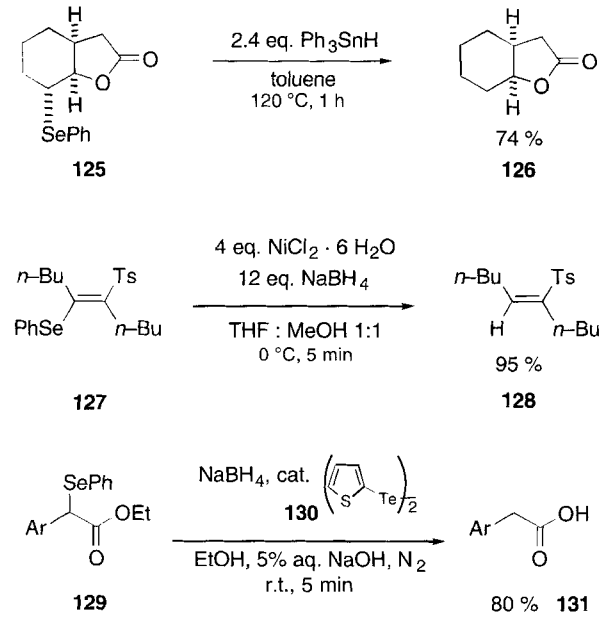
Another possibility to transform the phenyseleno group into a leaving group is the alkylation of phenyl selenides to give selenonium ions [6]. These intermediates are readily availabe from the reaction of selenides with alkylhalides [94, 180, 181], dihalocarbenes [94] or halogens [180, 182, 183]. The ternerization, though, is reversible and can be used for a selenium/iodide exchange. Thus upon heating, alkyl methyl phenylselenonium reagents, which are available by methylation of the parent alkyl phenyl selenides, decompose to alkyl iodides and methylphenyl selenide [1, 180–185].



123 **124**

Scheme 20 Electrophilic epoxide formation *via* a selenonium intermediate

β-Hydroxyalkyl selenonium salts (**123**, scheme 20) react with bases in a stereospecific manner to give the epoxides **124** [186]. Cyclic ethers (ring size n = 4–6) can be synthesized employing the same conditions to *n*-hydroxyalkyl phenylselenides [180]. Phenylseleno glycosides have been activated by oxidation with *N*-iodosuccinimide for the nucleophilic substitution of the seleno moiety [183].



Scheme 21 Some reductive deselenenylation methods

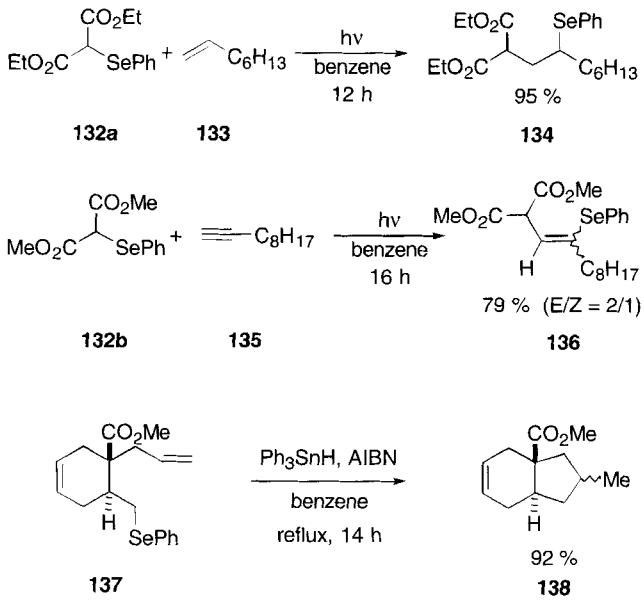
Reductive Removal

Various methods have been employed for the reductive cleavage of phenyl selenides. However, Raney nickel [180, 187–192], lithium in triethylamine [189], or lithium triethyl borohydride [193] can also reduce many other functionalities and therefore are useful only for a relatively constrained range of substrates.

More selective are the methods utilizing triphenyltin hydride (scheme 21, **125** → **126**) [194, 195], which also reduces selenoacetals to the corresponding alkanes, tributyltin hydride [27, 196, 197], or nickel boride (cf. **127** → **128**) [198], which is by far the mildest reagent to remove the phenylseleno substituent. In the presence of catalytic amounts of di(het)aryl dichalcogenides (*e.g.* **130**), or elemental tellurium, sodium borohydride smoothly deselenates α-phenylseleno esters **129** or α-phenylseleno carboxylic esters [199]. The deselenation of esters can be coupled with their hydrolysis if required, which also seems to benefit from the telluride catalysis (cf. arylacetic acid **131**).

