Main group organometallics in organic synthesis

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Received (in Cambridge) 21st April 1999

Covering: July 1997 to June 1998
Previous review: *J. Chem. Soc., Perkin Trans. 1*, 1998, 1343.

1 Introduction

The aim of this article is to provide a succinct overview of the applications of main group organometallics in synthetic organic chemistry over the period of July 97–June 98. Our emphasis is on novel methodologies, new features and emerging trends, and unprecedented or unusual observations. Certain specific examples of the uses of main group organometallics in natural product synthesis are outlined to highlight an extension to their application and versatility. However, for reasons of brevity, many excellent syntheses which routinely use main group organometallics in carbon–carbon bond formation are not included.

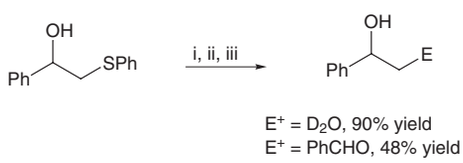
2 Group I

2.1 Lithium

Several structural studies of organolithium compounds (including lithium amides) in solid phase[1] or in solution,[2] and the influences of various ligating agents on their structure are reported.[3]

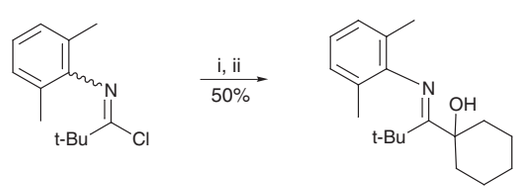
2.1.1 Alkyllithiums with no α-heteroatom

Deprotonation, halogen–metal exchange and conjugate addition are the more traditional methods for generation of organolithiums and they are commonly cited in the literature. Recently, however, reductive lithiation has been shown to be an equally excellent method for the regioselective synthesis of alkyllithiums. The use of lithium metal with naphthalene or DTBB (4,4′-di-*tert*-butylbiphenyl) has been widely explored. Since, unlike typical metal exchange reactions, there is no basic reagent involved, the methodology is particularly useful for the preparation of unusual organolithiums. For instance, Yus has shown that lithiated alkanes with leaving groups at the β position can be generated and reacted with electrophiles using this methodology with no significant β elimination observed (Scheme 1).[4]



Scheme 1 *Reagents*: i, n-BuLi, 2 min, THF, −78 °C; ii, Li, DTBB (5 mol%), THF, −78 °C; iii, E^+.

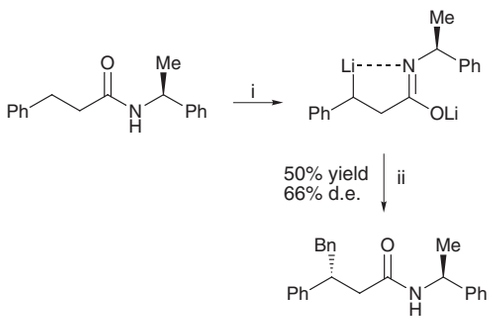
Propargylic (prop-2-ynyl) chlorides and benzylic chlorides can be lithiated by LiDTBB and reacted with electrophiles.[4,5] In addition to the carbon–halogen bond, reductive lithiation of a number of other bonds is also possible. Phenylsulfides,[7–9] ethers[10,12] and cyclic acetals[11] can undergo this reaction. Naphthalene, used only in catalytic quantities, in conjunction with lithium has been reported to reduce benzylic methyl ethers to the corresponding benzyllithium[12] and *N*-sulfonyl and *N*-allyl species to the corresponding amines.[13] The same reagent has been used for effective transmetallation of imidoyl chloride to its corresponding umpolong lithioiminyl (Scheme 2).[14] In the presence of $NiCl_2$, catalytic quantities of DTBB and excess lithium, ketones are reduced to the corresponding alcohols.[15]



Scheme 2 *Reagents*: i, Li, $C_{10}H_8$ (4 mol%), THF, −78 °C; ii, cyclohexanone.

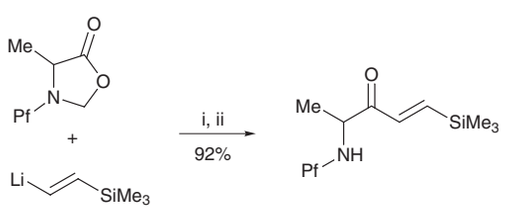
Conjugate addition is another important route for the preparation of organolithiums. Tandem conjugate addition–cyclisation is shown to afford the *trans* compound in the synthesis of tetrahydronaphthalene,[16] cyclobutanes[17] and cyclopropanes.[18] The conjugate addition can be made asymmetric either by addition of a chiral chelator such as (−)-sparteine,[18,19] or by the use of a chiral auxiliary.[20]

Iodine–lithium exchange mediated cyclisations have been explored by Bailey in the synthesis of functionally bare rings.[21,22] Other metal exchange reactions are considered under the relevant metals in this review. Finally, a complex induced proximity effect has been used to generate a synthetic equivalent of an enantioselective homoenolate (Scheme 3).[23]



Scheme 3 *Reagents*: i, s-BuLi, TMEDA, ether, −78 °C; ii, BnBr, −78 °C.

Diastereoselectivity in the addition of simple alkyllithiums to protected erythrulose and its oxime has been reported.[24,25] A two step transformation of 9-phenylfluoren-9-yl (Pf) protected α-amino acids to the corresponding ketones involving the reaction of an alkyllithium with a cyclic aminal is reported (Scheme 4).[26] Reactions of lithium silazides with aldehydes afford *N*-silylimines which undergo Barbier type reactions[27] as well as β-lactam formation.[28] Two examples of addition of organolithiums to homochiral hydrazones have appeared.[29,30] 1,2-Addition of organolithiums to both imines[31] and α,β-unsaturated imines[32] in the presence of a chiral ligator [(−)-sparteine] has been reported. The former affords only modest diastereoselectivities (up to 20% ee). Conjugate addition of organolithiums to α,β-unsaturated esters in the presence of (−)-sparteine has also been explored.[33] Additions to homochiral oximes bearing a chiral group on the oxygen proceed with modest stereoselectivities.[34]



Scheme 4 *Reagents*: i, −78 °C to 10 °C, 4 h; ii, EtOCOH, then AcOH.

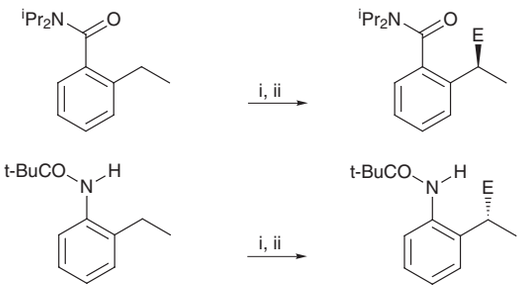
Beak and Clayden have further demonstrated remote stereoinduction in conformationally locked amides.[35,36] In particular, Beak has shown that the pathways of stereoinformation transfer in laterally lithiated *N*,*N*-diisopropyl-2-ethylbenzamide and *N*-pivaloyl-(2-ethylaniline) are different (Scheme 5).[36]

2.1.2 Alkyllithiums with an α-heteroatom

In this review, alkyllithiums which have a main group metal at the α-position are covered under the corresponding element.

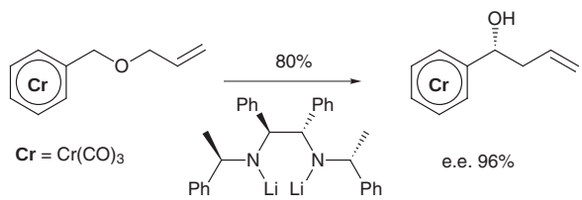
2.1.2.1 Alkyllithiums with an α-chalcogen atom

Deprotonation and conjugate addition are the more common methods for generation of these organolithiums. Enantiotopic



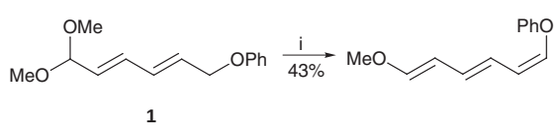
Scheme 5 *Reagents*: i, s-BuLi, −78 °C, THF, (−)-sparteine; ii, E^+.

deprotonation of the chromium arene complex of benzyl allyl ether followed by a [2,3]-Wittig rearrangement affords a homochiral benzylic alcohol (Scheme 6).[37]



Scheme 6

Trienic compounds are prepared from deprotonation of **1** (Scheme 7).[38] Sulfur–lithium exchange has been used for the synthesis of sulfur stabilised anions.[39] Synthesis of chiral allyl alcohols *via* desymmetrisation of epoxides has continued.[40,41] A synthesis of thiepines by desymmetrisation of thioxabicyclo-[3.2.1]octanes has been reported.[42] (−)-Sparteine mediated deprotonation of cyclooctene oxide has afforded a 5,5-fused bicyclic ring.[43] Further examples of enantioselective deprotonation include those reported by Gibson[37,44] and Hoppe.[45] Triphenyl sulfonium ylides react with imines in the presence of TMSCl to afford aziridines.[46] Kociénski has comprehensively studied the effect of sulfonyl substituent, solvent and the metal cation on the Julia reactions of benzothiazole and phenyltetrazole sulfonyl stabilised anions and has found lithium to be the least desirable cation.[47] A theoretical study has concluded that the carbon–lithium bond in 2-lithio-1,3-dithiane is equatorial.[48]



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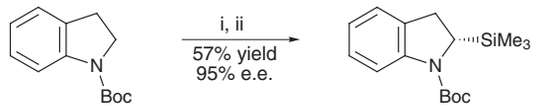
Scheme 7 *Reagents*: i, n-BuLi, −78 °C to rt.

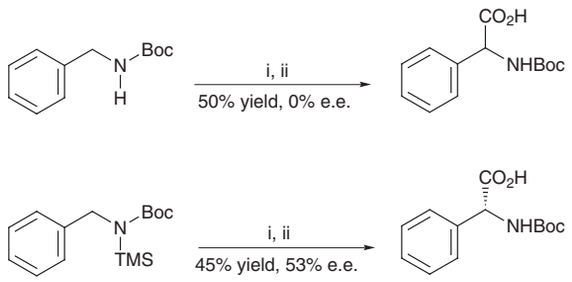
A synthesis of homochiral β-disulfoxides from the reaction between a homochiral sulfinate and a homochiral α-sulfinylcarbanion is reported.[49] *gem*-Disubstituted dichloroalkenes have been synthesised from the reaction of diethyl dichloromethylphosphonate and ketones or aldehydes.[50] Addition of the lithium salt of dithiane to *N*-Boc-*N*,*O*-isopropylideneserinal proceeds with excellent diastereoselectivity in favour of the corresponding *anti* adduct.[51]

2.1.2.2 Alkyllithiums with an α-nitrogen atom

Generation and reactions of non-stabilised α-phenyltriazole carbanions have been reviewed.[52] A synthesis of azepine by desymmetrisation of azaoxabicyclo[3.2.1]octanes has been reported.[42] (−)-Sparteine mediated deprotonation of indolene and the reactions of the corresponding anion with electrophiles gives excellent enantioselectivities (Scheme 8).[53] It has been shown that although (−)-sparteine mediated deprotonation of mono-Boc protected benzylamine is not selective, *N*-silylation results in enantioselective deprotonation (Scheme 9).[54]

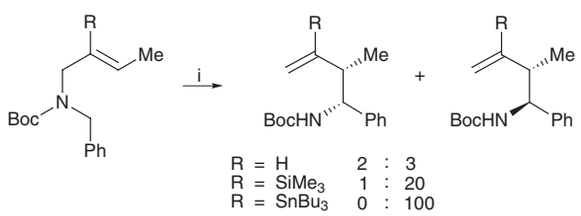


Scheme 8 *Reagents*: i, s-BuLi, −78 °C, cumene, (−)-sparteine; ii, TMSCl.



Scheme 9 *Reagents*: i, s-BuLi, −78 °C, THF, (−)-sparteine; ii, CO_2.

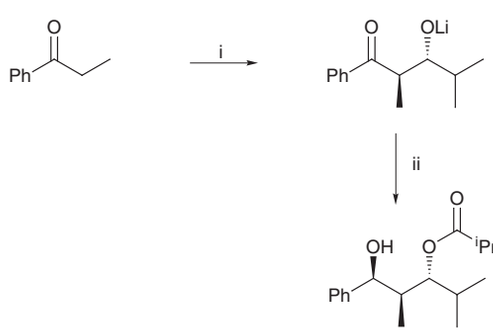
Reaction of this anion has been used in the synthesis of phenylglycine.[54] Beak has also demonstrated that *N*-aryl Boc protected benzylamines undergo asymmetric deprotonation at the benzylic position.[55] Borylation of nitrogen allows a diastereoselective lithiation of isoindolenes[56] and aziridines.[57] The stereoselectivity of the [2,3]-sigmatropic shift of nitrogen stabilised anions heavily depends on the nature of the R substituent (Scheme 10).[58]



Scheme 10 *Reagents*: i, LDA, THF–HMPA.

