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Covering: July 1996 to June 1997

Previous review: *Contemp. Org. Synth.*, 1997, 4, 136

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1 Introduction

This review describes the use of main group organometallic compounds in synthesis and follows on from the previous coverage.¹ Emphasis is placed on synthetic chemistry with organometallic compounds, rather than structural or mechanistic aspects.

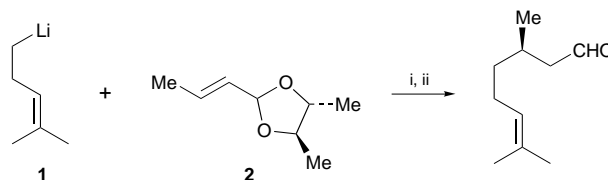
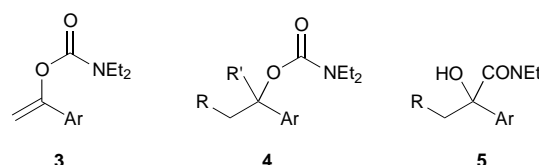
2 Group 1

2.1 Lithium

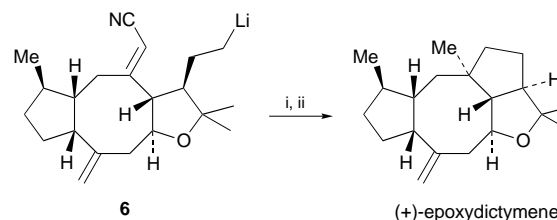
2.1.1 Non-stabilized organolithiums

Simple non-stabilized organolithium reagents are used in organic synthesis primarily for carbon–carbon bond formation by addition to π -systems. Addition to the alkene of allylic ethers or alkenyl acetals occurs in an S_N manner. For example, Alexakis *et al.* report the synthesis of citronellal by reaction of organolithium **1** with the alkene **2**, followed by acidic work-up (Scheme 1).² Ring opening of cyclic allylic ethers leads to decalins³ or polypropionates.⁴

The addition of organolithiums (RLi) to α -aryl *O*-vinyl carbamates **3** leads to the formation of carbamates **4** (after alkylation with $R'X$) or amides **5**, if the intermediate benzylolithium is allowed to warm to room temperature.⁵ Intramolecular addition to activated or unactivated dienes or enynes has led to the synthesis of cyclopentanes.⁶ Problems with radical cyclizations

Scheme 1 Reagents: i, Et₂O, 20 °C; ii, H₃O⁺

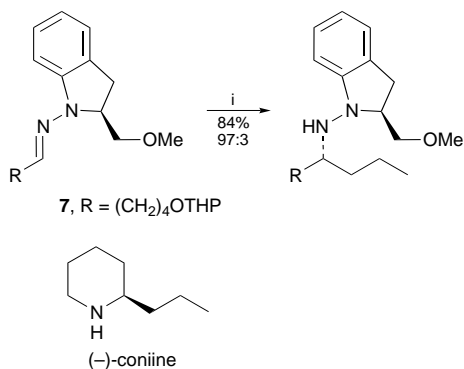
led Schreiber and co-workers to report iodine–lithium exchange (with Bu^tLi) for the formation of the organolithium **6**.⁷ After anionic cyclization and reductive decyanation, the diterpene (+)-epoxydictymene was synthesized (Scheme 2).

Scheme 2 Reagents: i, TMEDA, pentane–Et₂O; ii, K, 18-crown-6, PhMe

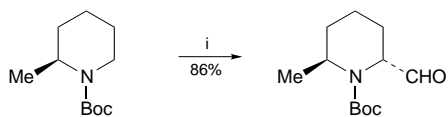
The intramolecular addition of organolithiums to carbonyl groups provides an alternative method for the preparation of ring systems, including cyclohexanones (and hence the terpene oppositol)⁸ and γ -lactams (and hence pyrrolidines).⁹ Inter-molecular addition of organolithiums with oxonium ions, generated from glycosyl chlorides, gives rise to *C*-glycols.¹⁰

A review on the addition of various organometallic reagents, including unstabilized organolithiums, to C=N double bonds has been published recently.¹¹ Addition to oxime ethers has led to the preparation of α -amino acids.¹² The alkaloid (–)-coniine has been synthesized by reaction of *n*-propyllithium with the hydrazone **7** (Scheme 3).¹³ 2-Acylamino-3-alkylpyrazines can be prepared by addition of organolithium reagents to 2-acylamino-pyrazines.¹⁴

Alternative methods for the preparation of amines make use of α -amino organolithiums in inter- or intra-molecular reactions. The organolithiums can be generated by tin–lithium exchange,¹⁵ reductive lithiation of benzotriazole derivatives¹⁶ or tosylates,¹⁷ or by proton abstraction.¹⁸ For example, the synthesis of the piperidine ring portion (and hence a total synthesis) of (+)-himbacine makes use of a Boc group to direct α -deprotonation (Scheme 4).¹⁹ Related reactions with piperazines have been reported.²⁰ A formal synthesis of (+)-conessine also makes use of a stereoselective alkylation of an α -amino organolithium (Scheme 5).²¹



Scheme 3 Reagents: i, PrⁿLi, THF

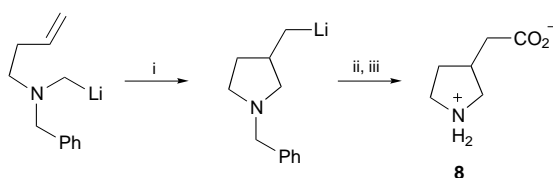


Scheme 4 Reagents: i, BuⁿLi, TMEDA, Me₂NCHO



Scheme 5 Reagents: i, BuⁿLi, TMEDA, MeI, -90 °C

Proton abstraction α to *N*-Boc derivatives has been studied extensively by Beak and an excellent account of some of this work has been published.²² Lithiation of *N*-Boc cyclopropylamines has given rise to substituted cyclopropylamines, including spirocyclic amines by cyclization onto an alkyl chloride.²³ Cyclizations onto alkenes (with *N*-alkyl rather than *N*-Boc amines) are known and this has allowed the preparation of the GABA uptake inhibitor **8** (Scheme 6).²⁴

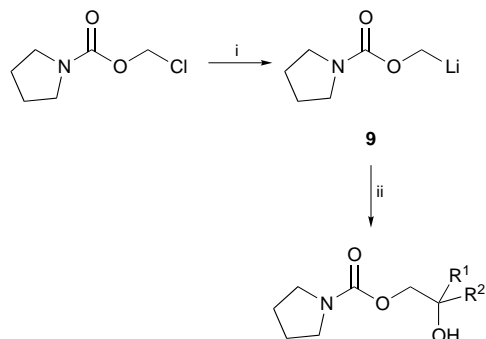


Scheme 6 Reagents: i, hexane-Et₂O, -78 °C to room temp.; ii, EtO₂CCl; iii, 6 M HCl

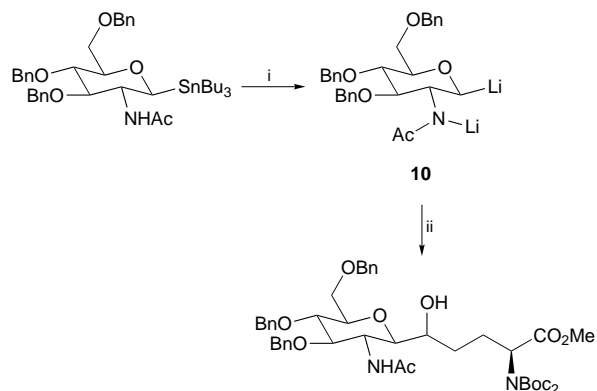
The formation of β -amino organolithiums and their reaction with electrophiles has been reported.²⁵ Alkylation of organolithiums bearing two nitrogen atoms, or one nitrogen and one oxygen atom, on the α -carbon gives rise to carbonyl compounds on hydrolysis.²⁶

Aziridinyl and oxiranyl anions are useful in organic synthesis and a review on these species has been published.²⁷ Simple α -oxy organolithiums such as PhCH₂OCH₂Li and MeOCH₂OCH₂Li have been used for the addition of a hydroxymethyl group to a ketone (leading to a preparation of taxusin²⁸ or montelukast derivatives)²⁹ or to a nitrile group [leading to (+)-digitoxigenin].³⁰ The α -oxy organolithium **9**, prepared from the corresponding chloride and lithium 4,4'-*tert*-butylbiphenyl (LiDBB), has been reported to add to carbonyl electrophiles and allows the synthesis of 1,2-diols (Scheme 7).³¹

The reagent LiDBB has also been used for the formation of β -oxy organolithiums from epoxides.³² Surprisingly, the β -*N,N*-diphenylmethyleamino group is compatible with an α -oxy organolithium.³³ The dianion **10** (containing a β -amido group) has been used for the synthesis of *C*-glycoside analogues of *N*-glucoasparagine (Scheme 8).³⁴



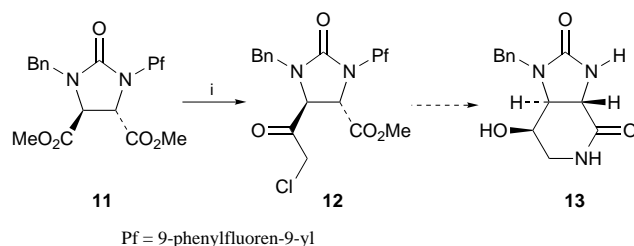
Scheme 7 Reagents: i, Li, DBB, THF; ii, R¹R²C=O then H₂O



Scheme 8 Reagents: i, MeLi then BuLi; ii, OHCCH₂CH₂CH(NBoc)₂-CO₂Me

Conversion of allylic alcohols to their allyl transposed homoallylic alcohols is possible using an α -oxy organolithium and [2,3] Still-Wittig rearrangement. This methodology has been applied to the synthesis of vitamin B₁₂ A-B-semicorrin³⁵ and cyathane-type diterpenoids.³⁶

α -Chloro organolithiums have found a number of uses in organic synthesis. Dichloromethylithium, Cl₂CHLi, generated from CH₂Cl₂ and LDA, allows the homologation of boronic esters and hence the synthesis of a boronic acid analogue of L-ornithine.³⁷ Chloromethylithium, ClCH₂Li, adds to the carbonyl group of the ureido ester **11** to give the ketone **12** (Scheme 9).³⁸ Ketone **12** was converted to the ureido amide **13**, incorporating the bicyclic core of streptolidine lactam. Addition of the organolithium Cl(I)CHLi to esters provides an alternative route to α -chloro ketones.³⁹ Formation of α -bromo organolithium species tends to lead to carbenoids and some interesting stereoselectivities from α -bromo- β - or γ -alkoxy organolithiums have been reported.⁴⁰

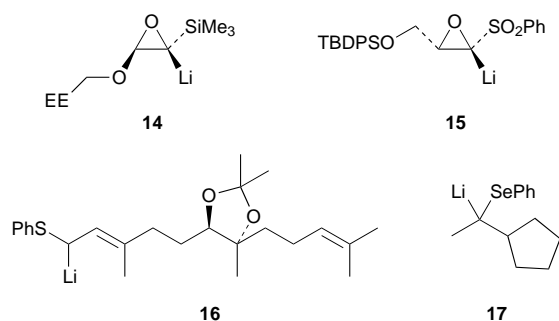


Scheme 9 Reagents: i, ClCH₂I, MeLi, LiBr, THF

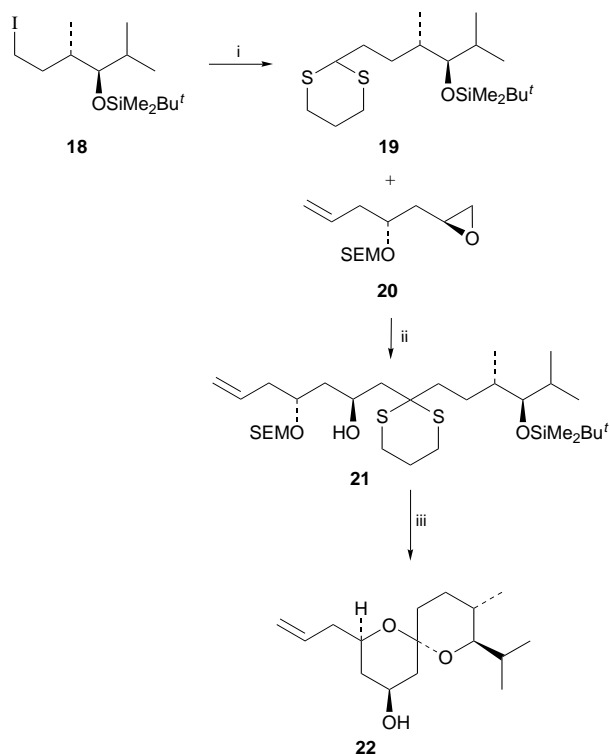
2.1.2 Organolithiums stabilized by silicon, selenium and sulfur