Homolytic Cleavage of Phenylselenides (Radical Formation)

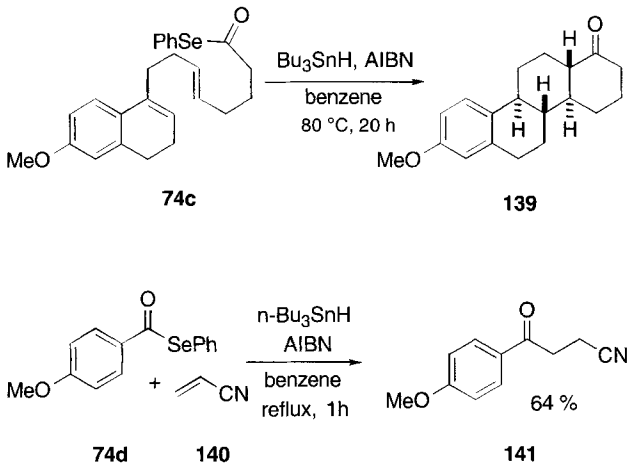
Upon photolysis or when heated with catalytic amounts of AIBN phenyl selenides with radical stabilizing substituents in α-position react to give benzenselenenyl radicals and the corresponding alkyl (scheme 22) or acyl radicals (scheme 23). These can be trapped *in situ* either by intermolecular or intramolecular reaction with alkenes (cf. **132/133** → **134** and **137** → **138**, resp.), alkynes (cf. **132/135** → **136**), enones, functionalized alk-



Scheme 22 Alkyl radical reactions from C–SePh homolytic bond dissociation

enes, *e.g.* enol ethers and enamines, or aldehydes [6, 79, 200–202]. *Anti*-addition is observed almost exclusively with cyclopentene (de = 100%) and phenyl vinyl sulfides (*de* = 80%) whereas *syn*-additon is found with *N*-aryl enamines (de = 80%) [203].

Acyl radicals can be generated from phenylseleno esters **74** with tributyltin hydride in the presence of AIBN as initiator (scheme 23). They are useful intermediates in the generation of (cyclic) ketones. Tandem processes allow the rapid stereoselective formation of complex systems like **139** [106]. A possible side reaction of these processes is the reduction of the acyl radicals to aldehydes. For a selection of the numerous applications of this methodology see ref. [204].



Scheme 23 Generation of acyl radicals from phenylseleno-esters

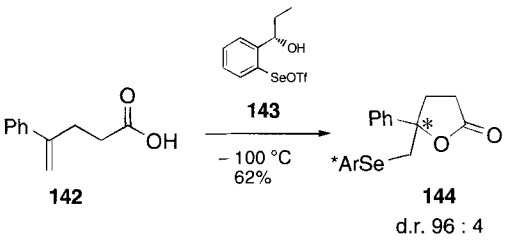
Selenium–Lithium Exchange

The C–SePh bond can be cleaved with alkyl lithium reagents [129–131]. This reaction has proven to be particularly useful for the synthesis of selenium free organolithium compounds whose carbanionic centre is well stabilized by electron withdrawing substituents [6, 205]. In diphenylseleno acetals one phenylseleno group can be exchanged (see the chapter about α-phenylseleno carbanions).

Miscellaneous

Asymmetric Benzeneselenenyl Derivatives

In recent years several chiral derivatives of benzeneselenenyl reagents have been developed. Pioneering work was done by Tomoda and coworkers [206–210] with binaphthylmonoselenides. [3]) However, *de*-values were low, generally less than 60%. Later approaches with the more accessible *ortho* (α-heteroalkyl) phenyl selenides like **143** gave somewhat better *de*-values, but usually only at very low reaction temperatures therefore demanding the use of super electrophilic seleno triflates **14** or hexafluorophosphates **10** [10, 212–214].

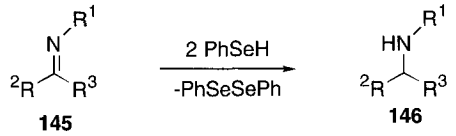


Scheme 24 Asymmetric selenolactonization with (*S*)-2-(1-hydroxyalkyl)benzeneselenenyl triflate

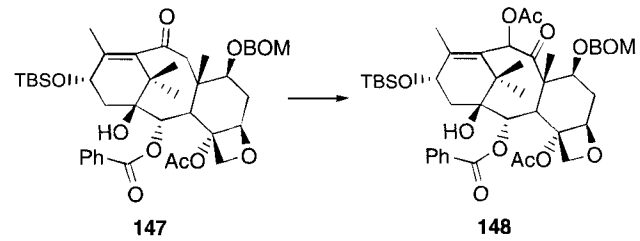
They were employed in the oxy-selenylation of alkenes [213, 215–219] [213, 216, 219] [10], selenolactonization [213, 216, 219], epoxide opening [220], and asymmetric catalytic reactions [220, 221]. A recent example from Wirth [215] is shown in scheme 24 (**142** → **143**).

Direct Reductions and Oxidations with Benzeneselenenyl Reagents

Selenophenol (**4**) is employed for the reductive cleavage of N=N-, N=O-, N–N- and N–O-bonds under mild conditions as well as for the reduction of imines to amines [222] (scheme 25, **145** → **146**) or for the reductive amination of ketones [223].



Scheme 25 Reduction of imines with selenophenol



Scheme 26 Enolate oxidation with benzene seleninic anhydride in the first paclitaxel synthesis. Reaction conditions: 1.) KO*t*Bu, THF, –78 °C; 2.) $(PhSeO)_2O$, 0 °C, 40 min; 3.) KO*t*–Bu, 0 °C, 10 min; 4.) Ac_2O, pyridine, DMAP, 20 h, 25 °C (TBS = *t*–butyldimethylsilyl, BOM = benzyloxymethyl).

[3]) Monomeric Biselenobinaphthol is not accessible [211].

Benzene seleninic acid anhydride can be used as a strong oxidant, *e.g.* in the synthesis of paclitaxel (Taxol®) to oxidize C-9 in the sterically hindered and strained B-ring of the taxoid **147** to the corresponding acyloin (cf. **148**)[224].