2.1.3 Lithium enolates and related compounds

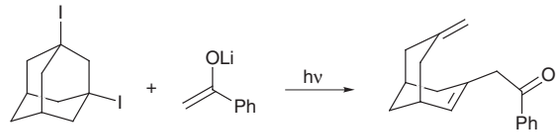
A kinetic isotope effect in the aldol-Tishchenko reaction (Scheme 11)[59] has been reported.[60] An unusual photo-catalysed reaction of an enolate and diiodoadamantane has also been reported (Scheme 12).[61]



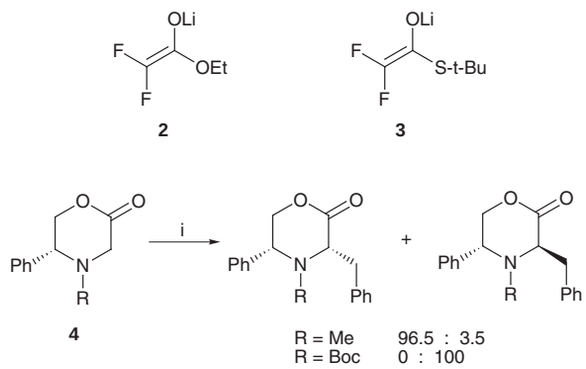
Scheme 11 *Reagents*: i, LDA, ^{i}PrCHO (1 equiv.); ii, ^{i}PrCHO (1 equiv.) warm to 22 °C.

It has been shown that although difluoroenolate **2** is unstable and prone to self-condensation, difluoroenolate **3** is stable and undergoes normal aldol reactions.[62] Both alkylation[63] and aldol reactions[64] of lithioalkylnitriles have been optimised.

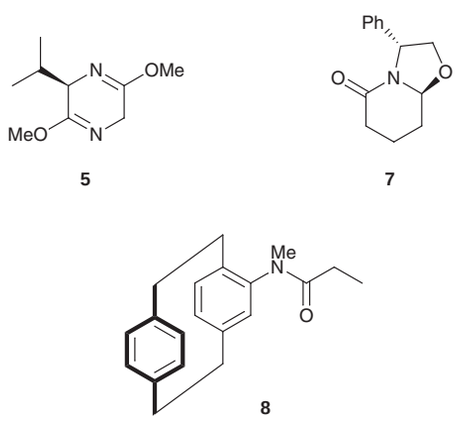
The Boc and methyl protected cyclic aminoesters **4** afford opposite stereoselectivity in reactions with electrophiles such as benzyl bromide (Scheme 13).[65] Stereoselective alkylation of **5** is



Scheme 12



Scheme 13 *Reagents*: i, LiHMDS, THF, $PhCH_2Br$, −78 °C.

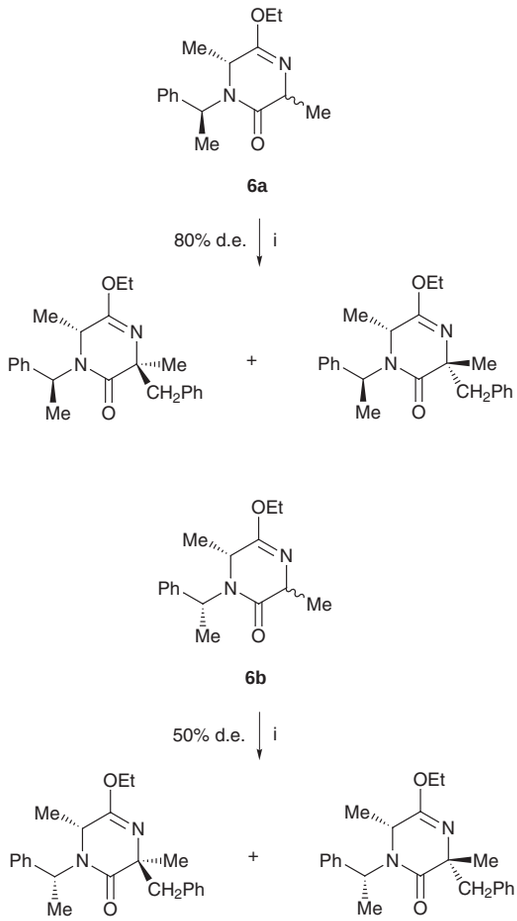


used in the synthesis of unnatural amino acids.[66] Matching of the two stereocentres gives a good selectivity in reactions of both diastereomers of **6** (Scheme 14).[67] Enantiopure 3-alkylpiperidines are prepared from the reaction of the lithium enolate of **7**.[68] The use of phenyl glycidol as a chiral auxiliary has been further explored[69,70] for the synthesis of chiral amines.[70] Addition of LiCl significantly improved the stereoselectivity of the alkylation of primary and secondary fluoroenolate anions.[71] Further examples of the use of **8** as a homochiral amide have been reported.[72] An asymmetric aldol reaction on a solid support has been reported.[73]

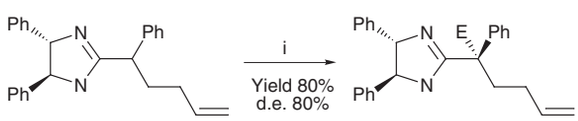
The regioselectivity of the reactions of the extended enolate derived from but-2-enoic acid is influenced by the reactivity of the alkyl halide employed.[74] Regioselective addition of extended enolates has been applied to the synthesis of Brefeldine.[75] A homochiral dihydroimidazole has been alkylated with good diastereoselectivity (Scheme 15).[76] Lithium enolates of cyclic ketones are enantioselectively alkylated in the presence of an alkyl halide, ligand **9** and 1 molar equivalent of LiBr.[77] Conjugate addition of diethyl malonate to cyclic α,β-unsaturated ketones proceeds with good (>80% ee) stereoselectivities in the presence of stoichiometric quantities of **10**.[78] Synthetic applications of [3,3]-sigmatropic rearrangements of homochiral imidates **11** have been explored.[79]

2.1.4 Alkenyl and alkynyllithiums

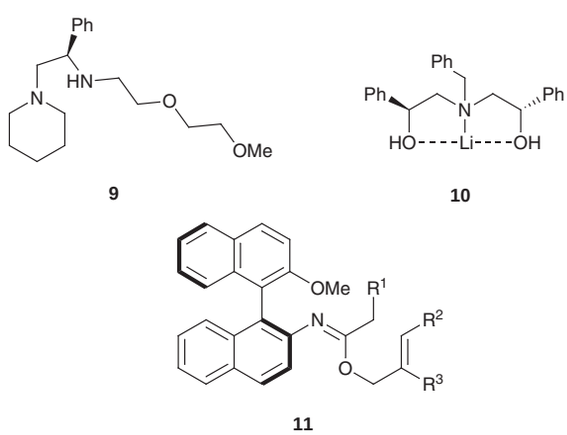
The subject of α-substituted vinyllithiums has been reviewed.[80] In addition, a synthetically convenient preparation of both *cis* and *trans* isomers of 1-chloro-1-lithiobutadiene[81] and a



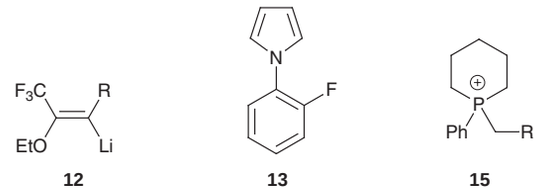
Scheme 14 *Reagents*: i, LiHMDS, THF, $PhCH_2Br$, −78 °C.



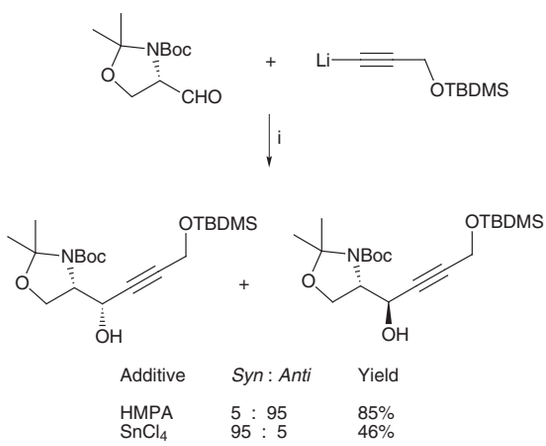
Scheme 15 *Reagents*: i, s-BuLi, −78 °C, THF; ii, E^+.



preparation of α-lithiated vinylsulfones[82] have been reported. *gem*-Diiodides have been reported to undergo consecutive regioselective halogen–metal exchange and reaction with electrophiles.[83] Unusual basic properties of α-ethoxy vinyllithium have been exploited in the deprotonation of dihydroisoxazole which, with a range of other bases, affords undesired aromatised products.[84] Vinyllithium **12** (R ≠ H), is configurationally stable and reacts with a variety of electrophiles.[85] Corey has reported a Shapiro reaction for stereoselective synthesis of trisubstituted olefins.[86]



Lithium acetylide has been shown to be stable only at very low temperature in solution. At around 0 °C it converts to dilithium acetylide, which appears as a white precipitate, and acetylene which evaporates.[87] Addition of alkynyllithiums to a variety of homochiral aldehydes has been reported.[88,89] In particular, contrasting *syn–anti* selectivities are observed in the addition to *N*-Boc-*N*,*O*-isopropylideneserinal (Scheme 16).[90] Addition of the lithium salt of methyl propionate to imine oxides is shown to be a versatile synthetic method for the preparation of a variety of compounds.[91]

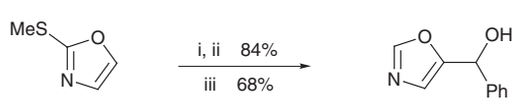


Additive	*Syn* : *Anti*	Yield
HMPA	5 : 95	85%
$SnCl_4$	95 : 5	46%

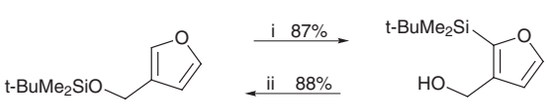
Scheme 16 *Reagents*: i, toluene, additive, −78 °C.

2.1.5 Aryllithiums

There has been further development of regioselective lithiation of heteroaromatic rings, including lithiation at the 4-position of 3,5-dimethylisoxazole,[92] use of 4-lithio-2-methylthiooxazole as a synthetic equivalent of 4-lithiooxazoles (Scheme 17),[93] and an unusual silyl migration in 3-(hydroxymethyl)furans (Scheme 18).[94]



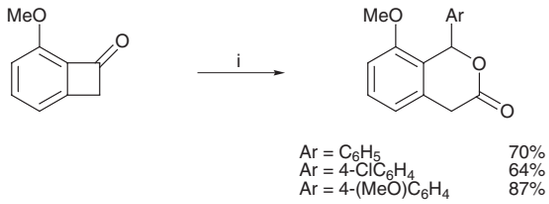
Scheme 17 *Reagents*: i, n-BuLi, −78 °C, TMEDA, THF; ii, PhCHO; iii, Raney nickel, EtOH.



Scheme 18 *Reagents*: i, n-BuLi, THF, −20 °C, 1 hour then HMPA; ii, NaH (5 equiv.), DMF, rt, 1 min.

