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METHODOLOGY TO ESTABLISH 1,2- AND 1,3-DIFUNCTIONALITY FOR THE SYNTHESIS OF CARBOHYDRATE DERIVATIVES

DAVID J. AGER* and MICHAEL B. EAST†
*NutraSweet Research and Development, 601 East Kensington Road, Mount Prospect, IL 60056, USA
†Department of Chemistry, Florida Institute of Technology, 150 West University Boulevard, Melbourne, FL 32901, USA

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1. INTRODUCTION

Sugars are ubiquitous in Nature. They are used as sources of energy, means for storing energy, and as parts of macromolecules either to modify properties, as in glycoproteins, or as building blocks such as in DNA and RNA. Synthetic organic chemists have found carbohydrates a valuable source of chiral centres for incorporation into a synthetic target. In this context, many of the reactions discovered by the early carbohydrate chemists are still invaluable as extensive modification of the sugar may be required before it can be incorporated into the synthetic sequence. An expansion of the 'chiral pool' would do much to alleviate this problem, as only a few monosaccharides are readily available from natural sources.

Many biologically important molecules contain sugar units, and the synthesis of modified analogues for biological activity testing is often tedious. In both the traditional synthetic organic and medicinal chemistry fields, it is advantageous to have useful synthetic methods to carbohydrate analogues.¶ The preparation of many analogues of 3′-azido-2′,3′-dideoxythymidine (AZT) for potential use in AIDS therapy admirably illustrates this point.[2]

The last few years have seen tremendous advances in the area of asymmetric synthesis. It is now possible to control the stereochemistry at two or three centres within an acyclic substrate with no induction being required from an existing asymmetric centre within the substrate molecule. The use of these powerful reactions, coupled with the use of chiral starting materials, will surely be the way synthetic strategy evolves.

Thus, from the viewpoints of both an organic chemist practicing the art of asymmetric synthesis from a chiral starting material and a medicinal chemist preparing analogues of natural sugars, the need has arisen for methods to prepare carbohydrates from acyclic, non-sugar derived precursors. Such an approach can be applied to the synthesis of natural, unnatural (e.g. L-isomers) sugars and a wide array of analogues containing a plethora of functional groups. This review will cover methods for the preparation of 1,2- and 1,3-difunctional compounds that have the potential to be used for the preparation of carbohydrate derivatives. Reactions discussed are not limited to those that result in an optically pure product; transformations which control only relative stereochemistry, or are stereoselective under certain conditions, have been included for completeness.¶ Kinetic resolutions have been included when appropriate.

This review falls into two parts. The first part covers synthetic methods which have been used

¶ The application of these synthetic methods for the synthesis of carbohydrate derivatives is discussed elsewhere.[1]

¶ Throughout this review, in the interest of space, only the *major* isomer of a reaction product is shown. In addition, when a racemic mixture results, only one isomer is illustrated.

for the preparation of 1,2-asymmetric centres with defined relative stereochemistry. The second part discusses 1,3-difunctional compounds where two 1,2-difunctional relationships may also be established. The emphasis of this report is on the synthetic methodology and control of stereochemical relationships rather than applications for carbohydrate synthesis.[1] Applications of the synthetic methodologies presented in this review for the synthesis of carbohydrate derivatives, and the use of methodologies that establish multiple asymmetric centres will be considered separately.[1]

Many of the reactions provide molecules where the relative, rather than absolute stereochemistry is defined. To avoid any ambiguity, as with the *erythro/threo* nomenclature system, the *pref/parf* and *syncat/ancat* nomenclature systems proposed by Carey will be employed throughout this chapter.[3] Alternative nomenclature systems have also been proposed to avoid this dilemma.[4]

Other reviews have addressed methods for the synthesis of carbohydrates,[5] while others have focused on advances in asymmetric synthesis,[6] or have considered topics discussed herein.[7] Of course, other classes of compounds, including ionophoric antibiotics,[8] insect pheromones[9] and macrolides,[10] benefit from the development of these methodologies.[11]

2. ONE-CARBON TRANSFORMATIONS

Although this review centres around the synthesis of contiguous chiral centres, some transformations at a single asymmetric centre are relevant as they extend the use of other methodologies.