Addition of the α -silyl oxiranyllithium **14** to the aldehyde nonadienal is the key step in the synthesis of (+)-cerulenin.⁴¹ The related α -sulfonyl oxiranyllithiums, such as **15**, have been used iteratively in the synthesis of hemibrevitoxin B.⁴² Ring opening of α -silyl epoxides by sulfur-stabilized organolithiums results in the preparation of allylic alcohols (and hence lipoxygenase metabolites).⁴³ Intramolecular opening of an epoxide provides

a route to (+)-cubitene,^{44a} whereas intermolecular alkylation of a similar organolithium **16** has been used for the synthesis of stereoisomers of quassiol A.^{44b} The α -selenyl organolithium **17**, generated by selenium–lithium exchange, adds to aldehydes to give β -hydroxy selenides which were used in the synthesis of the decalin unit of azadirachtin.⁴⁵



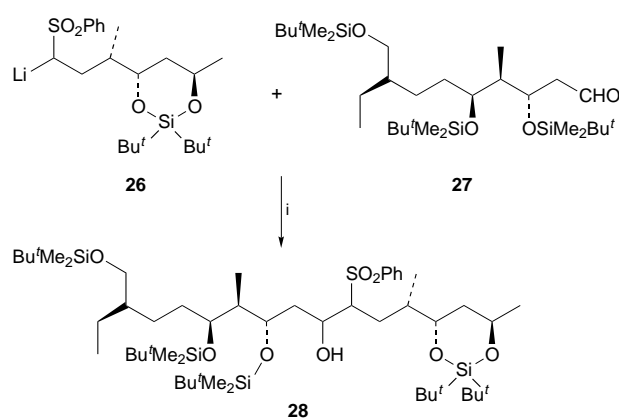
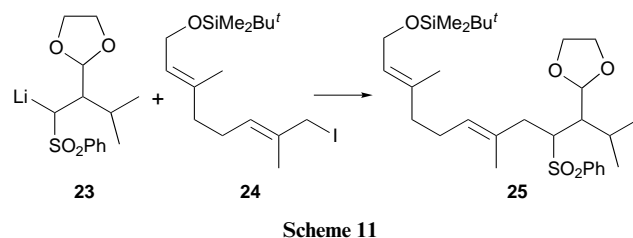
Sulfur-stabilized organolithiums, particularly 2-lithio-1,3-dithiane⁴⁶ and derivatives,⁴⁷ have featured in a number of synthetic sequences published during the period of this review. For example, formation of the organolithium from 1,3-dithiane and alkylation with the iodide **18** gives the 2-alkyl-1,3-dithiane **19** (Scheme 10).⁴⁸ A second proton abstraction and alkylation with epoxide **20** gives the 2,2-dialkyl-1,3-dithiane **21**, which was hydrolysed in a single step to the spiroketal **22**, used in a synthesis of milbemycin E.



Scheme 10 Reagents: i, 1,3-dithiane, Bu^nLi ; ii, Bu^tLi ; iii, HF, MeCN(aq)

Syntheses of (–)-rapamycin⁴⁹ and a segment of tautomycin⁵⁰ make use of the ability of 2-lithio-1,3-dithianes to undergo alkylation. Preparation of further segments of tautomycin and their coupling uses sulfone-stabilized organolithiums.⁵¹ Sulfone-stabilized organolithiums have been used extensively in organic synthesis. Effective alkylation takes place using alkyl halide,⁵² sulfonate,⁵³ epoxide,⁵⁴ enone,⁵⁵ ester⁵⁶ or aldehyde⁵⁷ electrophiles. This variety allows the construction of different functionalised carbon frameworks, using either inter- or intra-molecular carbon–carbon bond formation. For example, addition of the sulfone-stabilized organolithium **23** (Scheme 11)

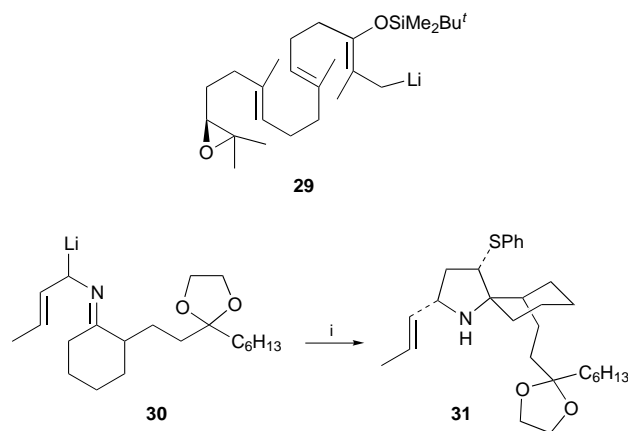
to the allyl iodide **24** gives the sulfone **25**, which was converted to a number of cembrenoids.^{52a} Addition of the organolithium **26** (Scheme 12) to the aldehyde **27** gives the β -hydroxy sulfone **28**.^{57a} After oxidation, desulfonation and desilylation, the β -hydroxy sulfone **28** was converted to the C-19 to C-34 spiroketal segment of the rutamycins. Sulfoxide-stabilized organolithiums provide an alternative to the use of sulfones, for example, for the synthesis of (–)-maytansinol^{46d} and (–)-podophyllo-toxin.⁵⁸



Scheme 12 Reagents: i, $\text{BF}_3 \cdot \text{OEt}_2$, THF, -78°C to room temp.

2.1.3 Allylic and benzylic organolithiums

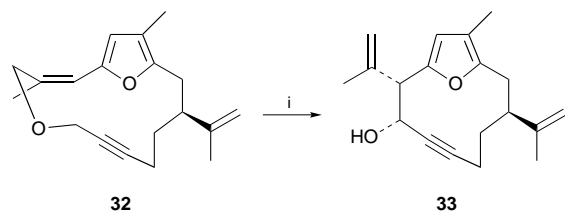
Allylic and benzylic organolithiums can be prepared by a number of methods, including proton abstraction with a strong base⁵⁹ and exchange of selenium⁶⁰ or chlorine⁶¹ for lithium. The latter process requires lithium metal and 4,4'-di-*tert*-butylbiphenyl (DBB) or naphthalene. Consecutive chlorine–lithium exchange and quench of the allylic organolithiums with carbonyl compounds has allowed access to perhydrofurofurans.⁶² Addition of 2-lithiopropene to an acylsilane gives rise, after Brook rearrangement, to the allylic organolithium **29**, an intermediate in the synthesis of dammarenediol II.⁶³ Tin–lithium exchange has been used for the preparation of the organolithium **30**, which undergoes cycloaddition with phenyl vinyl sulfide to give the pyrrolidine **31** (Scheme 13).⁶⁴ Further manipulations give 2,13-diepilepadiformine.



Scheme 13 Reagents: i, $\text{CH}_2=\text{CHSPh}$ then H_2O

Asymmetric deprotonation of allylic amines using BuLi and (–)-sparteine, followed by electrophilic quench gives, after hydrolysis or reduction, chiral aldehydes or amines.⁶⁵ Treatment of chiral allylic sulfoximines with BuLi, then ClTi(NEt₂)₃ or ClTi(OPrⁱ)₃ and an aldehyde, provides β-hydroxy sulfoximines with very high stereoselectivities.⁶⁶ Metallation of the prop-2-ynyl ether THPOCH₂C≡CSiMe₃ with Bu^tLi, followed by transmetalation with Ti(OPrⁱ)₄ and aldehyde quench, has been used to construct the decalin unit of erigerol.⁶⁷

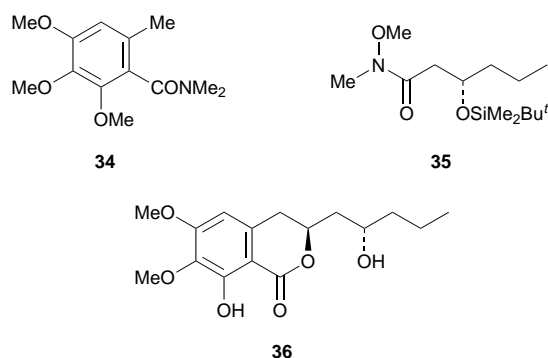
Proton abstraction of prop-2-ynyl or benzylic ethers⁶⁸ or benzylic amines⁶⁹ and subsequent [2,3] or [1,2] Wittig rearrangement has been used in organic synthesis. For example, a synthesis of (–)-kallolide B includes the [2,3] Wittig ring contraction of the prop-2-ynyl ether **32** to the alcohol **33** (Scheme 14).^{68a}



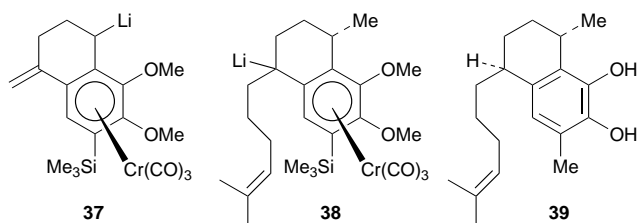
Scheme 14 Reagents: i, Bu^tLi, THF–pentane, 88%

In the same way as allylic organolithiums, benzylic organolithiums have been formed by proton abstraction with a base or exchange of sulfur, selenium, nitrogen (of benzotriazole) or chlorine for lithium (followed by intermolecular quench or cyclization).⁷⁰ Alternatively, reductive lithiation of a C–O bond with lithium metal and naphthalene provides benzylic organolithiums, used in the synthesis of isochromans.⁷¹

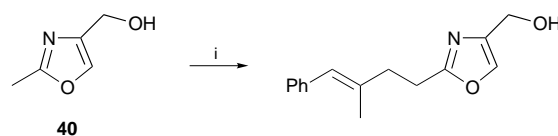
Butyllithium or LDA are common bases for direct proton abstraction to give benzylic organolithiums. A key step in the preparation of fusarentin 4,5-dimethyl ether **36** involves deprotonation of the benzamide **34** with *sec*-butyllithium and addition to the Weinreb amide **35**.⁷² A variety of naphthalenes including lignan derivatives have been synthesized by addition of benzylic organolithiums to α,β-unsaturated carbonyl compounds.⁷³



Benzylic organolithium species can be formed readily from tricarbonyl(η⁶-arene)chromium complexes. A synthesis of the 18-nor-seco-pseudopteris aglycone **39** makes good use of the stabilization afforded by the chromium complex, in two consecutive steps involving methylation of the benzylic organolithium **37**, followed by addition of homoprenyllithium to give organolithium **38**.⁷⁴ Other stereoselective alkylations of benzylic ether tricarbonylchromium(0) complexes have been reported.⁷⁵ Alkylations of laterally lithiated 2-alkyl-1-naphthamides proceed with high levels of diastereoselectivity.⁷⁶ Beak and co-workers report the formation of enantiomerically enriched products from alkylation of benzylic organolithiums in the presence of (–)-sparteine.⁷⁷ Conversion of benzylic amines to chiral α-, β- or γ-amino acids makes use of this methodology.⁷⁸



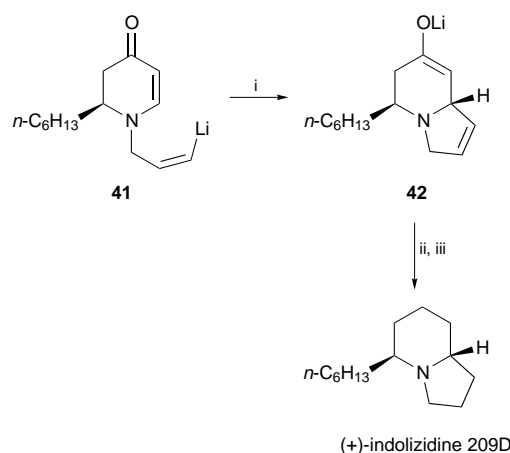
Aromatic heterocycles such as pyridines, pyrroles and indoles have been prepared from benzylic organolithiums.⁷⁹ A synthesis of (–)-tubifoline uses the Smith indolization of an ester with the benzylic organolithium generated from *o*-MeC₆H₄-NHSiMe₃ and butyllithium.⁸⁰ Alkylation of the organolithium derived from the oxazole **40** (Scheme 15) was used in the synthesis of phenoxan.⁸¹ Metallation of a 2-methylthiazole and condensation with an ester forms part of a synthesis of an advanced intermediate for the micrococci.⁸²



Scheme 15 Reagents: i, 2 equiv. LDA, THF, PhCH=C(Me)CH₂Br, 50%

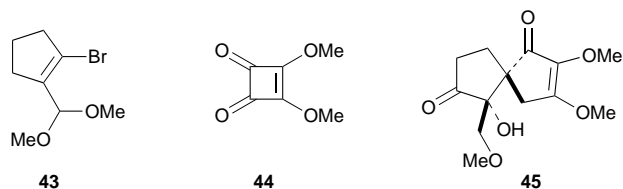
2.1.4 Alkenyl and alkynyl organolithiums

Direct proton abstraction⁸³ and the Shapiro reaction⁸⁴ have been used for the preparation of alkenyl organolithiums, although the most common methods involve halogen–lithium or tin–lithium exchange. Addition of alkenyl organolithiums, generated by iodine–lithium exchange, to carbonyl compounds has found use in the synthesis of (–)-galbonolide B⁸⁵ and calbistrin A.⁸⁶ The alkenyl organolithium **41** (Scheme 16), generated by iodine–lithium exchange with *tert*-butyllithium, cyclizes onto the unsaturated ketone to give the enolate **42**.⁸⁷ Trapping as the enol triflate and hydrogenation gave (+)-indolizidine 209D. Bromine–lithium exchange for the formation of alkenyl organolithiums which undergo anionic cyclization has also been reported.⁸⁸