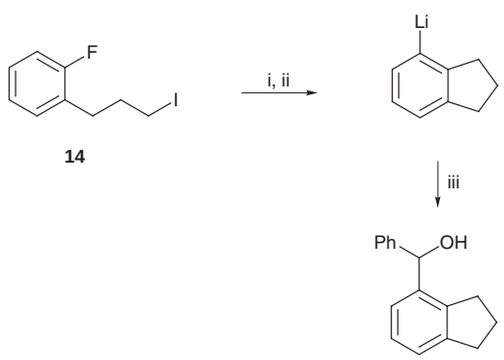
A Fries rearrangement of phenoxytetrazoles has been reported.[95] Asymmetric addition of aryllithiums to cinnamate esters in the presence of chiral ligators affords good stereoselectivities (up to 88% ee).[96] An unusual site selective ring opening of benzocyclobutanones leads to the formation of isochroman-3-ones (Scheme 19).[97]

Deprotonation of 1,2,4-tris(trifluoromethyl)benzene with LTMP affords 5- and 6-lithiated compounds in 80% and 20%



Scheme 19 *Reagents*: i, LiTMP + ArCHO (inverse addition), 0 °C.

yield, respectively,[98] whereas deprotonation of 1,3-bis(trifluoromethyl)benzene with BuLi–tBuOK affords the 2-lithiated anion exclusively.[99] *o*-Fluoroarylpyrrole **13** regioselectively lithiates at the position *ortho* to the fluorine atom on the benzene ring.[100] Lithiation at the position *ortho* to fluorine is also the case in fluoropyrazines.[101] Lithium–iodide exchange and *ortho* lithiation of **14** followed by elimination to benzyne, intramolecular cyclisation and reaction with electrophiles affords indanes (Scheme 20).[102] Overman has used regioselective *ortho* lithiation of 3- and 4-bromopyridines in the synthesis of opioid receptor binders.[103] Attempted lithiation of pyridines with BuLi usually affords butylated pyridine; however it has been shown that addition of *N*,*N*-dimethylaminoethanol (DMAE) allows formation of 2-lithiopyridines and subsequent alkylation to proceed very well under these conditions.[104] Quinolines can also be lithiated by this protocol although butylated quinoline is a significant byproduct.[104] Also, the use of dichloromethane as solvent in halogen–metal exchange of 2,5-dibromopyridine gives a good conversion to monolithiated 2-lithio-5-bromopyridine.[105] Schlosser has demonstrated that selective side chain and ring lithiation of alkylanisole are both possible.[106] Two reports of regioselective lithiation of a ferrocene ring have appeared.[107,108]



Scheme 20 *Reagents*: i, 3.2 equiv. t-BuLi, pentane–ether (4 : 1), 15 min, −78 °C; ii, THF, warm to rt; iii, PhCHO.

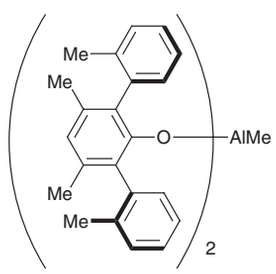
2.2 Sodium and potassium

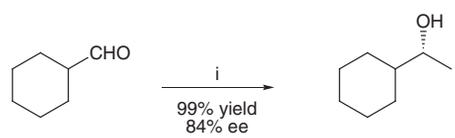
Treatment of sodium hydride with DMF at 80 °C releases one mole of hydrogen gas.[109] Although the nature of the resulting anion is unclear, it is shown to cause an unusual base induced intramolecular 1,3-hydride shift.[109] Sodium metal itself has been shown to be a mild and efficient reagent for desulfurisation.[110] The influence of various alkaline metals on the oxidation of enolates has been studied.[111] The sodium salts of *N*-benzylidene amino acids are enantioselectively alkylated in the presence of TADDOL.[112] The potassium salt of trifluoromethyl anion has been prepared by treatment of fluoroform with potassium metal in DMSO and, unusually, is stable at room temperature.[113] The potassium salt of phosphorane **15** affords a very high degree of *trans* selectivity.[114] A mixed potassium–lanthanum cation of BINOL affords modest enantioselectivity in the reaction of 2-nitropropane with benzaldehyde, whereas its lithium counterpart afforded none.[115] Finally, Schlosser has further investigated the *endo* preference of 2-alkyl branched alk-2-enylpotassium species.[116]

3 Group II

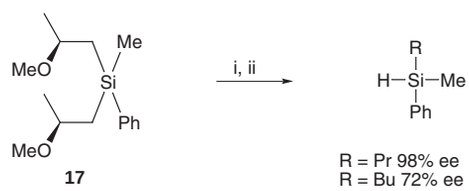
3.1 Magnesium

Further examples of stereoselective additions of Grignard reagents to chirally homogeneous hydrazones,[117] aldimines,[118] aldimine oxides,[119] ketimines,[120] aldehydes[121] and ketones[122] have appeared. In addition, chiral catalyst **16** (Scheme 21) has been developed for asymmetric addition of Grignard reagents to aldehydes.[123] Morpholine amides are shown to be superior to pyrrolidine amides in their reaction with Grignard reagents to afford ketones.[124] A conversion of solid supported ethyl esters to ketones has also been reported.[125] Contrasting selectivities have been observed in the addition of vinylmagnesium bromides to *N*-monosubstituted and *N*,*N*-disubstituted chirally homogeneous α-aminoaldehydes.[126] The first direct observation of an iodine ate complex in an iodine–magnesium exchange reaction has been reported.[127] Also the influence of solvent and metal cation in the addition of organometallics, including Grignard reagents, to chirally homogeneous α-aminoaldehydes has been explored.[128] Exceptionally high Felkin-Anh control in addition of Grignard nucleophiles to β-amidocyclopropyl aldehydes is reported.[129] A synthesis of chiral silanes *via* Grignard addition and reduction of **17** (Scheme 22),[130] and a very useful access to unsymmetrically substituted phosphines using consecutive reaction of **18** with Grignard reagent and then alkyllithium (Scheme 23) have been developed.[131] A new synthesis of (Z)-α,β-difluoroallylalcohols *via* Grignard addition has been reported (Scheme 24).[132] Grignard/cuprate addition to **19** proceeds stereoselectively with no fluoride elimination observed (Scheme 25).[133] Addition to nitroalkenes of Grignard reagents followed by concentrated mineral acid affords imidoyl chlorides.[134] α-Halovinylmagnesium species are prepared *via* metal exchange of the corresponding sulfoxides.[135]

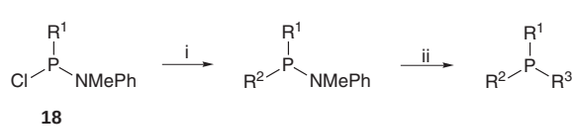




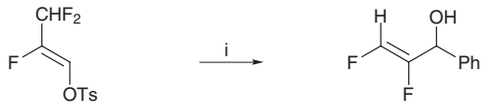
Scheme 21 *Reagents*: i, MeMgI, **16**.



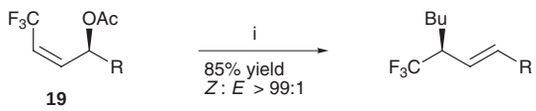
Scheme 22 *Reagents*: i, RMgBr; ii, $LiAlH_4$.



Scheme 23 *Reagents*: i, R^2MgBr; ii, R^3Li.

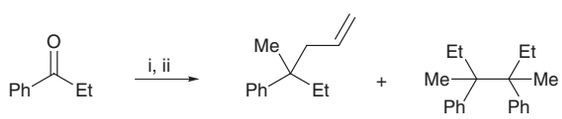


Scheme 24 *Reagents*: i, PhMgBr (3.0 equiv.), 50 °C, THF.

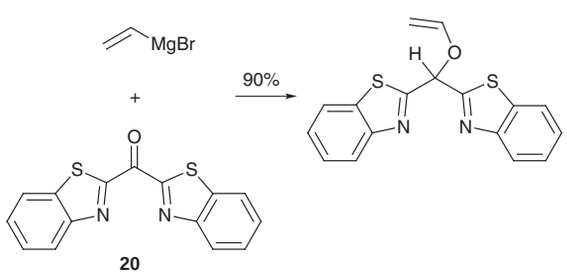


Scheme 25 *Reagents*: i, n-BuMgBr, CuCN (0.1 equiv.), Me_3SiCl (0.3 equiv.).

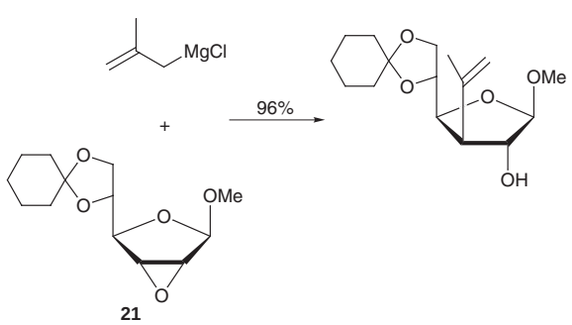
Additions of Grignard reagents to thiocarbonyls[136] and chirally homogeneous sulfimines[137] have been explored. The combination of Grignard reagents with vanadium(II) species has led to some interesting modifications of the behaviour of these reagents towards carbonyls. For instance, tertiary carbon centres are obtained from the reaction of a ketone with a Grignard reagent combined with VCl_2(TMEDA) in the presence of a catalytic amount of molecular oxygen (Scheme 26).[138] Organomanganese compounds are prepared from the corresponding Grignards and show interesting reactivity patterns.[139] Aryl glyco ethers undergo stereoselective rearrangement in the presence of MeMgBr and Pd(II) catalyst to afford α-arylsaccharides.[140] A magnesium promoted Simmons-Smith reaction is reported.[141] An unusual product is isolated from the reaction of **20** and allylmagnesium chloride (Scheme 27).[142] Ring opening of the epoxide **21** by 2-methylprop-2-enylmagnesium bromide proceeds at the sterically more congested position and is used in the synthesis of carbomycin (Scheme 28).[143]



Scheme 26 *Reagents*: i, MeMgBr, VCl_2, TMEDA; ii, allyl bromide.



Scheme 27

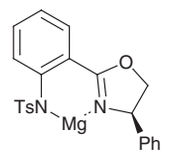


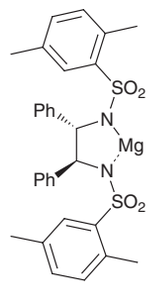
Scheme 28

Conjugate addition to cyclic ethers has been used as a route to the synthesis of homochiral allylic alcohols,[144] and zinc catalysed carbomagnesiation has been applied in the synthesis of fluvirucin B_1.[145]

Combination of ^iPrMgBr and $Ti(O^iPr)_4$ or $TiCl_2(O^iPr)_2$ affords a reduced titanium species which has been shown to have a range of applications in synthetic chemistry ranging from reduction of imines[146] to carbocyclisation.[147,148] Analogous reactions of ^iPrMgBr with $TiCp_2Cl_2$[149] and $ZrCp_2Cl_2$[150] are also reported.

Finally, the application of two chiral magnesium based catalysts, **22** and **23**, for asymmetric Diels–Alder reactions[151] and asymmetric amination of enolates[152] have appeared.





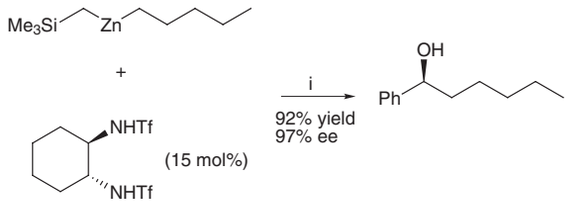
3.2 Barium and calcium

Further examples of the reaction of allylbarium compounds with aldehydes have appeared. As expected, additions to carbonyl functions occur at the least hindered, usually the α-position, of the allyl group. Modest enantioselectivities are reported in the presence of chiral crown ethers.[153] The C–Ca–C bond angle (150°) and C–Ca bond length (2.46 Å) are reported from an X-ray crystal structure.[154]

3.3 Zinc

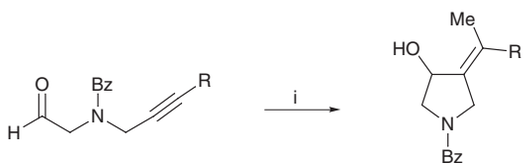
The popularity of organozinc compounds in organic synthesis continues to grow. Mediation of various chiral ligands in the asymmetric addition of diethylzinc to benzaldehydes,[155] benzaldimines,[156] nitroalkenes,[157] ketones[158] and cyclohexenones[159] has been explored. Addition of a number of organozinc compounds, other than diethylzinc, to ketones, aldehydes and activated double bonds has also been reported. For instance, the anti-HIV compound MKC-422 has been synthesised by the addition of allylzincate to a diaryl ketone.[160] Noteworthy amongst these are reports of an asymmetric addition of allylzinc bromide to aldehydes and ketones,[161] stereoselective intramolecular cyclisation of organozincates to ketones,[162] additions to imine *N*-oxides,[163] iminium species,[164] and nitriles (Blaise reaction),[165] as well as preparation of β-diketones from acyl cyanides.[166] Rychnovsky has obtained a highly diastereoselective addition of vinylzinc to a chiral 1,3-dioxane.[167]

Knochel has further demonstrated a selective transfer of an R group from mixed zincates to aldehydes (Scheme 29),[168] and cyclohexenones.[169] The use of solvents which are not usually associated with organozincates has been explored. In particular, dichloromethane has been used as a solvent in the addition of diethylzinc to acetophenone,[170] and dimethylformamide has been employed as solvent in the preparation of an organozincate.[171] Notably a chiral version of the Reformatski reaction in water containing chiral micelles has been carried out.[172] A Reformatski reaction in concentrated aqueous salt solution is reported to be accelerated with free radical promoters such as benzoyl peroxide, although the reason for this is not clear.[173] A Reformatski reaction of a saccharide sugar has been used in the synthesis of C-linked glycosides.[174] The use of light in the preparation of mixed zincates has also been reported.[175] Zinc halide mediated addition of an enolate anion to β-heterosubstituted nitroethylenes[176] and imines[177] as well as zinc halide mediated addition of enamine nucleophiles are explored.[178] Nucleophilic addition of organozincates to epoxides are described,[179] and nickel catalysed addition of zincates to homochiral vinyl sulfoxides and vinylpyridines is used in the synthesis of a number



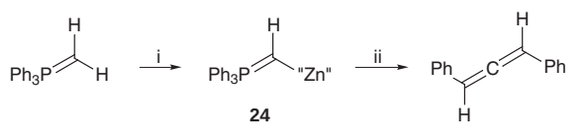
Scheme 29 *Reagents*: i, PhCHO, $Ti(O^iPr)_4$ (0.6 equiv.), Et_2O, −20 °C.

of phosphodiesterase (PDE) IV inhibitors.[180] Nickel catalysed carbozincation of arylalkynes has been reported to be significantly more facile than the corresponding reactions of cuprates[181] and is used in inter and intramolecular cyclisation of alkynes/aldehydes (Scheme 30).[182] Halogen–zinc exchange of β-iodoketones, esters and amides and the subsequent reaction of β-zincated carboxylic species with various electrophiles have been reported.[183]



Scheme 30 *Reagents*: i, $ZnMe_2$, $Ni(COD)_2$, 72%.