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References

[1] C. Paulmier, Selenium Reagents and Intermediates in Organic Synthesis, Pergamon Oxford 1986
[2] S. Patai, Z. Rappoport, The Chemistry of Organic Selenium and Tellurium Compounds, Part 1, Wiley New York 1986
[3] S. Patai, Z. Rappoport, The Chemistry of Organic Selenium and Tellurium Compounds, Part 2, Wiley New York 1987
[4] D. L. J. Clive, Tetrahedron **1978**, *34*, 1049
[5] K. C. Nicolaou, N. Petasis, Selenium in Natural Product Synthesis, Chemical Information System Philadelphia 1984
[6] A. Krief in: Main-Group Metal Organometallic in Organic Synthesis, Vol. 11 (Ed. A. McKillop), Pergamon Oxford, UK 1995, 515
[7] D. N. Jones, D. Mundy, R. D. Whitehouse, J. Chem. Soc., Chem. Commun. **1970**, 86
[8] K. B. Sharpless, R. F. Lauer, J. Am. Chem. Soc. **1973**, *95*, 2697
[9] M. Tiecco, M. Tingoli, L. Testaferri, Pure Appl. Chem. **1993**, *65*, 715
[10] S.-I. Fukuzawa, K. Takahashi, H. Kato, H. Yamazaki, J. Org. Chem. **1997**, *62*, 7711
[11] L. A. Paquette, Encyclopedia of Reagents for Organic Synthesis, John Wiley & Sons Chichester 1995
[12] H. J. Reich, M. L. Cohen, P. S. Clark, Org. Synth. **1974**, *59*, 141
[13] H. J. Reich, Acc. Chem. Res. **1979**, *12*, 22
[14] H. J. Reich, J. M. Renga, I. L. Reich, J. Am. Chem. Soc. **1975**, *97*, 5434
[15] O. Behagel, H. Seibert, Chem. Ber. **1932**, *65*, 812
[16] K. B. Sharpless, R. F. Lauer, A. Y. Teranishi, J. Am. Chem. Soc. **1973**, *95*, 6137
[17] G. H. Schmid, D. G. Garrat, Tetrahedron **1978**, *34*, 2869
[18] L. Engmann, J. Org. Chem. **1988**, *53*, 4031
[19] D. Houllemare, S. Ponthieux, F. Outorquin, C. Paulmier, Synthesis **1997**, 101
[20] A. Toshimitsu, S. Uemura, M. Okano, J. Chem. Soc., Chem. Commun. **1982**, 87
[21] T. Hori, K. B. Sharpless, J. Org. Chem. **1978**, *43*, 1689
[22] W. P. Jackson, S. V. Ley, A. J. Whittle, J. Chem. Soc., Chem. Commun. **1980**, 1173
[23] T. G. Back, K. R. Muralidharan, Tetrahedron Lett. **1990**, *31*, 1957
[24] S. Murata, T. Suzuki, Tetrahedron Lett. **1987**, *28*, 4415
[25] S. Murata, T. Suzuki, Chem. Lett. **1987**, 849
[26] S. Murata, T. Suzuki, Tetrahedron Lett. **1987**, *28*, 4297
[27] K. C. Nicolaou, D. A. Claremon, W. E. Barnette, S. P. Seitz, J. Am. Chem. Soc. **1979**, *101*, 3704
[28] K. C. Nicolaou, N. A. Petasis, D. A. Claremon, Tetrahedron **1985**, *41*, 4835
[29] H. J. Reich, J. M. Renga, J. Org. Chem. **1975**, *40*, 3313
[30] T. Hosay, L. Christiaens, G. Anthoine, P. Moniotte, Tetrahedron Lett. **1990**, *31*, 873
[31] G. Pandey, B. B. V. S. Sekhar, U. T. Bhalerao, J. Am. Chem. Soc. **1990**, *112*, 5650
[32] G. Pandey, B. B. V. S. Sekhar, J. Chem. Soc., Chem. Commun. **1993**, 780
[33] K. B. Sharpless, M. W. Young, J. Org. Chem. **1975**, *40*, 947
[34] P. A. Grieco, S. Gilman, M. Nishizawa, J. Org. Chem. **1976**, *41*, 1485
[35] D. Liotta, W. Markiewicz, H. Santiesteban, Tetrahedron Lett. **1977**, 4365
[36] K. Haraguchi, H. Tanaka, H. Kayakawa, T. Miyasaka, Chem. Lett. **1988**, 931
[37] K. Haraguchi, H. Tanaka, T. Miyasaka, Synthesis **1989**, 434
[38] P. Dowd, P. Kennedy, Synth. Commun. **1981**, *11*, 935
[39] S. V. Ley, I. A. O'Neill, C. M. R. Low, Tetrahedron **1986**, *42*, 5363
[40] H. J. Reich, F. Chow, S. V. Shah, J. Am. Chem. Soc. **1979**, *101*, 6638
[41] J. V. Comasseto, J. T. B. Ferreira, C. A. Brandt, N. Petragnani, J. Chem. Res. (S) **1982**, 212
[42] S. Torii, T. Inokuchi, N. Hasegawa, Chem. Lett. **1980**, 639
[43] R. G. Pearson, H. Sobel, J. Songsted, J. Am. Chem. Soc. **1968**, *90*, 319
[44] J. W. Anderson, G. K. Barker, J. E. Drake, S. M. Rodger, J. Chem. Soc., Dalton Trans. **1976**, 1716
[45] K. B. Sharpless, M. W. Young, J. Org. Chem. **1975**, *40*, 947
[46] S. Tomoda, Y. Takeuchi, Y. Nomura, Chem. Lett. **1981**, 1069
[47] R. A. Gancarz, J. L. Kice, Tetrahedron Lett. **1980**, 4155
[48] T. G. Back, J. Org. Chem. **1981**, *46*, 5443
[49] T. G. Back, K. R. Muralidharan, J. Org. Chem. **1989**, *54*, 121
[50] O. Ito, J. Am. Chem. Soc. **1983**, *105*, 850
[51] K. B. Sharpless, R. F. Lauer, J. Org. Chem. **1974**, *39*, 429
[52] H. J. Reich, J. Org. Chem. **1974**, *39*, 428
[53] D. Liotta, G. Zima, Tetrahedron Lett. **1978**, 4977
[54] A. Toshimitsu, K. Terao, S. Uemura, J. Chem. Soc. Perkin 1 **1987**, 1059
[55] L. Engmann, Tetrahedron Lett. **1987**, *28*, 1463
[56] S. Raucher, J. Org. Chem. **1977**, *42*, 2950
[57] T. Takahashi, H. Nagashima, J. Tsuji, Tetrahedron Lett. **1978**, 799
[58] T. Kametani, K. Suzuki, H. Kurobe, H. Nemoto, Chem. Commun. **1979**, 1128
[59] D. L. J. Clive, P. L. Beaulieu, Chem. Commun. **1983**, 307
[60] A. Toshimitsu, T. Aoai, H. Owada, S. Uemura, M. Okano, Chem. Commun. **1980**, 412