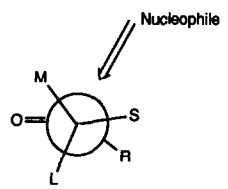
Nucleophilic substitution at an asymmetric centre allows for inversion of configuration. This approach can remedy a condensation reaction that provides the 'wrong' isomer as the major product. With regard to carbohydrates, inversion of a hydroxy group may be of importance. Reduction of a ketone may generate an additional asymmetric centre. Thus, these reactions will be considered briefly.

Electrophilic additions to alkenes can provide 1,2-functionality. In other cases, such as reaction of alkene with water, only one functional group is introduced. Both of these reactions are considered together in Section 3.

2.1. *Nucleophilic addition to a carbonyl compound*[12]

In addition to the plethora of synthetic methods which rely upon nucleophilic addition to a carbonyl group,[13] many stereoselective condensations have been developed from this simple reaction.

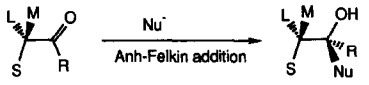
Condensation of a nucleophile with a carbonyl compound, with concurrent carbon–carbon bond formation, has proven to be one of the most powerful reactions in organic synthesis. Thus, the need to control and predict the direction of attack for the nucleophilic species has spawned many models.[14] These early rationalizations could be used in a predictive manner, but suffered from errors due to the assumption of a perpendicular approach for the incoming nucleophile relative to the carbonyl plane. Calculations have shown that the trajectory of the nucleophile is at an angle,[15] and closely relates to the model of Felkin.[14d,16] This model (Fig. 1 and Scheme 1) has become known



where S = small substituent
M = medium substituent
L = large substituent

Fig. 1.

as the Anh–Felkin model.¶[6i,15e,17] This model is powerful as it can also be used for α-substituted carbonyl compounds (Section 2.2). The major shortfall centres around identification of the 'large' group.[18] The interpretation of the Anh–Felkin model also gives powerful insight into means to optimize asymmetric induction: strong electrophilic assistance (i.e. complex formation between the carbonyl oxygen atom and a strong Lewis acid) aids selectivity, while use of a 'hard' nucleophile will be detrimental to high asymmetric induction.[19]



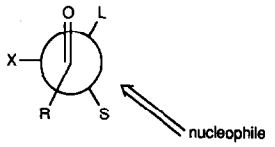
Scheme 1.

In cyclic carbonyl compounds, the approach of the nucleophile can be influenced greatly by the nature of the ring substituents, as well as the nucleophile itself.[20] In many respects, therefore, cyclic cases must be considered on an individual basis.[21]

2.2. *Chelation-controlled addition*

This type of addition is relatively simple to perform with carbohydrate precursors due to the prevalence of hydroxy groups. Although chelation-controlled addition can be accomplished with a wide variety of substrates, it is simplest to consider the rules by use of the models developed for α-substituted carbonyl compounds.

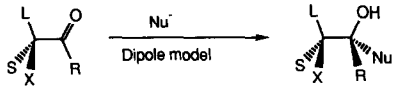
The addition of a nucleophile to an α-halo ketone, often referred to as the 'dipole model',[14b] is depicted in Fig. 2.[15a] The approach has been modified from the original proposal to be consistent with



where S = small substituent
L = large substituent
X = halogen

Fig. 2.

the favoured trajectory of the approaching nucleophile, although the overall product stereochemistry remains the same (Scheme 2).



Scheme 2.

Perhaps of more importance is the cyclic, or chelation model of Cram (Fig. 3),[22] where formation of the chelate can reverse the stereochemical outcome of a reaction compared to when a chelate is

¶ The direction of approach usually coincides with that determined by Cram (ref. 14*a*) who proposed the first model. Thus, it is not uncommon to see the use of 'Cram addition'. The chelate model described in Section 2.2 is often referred to as 'anti-Cram addition'.