Homochiral α-acetoxyferrocenes undergo displacement with zincates with retention of configuration.[184] Knochel has demonstrated a useful preparation of alcohols by oxygenation of zincates.[185] Zinc halide mediated alkylation of 2-substituted dithianes[186] has been reported. The use of zincate reagent **24** as a synthetic equivalent of a carbon atom has been demonstrated (Scheme 31).[187] Acylzinc species have been prepared and reported to undergo rapid rearrangement to the corresponding zinc enolates.[188]



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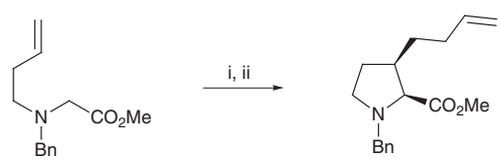
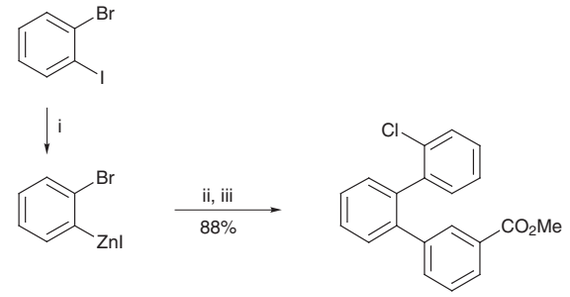
Scheme 31 *Reagents*: i, $Zn[N(TMS)_2]_2$; ii, PhCHO.

A new access to polysubstituted piperidines and pyrrolidines by intramolecular cyclisation of an organozinc intermediate onto an unactivated double bond has been reported (Scheme 32).[189]

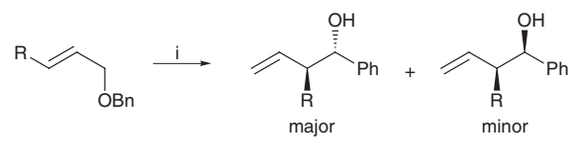


Scheme 32 *Reagents*: i, LDA, Et_2O, −40 °C, then $ZnBr_2$; ii, CuCN, allyl bromide.

Organozincates like a number of other organometallics can couple to vinyl and aryl halides in the presence of palladium catalysts (Negishi coupling).[190–193] Negishi coupling leading to biaryls has been reviewed.[194] The reaction can be performed on solid supported aryl halides[195] and is shown to have a preference for iodides over bromides.[196] This has led to the use of *o*-bromophenylzinc iodide as a synthetic equivalent of *o*-phenylene-1-anion-2-cation (Scheme 33).[197] Ketones can be prepared from Pd catalysed coupling of alkylzinc with thiolester[198] or acid chlorides.[199] Umpolong of a π allyl Pd cation has been developed by treatment of an allyl ether with diethylzinc in the presence of a Pd(0) catalyst. This reagent adds to benzaldehyde to give *syn* preference (Scheme 34).[200] Negishi has explored the role of various metals in the coupling of metal

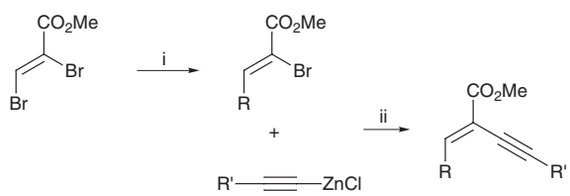


Scheme 33 *Reagents*: i, Zn powder, 70 °C, TMU; ii, Ar-CO_2Me, 1 h, rt, 2 mol% $Pd(PPh_3)_4$; iii, Ar-Cl, 18 h, 70 °C.



Scheme 34 *Reagents*: i, $Pd(PPh_3)_4$, Et_2Zn, PhCHCO.

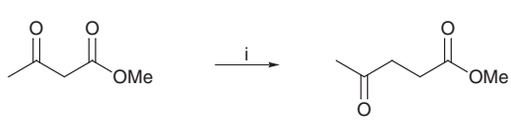
acetylides and aryl bromides and has found that zinc and magnesium derivatives are best.[201] Burton has exploited the coupling of vinylzinc to aryl halides in the preparation of a number of fluorinated styrenes.[202] A two step alkylation–alkynation of α,β-dibromoacrylates has been shown to proceed at the β position first (Scheme 35).[203]



Scheme 35 *Reagents*: i, RZnCl, $Pd(PPh_3)_4$; ii, $Pd(PPh_3)_4$.

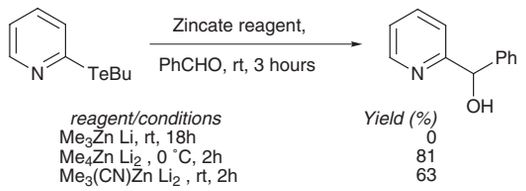
The combination of organozinc compounds with vanadium(IV) species has led to an interesting modification of the behaviour of these reagents towards carbonyls. For instance, aldehydes undergo alkylation at low temperature and pinacol formation at room temperature whereas reaction with ketones at higher temperature affords mostly deoxygenated products.[204,205] Carbozincation of enynes by the use of Et_2Zn and $Ti(OiPr)_4$ is shown to be more efficient and versatile than the alternative Me_3Al–Cp_2ZrCl_2 reagent.[206]

Reaction of the Simmons-Smith reagent continues to provide new synthetic methods. Aggarwal has used this reaction to prepare epoxides from aldehydes[207] and a report has appeared on a chain extension which affords γ-ketoesters from β-ketoesters using this reaction (Scheme 36).[208] Treatment of methylenecyclopropanes with bromoform and diethylzinc affords modest yields of the expected spiro Simmons-Smith product.[209] The Simmons-Smith reagent in conjunction with a palladium catalyst has been used for homologation of alkyl halides.[210]

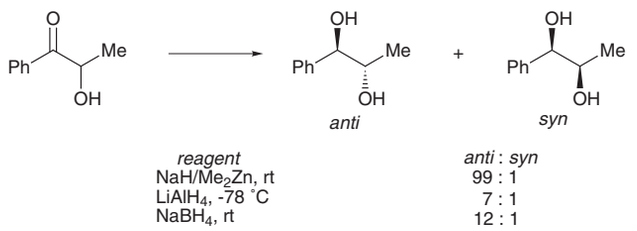


Scheme 36 *Reagents*: i, Et_2Zn, CH_2I_2.

One of the most important recent advances in the field of organozinc compounds is the development of ate complexes of zinc as synthetic reagents.[211] These compounds show higher and unique reactivities compared to other zincates which distinguishes them as valuable tools for synthesis (Scheme 37). In particular, dialkylzinc hydride ate complexes react very efficiently with carbonyls (Scheme 38).[212] The use of dialkylzinc



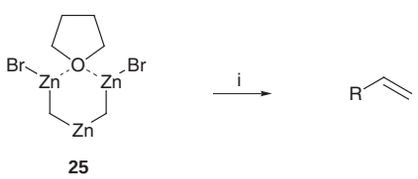
Scheme 37



Scheme 38

silylate complexes in conjugate additions are reported to require only catalytic quantities of copper[213] and zinc reagent.[214] An interesting method for the preparation of benzylzinc reagents *via* homologation of triorganozincates has been reported.[215]

Finally, the commercially available Nysted reagent **25** has been used for selective methylenation of aldehydes in the presence of ketones (Scheme 39).[216]



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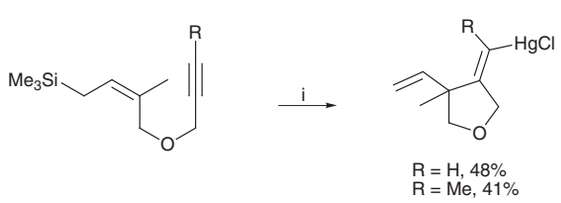
Scheme 39 *Reagents*: i, BF_3·OEt_2, RCHO.

3.4 Cadmium and mercury

Burton has exploited the coupling of arylcadmium reagents to vinyl halides in the preparation of a number of fluorinated styrenes.[202a] Mercury(II) mediated opening of bi and tercyclopropanes has been reported.[217] Hydromercuration of tetrahydropyrans followed by rapid reduction affords 2-hydroxytetrahydropyrans.[218] Triethylborane is reported to improve reductive demercuration.[219] An example of intramolecular alkyne carbomercuration by an allylic silane has also been reported (Scheme 40).[220] Benzene rings having an electron withdrawing substituent react with organomercury halides to afford *para* disubstituted benzenes.[221]



Scheme 40 *Reagents*: i, $HgCl_2$, CH_2Cl_2, HMDS (0.2 equiv.).

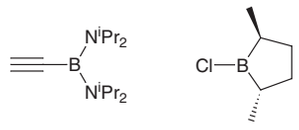
4 Group III

4.1 Boron

4.1.1 Preparations

Further examples of diborylation of carbon mutiple bonds under platinum catalysis have appeared. Stereospecific diborylation of terminal double bonds,[222] and diborylation of allenes are both reported.[223] Diborylation of alkynes is applied in the synthesis of a library based on the Tamoxifen structure.[224]

Bis(*N*,*N*-diisopropylamino)ethyneborate **26** is proposed as a more efficient alternative to ethynetrimethylsilane as a synthetic



26 **27**

equivalent to acetylene.[225] A transborylation reaction has been used in preparation of vinyl-9-BBN from dicyclohexylvinylborane.[226] Further examples of the use of vinylboranes in Diels–Alder[227] and dipolar cycloadditions[228] have appeared.

Other preparative highlights include a convenient synthesis of the C_2-symmetric borolane **27**,[229] a new method for the preparation of arylboronic esters *via* a palladium catalysed reaction between a hydroborate and an aryl halide[230] and the preparation of an ω-borono-α-amino acid.[231]

4.1.2 Reactions

4.1.2.1 Suzuki coupling

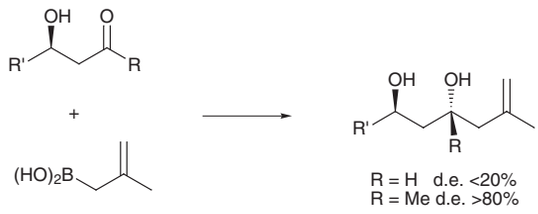
The best known application of organoboron compounds is the arylation or alkylation of an aryl or alkylborane with a halide. The preparation of biaryls by Suzuki and other coupling protocols has been reviewed.[194]

A number of significant innovations in the Suzuki coupling have been reported this year including coupling of arylboronic acids[232] and esters[233] to aryl chlorides which is made possible by the use of a nickel catalyst in place of a palladium catalyst; coupling of boronic acids to sulfonium salts which is more efficient than coupling to the corresponding halides;[234] the use of ligandless palladium in the reaction between arylboronic acids and tetraphenylborate in water;[235] an optimised coupling of hindered biaryls using thallium hydroxide as base and DMA as co-solvent;[236] preparation and coupling of otherwise difficult to handle pyridine-4-boronic esters;[237] preparation of chiral cyclopropylboronic acid[238] and their coupling to alkenyl halides;[238,239] addition of phenylboronic acids to imines;[240] coupling of phenylboronic acid to cyclohexenone with a homochiral rhodium catalyst;[241] and the use of an intramolecularly bound borate ester.[242] A co-polymerisation of dibromobenzenes and phenylenediboronic acids is reported.[243] In addition, examples of aryl–alkyl coupling of alkylboranes with aryl bromides,[244] vinyl iodides[245] and *in situ* generated "alkyl-palladium" species with arylboronic acids have been reported.[246] Two mechanistic studies on the Suzuki coupling have been carried out and one has shown that transmetallation of alkylboranes to palladium proceeds with retention of stereochemistry.[247]

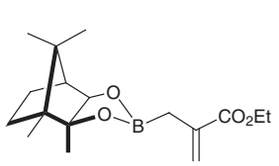
4.1.2.2 Allylboranes

Allylboranes undergo efficient reactions with carbonyls. An unexpected observation is that addition of 2-methylprop-1-en-3-ylboronic acid to β-hydroxy methyl ketones is more stereoselective than it is to β-hydroxy aldehydes (Scheme 41).[248] Triallylborane and allylzincate have been shown to have the opposite selectivity in the addition to *N*-benzylidenevaline methyl ester.[249] Addition of homochiral borane **28** to imines has been used as an enantioselective route to α-methylene-γ-lactams.[250] Addition of allyldiisopinocampheylborane to Boc protected α-aminopropanal has been employed in the total synthesis of Fumonisin B_2.[251] Surprisingly, addition of homochiral **29** to aldehydes afforded almost no stereoselectivity.[252] C_2-Symmetric ligand **30** has been synthesised by application of allylborane chemistry.[253]

Arylboronic acids are easily transformed to the corresponding iodides by treatment with *N*-iodosuccinimide.[254] Electrophilic amination of chiral alkylboranes is used in the synthesis of chiral primary amines.[255] Two very useful applications of homochiral boron catalysts in an enantioselective allylation of aldehydes[256] and an enantioselective Claisen rearrangement[257] have been reported.