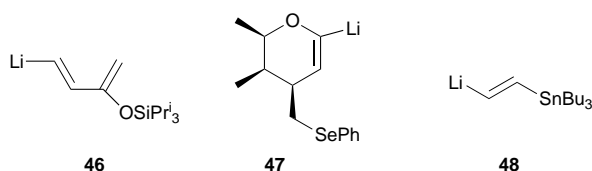
Scheme 16 Reagents: i, THF, –78 °C, 1 h; ii, *N*-(5-chloro-2-pyridyl)-triflimide; iii, H₂, Pt/C, EtOAc, Li₂CO₃

A number of examples of the formation of alkenyl organolithiums by bromine–lithium exchange and addition to aldehydes or ketones have been reported.⁸⁹ Addition to imines followed by oxidative cleavage of the alkene provides α-amino acids.⁹⁰ Addition to squarate esters has proved popular.⁹¹ For example, addition of the organolithium generated from the alkenyl bromide **43** to the squarate ester **44** was used in the

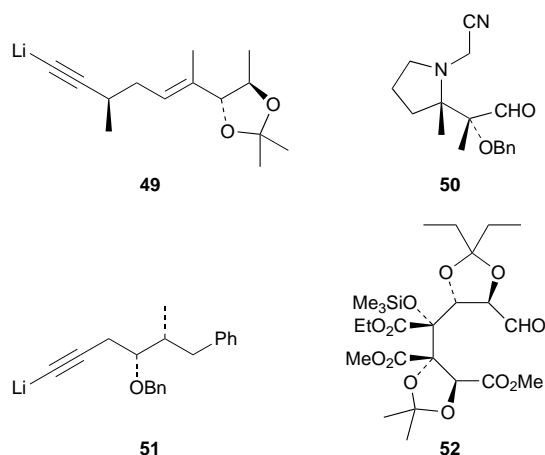


synthesis of dimethyl gloiosiphone A **45**.⁹² Syntheses of espintanol and precapnelladiene also use alkenyllithium additions to squarate esters.⁹³

Formation of alkenyl organolithiums by reductive lithiation of vinyl chlorides⁹⁴ or tin–lithium exchange⁹⁵ are possible. The organolithiums **46–48** were prepared by tin–lithium exchange of the corresponding trialkylstannanes with butyllithium and used as part of the synthesis of a taxinine analogue,⁹⁶ of the 18-*O*-methyl ether of mycalamide B⁹⁷ and of alisamycin,⁹⁸ respectively.



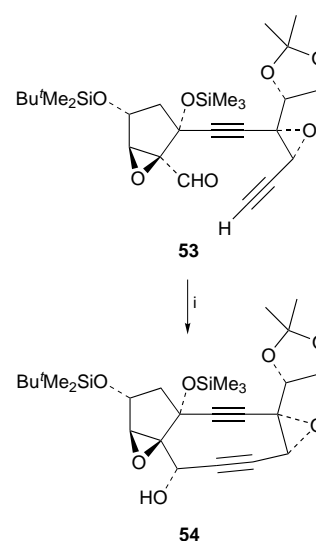
Alkynyl organolithiums, formed by proton abstraction of terminal alkynes, continue to play an important role in organic synthesis. Particularly prominent is the formation of carbon–carbon bonds by addition to carbonyl compounds.⁹⁹ Various alkynyl organolithiums, such as **49**, add to the aldehyde **50** in syntheses of allopumiliotoxins, such as allopumiliotoxin 339A.¹⁰⁰ Syntheses of the azetidine alkaloids penaresidin A and B¹⁰¹ and of estradiols¹⁰² make use of alkynyl organolithium addition to carbonyl groups. Addition of organolithium **51** to the aldehyde **52** was used in a synthesis of zaragozic acid C.¹⁰³ Intramolecular addition onto aldehydes¹⁰⁴ or alkyl halides¹⁰⁵ allows the formation of cycloalkadiynes. For example, a synthesis of neocarzinostatin chromophore aglycon was accomplished by treatment of the alkynyl aldehyde **53** (Scheme 17) with a base, followed by further elaborations of the diyne **54**.^{104a}



Addition of alkynyl organolithiums to primary alkyl halides has been used in the syntheses of dolatrienoic acid (a subunit of dolastatin 14)¹⁰⁶ and of carbazoquinocins A and D.¹⁰⁷ Alkynyl organolithiums also add to Fischer-type carbene complexes¹⁰⁸ and to epoxides,¹⁰⁹ the latter finding use in the synthesis of tetrahydrofurans such as 15-*epi*-annonin I and *trans*-(+)-deacetylkumausyne.

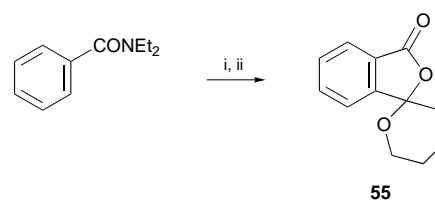
2.1.5 Aryl organolithiums

Carboxylic amides are known to assist proton abstraction in the *ortho* position of an aromatic ring. *ortho*-Lithiation of *N,N*-



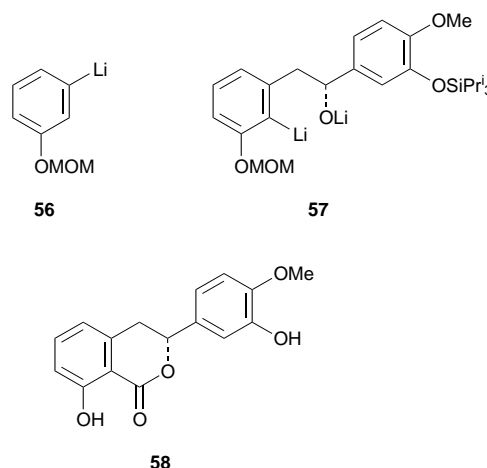
Scheme 17 Reagents: i, LiN(SiPhMe₂)₂, LiCl, THF, –78 °C, 79%

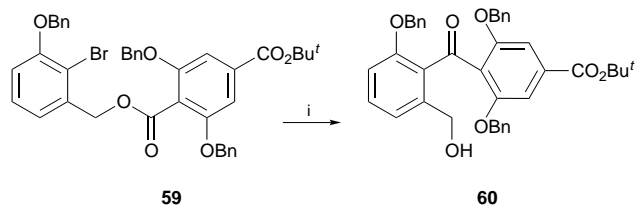
diethylbenzamide and quench with lactones, followed by acidic hydrolysis of the amide gives aryl spiroacetals, such as **55** (Scheme 18), related to the papulacandins.¹¹⁰ *N*-Pivaloylanilines and carbamates are known to direct *ortho*-lithiation.¹¹¹ Sequential alkylations *ortho* to methoxy groups has given access to benzoquinones and to pongapinone A and ponganone II.¹¹² Directed dilithiation of diphenyl ethers and cyclization leads to tricyclic products.¹¹³



Scheme 18 Reagents: i, Bu^tLi, THF, TMEDA, –78 °C, δ -valerolactone; ii, TsOH, THF–H₂O

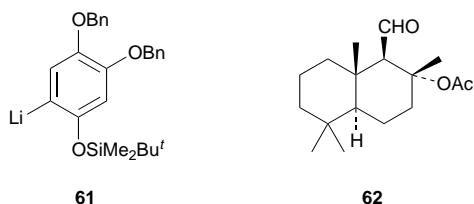
The natural product phyllodulcin **58** has been prepared using the two aryl organolithium intermediates **56** (formed by bromine–lithium exchange) and **57** (formed by proton abstraction).¹¹⁴ Anionic cyclization of aryl organolithiums, generated by bromine–lithium exchange or organolithium addition to a benzyne, provides indanes or indolines.¹¹⁵ Bromine–¹¹⁶ or iodine–lithium¹¹⁷ exchange have been used for the formation of aryl organolithiums. For example, synthesis of the benzophenone subunit of balanol, and hence a total synthesis of balanol, was achieved by treatment of the bromide **59** with *n*-butyllithium (Scheme 19).¹¹⁸ The resulting organolithium rearranges to give the benzophenone **60**.



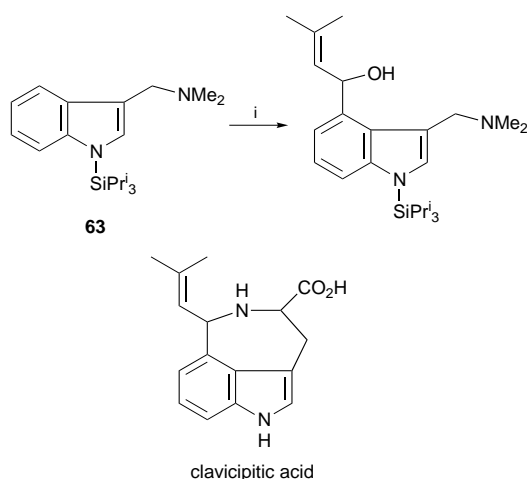


Scheme 19 Reagents: i, BuⁿLi, THF, -78 °C, 51%

Addition of the organolithium **61**, formed by bromine–lithium exchange, to the aldehyde **62** allows a synthesis of (+)-puupehenone.¹¹⁹ A variety of aryl and heteroaromatic organolithiums have been reported to add to cyclobutenediones to give substituted xanthenes.¹²⁰



Heteroaromatic organolithiums have found widespread use for the synthesis of substituted heterocycles. Both *cis*- and *trans*-clavicipitic acids have been prepared using directed lithiation of the indole **63** (Scheme 20).¹²¹ The organolithium **64**, prepared by bromine–lithium exchange, has been used in the synthesis of the indole alkaloid decarbomethoxytetrahydrosecodine.¹²²



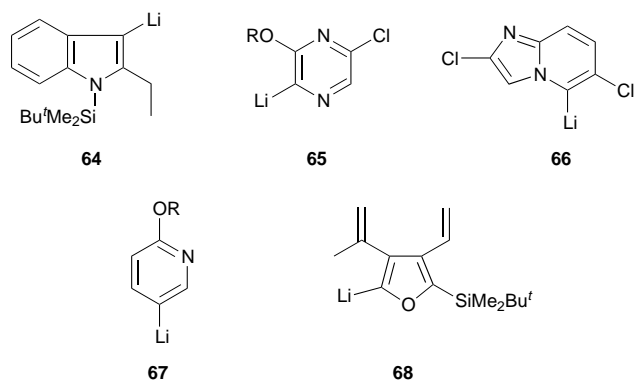
Scheme 20 Reagents: i, Bu^tLi, Et₂O, 0 °C, Me₂C=CHCHO, 82%

Lithiation of diazines,¹²³ imidazoles¹²⁴ and pyridines¹²⁵ has allowed access to a variety of heterocyclic products. Examples of each of these heteroaromatic organolithiums, **65–67** add to protected ribonolactones to give C-nucleosides.¹²⁶ Addition of 5-lithio-2-chloropyridine (or its 2-methoxy analogue **67**, R = Me) to the 7-azabicyclo[2.2.1]heptane ring system has provided two routes to epibatidine.¹²⁷

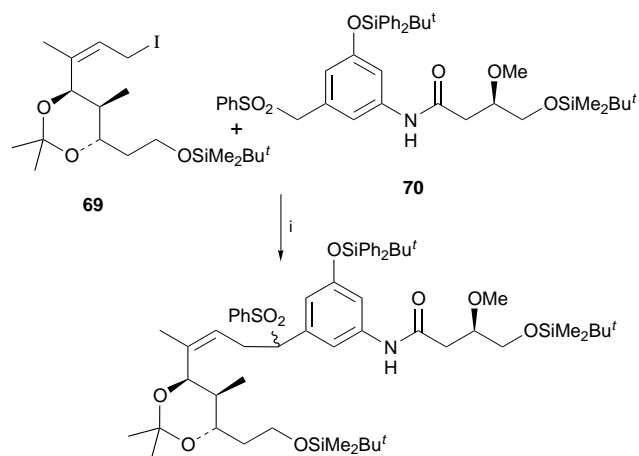
Heteroaromatic organolithiums based on furan and thiophene have been reported.¹²⁸ For example, a synthesis of (+)-xestoquinone uses the addition of furan **68** to a naphthoyl chloride, followed by a palladium-catalysed polyene cyclization to set up the required pentacycle.¹²⁹

2.2 Sodium and potassium

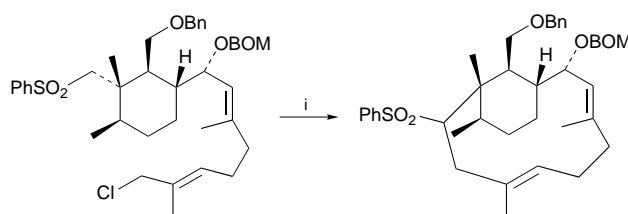
Although much rarer than organolithium species, organosodium and organopotassium reagents have found some applications in organic synthesis. Of particular merit is the ease of formation and subsequent alkylation of sulfone-stabilized organosodiums and organopotassiums. Sodium hexamethyl-



disilazide (NaHMDS) is an effective base and has been employed in the synthesis of (+)-U-106305¹³⁰ and (+)-trienomycins A and F,¹³¹ the latter using alkylation of the iodide **69** with the sulfone **70** (Scheme 21). Potassium hexamethyldisilazide (KHMDS) is also effective and has been used for intramolecular Michael addition to give an eight-membered ring¹³² and cyclization to give the ring system of phomactin D (Scheme 22).¹³³



Scheme 21 Reagents: i, NaHMDS, THF, -78 °C, 91%



Scheme 22 Reagents: i, KHMDS, THF, room temp.