[61] A. P. Kozikowski, K. L. Sorgi, R. J. Schmiesing, Chem. Commun. **1980**, 477
[62] M. Tiecco, L. Testaferri, M. Tingoli, D. Chianelli, D. Bartoli, Tetrahedron **1988**, *44*, 2261
[63] G. Jaurand, J.-M. Beau, P. Sinay, Chem. Commun. **1981**, 572
[64] S. Torii, K. Uneyama, M. Ono, Tetrahedron Lett. **1980**, *21*, 2741
[65] K. C. Nicolaou, Tetrahedron **1981**, *37*, 4097
[66] D. L. J. Clive, C. G. Russel, Tetrahedron **1980**, *36*, 1399
[67] K. C. Nicolaou, S. P. Seitz, W. J. Sipio, J. F. Blount, J. Am. Chem. Soc. **1979**, *101*, 3884
[68] R. Vukicevic, S. Konstantinovic, M. L. Mihailovic, Tetrahedron **1991**, *47*, 859
[69] Lactonizations: K. C. Nicolaou, Z. Lysenko, J. Am. Chem. Soc. **1977**, *99*, 3185; D. L. J. Clive, G. Chittattu, J. Chem. Soc., Chem. Commun. **1977**, 484; N-Heterocycles: D. Clive, L. J., V. Farina, A. Singh, C. K. Wong, W. A. Kiel, S. M. Menchen, J. Org. Chem. **1980**, *45*, 2120; A. M. Morella, A. D. Ward, Aust. J. Chem. **1995**, *48*, 445; A. Toshimitsu, K. Terao, S. Uemura, J. Org. Chem. **1986**, *51*, 1724; D. De Smaele, N. De Kimpe, J. Chem. Soc., Chem. Commun. **1995**, 2029; Ethers: see ref. [24, 26, 31, 68, 187]; S. Konstantinovic, Z. Bugarcic, S. Milosavljevoc, G. Schroth, M. L. Mihailovic, Liebigs Ann. Chem. **1992**, 261; D. L. J. Clive, G. Chittattu, N. J. Curtis, W. A. Kiel, C. K. Wong, J. Chem. Soc., Chem. Commun. **1977**, 725; K. C. Nicolaou, Z. Lysenko, Tetrahedron Lett. **1977**, 1257; N. Greeves, W.-M. Lee, J. V. Barkley, Tetrahedron Lett. **1997**, *38*, 6453; B. H. Lipshutz, T. Gross, J. Org. Chem. **1995**, *60*, 3572; Enols: see ref. [22] Additions to triple bonds: see ref. [23] Additions to double bonds: see ref. [20] Enynes: see ref. [32]
[70] K. C. Nicolaou, R. L. Magolda, W. J. Sipio, Synthesis **1979**, 982
[71] R. Baudat, M. Petrzilka, Helv. Chim. Acta **1979**, *62*, 1406
[72] I. Ryu, S. Murai, I. Niwa, N. Sonoda, Synthesis **1977**, 874
[73] D. L. J. Clive, J. Chem. Soc., Chem. Commun. **1973**, 695
[74] D. R. Williams, K. Nishitani, Tetrahedron Lett. **1980**, *21*, 4417
[75] H. J. Reich, I. L. Reich, J. M. Renga, J. Am. Chem. Soc. **1973**, *95*, 5813
[76] L.-F. Tietze, G. v. Kiedrowski, B. Berger, Tetrahedron Lett. **1982**, *23*, 51
[77] N. Miyoshi, T. Yamamoto, N. Kambe, S. Murai, N. Sonoda, Tetrahedron Lett. **1982**, *46*, 4813
[78] S. Torii, K. Uneyama, K. Handa, Tetrahedron Lett. **1980**, *21*, 1863
[79] D. L. J. Clive, H. W. Manning, T. L. B. Boivin, M. H. D. Postema, J. Org. Chem. **1993**, *58*, 6857
[80] M. R. Roberts, R. H. Schlessinger, J. Am. Chem. Soc. **1981**, *103*, 724
[81] S. Ponthieux, F. Outorquin, C. Paulmier, Tetrahedron Lett. **1995**, *36*, 6453
[82] C. Paulmier, P. Lerouge, Tetrahedron Lett. **1982**, *23*, 1557