Scheme 41



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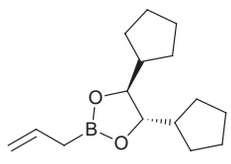

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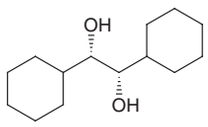

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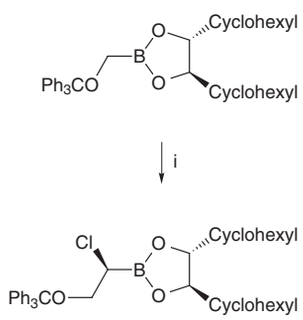
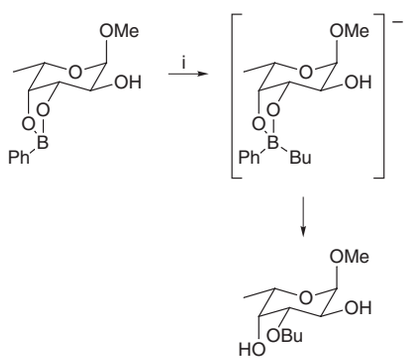
4.1.2.3 Miscellaneous

Undoubtedly, a very exciting development in recent years in the field of organoboranes is the application of ate complexes of boron in carbon–carbon bond forming reactions, particularly the Matteson reaction (Scheme 42).[258] The mechanism of the reaction has been investigated[259] and a theoretical study has been carried out to determine the transition state for rearrangement.[260] Further examples of the use of ate complexes of boron as alkyl transfer agents have appeared.[261–264] A particularly interesting example is that of regioselective alkylation of saccharides (Scheme 43).[265]



Scheme 42 *Reagents*: i, Cl_2CHLi, $ZnCl_2$.



Scheme 43 *Reagents*: i, Ag_2O, Et_3N, n-BuI, 50%.

Interestingly, a report has appeared on the preparation of a stable α-lithio-β-aminobutanoic ester in the presence of trimethylborate. With this additive, the anion is not prone to elimination and is efficiently alkylated.[266] α-Halo alkylboronic esters have also found an application as a source of α-boryl radicals.[267]

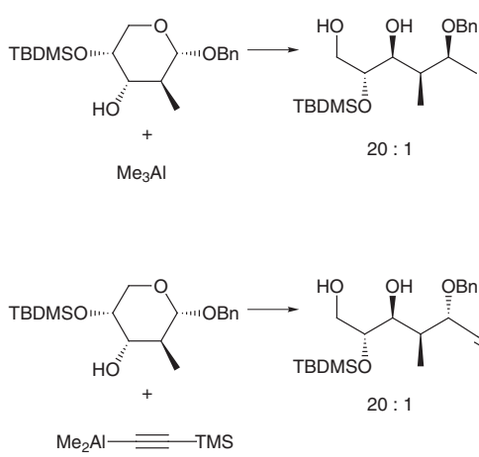
4.2 Aluminium

Nickel catalysed coupling of vinylaluminates with benzylic or allylic chlorides affords non-conjugated alkenyl aromatics.[268] This methodology has been used in a synthesis of vitamin K.[269]

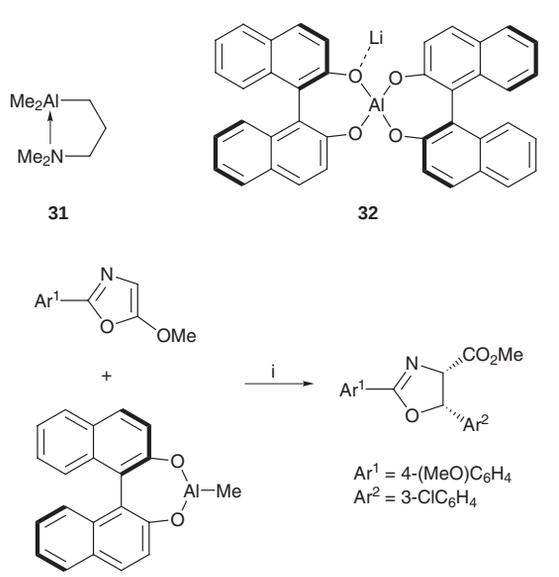
Zirconium catalysed carboalumination of alkynes to afford aluminacycles has been further exploited by Negishi for the synthesis of cyclopentenones and alkenylcyclopropanes,[270] although the use of zinc in place of aluminium has been shown to be superior.[206] Novel oxovanadyl-induced oxidation of ate complexes of aluminium has been used in the synthesis of enynes.[271]

Contrasting selectivities are observed in the reaction of cyclic acetals with alkyl and alkynyl aluminium reagents (Scheme 44).[272] Trimethylaluminium adds to acid chlorides in the presence of a stoichiometric quantity of aluminium trichloride to afford the corresponding methyl ketones.[273] Other ketones can be similarly prepared from the reaction of an organozincate and acid chlorides in the presence of a stoichiometric quantity of aluminium trichloride.[273] Intramolecular chelation in **31** makes this reagent more easy-to-handle than trimethylaluminium.[274] Asymmetric conjugate addition of alkylaluminates to α,β-unsaturated ketones has been reported.[275]

The use of aluminium catalysts and reagents has been



Scheme 44



Scheme 45 *Reagents*: i, Ar^2CHO, 5 °C, 42 h, MeCN, 75%.

reviewed.[276] An interesting example of an aluminium catalysed heterocycloaddition reaction has been reported (Scheme 45).[277] Heterobimetallic multifunctional asymmetric complexes such as **32** are used for a number of asymmetric transformations.[278]

4.3 Indium and gallium

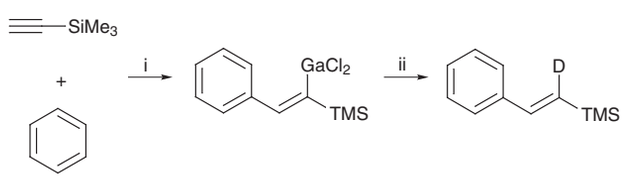
The most noteworthy feature of organoindium species is their stability in aqueous media. Thus both catalytic and stoichiometric uses of indium are the basis for a number of economic and "environmentally friendly" synthetic protocols.

Allylindium species are the best known organoindiums and not surprisingly continue to be the main focus of attention in this area. Further examples of addition of allylindium species to carbonyls have appeared[279,280] including a number of applications in total synthesis.[281,282] Allylindation of 2,3-azetidinones has been investigated by Bose[283] and Paquette.[284,285] Paquette has also reported a strong chelation effect in the addition of allylindiums to α-hydroxycyclohexanones[286] and an effective 1,4-asymmetric induction in indium promoted coupling of oxygenated allyl bromides.[287] Addition of allylindiums to both acid chlorides[288] and acylpyrazoles[289] have been reported to afford unconjugated ketones, although in the latter case, a major byproduct of the reaction is the tertiary alcohol obtained from further reaction of the ketone product with excess allylic indium species. In both reactions, the allylic moiety adds through the γ-carbon. There appears to be a discrepancy regarding the role of $InCl_3$ in the catalysis of the aldol reaction between silyl enol ethers and aldehydes. Although an efficient Mannich-type reaction between a silyl enol ether, an aldehyde and an amine in water is described,[290] in another report, the reactions of silyl enol ether and aldehydes are said to be sluggish.[291]

Addition of allylindiums to two other electrophiles, sodium alkyl thiosulfate[292] and 1,1-dicyano-2-arylethene[293] have also been reported. Indium is reported to mediate the pinacol reaction of aromatic aldehydes in water under sonication.[294]

The use of both lithium gallium hydride[295] and lithium indium hydride[296] as reducing agents have been reported. The latter is also reported to reduce β-hydroxyketones with better *meso* selectivity than lithium aluminium hydride does.[296] Dichloroindium hydride has been prepared and reported to reduce alkyl bromides under mild conditions.[297]

Non-activated aromatics are reported to undergo an addition reaction to acetylenetrimethylsilane. The presumed vinylgallate intermediate was not characterised but upon metal exchange affords a vinyllithium species which reacts with electrophiles (Scheme 46).[298]



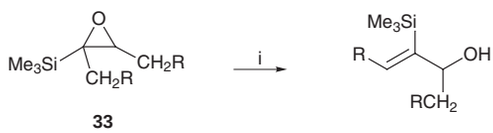
Scheme 46 *Reagents*: i, $GaCl_3$; ii, BuLi then D_2O.

5 Group IV

5.1 Silicon

5.1.1 Preparations

New methods for the synthesis of arylsilanes from aryl halides *via* a palladium catalysed reaction of triethoxysilane,[299] and fluoride mediated silylation with diphenyldisilane[300] have been disclosed. In both reactions, little reduction of aryl halide is observed. Vinylsilanes are prepared from reduction of hexacarbonyldicobalt alkynes with triethylsilane but the reaction is not regioselective.[301] Hydroboration of alkynylsilanes followed by a palladium catalysed alkylation of the *gem*-substituted vinylsilane/borane affords stereoselective access to *trans* vinylsilanes.[302] Deprotonation of silylepoxide **33** results in the exclusive formation of a vinylsilane (Scheme 47).[303] Silylated vinyl oxiranes undergo stereocontrolled rearrangement with a Pd(0) catalyst to afford α-silylated β,γ-aldehydes.[304] Reports of an unusual reaction of silylalkynes leading to the formation of vinylsilanes have appeared (Scheme 48).[305] Vinylsilanes are also reported from both inter and intramolecular $HfCl_4$ catalysed additions of allylsilanes to alkynes (see later).[306,307] Regioselective alkylation of allylsilanes[308] has been achieved by treatment of **34** with KH followed by C-lithiation and treatment with electrophiles (Scheme 49).[309]



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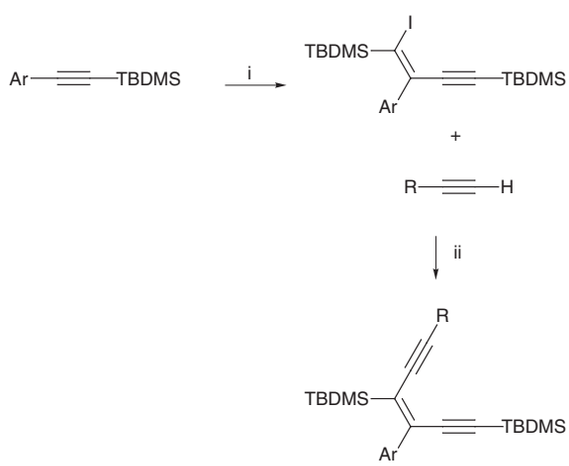
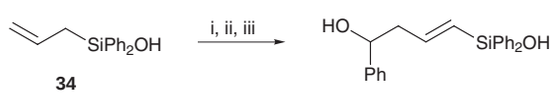
Scheme 47 *Reagents*: i, LDA.



Scheme 48 *Reagents*: i, I(pyridine)$_2$BF$_4$, −80 °C to −30 °C CH_2Cl_2, HBF_4, 95%; ii, $PdCl_2(PPh_3)_2$, CuI, Et_3N–DMF, rt, 3 hours.