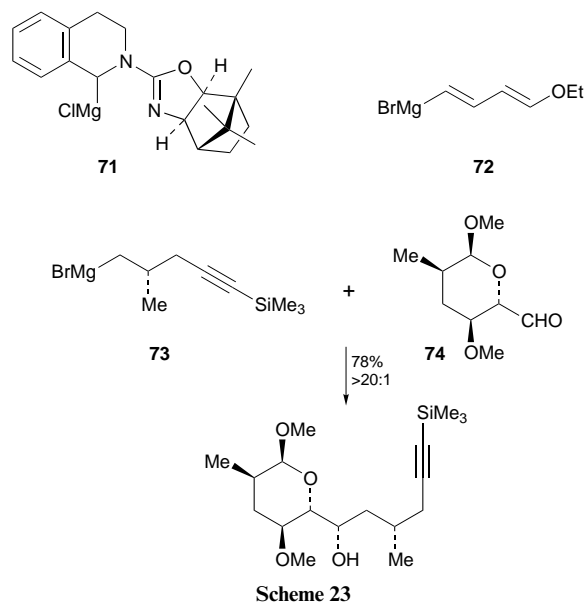
The Ramberg–Bäcklund reaction, involving potassium hydroxide promoted deprotonation of a sulfone, has been used in a synthesis of C-aryl glycosides related to the chryso-mycins.¹³⁴ A synthesis of a subunit of tricolorin A uses the reagent potassium 3-aminopropylamide (KAPA) to rearrange an internal alkyne to the terminal position.¹³⁵ Alkenyl potassiums, prepared by metallation of alkenes with BuLi–KOBu^t (LICKOR), have been used for the preparation of allyl-silanes.¹³⁶ A synthesis of a mitosene analogue¹³⁷ and of triaryl-methanes¹³⁸ make use of metallation at the benzylic position with NaOMe or KOBu^t. Finally in this section, NaHMDS and KHMDS have been found to allow metallation of nitroaromatics with *in situ* trimethylsilyl quench.¹³⁹

3 Group 2

3.1 Magnesium

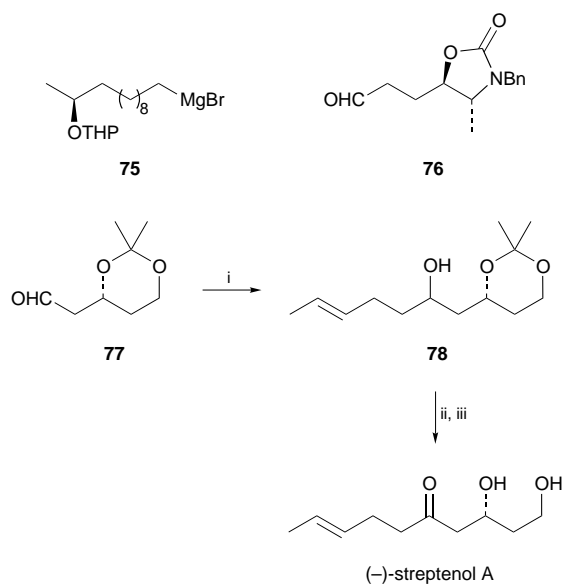
The addition of organomagnesium reagents to, in particular,

carbonyl or C=N groups remains popular for carbon-carbon bond formation in organic synthesis. A number of Grignard reagents have been reported to add to serine-derived aldehydes, for example, for the synthesis of β -hydroxy-leucine or tyrosine derivatives.¹⁴⁰ Addition of the Grignard reagent **71** to piperonal has allowed a diastereoselective synthesis of (+)-corlumine.¹⁴¹ A synthesis of the polyene macrolide roflamycoin uses the Grignard reagent **72**, derived from the corresponding stannane by sequential tin-lithium and lithium-magnesium exchanges.¹⁴² Sequential iodine-lithium and lithium-magnesium exchanges have been used to prepare the reagent **73**, which adds to the aldehyde **74** to set up a subunit (and hence a total synthesis) of FK-506 (Scheme 23).¹⁴³



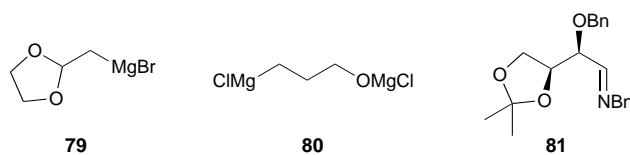
Scheme 23

A synthesis of the alkaloid (-)-carnavaline uses, as a key carbon-carbon bond forming step, the addition of the Grignard reagent **75** to the aldehyde **76**.¹⁴⁴ The Grignard reagent derived from 1-bromopent-3-ene adds to the aldehyde **77** (Scheme 24);¹⁴⁵ oxidation of the resulting alcohol **78** and hydrolysis of the ketal gives (-)-streptenol A. Other synthetic applications of addition of Grignard reagents to aldehydes include the preparation of trifluorophedrine and substituted [2.2]paracyclophanes.¹⁴⁶

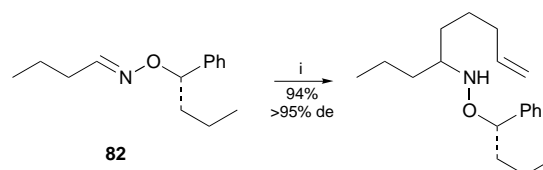


Scheme 24 Reagents: i, C_5H_9MgBr , Et_2O ; ii, PDC, CH_2Cl_2 ; iii, $AcOH-H_2O$

Various Grignard reagents, for example **79**, have been reported to add to aldehydes or ketones derived from carbohydrates.¹⁴⁷ Addition of the organomagnesium reagent **80** to cyclic ketones, followed by *O*-tosylation, gives spirocyclic ethers.¹⁴⁸ Grignard reagents add to carboxylic acid derivatives to give ketones.¹⁴⁹ For example, Grignard addition to the *N,N*-dimethylamide analogue of the aldehyde **76** has provided a route to (-)-cassine.¹⁵⁰

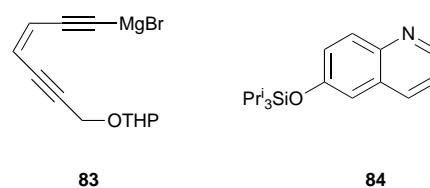


Nucleophilic addition of organometallic reagents to C=N double bonds (to give chiral amines) has been described in a recent review.¹⁵¹ Homochiral amino acid derivatives and α -aryl substituted amines can be prepared by Grignard addition to chiral imines.¹⁵² A synthesis of deacetylanisomycin and analogues uses organometallic addition to the imine **81**.¹⁵³ The key step in a synthesis of (-)-coniine and (+)-pseudoconhydrine uses nucleophilic addition of the Grignard reagent derived from 1-bromopent-4-ene to the imine **82** (Scheme 25).¹⁵⁴



Scheme 25 Reagents: i, $BF_3 \cdot OEt_2$, PhMe, $CH_2=CHCH_2CH_2CH_2MgBr$

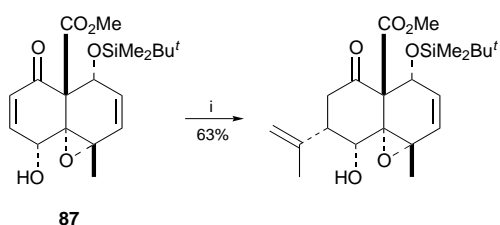
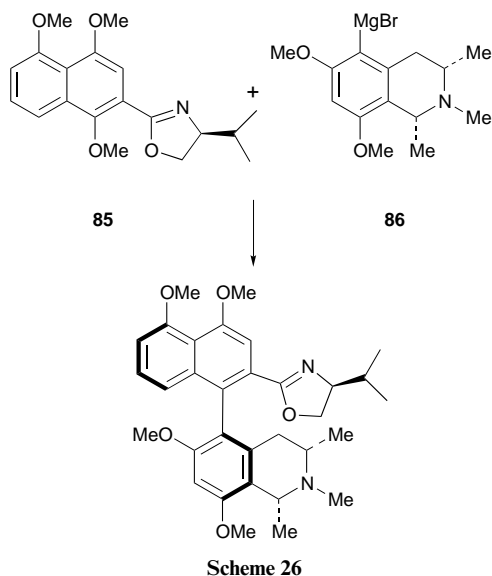
An alternative approach for the asymmetric synthesis of amines involves Grignard addition to chiral iminium ions¹⁵⁵ or nitrones.¹⁵⁶ Addition of the alkynyl Grignard reagent **83** to the iminium ion derived from the quinoline **84** and an acid chloride, was used in the synthesis of the enediyne core of dynamycin A.¹⁵⁷ Quinolone alkaloids can be prepared in a similar way.¹⁵⁸ The formation of imines by addition of Grignard reagents to nitriles has been reported.¹⁵⁹



Grignard reagents can add to activated aromatic compounds, such as (arene)chromium complexes (to give axially chiral biaryls),¹⁶⁰ purin-2-ones¹⁶¹ and naphthalenes substituted by an electron-withdrawing group.¹⁶² For example, a synthesis of (+)-*O*-methylancistrocline has been achieved by coupling the naphthalene **85** with the Grignard reagent **86** (Scheme 26).^{162a}

Addition of Grignard reagents to alkenes activated by electron-withdrawing substituents has been reported.¹⁶³ Conjugate addition of isopropenylmagnesium bromide to the enone **87** (Scheme 27) was used in the synthesis of euonyminol and 3,4-dideoxymaytol.¹⁶⁴ The isopropenyl group is delivered to the α face by prior complexation to the 6α -hydroxy substituent.

The reaction of Grignard reagents with a variety of electrophiles can be promoted by transition metal catalysts. Nickel- or palladium-catalysed cross coupling of Grignard reagents with vinyl halides,¹⁶⁵ aryl triflates,¹⁶⁶ allylic ethers¹⁶⁷ and prop-2-ynyl dithioacetals¹⁶⁸ have been reported. A chiral zirconocene complex has been used for the asymmetric carbomagnesiation of unactivated alkenes.¹⁶⁹ Methyltrisopropoxytitanium

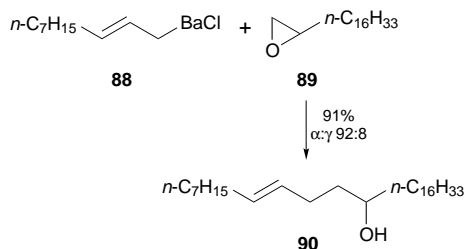


Scheme 27 Reagents: i, LDA, 15-crown-5, $\text{CH}_2=\text{C}(\text{Me})\text{MgBr}$, THF

$[\text{MeTi}(\text{OPr}^i)_3]$ has been found to mediate the synthesis of cyclopropylamines from *N,N*-dialkyl carboxylic amides and Grignard reagents.¹⁷⁰

3.2 Barium

Allylic Grignard (and other organometallic) reagents normally react with electrophiles through the γ -carbon of the allyl reagent. In contrast, allylic barium reagents have been found to couple to allylic phosphates (and other allylic electrophiles) with high α,α' selectivity, giving rise to 1,5-dienes.¹⁷¹ The regioselective coupling of allylic barium reagents with epoxides also occurs with high α selectivity. For example, the organobarium reagent **88** adds to the epoxide **89** to give the alcohol **90** as the major product (**Scheme 28**).¹⁷²

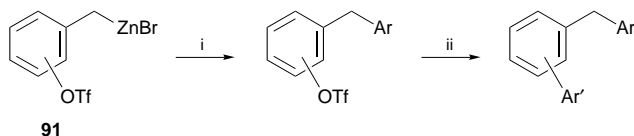


3.3 Zinc

Organozinc compounds play an important role in organic synthesis, aided by their ability to tolerate a range of functional groups. They can be prepared by halogen–zinc exchange with dialkylzincs,¹⁷³ lithium zincates¹⁷⁴ or activated zinc metal.¹⁷⁵ Other methods include boron– or tellurium–zinc exchange¹⁷⁶ and hydrozincation of terminal alkenes.^{173a}

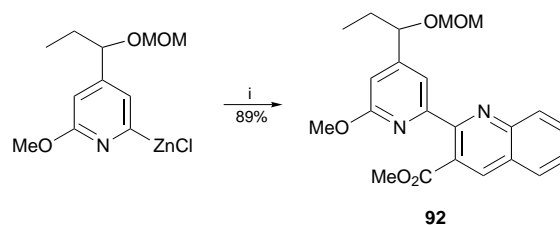
In the presence of transition metal catalysts, organozinc reagents react with a variety of electrophiles. Ketones can be prepared by reaction of diorganozinc compounds with acid chlorides in the presence of CoBr_2 .¹⁷⁷ Addition of phosphino

halides provides phosphines or diphosphines.¹⁷⁸ An alternative preparation of ketones involves reaction of organozinc halides, under an atmosphere of carbon monoxide in the presence of palladium(0), with aryl halides.¹⁷⁹ The direct coupling of an organozinc halide with an aryl or vinyl halide (or triflate) under palladium catalysis has found use by a number of research groups.¹⁸⁰ For example, substituted aromatic compounds can be prepared by coupling benzylic zinc bromides **91** with aryl iodides (**Scheme 29**).¹⁸¹ The product aryl triflate can be used in a second zinc bromide coupling at higher temperature.