[83] P. Lerouge, C. Paulmier, Tetrahedron Lett. **1984**, *25*, 1983
[84] M. Jefson, J. Meinwald, Tetrahedron Lett. **1981**, *22*, 3561
[85] M. Tiecco, L. Testaferri, M. Tingoli, D. Chianelli, M. Montanucci, Tetrahedron Lett. **1984**, *25*, 4975
[86] H. J. Reich, M. C. Clark, J. Willis, W.W., J. Org. Chem. **1982**, *47*, 1618
[87] S. Saito, S. Hamano, M. Inaba, T. Moriwake, Synth. Commun. **1984**, *14*, 1105
[88] M. J. Dabdoub, J. V. Comasseto, A. L. Braga, Synth. Commun. **1988**, *18*, 1979
[89] K. B. Sharpless, M. W. Young, R. F. Lauer, Tetrahedron Lett. **1973**, *22*, 1979
[90] M. Sevrin, A. Krief, Chem. Commun. **1980**, 656
[91] M. M. Joillié, P. C. Wang, J. E. Semple, J. Am. Chem. Soc. **1980**, *102*, 887
[92] P. A. Grieco, J. Y. Jaw, D. A. Claremon, K. C. Nicolaou, J. Org. Chem. **1981**, *46*, 1215
[93] M. Clarembeau, A. Krief, Tetrahedron Lett. **1984**, *25*, 3625
[94] A. Krief, J. L. Laboureur, W. Dumont, D. Labar, Bull. Soc. Chim. Fr. **1990**, *127*, 681
[95] D. Liotta, U. Sunay, H. Santiesteban, W. Markie-wiecz, J. Org. Chem. **1981**, *46*, 2605
[96] D. Liotta, H. Santiesteban, Tetrahedron Lett. **1977**, 4369
[97] H. J. Cristau, B. Chabaud, R. Labaudiniere, H. Christol, J. Org. Chem. **1986**, *51*, 875
[98] M. Sakakibara, K. Katsumata, Y. Watanabe, T. Toru, Y. Ueno, Synthesis **1992**, 1992
[99] M. Shimizu, R. Ando, I. Kuwajiama, J. Org. Chem. **1984**, *49*, 1230
[100] M. Clarembeau, A. Cravador, W. Dumont, L. Hevesi, A. Krief, J. Lucchetti, D. Van Ende, Tetrahedron **1985**, *41*, 4793
[101] D. J. Goldsmith, D. Liotta, C., M. Volmer, W. Hoekstra, L. Waykole, Tetrahedron **1985**, *41*, 4873
[102] M. Sakakibara, K. Katsumata, Y. Watanabe, T. Toru, Y. Ueno, Synlett **1992**, 965
[103] P. Grieco, M. Miyashita, Tetrahedron Lett. **1974**, *21*, 1869
[104] P. A. Grieco, Y. Yokoyama, E. Williams, J. Org. Chem. **1978**, *43*, 1283
[105] S. Masamune, Y. Hayase, W. Schilling, W. K. Chan, G. S. Bates, J. Am. Chem. Soc. **1977**, *99*, 6756
[106] L. Chen, G. B. Gill, G. Pattenden, H. Simonian, J. Chem. Soc. Perkin 1 **1996**, 31
[107] A. Ogawa, N. Sonoda in Comprehensive Organic Synthesis, Vol. 6 (Ed. B. M. Trost, I. Fleming), Perga-mon Press Oxford **1991**, p. 461
[108] T. G. Back, S. Collins, J. Org. Chem. **1981**, *46*, 3249
[109] Y.-H. Kang, J. L. Kice, Tetrahedron Lett. **1982**, *23*, 5373
[110] T. G. Back, S. Collins, R. G. Kerr, J. Org. Chem. **1983**, *48*, 3077
[111] T. G. Back, S. Collins, U. Gokhale, K.-W. Law, J. Org. Chem. **1983**, *48*, 4776
[112] T. Miura, M. Kobayashi, J. Chem. Soc., Chem. Commun. **1982**, 438
[113] J. V. Comasseto, L. W. Ling, N. Petragnani, H. A. Stefani, Synthesis **1997**, 373
[114] A. Ogawa, N. Sonoda, J. Synth. Org. Chem., Jpn. **1996**, *54*, 894