34

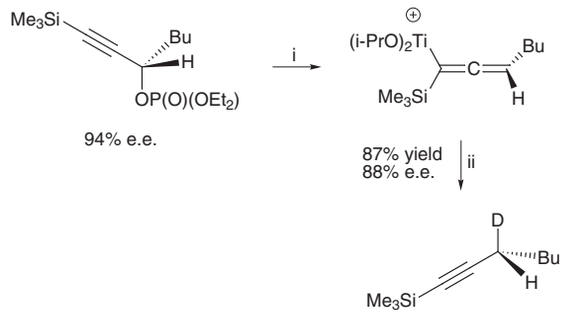
Scheme 49 *Reagents*: i, KH; ii, BuLi in THF–HMPA; iii, PhCHO.

A highly regioselective zirconium catalysed carbocyclisation–hydrosilation of 2-methylhexa-1,5-diene[310] and an enantioselective carbocyclisation–hydrosilation of bisallyl malonate using a chiral catalyst has been reported.[311] An intramolecular silylformylation of alkenes[312] and a silylformylation of alkynes leading to *cis* β-silyl-α,β-unsaturated amides[313] have also been documented.

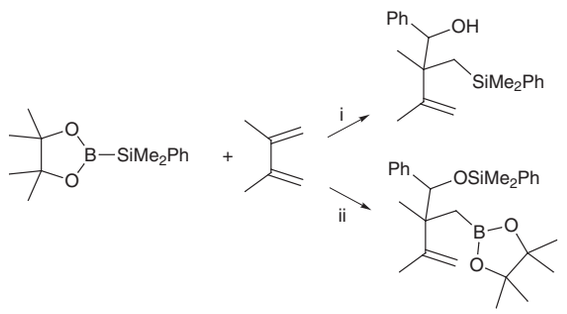
1,2-Silyl shifts continue to be investigated in synthetic[314] and mechanistic contexts.[315] It is shown that they proceed with retention of configuration at the migrating terminus.[315] Inter and intramolecular reactions of silylallene with electrophiles afford silylalkenes and silylalkynes in good yields (Scheme 50).[316,317]

Platinum catalysed borasilation of dienes and the subsequent reaction of the product with benzaldehyde has been investigated and it is reported that the course of the reaction depends on the timing of benzaldehyde addition (Scheme 51).[318]

Reagent $Cp_2Ti[P(OEt)_3]_2$ is used in desulfurative silation, germation and stannation of thioacetals[319] as well as transformation of silylated thioacetals to allylsilanes. The latter occurs with modest *E*:*Z* selectivity (Scheme 52).[320] A rhodium catalysed insertion of ethyl α-diazoacetate into the β C–H bond of silacycloalkanes is reported.[321] An efficient and practical synthesis of optically pure 5-silylated cyclohex-2-enone is reported



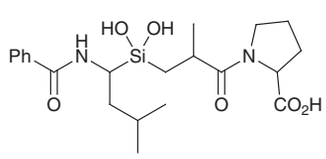
Scheme 50 *Reagents*: i, $Ti(O\text{-}i\text{-}Pr)_4$, 2 equiv. i-PrMgCl; ii, D_2O.



Scheme 51 *Reagents*: i, $(Ph_3P)_2Pt(C_2H_4)$, octane, reflux, 24 hours, then PhCHO; ii, PhCHO then $(Ph_3P)_2Pt(C_2H_4)$, octane, reflux, 24 hours.

Scheme 52 *Reagents*: i, $Cp_2Ti[P(OEt)_3]_2$, RCO_2Et.

and this compound is shown to be a chiral cyclohexa-2,5-dienone synthon.[322] Finally, silicon-containing pseudopeptide **35**, has been prepared.[323]



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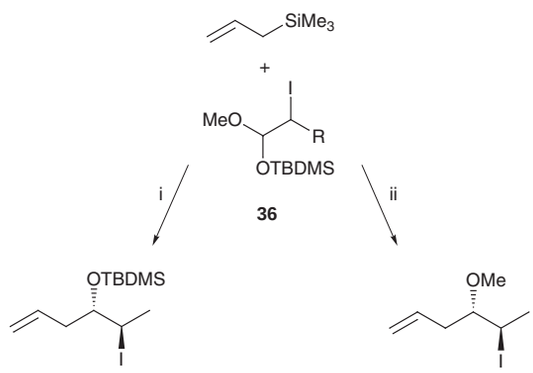
5.1.2 Reactions

Silicon compounds have many uses in preparative chemistry. In particular, the use of allylsilanes has been a popular subject of investigation in recent years. They are also employed in a variety of other methodologies exploiting their use as a masked proton or hydroxy group or their use as protecting groups. The use of silicon tethered groups in organic synthesis has been reviewed.[324]

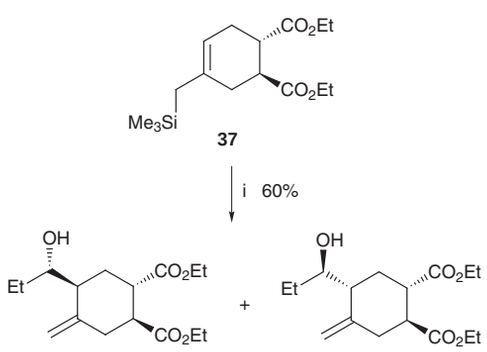
5.1.2.1 Allylsilanes

Allylsilanes when used in conjunction with an activating agent, usually a Lewis acid or fluoride, can be a convenient source of an allyl anion in reactions with a range of functionalities but particularly aldehydes or acetals (Sakurai reaction). An 8-membered transition state for this reaction is proposed based on computer modelling and some experimental data.[325] There have been recent advances both in catalytic asymmetric Sakurai reactions and also in finding more convenient or economical activating agents. For example, $BiBr_3$ has been shown to catalyse the addition of allyltrimethylsilane to benzaldehyde and its dimethylacetal.[326] Propenyltrichlorosilane is shown to add to aldehydes in the presence of a chiral formamide and HMPA with good (88–95% ee) selectivity.[327] *o*-Bis(allyldimethylsilyl)benzene in the presence of catalytic fluoride is shown to be a good reagent for allylation of aldehydes, even though allyldimethylsilylbenzene is not as efficient.[328] Three examples of the addition of allyltrimethylsilane to α-halo acetals have been reported,[329–331] although the reaction of allyltrimethylsilane with iodohydrins has been reported to result in stereospecific conversion into alkenes.[331] A chelation effect in the addition of allylsilanes to α-amino aldehydes has been demonstrated.[332]

A particularly interesting observation is that allylsilane addition to mixed acetal **36** affords different products depending on the Lewis acid employed (Scheme 53),[330] although this is not the only example of different behaviour of allylsilane with different catalysts.[333,334] Reaction of the Diels–Alder cycloadduct **37** with aldehydes affords a modest ratio of stereoisomers (Scheme 54).[335] A highly stereoselective synthesis of tetrahydrofurans has been developed based on the use of cyclic allylsilanes.[336] Silyl enol ethers are also shown to undergo mixed oxidative coupling in the presence of a vanadium compound.[337]



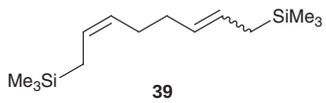
Scheme 53 *Reagents*: i, $TiCl_4$; ii, TMSOTf.



Scheme 54 *Reagents*: i, $TiCl_4$, −60 °C, EtCHO.

Homochiral solid supported silanes undergo highly *syn* selective addition to aldehydes and dimethylacetals.[338] Addition of stoichiometric quantities of chiral catalyst in this reaction affords adducts with high enantiomeric excesses.[339]

Additions of allylsilanes to other electrophiles have also been investigated, including Lewis acid catalysed addition of allylsilanes to epoxides,[340] amination with nosylatehydroxylamine **38** which allows access to α-amino acids,[341] and nitration which provides an efficient asymmetric C–N bond formation protocol with homochiral crotylsilanes.[342] Addition of bisallylsilane **39**, generated from butadiene, Li metal and TMSCl, to α,β-unsaturated ketones proceeds stereoselectively and gives a one-step control of four stereocentres.[343] Addition of this reagent to ketones[344] and acetals[345] has also been reported. Addition of allylsilanes to naphthaquinone in the presence of $TiCl_4$ affords a Michael adduct but in the presence of Me_2AlCl a mixture of [2+2] and [2+3] cycloadducts is obtained.[333] Interestingly, addition of allylsilanes to the α,β-unsaturated ketone **40** in the presence of $TiCl_4$ affords a ring expanded product (Scheme 55).[334]



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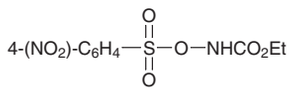

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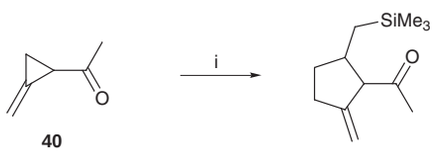


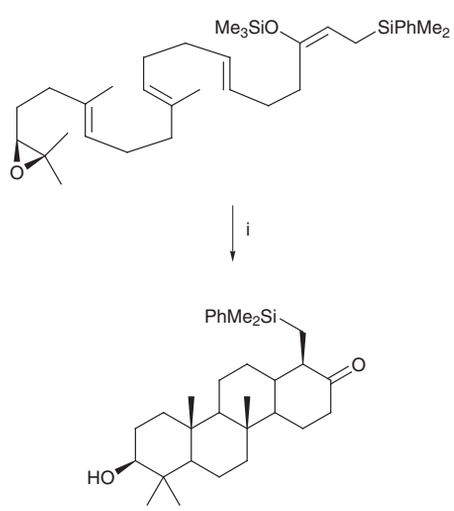
40

Scheme 55 *Reagents*: i, $TiCl_4$, allyltrimethylsilane.

A method for C-allylation of unprotected sugars is reported using allylsilanes.[346] Interestingly, BF_3 failed to give any product in this reaction. In a related example, Lewis acid catalysed addition of silylated alkynes is reported to proceed with significant 1,4-*anti*-selectivity.[347] Reports of both intra and intermolecular $HfCl_4$ catalysed *anti* addition of allylsilanes to unactivated alkynes have appeared.[306,307] Interestingly, an *endo-trig* carbocyclisation is the exclusive outcome of the intramolecular reaction.[306]

The use of allylsilanes in enantioselective (ee up to 85%) free radical allylation promoted by a homochiral Lewis acid is reported.[348] This complements a similar reaction observed with allyltin reagents (see later).[349]

Addition of allyltrimethylsilane to a homochiral aldehyde has been used in the synthesis of butenylglycine.[350] Intramolecular cyclisation of allylsilanes has been widely used in synthetic methodology, including a synthetic approach to the right wing of taxol,[351] synthesis of Myrtine[352] (*via* intramolecular addition to an aminal), synthetic approaches to substituted piperidines[353] (*via* an oxidative process to prepare a formaldimine *in situ*) and *trans* hydroazulenol (from cyclodec-5-enone in two steps).[354] Panek has elegantly used inter-[355] and intramolecular carbocyclisation of homochiral (*E*)-crotylsilanes as an efficient methodology for natural product synthesis.[356] Finally, Corey has reported an elegant and short synthesis of the marine sesterpene scalarendial *via* a tetracyclisation of allylsilane epoxide (Scheme 56).[357]



Scheme 56 *Reagents*: i, $MeAlCl_2$.