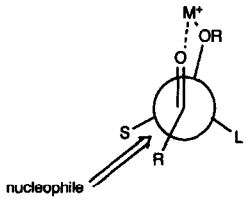
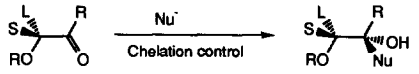


Fig. 3.

not formed (Scheme 3) (*vide infra*).[23] Once again the model has been modified to conform with Anh's results.



Scheme 3.

A varient of these rules is provided for α-keto esters by Prelog's generalization (Fig. 4).[24] However, as with all of these generalizations, care must be exercised in their application as 'exceptions' do exist, particularly when the models are pushed to their limits.[25]

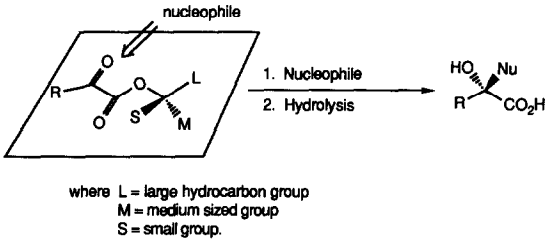
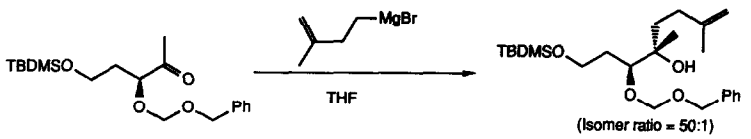


Fig. 4.

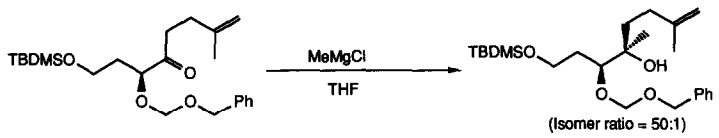
In some cases, high diastereoselectivity during an enolate reaction may not be due to a chelate-controlled mechanism, but can be attributed to enolate conformations within an aggregate.[26] However, it has been demonstrated that chelates are true intermediates for the addition of an organometallic reagent to an α-alkoxycarbonyl compound.[27]

The mechanism of a reaction can also have important stereochemical consequences; for example, reduction of an acyclic ketone by an electron transfer process can provide the opposite stereochemistry to the more traditional metal hydride reagents.[28]

As complex formation is often crucial for high stereoselectivity, the nature of the oxygen-protecting group and solvent play an important role to determine the selectivity of the addition. Obviously, this oxygen-protecting group must also be easily and cleanly removed. For these reasons, the use of benzyl, benzyloxymethyl, or furfurylmethyl protection has been advocated with Grignard reagents. The use of the Anh–Felkin or chelation-controlled addition allows regulation of the product stereochemistry as these two modes of addition usually give rise to different diastereoisomers (see Schemes 4 and 5).[29]

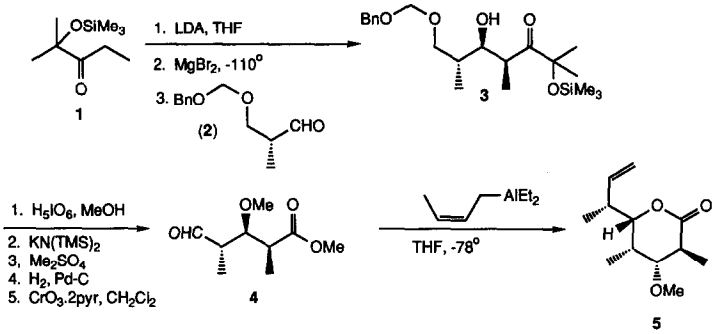


Scheme 4.



Scheme 5.