[115] A. Ogawa, R. Obayashi, M. Sekiguchi, T. Masawaki, N. Kambe, N. Sonoda, Tetrahedron Lett. **1992**, *33*, 1329
[116] N. Petragnani, G. Schill, Chem. Ber. **1970**, *103*, 2271
[117] R. Pellicciari, M. Curini, P. Ceccherelli, R. Fringuelli, J. Chem. Soc., Chem. Commun. **1979**, 440
[118] M. J. Dabdoub, C. C. Silveira, P. G. J. Guerrero, J. Organomet. Chem. **1993**, *460*, 31
[119] D. J. Buckley, S. Kulkowit, A. McKervey, J. Chem. Soc., Chem. Commun. **1980**,
[120] T. G. Back, R. G. Kerr, J. Organomet. Chem. **1985**, *286*, 171
[121] P. J. Giddings, D. I. John, E. J. Thomas, Tetrahedron Lett. **1980**, *21*, 399
[122] P. J. Giddings, D. I. John, E. J. Thomas, Tetrahedron Lett. **1980**, *21*, 395
[123] N. Petragnani, R. Rodrigues, J. V. Comasseto, J. Organomet. Chem. **1976**, *114*, 281
[124] P. J. Giddings, D. I. John, E. J. Thomas, J. Chem. Soc. Perkin 1 **1982**, 2757
[125] T. G. Back, R. G. Kerr, Tetrahedron **1985**, *41*, 4759
[126] Y. Nishibayashi, K. Ohe, S. Uemura, J. Chem. Soc., Chem. Commun. **1995**, 1245
[127] H. J. Reich in Organoselenium Chemistry, (Ed.: D. Liotta), Wiley New York 1987, 243
[128] S. Halazy, A. Krief, J. Chem. Soc., Chem. Commun. **1979**, 1136
[129] D. Seebach, N. Peleties, Chem. Ber. **1972**, *105*, 511
[130] D. Seebach, A. K. Beck, Angew. Chem. **1974**, *86*, 859
[131] D. Seebach, N. Meyer, A. K. Beck, Liebigs Ann. Chem. **1977**, 846
[132] W. Dumont, P. Bayet, A. Krief, Angew. Chem. **1974**, *86*, 857; Angew. Chem. Int. Ed. Engl. **1974**, *13*, 804
[133] S. Halazy, J. Lucchetti, A. Krief, Tetrahedron Lett. **1978**, *41*, 3971
[134] A. Krief, G. Evrard, E. Badaoui, V. De Beys, R. Dieden, Tetrahedron Lett. **1989**, *30*, 5635
[135] R. W. Hoffmann, M. Bewersdorf, Liebigs Ann. Chem. **1992**, 643
[136] A. Krief, E. Badaoui, W. Dumont, Tetrahedron Lett. **1993**, *34*, 8517
[137] H. J. Reich, S. K. Shah, J. Am. Chem. Soc. **1975**, *97*, 3250
[138] R. H. Mitchell, J. Chem. Soc., Chem. Commun. **1974**, 990
[139] H. J. Reich, J. Org. Chem. **1975**, *40*, 2570
[140] M. Clarembeau, A. Krief, Tetrahedron Lett. **1986**, *27*, 1723
[141] M. Clarembeau, A. Krief, Tetrahedron Lett. **1984**, *25*, 3629
[142] Y. Yamamoto, Y. Saito, K. Maruyama, Tetrahedron Lett. **1982**, *23*, 4597
[143] Y. Yamamoto, H. Yatagai, Y. Saito, K. Maruyama, J. Org. Chem. **1984**, *49*, 1096
[144] H. J. Reich, S. K. Shah, P. M. Gold, R. E. Olson, J. Am. Chem. Soc. **1981**, *103*, 3112
[145] H. J. Reich, F. Chow, S. V. Shah, J. Am. Chem. Soc. **1979**, *101*, 6648
[146] L. A. Wessjohann, A. L. Braga, C. C. Silveira, L. Dornelles, Reformatsky Reactions of *a*-Haloselenides, unpublished results, Ludwig-Maximilians-Universität München (Universidade Federal de Santa Maria) 1997