5.1.2.2 Other organosilanes

Stereoselective intramolecular ene reactions of vinylsilanes and allylsilanes have been described.[358,359] An aluminium trichloride addition of alkynesilanes to acid chlorides is reported to afford the corresponding ketones.[360] A report of the preparation and reactions of polyenylsilanes has appeared.[361] A difluorocyclopropyl anion has been prepared from the corresponding silylated compound and is shown to react with aldehydes in good yield.[362] Preparation and reactions of the trifluoromethyl anion have also been reported from trifluoromethyltrimethylsilane and TBAF.[363,364] Ate complexes of silicon are used in alkylation of aldehydes[365] and phenylation of allylic alcohols.[366] Silaranes provide an array of very interesting chemistry. For instance, their treatment with base and an aldehyde affords a product not dissimilar to that expected from a Sakurai reaction.[367,368]

Further examples of the role of silicon as a masked hydroxy group[369] or proton[369,370] have appeared. The scope and limitations of intermolecular radical cyclisations of acyl silanes have been explored,[371] and Corey has provided a stereospecific synthesis of tetrasubstituted *Z*-enol silyl ethers using acylsilanes.[372] Seven membered rings have been prepared from [3+4] annulation of α,β-unsaturated acylsilanes with enolates of α,β-unsaturated ketones.[373] α-Hydroxysilanes obtained from reduction of acylsilanes have been used in the synthesis of homochiral cyclopropyl carboxylic acids.[374]

Finally three very interesting reports which have appeared document an "inside selective" silylation protocol for 1,2-diols,[375] the use of the tris(trimethylsilyl) group as a photolabile, fluoride resistant protecting group,[376] and a method for selective deprotection of nonaromatic silyl ethers in the presence of aromatic silyl ethers.[377]

Hydrosilanes are used in copper mediated chemoselective reduction of α,β-unsaturated ketones,[378] reduction of amides to the corresponding amines catalysed by Wilkinson's catalyst,[379] and also in generation of tin hydrides.[380,381]

5.2 Germanium

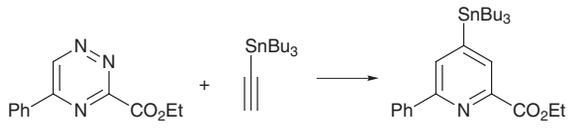
Tris(trimethylsilyl)germane adds to mono-substituted alkynes to give exclusively *cis* alkenes in excellent yield; however addition of this reagent to alkenes is reversible.[382] Treatment of (α-fluoroalkyl)phenylsulfides with the triethylgermane anion generates the corresponding fluoroalkyl anion.[383,384] Metallic germanium, produced by reduction of a germanium tetrachloride in the presence of potassium metal, promotes diastereoselective Reformatski reactions between α-bromophenones and aldehydes although the main product is the debrominated phenone.[385] The combination of triphenylphosphine and germanium tetrachloride also effectively and selectively reduces α-bromoketones, esters, amides, acids and thioesters.[386] Triethylallylgermane chemoselectively adds to imines in the presence of aldehydes.[387] Finally the generation and detection of a number of germylenes (equivalents of carbenes) are reported both in the gas phase[388] and solution.[389,390] As yet they have very limited preparative applications.[390]

5.3 Tin

5.3.1 Preparations

3-Stannylated pyridines have been prepared from the reaction of 3-bromopyridines and hexamethyldistannane thus avoiding the use of lithiation which can be incompatible with the pyridine ring system.[391] Cycloaddition of pyrazine **41** to ethynyltributyltin affords a 4-stannylated pyridine **42** which was subsequently used in coupling reactions. Hence ethynyltributyltin is a synthetic equivalent to aryl, alkyl and haloalkynes which on their own do not undergo cycloaddition–nitrogen extrusion with pyrazine **41** (Scheme 57).[392]

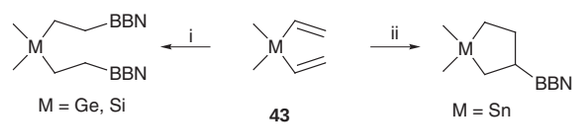
A new method for the preparation of benzylstannane, *via in situ* generation of a Grignard reagent, has been devised.[393] Bisvinylstannane **43** undergoes cyclisation in the presence of



41 42

Scheme 57

9-BBNH, although the same does not occur with the germanium or silicon analogues (Scheme 58).[394] Synthesis of stannacyclopentanes *via* metal exchange from the corresponding zirconium pentacycle is also described.[395] No application for either tin heterocycle is disclosed.



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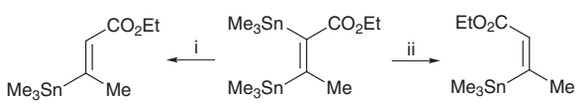
Scheme 58 *Reagents*: i, 9-BBNH (2 equiv.); ii, 9-BBNH (1 equiv.).

Vinyltin compounds have a diverse range of chemical reactivities and therefore their synthesis is particularly relevant. Two new methods for the preparation of stannylated α,β-unsaturated carboxylic acids are disclosed. Treatment of bisstannylated **44** with CuCl in wet DMF affords *trans* β-stannylated ethyl crotonate whereas its treatment with hydrochloric acid in DMF affords the *cis* analogue (Scheme 59).[396] Michael addition of a stannylcuprate to alkynoate acids and a copper catalysed stannylation using an aluminate tin reagent gave access to both regioisomers of stannylated cinnamic acid.[397] An improved method for the synthesis of 3,3-bis(trialkylstannyl)acrylate is reported.[398]



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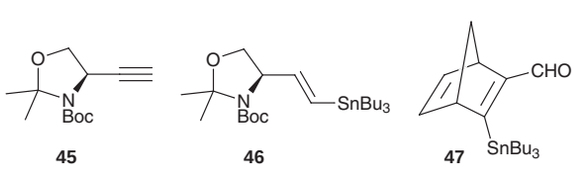
Scheme 59 *Reagents*: i, CuI, DMF, H_2O; ii, HCl, DMF.

Hydrostannylation of alkynes remains a most convenient route to vinyltin compounds and can be performed either by radical hydrostannylation, Pd-catalysed hydrostannylation or stannylcuprate addition. The regio and stereoselectivity of these three types of hydrostannylation have been compared and the latter two are found to be complementarily selective.[399] Hydrostannation–cyclisation of 1,6-diynes has been shown to proceed well with Pd catalysis but since phosphine ligands retard the reaction, Perlman's catalyst should be used.[400] Perlman's catalyst has also been used in hydrostannation of allenes.[401] However, hydrostannylation of thioalkynes does proceed in the presence of phosphine ligated palladium.[402]

To preempt the handling of tin hydrides, a method for *in situ* formation and hydrostannylation of alkynes has been developed using a stoichiometric amount of triethylsilane and tributyltin chloride.[380] On a similar note, a new synthesis of tributyltin hydride has been demonstrated using phenylsilane as the reducing agent for *N*,*N*-dimethyltributyltin.[381] Stannylcuprate addition to **45** affords a new methodology for the synthesis of homochiral amino acids *via* **46**.[403] Other routes to



45 46 47

vinylstannanes include reduction of alkynestannane using $Ti(O^iPr)_4$–^{i}PrMgCl,[404] a tin mediated Pummerer reaction[405] and cycloaddition of stannylated propionaldehyde with cyclopentadiene under chiral Lewis acid catalysis to afford **47**.[406]

Carbostannylation of alkynes catalysed by an iminephosphine palladium complex is shown to be efficient and regioselective.[407]

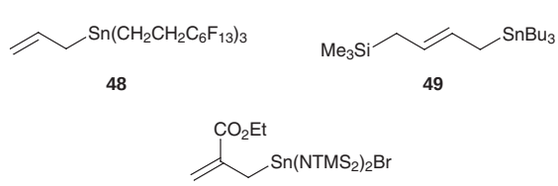
Addition of tin anions to aldehydes has found two important applications. α-Amino and α-hydroxy boronic acids are synthesised *via* metal exchange and chemical manipulation of α-hydroxystannanes.[408] Alkene metathesis of α-hydroxystannanes affords access to medium size cyclic ethers.[409]

5.3.2 Reactions

Tin compounds have a diverse range of applications in preparative chemistry. The most common of these are the use of allylstannanes in addition to electrophiles, Stille-type couplings, regio and stereoselective metal exchange for formation of carbanions, and finally their use for generation of carbon centred radicals by homolytic bond fission.

5.3.2.1 Allylstannanes

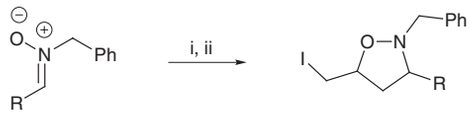
Addition of an allyl group to aldehydes remains one of the most common uses of allyltin compounds. Reactions are usually Lewis acid mediated although Curran has discovered a convenient, easy-to-purify method for thermal, non-Lewis acid catalysed allylation of aldehydes, using reagent **48**.[410] Reagent



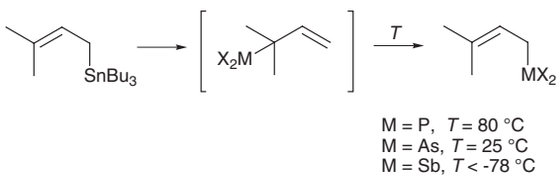
48 49 50

48 has found further application in easy-to-purify Stille couplings,[411,412] including one under microwave conditions.[412] Addition of allyl bromide to aldehydes in the presence of catalytic Sn(II)–CuCl and a chiral catalyst is shown to be modestly enantioselective (ee below 33%).[413] In the presence of AgOTf and BINAP, pentadienyltributyltin reacts with aldehydes through its γ-position whereas in the presence of more conventional Lewis acids, α-adducts predominate.[414] Compound **49** reacts with aromatic aldehydes as an allylstannane.[415] A Lewis acid is not essential for improving the chemical yield of the reaction but it reverses the stereoselectivity.[415] Trimethylborate mediated reaction of allylstannane with aldehydes is modestly stereoselective in the presence of a BINOL–Ti(IV) complex.[416] Allenestannane is significantly more stereoselective but affords a mixture of allene and alkyne adducts.[416]

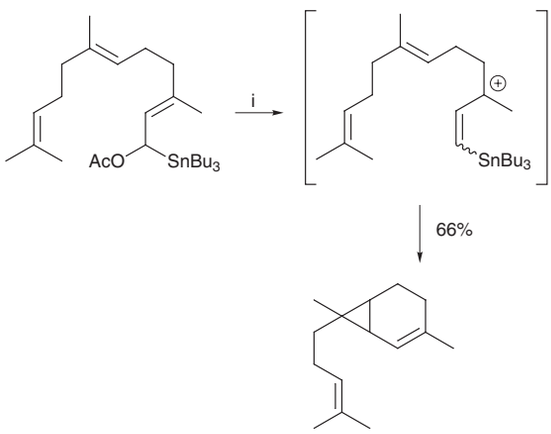
Addition of allyltin to imine *N*-oxides followed by treatment with NIS afforded **51** (Scheme 60),[417] and addition to imines using a chiral Pd catalyst has afforded modest (80%) enantiomeric excesses.[418] Allyltributyltin is shown to react chemoselectively with aldimines in the presence of aldehydes using $Zr(OTf)_4$ as a catalyst.[419] Addition of tributylcrotyltin to group IV (P, As, Sb) halides afford, *via* an intramolecular rearrangement, but-2-enylated products, although the temperature for rearrangement varied significantly between the atoms (Scheme 61).[420] Evans has demonstrated that the addition of allylstannanes to glycoepoxides affords β-allylated saccharides in high diastereomeric excesses.[421] Compound **50** is used as a monoallylating agent for benzylic bromides under palladium and fluoride catalysed conditions.[422] The ability of tin to stabilise a carbocation at the γ-position (the γ-effect) has been employed in a very elegant synthesis of sesquicarene (Scheme 62).[423]



Scheme 60 *Reagents*: i, TMSOTf, allyltributyltin; ii, NIS.



Scheme 61 *Reagents*: i, MCl_3, temperature *T*.

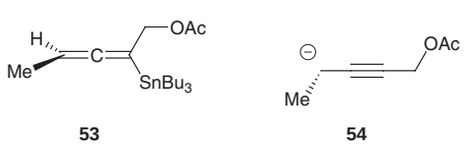


Scheme 62 *Reagents*: i, $BF_3{\cdot}OEt_2$, MeCN.