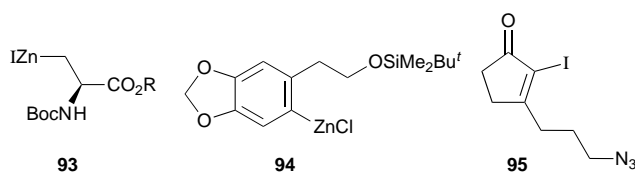
Scheme 29 Reagents: i, ArI, $\text{Pd}(\text{dba})_2$, tri-*o*-furylphosphine (tfp), THF, room temp.; ii, $\text{Ar}'\text{ZnBr}$, $\text{Pd}(\text{dba})_2$, dppf, 70 °C

The coupling of arylzinc halides with aryl halides under palladium catalysis (Negishi cross-coupling) provides a mild method for the generation of biaryls.¹⁸² Syntheses of biaryls related to korpenamine and michellamine¹⁸³ and to lamellarins¹⁸⁴ have been reported using this methodology. The pyridine **92**, applied to a formal synthesis of camptothecin, was prepared by an arylzinc chloride coupling (**Scheme 30**).¹⁸⁵ Indolylzinc halides couple with aryl halides to provide indole alkaloids.¹⁸⁶ Couplings with nucleic acid bases give aryl-substituted nucleosides.¹⁸⁷



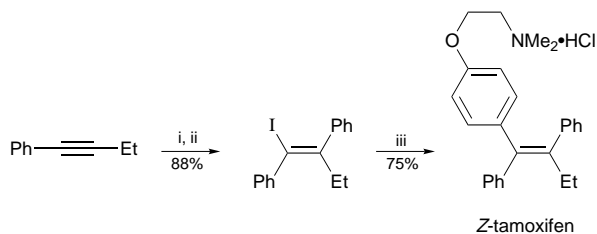
Scheme 30 Reagents: i, methyl 2-chloroquinoline-3-carboxylate, 5 mol% $\text{Pd}(\text{PPh}_3)_4$, THF, reflux

The serine-derived organozinc iodide **93** couples to aryl halides under palladium catalysis to give isodityrosine, pyridylalanines and chromium-complexed phenylalanine derivatives.¹⁸⁸ An approach toward the synthesis of cephalotaxine makes use of the arylzinc chloride **94**, which couples to the vinyl iodide **95**.¹⁸⁹



The cross-coupling of vinylzinc halides with vinyl halides has led to the synthesis of polyenes¹⁹⁰ and nakienones A and B.¹⁹¹ A synthesis of tamoxifen (**Scheme 31**) uses a nickel-catalysed carbonylation of 1-phenylbut-1-yne, followed by a palladium-catalysed coupling of the product vinyl iodide with an arylzinc bromide.¹⁹²

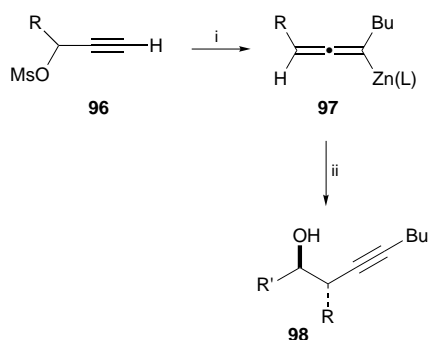
Palladium- or nickel-catalysed radical cyclizations of unsaturated iodides or bromides are promoted by dialkylzincs.¹⁹³ The product organozinc halide, including the related pyrrolidines formed by zinc enolate cyclization,¹⁹⁴ can be trapped with a variety of electrophiles. Cyclization of enones possessing unsaturated side chains has been reported using $\text{Ni}(\text{cod})_2$ and organozinc reagents.¹⁹⁵ Copper salts or the cobalt complex $\text{Co}(\text{acac})_2$ promote conjugate addition of dialkylzincs to



Scheme 31 Reagents: i, Ph_2Zn , $\text{Ni}(\text{acac})_2$; ii, I_2 ; iii, ArZnBr , $\text{Pd}(\text{dba})_2$, Ph_3P , then HCl

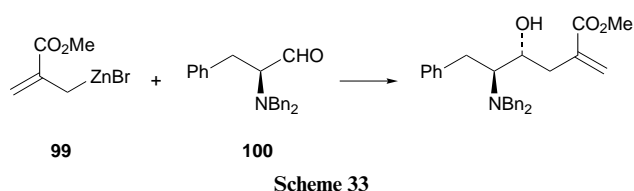
enones.¹⁹⁶ Copper-catalysed alkylations of organozinc halides with allylic epoxides¹⁹⁷ or glycols¹⁹⁸ has been reported.

The reaction of terminal alkynes with triorganozincates allows the formation of alkynyl and allenyl zinc reagents.¹⁹⁹ For example, addition of lithium tributylzincate to the alkyne **96** gives the zinc reagent **97** (Scheme 32).^{199a} Subsequent reaction with an aldehyde (or other electrophile) gives predominantly the *anti*-but-3-ynyl alcohol **98**.



Scheme 32 Reagents: i, Bu_3ZnLi , THF ; ii, $\text{R}'\text{CHO}$

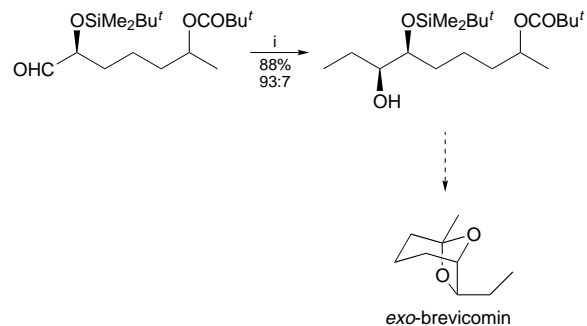
The allylzincation of alkynyl- or vinyl-lithium species has allowed the synthesis of novel unsaturated compounds, *via* organo-*gem*-bismetallics.²⁰⁰ Allylzinc bromides are popular reagents for allylation of aldehydes.²⁰¹ For example, a key step in a synthesis of Phe-Phe hydroxyethylene dipeptide isosteres involves the use of the allylzinc bromide **99** and the aldehyde **100** (Scheme 33).^{201a} Propynylation of sugar aldehydes has resulted in a synthesis of 6-deoxyheptoses.²⁰² Allylation of imines and oximes gives homoallylic amines or allyl glycine derivatives.²⁰³



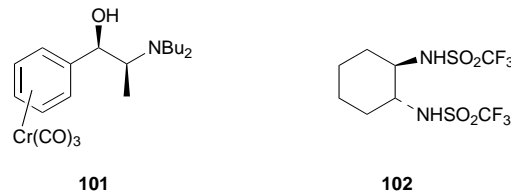
Scheme 33

The formation of chiral alcohols by addition of aldehydes to organozinc reagents continues to receive considerable attention.²⁰⁴ Enantioselective syntheses of (–)-phoracantholide and (+)-lasiodiplodin have been achieved using addition of aldehydes to dimethylzinc in the presence of the chiral catalyst **101**.²⁰⁵ Autocatalytic reactions with diisopropylzinc and heteroaryl aldehydes or isophthalaldehyde have been examined.²⁰⁶ Highly enantioselective formation of a range of secondary alcohols, including the natural product ginnol, has been achieved using dialkylzinc, the chiral catalyst **102** and $\text{Ti}(\text{OPr}^i)_4$.^{176a} The same catalyst has been used in syntheses of (–)-*exo*- and (–)-*endo*-brevicomins (Scheme 34).²⁰⁷

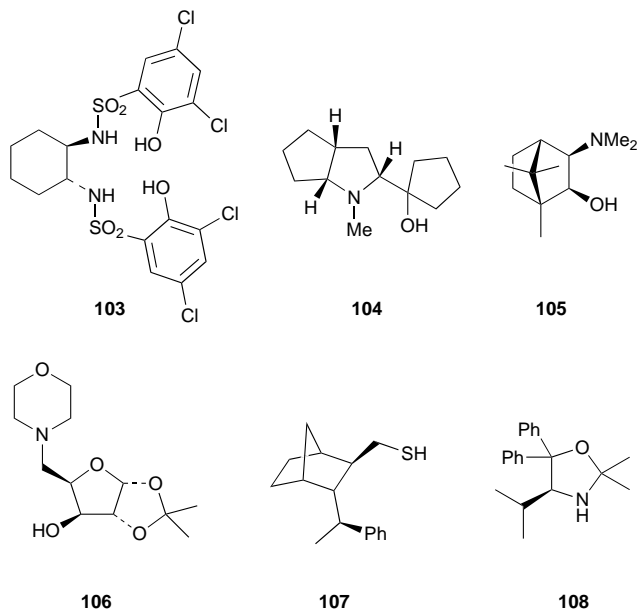
The enantioselective addition of diethylzinc to a variety of aldehydes, including non-aromatic aldehydes, has been achieved using the catalyst **103**.²⁰⁸ Other catalysts in the addition of benzaldehyde to diethylzinc are known to provide the



Scheme 34 Reagents: i, Et_2Zn , $\text{Ti}(\text{OPr}^i)_4$, 5 mol% **102**

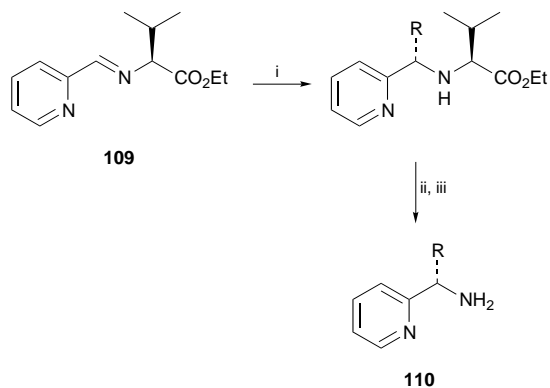


product 1-phenylpropan-1-ol in greater than 90% enantiomeric excess. These are often based on β -amino alcohols²⁰⁹ such as **104** (giving 1-phenylpropan-1-ol, 99% ee)²¹⁰ and **105** (98% ee),²¹¹ the latter displaying chirality amplification (catalyst of 15% ee gave product of 95% ee). Related catalysts **106**,²¹² **107**²¹³ and **108**²¹⁴ based on β -amino alcohols, all give 1-phenylpropan-1-ol in excellent 96–100% ee. The catalyst prepared by mixing binaphthol and $\text{Ti}(\text{OPr}^i)_4$ has been reported to give 1-phenylpropan-1-ol in 95.6% ee at -78°C (64% conversion) or 91.9% ee at 0°C (100% conversion).²¹⁵



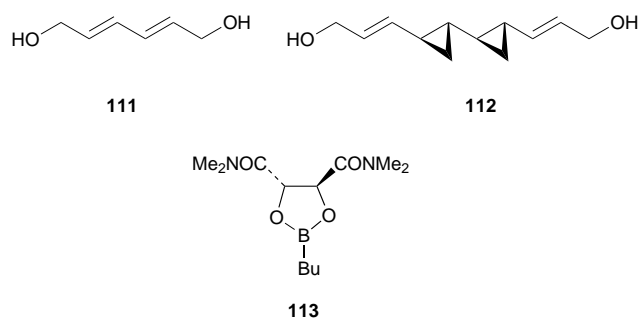
Chiral catalysts have been used to promote the enantioselective addition of diethylzinc to *N*-diphenylphosphinoylimines²¹⁶ and to nitrones.²¹⁷ Diastereoselective addition to imines bearing a chiral auxiliary on the nitrogen atom is possible.²¹⁸ For example, addition of triorganozincate reagents to the imine **109** has provided a synthesis of chiral 1-(2-pyridyl)alkylamines **110** (Scheme 35).^{218a} Diarylzincs have been reported to add to glycine cation equivalents to give α -aryl α -amino esters.²¹⁹

Diethylzinc in the presence of diiodomethane is thought to generate the organozinc reagent $\text{Zn}(\text{CH}_2\text{I})_2$, an effective agent for cyclopropanation of, in particular, allylic alcohols. This reagent has found use in the synthesis of taxusin,²⁸ the cyclopropane unit of curacin A,²²⁰ (+)-ptilocaulin²²¹ and



Scheme 35 Reagents: i, RMe_2ZnLi or RMe_2ZnMgX , THF; ii, $LiAlH_4$; iii, H_5IO_6 , $MeNH_2$

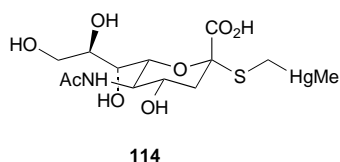
(-)-pinidine (using CH_3CHI_2 and Et_2Zn).²²² Considerable effort has been applied to the synthesis of the polycyclopropanes U-106305 and FR-900848.²²³ For example, double cyclopropanations of the allylic alcohols **111** and **112** with $Zn(CH_2I)_2$ and the chiral ligand **113** were used in a synthesis of the antifungal agent FR-900848.²²⁴