[147] M. Sevrin, J. N. Denis, A. Krief, Angew. Chem. **1978**, *90*, 550; Angew. Chem. Int. Ed. Engl. **1978**, *7*, 526
[148] S. Raucher, G. A. Koolpe, J. Org. Chem. **1978**, *43*, 4252
[149] R. W. Hoffmann, R. Dress, T. Ruhland, A. Wenzel, Chem. Ber. **1995**, *128*, 861
[150] V. K. Aggarwal, Angew. Chem. **1994**, *106*, 185
[151] W. Klute, M. Krüger, R. W. Hoffmann, Chem. Ber. **1996**, *129*, 633
[152] R. W. Hoffmann, W. Klute, Chem. Eur. J. **1996**, *2*, 694
[153] R. W. Hoffmann, W. Klute, R. K. Dress, A. Wenzek, J. Chem. Soc., Perkin Trans. 2 **1995**, 1721
[154] L. Hevesi, Phosphorus and Sulfur **1988**, *38*, 191
[155] L. Hevesi, Bull. Soc. Chim. Fr. **1990**, *127*, 697
[156] C. C. Silveira, E. J. Lenardão, J. V. Comasseto, M. J. Dabdoub, Tetrahedron Lett. **1991**, *32*, 5741
[157] C. C. Silveira, G. L. Fiorin, A. L. Braga, Tetrahedron Lett. **1996**, *37*, 6085
[158] C. C. Silveira, A. L. Braga, A. Machado, G. L. Fiorin, Tetrahedron Lett. **1996**, *37*, 9173
[159] B. M. Trost, T. N. Salzmann, K. Hiroi, J. Am. Chem. Soc. **1976**, *98*, 4887
[160] H. J. Reich, J. M. Renga, I. L. Reich, J. Org. Chem. **1974**, *39*, 2133
[161] P. Grieco, M. Miyashita, J. Org. Chem. **1974**, *39*, 120
[162] H. J. Reich, S. Wollowitz, J. E. Trend, F. Chow, D. F. Wendelborn, J. Org. Chem. **1978**, *43*, 1697
[163] R. L. Dorta, C. G. Francisco, R. Freire, E. Suarez, Tetrahedron Lett. **1988**, *29*, 5429
[164] K.-C. Woo, K. Jones, Tetrahedron Lett. **1991**, *32*, 6949
[165] K. M. Nsunda, L. Hevesi, Tetrahedron Lett. **1984**, *25*, 4441
[166] D. Labar, L. Hevesi, W. Dumont, A. Krief, Tetrahedron Lett. **1978**, 1141
[167] A. Krief, W. Dumont, J. N. Dinis, G. Evrad, B. Norberg, J. Chem. Soc., Chem. Commun. **1985**, 569
[168] S. Uemura, S. Fukuzawa, J. Chem. Soc. Perkin 1 **1985**, 471
[169] A. Toshimitsu, C. Hirosawa, S. Tanimoto, S. Uemura, Tetrahedron Lett. **1992**, *33*, 4017
[170] A. Krief, W. Dumont, A. F. De Mahieu, Tetrahedron Lett. **1988**, *29*, 3269
[171] P. Ceccherelli, M. Curini, F. Epifano, M. C. Marcotulio, O. Rosati, J. Org. Chem. **1995**, *60*, 8412
[172] M. Shimizu, I. Kuwajima, J. Org. Chem. **1980**, *45*, 4063
[173] R. Ando, T. Sugawara, M. Shimizu, I. Kuwajima, Bull. Chem. Soc. Jpn. **1984**, *57*, 2987
[174] M. Tiecco, D. Chianelli, L. Testaferri, M. Tingoli, D. Bartoli, Tetrahedron **1986**, *42*, 4889
[175] S. Uemura, K. Ohe, N. Sugita, J. Chem. Soc., Chem. Commun. **1988**, 111
[176] M. Shimizu, R. Ando, I. Kuwajima, J. Org. Chem. **1981**, *46*, 5246
[177] S. Uemura, S. Fukuzawa, A. Toshimitsu, J. Chem. Soc., Chem. Commun. **1983**, 1501
[178] M. Tiecco, D. Chianelli, L. Testaferri, M. Tingoli, D. Bartoli, Tetrahedron **1986**, *42*, 4897
[179] A. Krief, W. Dumont, J.-N. Denis, J. Chem. Soc., Chem. Commun. **1985**, 571