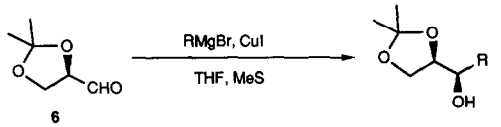
The philosophy of chelation control was employed to control the aldol reactions (Section 4.2) in Still's synthesis of monensin.[30] Condensation of the kinetic enolate (formed from the ketone **1**) with the aldehyde **2** in the presence of magnesium bromide afforded a 5 : 1 mixture of the diastereomeric adducts in favour of the chelation-controlled product. Subsequent transformations of the adduct, **3**, and removal of the minor diastereomer by chromatography provided the aldehyde **4**. This aldehyde **4** was subjected to a second aldol reaction, but as Anh–Felkin control was required, the branched nature of C-3 had to override the ability of the methoxy group to form a chelate. This control was achieved by the use of *cis*-2-butenyldiethylaluminium as a propanal enolate equivalent, and yielded about a 3 : 1 diastereoisomeric mixture of lactone **5** (Scheme 6).[30b]



Scheme 6.

The condensation of lithium enolates derived from esters and ketones with α-alkoxy aldehydes follows Anh–Felkin control, if the alkoxy substituent is assumed to be the 'large' group.[31] This former mode of addition is also observed with other organometallic reagents.[32] The use of triisopropylsilyl has been advocated for the protection of an α- or β-hydroxy group when chelation-controlled addition is not required.[27,33]

The use of a Grignard reagent with a β-alkoxy aldehyde does not, however, result in high induction. This situation can be alleviated by use of a cuprate, although chemical yields may be diminished. A β-substituent, when an α-substituent is also present, can have a marked effect on selectivity.[34] An excellent illustration is provided by the cuprate addition to 2,3-*O*-isopropylideneglyceraldehyde (**6**) (Scheme 7); organometallics usually provide the *ancat* isomer.[35] An alternative procedure to effect chelation control with a β-alkoxy aldehyde is to use an organotitanium reagent.[36] The selective cuprate reaction with β-alkoxy aldehydes does not translate to α-alkoxy aldehydes.[34]



Scheme 7.

The addition of a nucleophilic reagent to a carbonyl group is influenced by many variables, many of which can be determined through the reaction conditions and reagents. Although the interplay between these variables is not completely understood, the rules described above can be used in a predictive manner. For example, the size of a reducing agent for a ketone can have an effect on the facial selectivity (cf. Section 3.4.2.2).[37]

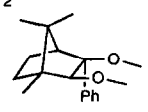
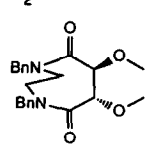
2.3. *Use of 'extended' organometallic reagents*[38]

The use of an organometallic reagent which contains functionality allows further modification of the adducts derived from addition to carbonyl compounds. This approach has provided alternatives to the aldol (Section 4.2), and the homoaldol reactions.[1] In this regard, many heteroatoms have been incorporated into the organometallic unit along with unsaturation to afford a substituted allyl anion.[38a]

The flexibility of such an approach does rely somewhat upon the configurational stability of the ambident allyl anion and its site of reaction.[39] Examples of metals that fulfill these regiochemical criteria are included in Table 1. In addition to carbonyl compounds, a wide variety of electrophiles have been condensed with allyl anions.[40]

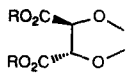
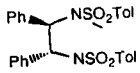
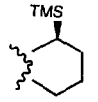
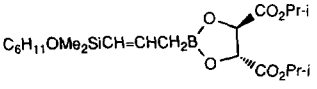
Table 1.

Examples of allylic moieties that condense with carbonyl compounds.