3.4 Cadmium and mercury

Organocadmium reagents,²²⁵ being less basic than their corresponding organolithium or organomagnesium salts, can couple with reactive electrophiles under relatively mild conditions. This is important for forming sensitive β,γ -unsaturated ketones, which can be prepared by allylation of acid chlorides using allyl bromides and cadmium metal in THF at room temperature.²²⁶ Diarylcadmium reagents have been used for the synthesis of C-nucleosides.²²⁷

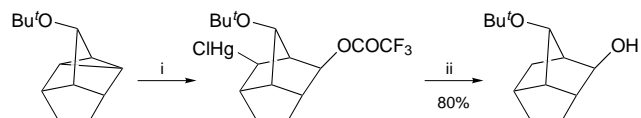
The mercury-containing *N*-acetylneuraminic acid analogue **114** has been prepared by *S*-alkylation with iodomethyl (methyl)mercury ($I(CH_2HgMe)$).²²⁸ Oxymercuration of allylic ethers²²⁹ or cyclopropanes²³⁰ have been used in synthesis. Functionalized diquinanes can be prepared by regio- and stereo-selective cyclopropane ring opening (Scheme 36).²³¹ A synthesis of (-)-solavetivone uses cyclization of the organomercury chloride **116**, generated by selective ring opening of the cyclopropane **115** (Scheme 37).²³² Use of *tert*-butylmercury halides for radical-mediated cyclizations or reductive *tert*-butylations have been reported.²³³



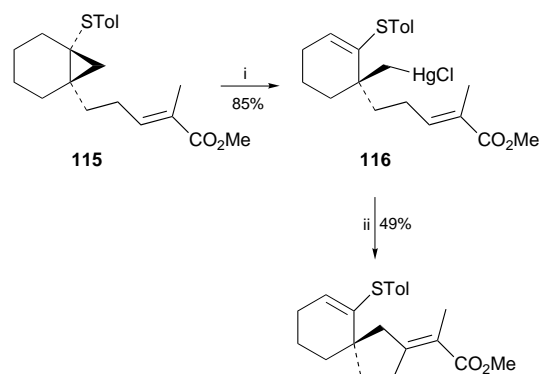
4 Group 13

4.1 Aluminium

Organoaluminium reagents have been used for the alkylation of aldehydes and ketones,²³⁴ oxonium ions²³⁵ and α -bromo glycine derivatives.²³⁶ For example, lactol acetates **117** react with the

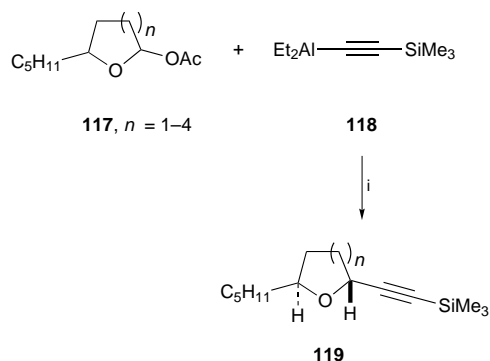


Scheme 36 Reagents: i, $Hg(OCOCF_3)_2$, CH_2Cl_2 , then $NaCl$; ii, $LiAlH_4$, THF



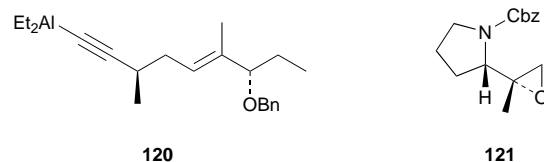
Scheme 37 Reagents: i, $Hg(OCOCF_3)_2$, CH_2Cl_2 , $NaOAc$, then $NaCl$; ii, Li_2PdCl_4 , THF-DMF, $KHCO_3$

organoaluminium reagent **118** to give the alkynes **119** with high *trans:cis* selectivity (Scheme 38).^{235a}

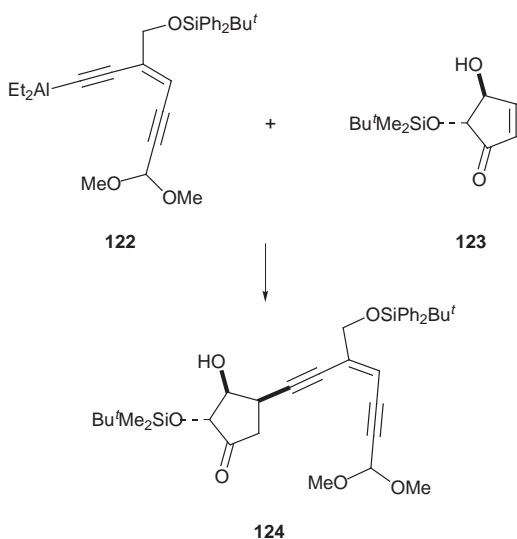


Scheme 38 Reagents: i, $BF_3 \cdot OEt_2$, CH_2Cl_2 , $-78^\circ C$, 93–97%

Alkylation of epoxides with organoaluminium reagents can occur with high regioselectivity.²³⁷ Alkynyl organoaluminium species, such as **120**, were used by Overman and co-workers for the synthesis of pumiliotoxins A and B, by ring opening of the epoxide **121**.²³⁸ The alkynyl organoaluminium species **122** adds to the enone **123** to give the enediyne **124** (Scheme 39).²³⁹ Acetal cleavage of **124** and intramolecular aldol condensation provides the ring system of neocarzinostatin and kedarcidin chromophores. Conjugate addition of a methyl group using Me_3Al and $Ni(acac)_2$ onto a cyclopentenone was used in a four step synthesis of α -cuparenone.²⁴⁰ β -Alkyl α -halo carboxylic acid derivatives have also been prepared by 1,4-addition using organoaluminium reagents.²⁴¹

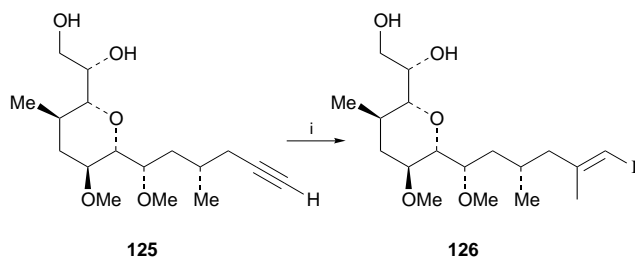


The asymmetric alkylaluminum of alkenes has been reported to proceed with excellent enantioselectivities in the presence of chiral zirconocene catalysts.²⁴² Carboalumination of alkynes have been investigated²⁴³ and applied to the synthesis of FK-506 (Scheme 40).¹⁴³ Methylalumination of the alkyne **125** in the presence of Cp_2ZrCl_2 gave, after trapping with



Scheme 39

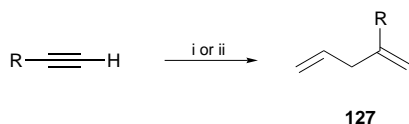
iodine, the vinyl iodide **126**, the C-8 to C-20 portion of FK-506. Vinylaluminium species can also be prepared by tellurium-aluminium exchange,²⁴⁴ or by hydroalumination of alkynes.²⁴⁵



Scheme 40 Reagents: i, Me_3Al , Cp_2ZrCl_2 then I_2

4.2 Gallium and indium

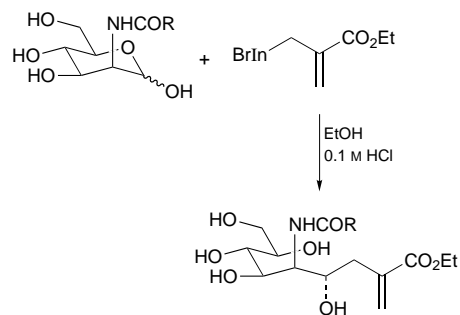
The organogallium reagent Me_2GaCl has been used to activate glycosyl fluorides to glycosidation.²⁴⁶ The allylation of alkynes with allylgallium or allylindium reagents provides 1,4-dienes **127** (Scheme 41).²⁴⁷



Scheme 41 Reagents: i, $\text{CH}_2=\text{CHCH}_2\text{SiMe}_3$, GaCl_3 , then MeMgBr , H_2O ; ii, $\text{CH}_2=\text{CHCH}_2\text{I}$, In , THF , then HCl

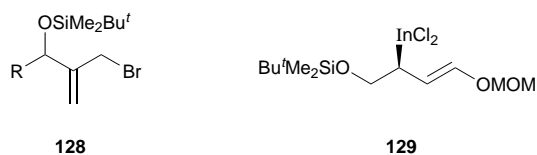
A number of allylations of carbonyl compounds using allylindium reagents have been reported during the period of this review.²⁴⁸ The homoallylic alcohol products result from γ -addition of the allyl unit to the aldehyde or ketone. The ability to effect allylation in aqueous solution or alcoholic solvents allows the use of unprotected hydroxy carbonyl compounds. Syntheses of *N*-acetylneuraminic acid analogues by indium-mediated allylation of unprotected carbohydrates makes use of this methodology, an example of which is shown in Scheme 42.²⁴⁹

Addition of allylindium reagents to α -hetero aldehydes can occur with reasonable diastereoselectivity.²⁵⁰ High levels of diastereoselectivity result from allylations of aldehydes with the allylindium reagents **128**.²⁵¹ Diastereoselective allylation of imines has also been reported.²⁵² Fluorinated or chlorinated homoallylic alcohols can be prepared using allylindium addition to aldehydes.²⁵³ The allylindium reagents can be made by insertion of indium metal into allylic halides or by transmetalation of allylstannanes with InCl_3 or InI_3 .²⁵⁴ The use of



Scheme 42

α,δ -bisoxygenated allylstannanes gives rise to allylindium reagents, such as **129** and hence, on addition to aldehydes, carbohydrate precursors.^{254a} Reaction of allylindium reagents with diselenides gives allyl or prop-2-ynyl selenides.²⁵⁵

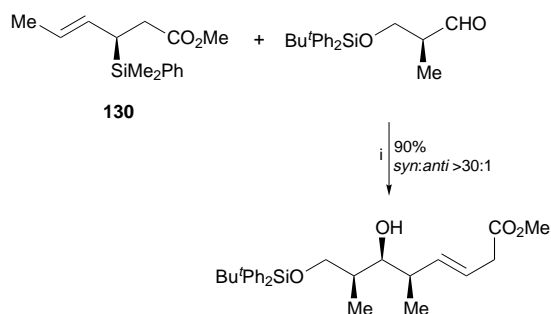


5 Group 14

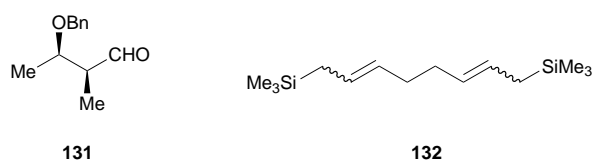
5.1 Silicon

5.1.1 Allylsilanes

The ability of allylsilanes (or allenylsilanes) to undergo efficient allylation (or propynylation) reactions has resulted in a number of publications reporting methods for their preparation.²⁵⁶ The addition of allylsilanes to aldehydes under Lewis acid catalysis, has found use for the synthesis of homoallylic alcohols, oxetanes and dioxanes.²⁵⁷ Panek and co-workers have described the stereoselective additions of allylsilanes, such as **130** (Scheme 43), to aldehydes in syntheses of the C-1 to C-17 and C-19 to C-34 fragments of rutamycin²⁵⁸ and the C-1 to C-17 and C-19 to C-34 fragments of ulapualide A.²⁵⁹ Stereoselective addition of allyltrimethylsilane to the chiral aldehyde **131**, using TiCl_4 catalysis, provides a building block for a synthesis of pederic acid derivatives.²⁶⁰ High enantioselectivities can be obtained in the asymmetric allylation of achiral aldehydes using allylsilanes.²⁶¹

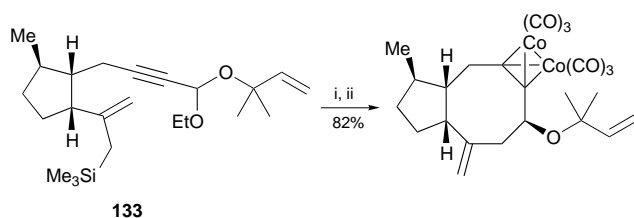


Scheme 43 Reagents: i, TiCl_4 , CH_2Cl_2



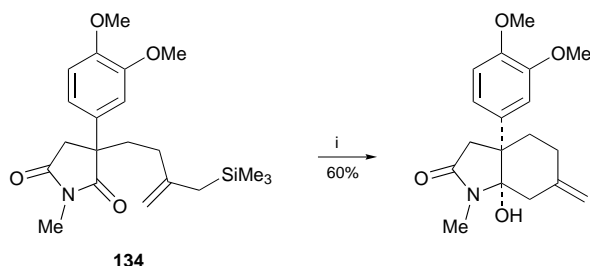
Diallylation of the carbonyl group of an acid anhydride or of oxonium ions, to give carbocycles, is possible using the bis-(allylsilane) **132**.²⁶² Monoallylation of acid chlorides to give β,γ -unsaturated ketones has been reported.²⁶³ Oxonium ions

can act as electrophiles in inter-²⁶⁴ or intra-molecular²⁶⁵ allylations. For example, *C*-glycosidation of ribofuranosides can be achieved with allyltrimethylsilane and a Lewis acid.²⁶⁶ A synthesis of (+)-epoxydictymene uses, as a key step, the intramolecular closure of the allylsilane **133** (Scheme 44).⁷



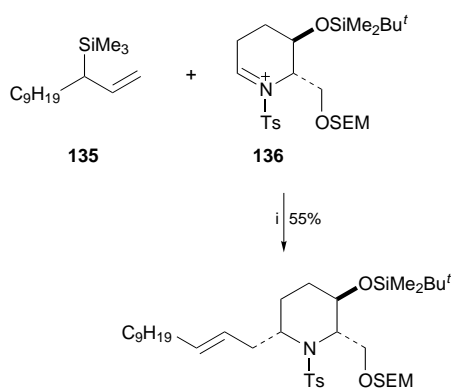
Scheme 44 Reagents: i, $\text{Co}_2(\text{CO})_8$, Et_2O ; ii, Me_3SiOTf , Et_2O , $-78\text{ }^\circ\text{C}$

Intramolecular closure of an allylsilane can be accomplished onto a ketone²⁶⁷ or onto the carbonyl group of an imide.²⁶⁸ The latter reaction was used in a synthesis of mesembrine by cyclization of the allylsilane **134** with CsF (Scheme 45).