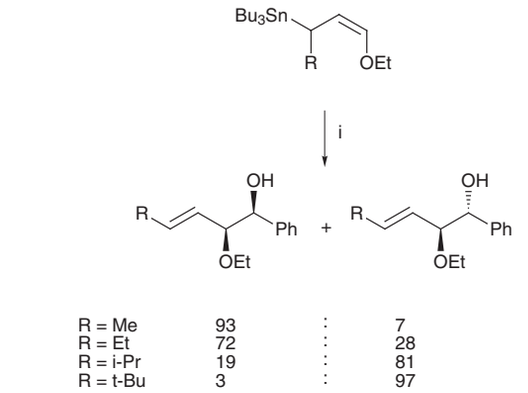
Although allylation of aldehydes and ketones with allylstannanes usually requires Lewis acid catalysis, under certain conditions protic acids also promote this reaction. For instance, 1,8-(bisallylstannyl)naphthalene reacts as a monoallylating agent with ketones and aldehydes in 1,1,1-trifluoroethanol.[424] Similarly, tetraallyltin is shown to react with acetals in the presence of TFA or silica gel in methanol.[425] A catalytic version requiring 0.05 equivalents of tetraallyltin and using allyltributyltin as the allylating reagent in aqueous acid media has been reported.[426]

The size of the α-substituent has a significant effect on the diastereoselectivity of the additions of γ-alkoxyallylstannanes to aldehydes (Scheme 63).[427,428] With bulky alkyl groups at the α-position, *anti* products dominate.[427] However, if the α-substituent is another stannyl group, the *syn* adduct is reported to be the major isomer.[428] Thomas has demonstrated a doubly stereoselective allylation of aldehydes using tin tetrachloride as catalyst.[429] Intramolecular cyclisation of allylstannane **52** proceeds with different diastereoselectivity depending on the Lewis acid used (Scheme 64).[430] The unusual Lewis acid $InCl_3$ is used to catalyse the reaction of allylstannane and an aldehyde to give a product which was subsequently converted to Forskolin.[431] Coupling of alkynylstannanes to acetals is found to be more stereoselective than the coupling of the zincate derivatives.[432]

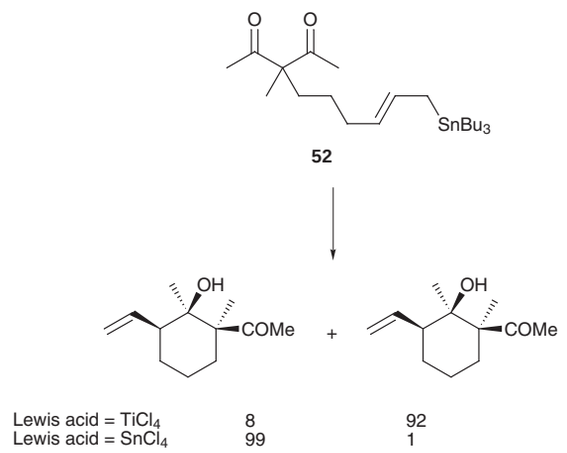
Homochiral stannylated allene **53** is prepared from a homochiral propargyl mesylate and has found a very useful application as a chiral synthon for **54**. In the presence of a number of tin Lewis acids, allenylstannane **53** adds to aldehydes with



53 **54**



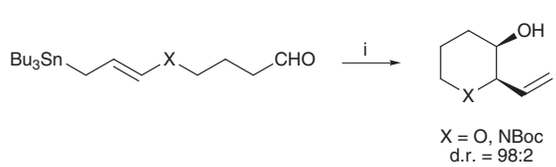
Scheme 63 *Reagents*: i, PhCHO, $BF_3{\cdot}OEt_2$, CH_2Cl_2, −78 °C.



Scheme 64 *Reagents*: i, Lewis acid.

a high degree of stereoselectivity. The methodology has been applied to the synthesis of subunits of a number of natural products such as Zincophorin, Rifamycin and Discodemolide.[433] Synthesis of γ-silyloxyallenylstannanes is also reported from thermal rearrangements of [(α-silyloxy)propargyl]-stannanes.[434]

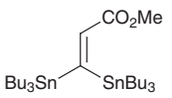
Intramolecular cyclisations of allylstannanes continue to provide useful synthetic methods for preparation of carbocyclic and heterocyclic rings. Intramolecular cyclisation of an allylstannane–aldehyde is used for the diastereoselective formation of 2,3-disubstituted tetrahydropyran[435] and piperidines (Scheme 65)[436] and the synthetic utility of this methodology is demonstrated in the total synthesis of Desoxoprosopinine.[437] A modestly enantioselective destannation–protonation of allyltins with Lewis acids, in the presence of catalytic quantities of a chiral Brønsted acid has been reported.[438]



Scheme 65 *Reagents*: i, $BF_3{\cdot}OEt_2$, toluene.

5.3.2.2 Stille coupling

The formation of biaryls by Stille coupling has been reviewed.[194] Another example of "no-palladium" Stille coupling has appeared using both CuI and $MnBr_2$ as catalyst instead.[439] In the Stille coupling of *gem*-substituted bis(trialkylstannyl)alkenes **55** and **56**, it is shown that coupling occurs at the *cis* tin although selectivity is not very high.[440] A mechanistic study by the same author suggests that these substitutions are *cine* and not *ipso*.[441] The electronic nature of the aromatic



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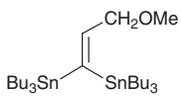

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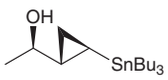

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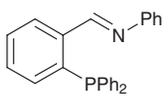
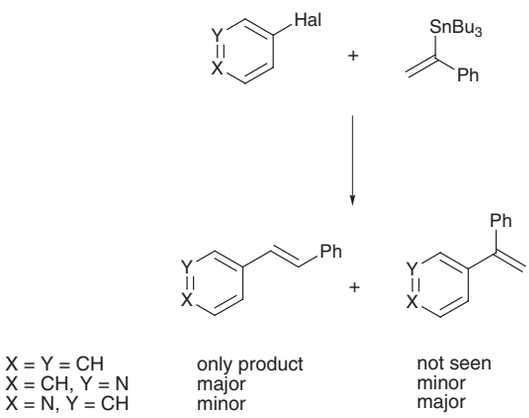


58

halide is reported to have a significant effect on the regiochemistry of substitution. Hence, although halo benzenes and 3-halopyridines give mostly *cine* substituted products when reacted with α-stannylated styrenes, 2-halopyridines afford mostly the *ipso* product (Scheme 66).[442]

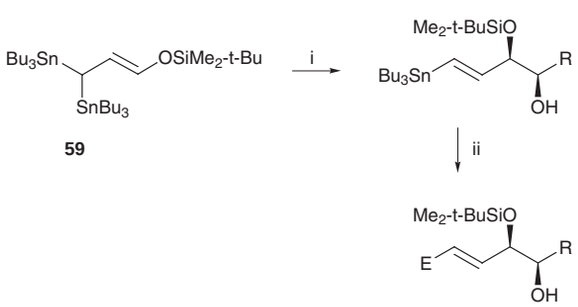


Scheme 66

Coupling of stannanes to arylsulfonium species is reported to proceed more efficiently than to the corresponding aryl halide[443] and coupling of stannanes to aryliodonium salts, using manganese catalysis is also reported.[444]

Enantiopure cyclopropyltributyltin **57** has been prepared by selective enzymatic hydrolysis of the *S* isomer.[445] Both this[445] and a boronic[238,239] acid analogue have now been used in coupling to aryls. Ligand **58**, in the presence of Pd(0), catalyses homocoupling of both electron rich and electron deficient arylstannanes.[446] Under these conditions, alkyne stannanes homocouple only poorly, although they do undergo other reactions.[407] Oxidative homocoupling of vinylstannanes and that of allylstannanes to vinylstannanes has been shown.[447]

A combined methodology for allylation–Stille coupling has been developed. Bisstannyl allyl ether **59** undergoes reaction with aldehydes to afford vinylstannanes with high *syn* selectivity that undergo Stille couplings (Scheme 67).[428] Stille coupling is used for alkenylation of imidoyl chloride and cyanuric chloride.[448]



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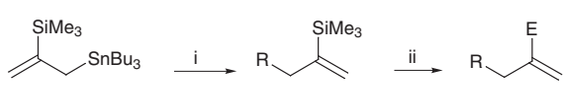
Scheme 67 *Reagents*: i, RCHO; ii, E^+.

Stille coupling has been employed for the synthesis of analogues of Huprazine,[449] *para*-substituted phenylalanines,[450] and bicyclic β-lactams.[451] The elegant use of Stille coupling in the synthesis of neocarzinostatin analogues is also reported.[452] Other noteworthy applications of Stille coupling in natural product synthesis include assembly of Macrolactin A *via* three Stille couplings,[453] the application of Stille coupling in the total synthesis of Rhizoxin[454] and Forskolin,[431] and the ring closure of Mycotrienol *via* a one-pot coupling of *trans* 1,2-bisstannylated ethylene and bisiodide to form a triene.[455] Synthesis of trienes *via* a two step coupling of 1,2-bisstannylatedethylene has also been demonstrated.[456]

Combination of Ni(0) with alkynestannanes continues to provide very interesting chemistry. A nickel catalysed three-component coupling of norbornene, trimethylallyltin and an α,β-unsaturated ketone is reported.[457] Also both inter- and intramolecular dialkylation of a monosubstituted alkyne with alkynestannane and allyl acetate are reported.[458] Finally, palladium catalysed diarylation and dialkenylation of norbornene in the presence of α-chloroacetone is also reported.[459]

5.3.2.3 Radical reactions involving tin

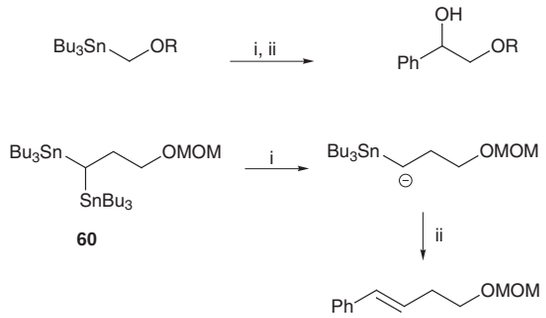
Homolytic fission of alkylstannanes is a common method of generating alkyl radicals. Some of the most significant applications of this method in organic synthesis over the period of the review are outlined here. Asymmetric aluminium mediated radical allylation of an α-iodo ester with a binaphthol[460] and diamine[461] chiral catalyst are reported. Allylation of a solid supported α-bromoester is disclosed.[462] Addition of trimethylaluminium at the end of reductions with tributyltin hydride is reported to significantly remove traces of tin from reaction mixtures.[463] A synthetic methodology for the preparation of naturally occurring oxepanes such as ciguatoxin and brevetoxin *via* cyclisation onto a β-oxy-α,β-unsaturated ester is being developed.[464] In this reaction triethylborane is a better radical initiator than AIBN. Photolytic generation of the glycoradical and reaction with allyltributylstannane results in the formation of mostly the β-diastereomer of saccharides.[465] A methodology for radical allylation followed by ionic reaction of β-silylated allyltins is developed (Scheme 68).[466] It has been shown that *O*-stannylsubstituted alkylarylsulfones undergo unusually facile homolytic sulfone cleavage to generate alkyl radicals.[467] Dibutyltinchloride hydride is shown to be a chemoselective reagent for reduction of ketimines in the presence of ketones.[468] Finally, a procedure for reduction of aryl halides with tin hydrides in water is described.[469]



Scheme 68 *Reagents*: i, RX, AIBN, PhH, reflux; ii, TBAF, E^+.

5.3.2.4 Metal exchange for regiospecific anions

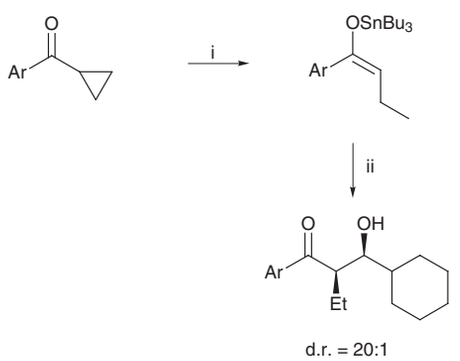
Metal exchange (usually with lithium) is a particularly useful and common method for generation of regiospecific anions from alkylstannanes. The main highlights of this aspect of the use of alkylstannanes in synthesis are as follows. Bisstannyl ether **60** is used in a methodology for three carbon elongation of carbonyls[470] (Scheme 69) as well as preparation of cyclopropylstannanes in a highly stereocontrolled fashion.[471] A convenient and general one pot procedure for preparation of primary α-alkoxystannanes and their use as hydroxymethyl anion equivalents is reported.[472] A novel synthesis of the indolizidine ring system *via* cycloaddition of a 2-azaallyl anion and an azomethine ylide is disclosed.[473] Wittig rearrangement of an enantio-defined anion derived from α-propargyloxystannane is shown to proceed with complete retention at the anion bearing terminus, although periselectivity ([2,3] *versus* [1,2]) depends on the alkyne substituent.[474]



Scheme 69 *Reagents*: i, BuLi; ii, PhCHO.

5.3.2.5 Tin enolates

Two interesting and contrasting features of the reactivity of tin enolates have been disclosed by Baba. Reaction of a tin enolate with α-chloroketones in the presence of $ZnCl_2$ efficiently affords a 1,4-diketone *via* a formal nucleophilic displacement of halide function. In the absence of a Lewis acid however, the major product is that of a nucleophilic addition to the ketone function.[475] The same group has also found that preference of a tin enolate for reaction towards carbonyl and carboxy functions in the presence of an alkyl halide function can be fully reversed if that enolate is converted into an ate complex by treatment with the bromide anion first.[476] Enholm has investigated a number of features of tin enolate radicals. For instance, addition of a tin radical to an α,β-unsaturated ketone sets up a ketyl radical which undergoes a [3,3] sigmatropic shift to the corresponding α-hydroxy ketone.[477] Tin enolates generated through reduction of cyclopropyl ketone are shown to react with aldehydes with high *erythro* selectivity (Scheme 70).[478]



Scheme 70 *Reagents*: i, Bu_3SnH, AIBN, PhH, 80 °C; ii, cyclohexanecarboxaldehyde.

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Review 8/02867B