[180] A. Krief, Tetrahedron **1980**, *36*, 2531
[181] H. Rheinboldt in Methoden der Organischen Chemie (Houben-Weyl), Vol. 9 (Ed. E. Müller), Georg Thieme Verlag Stuttgart 1955, S. 1034
[182] M. Sevrin, W. Dumont, L. Hevesi, A. Krief, Tetrahedron Lett. **1976**, 2647
[183] M.-K. Cheung, N. L. Douglas, B. Hinzen, S. V. Ley, X. Pannecoucke, Synlett **1997**, 257
[184] S. Halazy, A. Krief, Tetrahedron Lett. **1979**, *43*, 4233
[185] A. Krief, Topics in Current Chemistry: Small Ring Compounds in Organic Synthesis, Vol. 135, Sprin-ger-Verlag Berlin **1987**, 1
[186] A. Krief, W. Dumont, D. Van Ende, S. Halazy, D. Labar, J.-L. Laboureur, T. Q. Le, Heterocycles **1989**, *28*, 1203
[187] K. C. Nicolaou, R. L. Magolda, W. J. Sipio, W. E. Barnette, Z. Lysenko, M. M. Joullie, J. Am. Chem. Soc. **1980**, *102*, 3784
[188] D. H. R. Barton, M. R. Britten-Kelly, D. Ferreira, J. Chem. Soc. Perkin 1 **1978**, 1682
[189] M. Sevrin, D. Van Ende, A. Krief, Tetrahedron Lett. **1976**, 2643
[190] D. L. J. Clive, G. Chittattu, C. K. Wong, Can. J. Chem. **1977**, *55*, 3894
[191] S. V. Ley, P. J. Murray, J. Chem. Soc., Chem. Commun. **1982**, 1252
[192] B. Danieli, G. Lesma, G. Palmisano, S. Tollari, J. Chem. Soc. Perkin 1 **1984**, 1237
[193] R. O. Hutchins, K. Learn, J. Org. Chem. **1982**, *47*, 4380
[194] D. L. J. Clive, G. J. Chittattu, V. Farina, W. A. Kiel, S. M. Menchen, C. G. Russel, A. Singh, C. K. Wong, N. J. Curtis, J. Am. Chem. Soc. **1980**, *102*, 4438
[195] D. L. J. Clive, G. Chittattu, C. K. Wong, J. Chem. Soc., Chem. Commun. **1978**, 41
[196] E. J. Corey, H. L. Pearce, I. Szekly, M. Ishiguro, Tetrahedron Lett. **1978**, 1023
[197] K. C. Nicolaou, W. E. Barnette, R. L. Magolda, P. A. Grieco, W. Owens, C.-L. J. Wang, J. B. Smith, M. Ogle tree, A. M. Lefer, Prostaglandins 1978, *16*, 789
[198] T. G. Back, V. I. Birss, M. Edwards, M. V. Krishna, J. Org. Chem. **1988**, *53*, 3815
[199] C. C. Silveira, E. J. Lenardão, J. V. Comasseto, Synth. Commun. **1994**, *24*, 575
[200] D. L. J. Clive, A. C. Joussef, J. Org. Chem. **1990**, *55*, 1096
[201] L. Engman, V. Gupta, J. Org. Chem. **1997**, *62*, 157
[202] J. H. Byers, G. C. Lane, J. Org. Chem. **1993**, *58*, 3355
[203] D. P. Curran, G. Thoma, J. Am. Chem. Soc. **1992**, *114*, 4436
[204] N. Herbert, G. Pattenden, Synlett **1997**, 69; D. L. Bo ger, R. J. Mathvink, J. Org. Chem. **1992**, *57*, 1429; J. Pfenninger, C. Heuberger, W. Graf, Helv. Chim. Acta **1980**, *63*, 2328; D. Crich, S. M. Fortt, Tetrahedron Lett. **1988**, *29*, 2585; D. Crich, D. Batty, J. Chem. Soc. Perkin 1 **1992**, 3193; D. Crich, K. A. Eustace, T. J. Ritchie, Heterocycles **1989**, *28*, 67; D. Crich, S. M. Fortt, Tetrahedron Lett. **1987**, *28*, 2895; D. L. Boger, R. J. Mathvink, J. Org. Chem. **1990**, *55*, 5442; D. L. Boger, R. J. Mathvink, J. Org. Chem. **1989**, *54*, 1777; D. L. Boger, K. D. Robarge, J. Org. Chem. **1988**, *53*, 3377; D. L. Boger, R. J. Mathvink, J. Am. Chem. Soc. **1990**, *112*, 4003; D. L. Boger, R. Mathvink, J. Am. Chem. Soc. **1990**, *112*, 408; D. L. J. Clive, D. R. Cheshiire, J. Chem. Soc., Chem. Commun. **1987**, 1520; A. G. Angoh, D. L. J. Clive, J. Chem. Soc., Chem. Commun. **1985**, 941; M. D. Bachi, E. Bosch, Tetrahedron Lett. **1986**, *27*, 641; see also ref. [79, 106, 202]
[205] A. Krief, A. Nazih, M. Hobe, Tetrahedron Lett. **1995**, *36*, 8111
[206] K.-I. Fujita, K. Murata, M. Iwaoka, S. Tomoda, Heteroat. Chem. **1995**, *6*, 247
[207] S. Tomoda, M. Iwaoka, Chem. Lett. **1988**, 1895
[208] S. Tomoda, M. Iwaoka, J. Chem. Soc., Chem. Commun. **1988**, 1283
[209] S. Tomoda, K. Fujita, M. Iwaoka, J. Chem. Soc., Chem. Commun. **1990**, 129
[210] K. Fujita, M. Iwaoka, S. Tomoda, Chem. Lett. **1992**, 1123
[211] S. Murata, T. Suzuki, A. Yanagisawa, S. Suga, J. Heterocycl. Chem. **1991**, *28*, 433
[212] R. Déziel, E. Malenfant, G. Bélanger, J. Org. Chem. **1996**, *61*, 1875
[213] K.-I. Fujita, K. Murata, M. Iwaoka, S. Tomoda, J. Chem. Soc., Chem. Commun. **1995**, 1641
[214] T. Wirth, K. J. Kulicke, G. Fragale, Helv. Chim. Acta **1996**, *79*, 1957
[215] T. Wirth, Angew. Chem. **1995**, *107*, 1872
[216] K.-I. Fujita, K. Murata, M. Iwaoka, S. Tomoda, Tetrahedron Lett. **1995**, *36*, 5219
[217] R. Déziel, S. Goulet, L. Grenier, J. Bordeleau, J. Bernier, J. Org. Chem. **1993**, *58*, 3619
[218] R. Déziel, E. Malenfant, J. Org. Chem. **1995**, *60*, 4660
[219] K.-I. Fujita, M. Iwaoka, S. Tomoda, Chem. Lett. **1994**, 923
[220] T. Wirth, Tetrahedron Lett. **1995**, *36*, 7849
[221] T. Wirth, K. J. Kulicke, G. Fragale, J. Org. Chem. **1996**, *61*, 2686
[222] K. Fujimori, H. Yoshimoto, S. Oae, Tetrahedron Lett. **1979**, 4397
[223] K. Fujimori, H. Yoshimoto, S. Oae, Tetrahedron Lett. **1980**, *21*, 3385
[224] R. A. Holton, H.-B. Kim, C. Somoza, F. Liang, R. J. Biediger, P. D. Boatman, M. Shindo, C. C. Smith, S. Kim, H. Nadizadeh, Y. Suzuki, C. Tao, P. Vu, S. Tang, P. Zhang, K. K. Murthi, L. N. Gentile, J. H. Liu, J. Am. Chem. Soc. **1994**, *116*, 1599

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