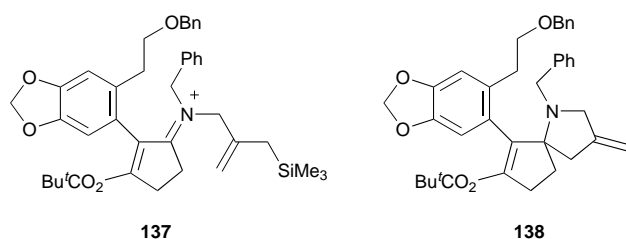
Scheme 45 Reagents: i, CsF , DMF , room temp.

Addition of allylsilanes to iminium ions gives rise to homoallylic amines²⁶⁹ or new iminium ions (by ene reaction).²⁷⁰ The allylsilane **135** (Scheme 46) adds to the iminium ion **136**, generated from the α -ethoxysulfonamide, in a synthesis of desoxoprosophylline.²⁷¹

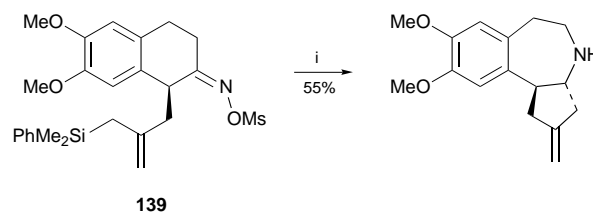


Scheme 46 Reagents: i, $\text{BF}_3 \cdot \text{OEt}_2$, -78 to $-30\text{ }^\circ\text{C}$

Irradiation of the allylsilane **137** effects intramolecular closure to the spirocyclic amine **138** in a formal synthesis of cephalotaxine.²⁷² Cyclizations of isonitriles provide pyrrolines.²⁷³ Intramolecular ene reactions of allenylsilanes with imines have been used for syntheses of (–)-pancracine, (–)-coccinine and 5,11-methanomorphanthridines.²⁷⁴



An alternative approach to the cephalotaxine framework uses the cyclization of the allylsilane **139** under Beckmann rearrangement conditions (Scheme 47).²⁷⁵ Intra- or intermolecular reactions of allylsilanes with carbocation intermediates have been reported.²⁷⁶ Syntheses of γ -cyclohomocitral, pallelescensone and ancistrodial make use of an intramolecular reaction of an allylsilane with an epoxide.²⁷⁷ Ring opening of aziridines by allylsilanes provides γ -amino alkenes.²⁷⁸ Cyclopropanes can be formed by cyclization onto alkyltriflates.²⁷⁹ Allylation of phenylthio- or phenylseleno-containing acetals, or of sulfines gives access to homoallylic sulfides, selenides or allylic sulfoxides.²⁸⁰



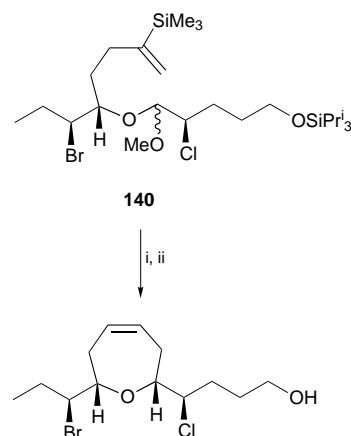
Scheme 47 Reagents: i, Bu_2AlH , CH_2Cl_2 , -78 to $0\text{ }^\circ\text{C}$

Titanium tetrachloride promotes the intermolecular conjugate addition reaction with allylsilanes.²⁸¹ Intramolecular conjugate addition has been applied to the synthesis of bicyclo-[4.3.0]nonanes,²⁸² endiandric acid²⁸³ and the *Strychnos* alkaloids tubifolidine, dihydroakuammicine and akuammicine.²⁸⁴

Allylsilanes have found use in palladium-catalysed cyclization reactions.²⁸⁵ Allylations of alkynes (with allylsilanes and EtAlCl_2) or of allylsilanes (with allylboranes) have been reported.²⁸⁶

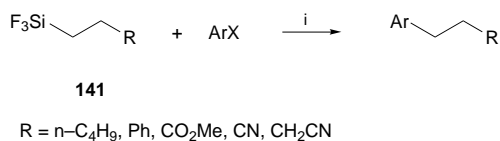
5.1.2 Other organosilanes

Many organosilanes other than allylsilanes have been used in organic synthesis. Vinylsilanes can be prepared by a number of methods, particularly from alkynes,²⁸⁷ but also from allenes, ketones, α -silyl epoxides or β -silyl sulfones.²⁸⁸ They have found use for the preparation of vinyl iodides²⁸⁹ and for carbon-carbon bond forming reactions with acid chlorides²⁹⁰ (in a synthesis of a fragment of desepoxyrosaramycin), with ketones²⁹¹ and with intramolecular oxonium ions.²⁹² The latter chemistry has allowed syntheses of cyclic ethers, including (+)-isolaurepinnacin by cyclization of the vinylsilane **140** with BCl_3 (Scheme 48).^{292a}



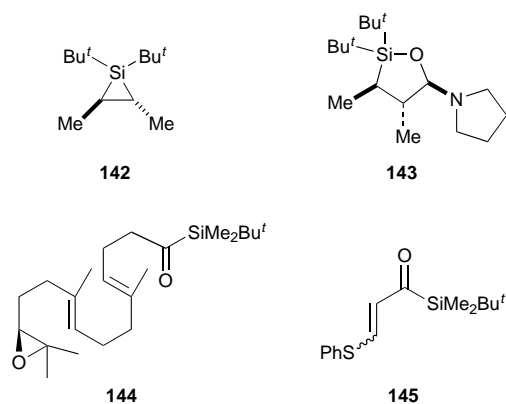
Scheme 48 Reagents: i, BCl_3 , CH_2Cl_2 , -78 to $0\text{ }^\circ\text{C}$; ii, TBAF , THF

Coupling of vinylsilanes with aryl halides using palladium catalysis can be used for the preparation of functionalized styrenes.²⁹³ Homocoupling reactions of vinyl- or aryl-silanes to give dienes or biaryls can be achieved under palladium or copper(I) catalysis.²⁹⁴ The palladium-catalysed coupling of alkyltrifluorosilanes **141** with aryl halides has been reported (Scheme 49).²⁹⁵

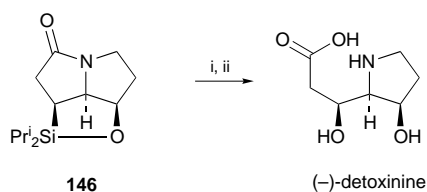


Scheme 49 Reagents: i, 5 mol% Pd(PPh₃)₄, TBAF, THF, 100 °C

α -Silyl epoxides, generated by epoxidation of vinylsilanes, have found use for the synthesis of alkenes, aldehydes, epoxides (e.g. disparlure) and furans.²⁹⁶ Siliranes, such as **142**, react with formamides, such as 1-formylpyrrolidine, to give the insertion product **143**.²⁹⁷ Acylsilanes are versatile synthetic intermediates, finding use for the synthesis of vinyl sulfones and vinylsilanes,²⁹⁸ alcohols²⁹⁹ and ketones as part of C-disaccharides.³⁰⁰ Nucleophilic additions (by a vinyl lithium or an enolate) to the acylsilanes **144**⁶³ and **145**³⁰¹ are key steps in syntheses of the terpene dammareniol II and the cyclopentenones clavulones II and III, respectively. α -Silyl γ -lactones can be prepared by lithiation and carbonylation of trimethylsilyldiazomethane, followed by epoxide ring-opening.³⁰²



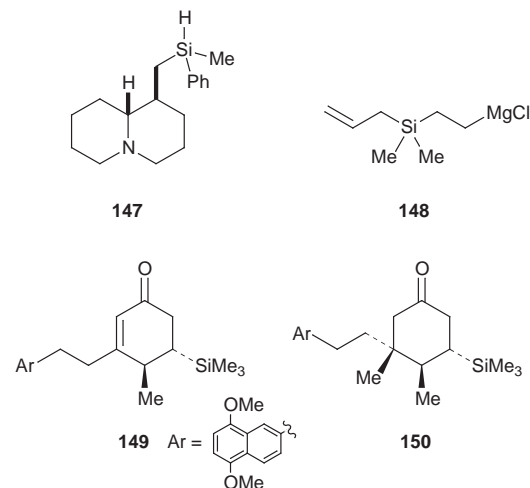
The ability to convert a silyl group stereospecifically to a hydroxy group is a useful feature of organosilicon chemistry. Cleavage of the carbon–silicon bond of allylsilanes to give allylic alcohols has found use in syntheses of (+)-conduritol E and (–)-2-deoxy-*allo*-inositol,³⁰³ (–)-swainsonine³⁰⁴ and the C-21 to C-42 fragment of rapamycin.³⁰⁵ Cycloaddition reactions with vinylsilanes, followed by conversion of the product alkylsilanes to alcohols, have been used in syntheses of (+)-crotanecine and (–)-detoxinine.³⁰⁶ For example, oxidation of the silane **146** provides, after acidic hydrolysis (–)-detoxinine (Scheme 50).^{306b}



Scheme 50 Reagents: i, KF, H₂O₂, THF, MeOH, 60 °C; ii, HCl

The final step in a synthesis of the alkaloid epilupinine involves oxidative cleavage of the silane **147**.³⁰⁷ Other silyl-to-hydroxy conversions are reported in syntheses of lavandulol, triptoquinones B and C, triptocallol and the δ -lactone of compactin.³⁰⁸ The Grignard reagent **148** acts as a β -hydroxyethyl carbanion equivalent, with conversion of the silyl to the hydroxy group using KHF₂ and CF₃CO₂H, followed by H₂O₂.³⁰⁹ Bis-silylation of alkenes allows the preparation of 1,2-diols and hence a formal synthesis of (–)-avenaciolide.³¹⁰

Silyl groups are useful in organic synthesis as control elements in regioselective allylations³¹¹ or Nazarov cyclizations for the synthesis of silphinene and pentalene.³¹² Stereoselective

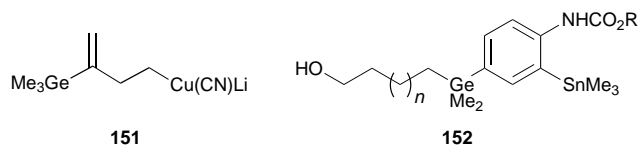


reactions mediated by a silyl group include conjugate additions,³¹³ aldol condensations,³¹⁴ cycloadditions³¹⁵ and cyclizations.³¹⁶ For example, a synthesis of (–)-cordiaquinone B makes use of a silyl group in cyclohexenone **149** to direct conjugate addition of Me₂CuLi to give the diastereomerically pure cyclohexenone **150**.^{313a}

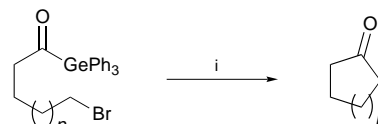
Cleavage of carbon–silicon bonds with fluoride has provided a route to azomethine ylides³¹⁷ or benzofuran 2,3-quinodimethanes³¹⁸ and hence cycloaddition products on trapping with electron-deficient alkenes. Fluoride ion-induced cyclization to 1(2*H*)-isoquinolones³¹⁹ and silyl-directed fragmentation of a bridging carbon–carbon bond to give medium-ring alkenes³²⁰ have been reported.

5.2 Germanium

Vinyl- or aryl-germanes can act as masked vinyl or aryl halides and have therefore found application in organic synthesis (using vinylgermane **151**)³²¹ and as linkers in solid phase synthesis (from arylgermane **152**).³²² As an alternative deprotection strategy, the arylgermane or alkynylgermane³²³ can undergo protodegermylation. Vinylgermanes can be prepared from ketones³²⁴ and their use in the germanium-Peterson reaction has been investigated.³²⁵



In the presence of scandium(III) triflate, allylgermanes act as allylating agents for aldehydes or ketones in aqueous media.³²⁶ Inter- or intra-molecular reaction of alkyl halides with acylgermanes occurs under radical conditions to provide ketones.³²⁷ An in-depth study has been reported of the formation of cyclopentanones and cyclohexanones by this method (Scheme 51).^{327a}



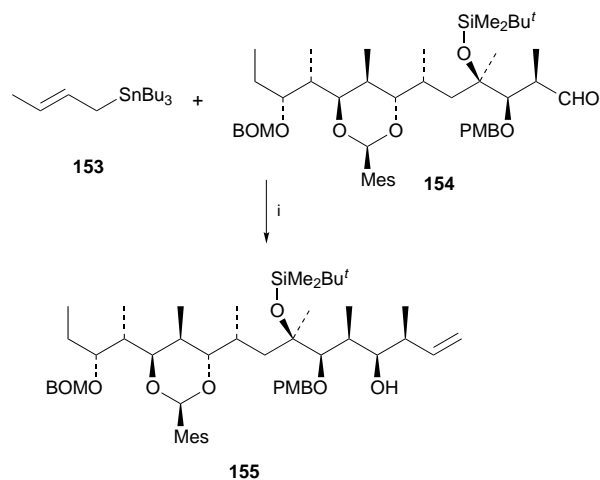
Scheme 51 Reagents: i, Ph₃SnH, AIBN or *h* ν

5.3 Tin

5.3.1 Allylstannanes

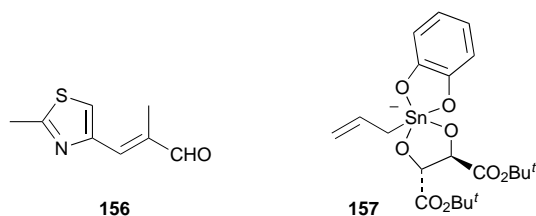
Allylstannanes can be prepared by various methods³²⁸ and act as useful allylating agents by either heterolytic or homolytic pathways. This review will focus on heterolytic cleavage of the carbon–tin bond, a process commonly used for the allylation of

aldehydes (or ketones).³²⁹ The addition of allylstannanes to chiral aldehydes can occur with high diastereoselectivity. A synthesis of erythromycin B involves the addition of the crotylstannane **153** to the aldehyde **154**, which occurs to give all four diastereomeric homoallylic alcohols, but in which the major, separable product **155** is the desired isomer (Scheme 52).³³⁰



Scheme 52 Reagents: *i*, BF₃·OEt₂, 69% (+24% other isomers)

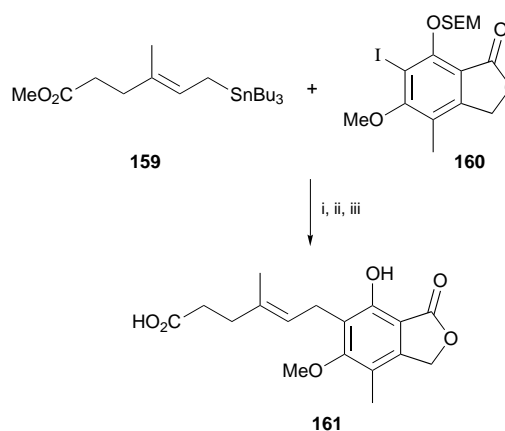
Diastereoselective allylation of chiral aldehydes are important carbon-carbon bond forming steps in syntheses of the elaiophyllin aglycon³³¹ and a fragment of epothilone A.³³² An alternative route to epothilone A uses asymmetric allylation of the aldehyde **156** with allyl tributyltin and BINOL-Ti(OPr^t)₄.³³³ This reagent combination gives high enantioselectivities in the allylation of a range of aldehydes³³⁴ and has found application in the preparation of the C-1 to C-21 fragment of rapamycin³³⁵ and the C-32 to C-40 fragment of phorbaxozoles A and B.³³⁶ Asymmetric allylations with BINAP-silver(i) or bis(oxazoline)-zinc(ii) complexes have also been reported.³³⁷ An alternative reagent (other than allyltributyltin and a chiral metal complex) for asymmetric allylation is the allylstannane **157**, which gives high enantiomeric excesses of the product homoallylic alcohols with aromatic aldehydes.³³⁸



Scheme 53 Reagents: *i*, BF₃·OEt₂, CH₂Cl₂, -90 °C

amines with high diastereoselectivities.³⁴⁷ Conversion of allylstannanes to allylic alcohols can be effected using selenium dioxide.³⁴⁸

Some transition metal-catalysed couplings with allylstannanes have been reported. 1,4-Dienes are formed on coupling to alkynes using ZrCl₄.³⁴⁹ Allylation of allylstannanes can be performed using CuI.³⁵⁰ A synthesis of mycophenolic acid **161** uses the coupling of the allylstannane **159** with the aryl iodide **160** (Scheme 54).³⁵¹



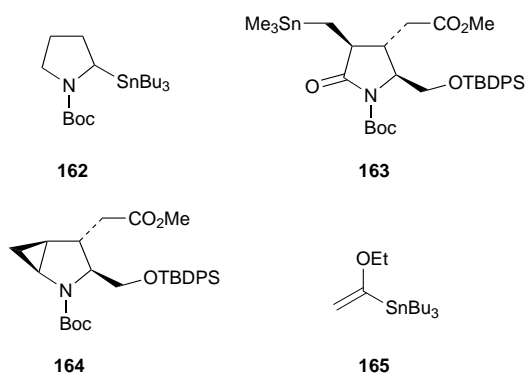
Scheme 54 Reagents: *i*, Pd(dba)₂, Ph₃As, NMP, 110 °C; *ii*, H₂SO₄, MeOH, THF; *iii*, LiOH, THF, H₂O

5.3.2 Other organostannanes

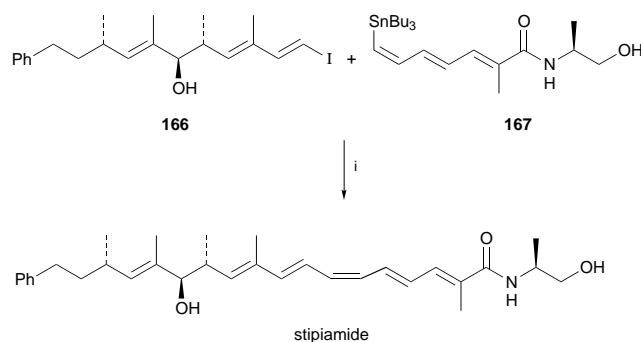
Organostannanes substituted by α -amino or α -oxy groups can be prepared in high yields and used in a number of different ways in organic synthesis.³⁵² The stannane **162** couples with silyl enol ethers under oxidative conditions and has been used in a synthesis of stemonamide.³⁵³ Partial reduction and cyclopropanation of the stannyl lactam **163**, itself prepared by tin-mediated radical cyclization, gives the pyrrolidine **164**.³⁵⁴ Other cyclopropanations with organostannanes or ring-opening of methylenecyclopropanes to give organostannanes have been reported.³⁵⁵

Vinylstannanes, prepared by hydrostannylation of alkynes³⁵⁶ or by other methods,³⁵⁷ are important intermediates in organic synthesis. Palladium-catalysed cross-coupling reactions of vinylstannanes with organohalides have been used as key carbon-carbon bond forming steps in many syntheses. Couplings to aryl³⁵⁸ or heteroaryl halides³⁵⁹ or triflates³⁶⁰ provide aryl-substituted alkenes. Syntheses of dimethyl sulfomycinamate and ellipticine both involve coupling the vinylstannane **165** with a bromopyridine.³⁶¹

Palladium-catalysed couplings of vinylstannanes with vinyl iodides³⁶² or triflates³⁶³ provide dienes with control of alkene geometry. Such intermolecular couplings have found applic-

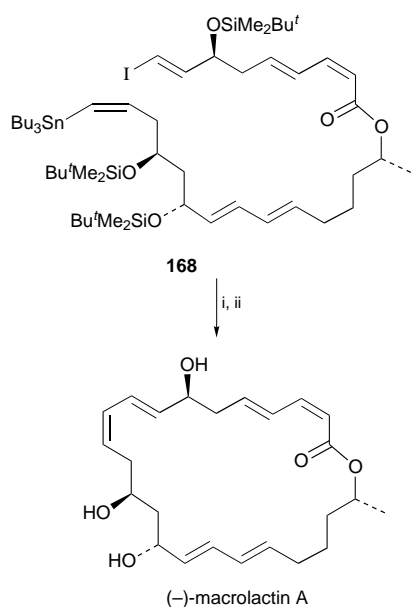


ation in syntheses of calyculin C,³⁶⁴ limocrocin,³⁶⁵ alisamycin,⁹⁸ stipiamide³⁶⁶ and bafilomycin A₁.³⁶⁷ For example, coupling the vinyl iodide **166** with the vinylstannane **167** gives the polyene stipiamide (Scheme 55).



Scheme 55 Reagents: i, (MeCN)₂PdCl₂, NMP

Both inter- and intra-molecular couplings of vinylstannanes with vinyl iodides were used to construct all three diene moieties of (–)-macrolactin A, the final coupling involving the stannane **168** (Scheme 56).³⁶⁸ Other intramolecular couplings of vinylstannanes with vinyl iodides have allowed macrocyclizations to give (–)-rapamycin,³⁶⁹ (–)-haliclomadamine³⁷⁰ and the core of elaiophylin³⁷¹ and pateamine.³⁷²

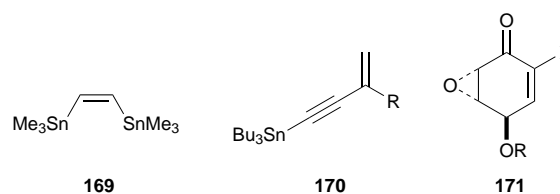


Scheme 56 Reagents: i, Pd(dba)₂, NMP, Pr₂NEt; ii, Bu₄NF, AcOH, THF

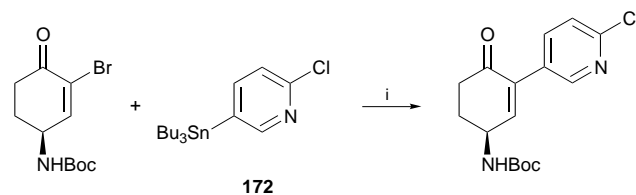
A synthesis of oleandolide makes use of the palladium-catalysed coupling of a vinylstannane with an acid chloride to give an α,β -unsaturated ketone.³⁷³ Other unsaturated ketones

can be prepared by carbonylative Stille couplings of vinylstannanes.³⁷⁴ Couplings or carbonylative couplings of organostannanes with fluoroalkyl-substituted alkyl halides have been reported.³⁷⁵ Couplings with 2-bromothiazolines provide 2-substituted thiazolines.³⁷⁶ Palladium-catalysed allylations of organostannanes can be carried out.³⁷⁷ Intramolecular copper-catalysed conjugate addition of vinylstannanes leads to cyclopentenes.³⁷⁸

A method for the synthesis of enediynes, including dymnicin A, makes use of the coupling of the bis-stannane **169** with bis-iodoalkynes.³⁷⁹ Electrophilic reactions of **169** are known.³⁸⁰ Coupling reactions with alkynylstannanes can also access enediynes.³⁸¹ Alkynylstannanes can undergo palladium- or nickel-catalysed cross-couplings.³⁸² Couplings of the alkynylstannanes **170** (R = Me or CH₂CH₂CH=CMe₂) with vinyl iodides **171** (R = H or SiMe₂Bu^t) give harveynone and (–)-tricholomenyn A.³⁸³



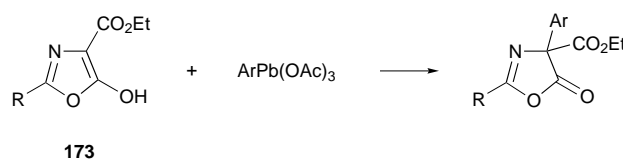
Aryl-³⁸⁴ and heteroaryl-stannanes³⁸⁵ have found application in a number of synthetic endeavours. Palladium-catalysed couplings with aryl halides or triflates have led to syntheses of fenanthroviridone, lamellarins, garcifuran B, pindikamine A and meridine.^{386,184} A synthesis of (–)-epibatidine uses the arylstannane **172** to insert the pyridine ring (Scheme 57).³⁸⁷



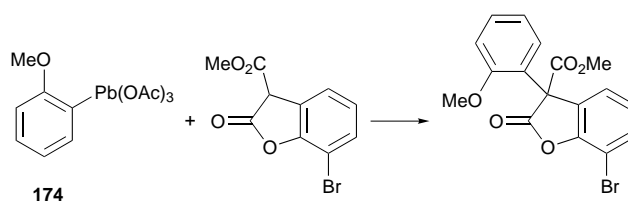
Scheme 57 Reagents: i, 2.5 mol% (dba)₃Pd-CHCl₃, 15 mol% Ph₃As, THF

5.4 Lead

Aryl- or alkynyl-lead compounds are known to react with enolates to give α -aryl or α -alkynyl carbonyl compounds.³⁸⁸ Arylation of the oxazolones **173** (R = Ph or Me) has provided a route to α -arylglycines (Scheme 58).³⁸⁹ A fragment of diazamide A has been prepared using the aryllead triacetate **174** (Scheme 59).³⁹⁰ Aryllead triacetates allow the arylation of phenols³⁹¹ and the *N*-arylation of amides.³⁹²



Scheme 58



Scheme 59

6 References

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