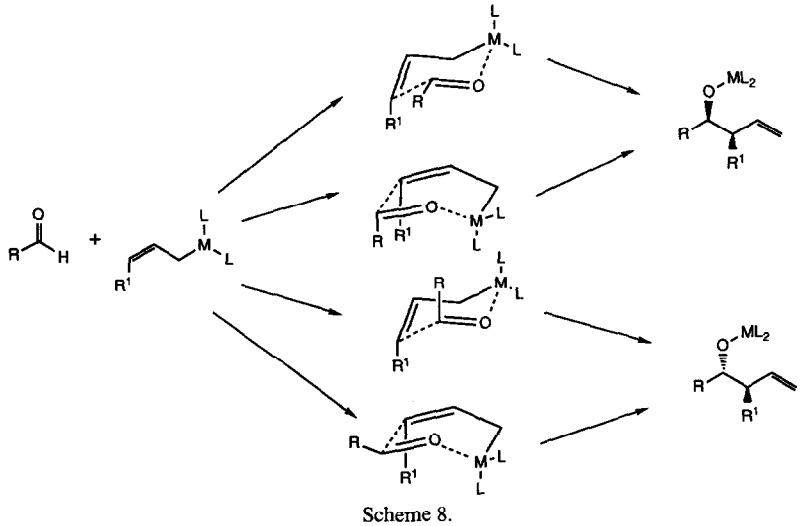
Allylic Compound	Base or Catalyst	Major isomer[a]	Reference	Allylic Compound	Base or Catalyst	Major isomer[a]	Reference
$XCH_2CH{=}CHR$[b]	Li or Mg, Cp_2ZrCl_2	A	41	$ROCH_2CH{=}CHR$[h]	Base,[i] Et_3Al	A	58
	SnX_2	-[c]	42		Base,[i] Cp_2ZrCl_2	S	58a
	$CrCl_2$	A	41b,42a,43		t-BuLi, Cp_2TiCl	A	54
	Zn	S	44		BuLi, $BF(OMe)_2$	S	59
	$CpTiCl_2$	A	43a,45				
	MoCpClNO	A	46	$R'SCH_2CH{=}CHR$	Base,[i] Bu_3SnCl, BF_3	A	58a
	Pd-$SnCl_2$[d]	A	47		Base,[i] Cp_2ZrCl_2	S	58a
	LDMAN-$CeCl_3$[e]	-	48		Base[i]	γ	60
	Sb	S	49		t-BuLi, $Ti(OPr\text{-}i)_4$	A	61
					Base,[i] $ClB(NMe_2)_2$.MeI $[Me_2C(OH)_2]_2$	A	62
$R'_3SiCH_2CH{=}CHR$	F^-	A	50		Base,[i] $ClB(NMe_2)_2$.MeI		
	$TiCl_4$	γ[f]	51		$[Me_2C(OH)_2]_2$	S[g]	62
	$SnCl_4$	-	52				
	s-BuLi, TMEDA	γ	53				
	s-BuLi, TMEDA, Et_3Al	-	53	$RSOCH_2CH{=}CH_2$	LDA, Me_3P	-[j]	63
	t-BuLi, Cp_2TiCl	A	54				
				$R'SeCH_2CH{=}CH_2$	s-BuLi, TMEDA	γ	53
$R'_3SnCH_2CH{=}CHR$	$BF_3{\cdot}OEt_2$	S[g]	55		s-BuLi, TMEDA, Et_3Al	-	53
	$BF_3{\cdot}OEt_2$	S	56				
	$MgBr_2$	S	56c	$R'_2NOCOCH_2CH{=}CHR$	BuLi, TMEDA, i-Bu_2AlX	S	64
	Δ	A[g]	56e,57		BuLi, $ClTi(OPr\text{-}i)_3$	S	65
					BuLi, TMEDA, i-Bu_2AlX	S[g]	64a,66
$R'_2BCH_2CH{=}CHR$ R'_2B = 	-	A	67	$R'_2BCH_2CH{=}CHR$ R'_2B =  2-Icr	-	-	79
$(Me_2C\text{-}O)_2$	-	A	68,69		-	-	80
		S[g]	68-70		-	A	80
$[(C_6H_{11})CH\text{-}O]_2$	-	S[g]	71				

(cont.)

Table 1 (cont.)

Allylic Compound	Base or Catalyst	Major isomer[a]	Reference
9-BBN	-	A	56d,72
(o-$C_6H_4O_2$)	-	A	73
Ipc_2	-	-	74
	-	A	75
		S[g]	75
	-	A	76
		S[g]	77
	-	-	78
$RCH{=}CRCH(CH_2OBz)SnBu_3$	-	S	85
$ROCH{=}CHCH_2B(OCMe_2)_2$	-	A	86
		S[g]	86,87
$RSCH{=}CHCH_2B(OCMe_2)_2$	-	S[g]	62,88
$CH_2{=}CHCH(OEE)TMS$	s-BuLi	-	89
$R_2NCO_2CH_2CH{=}CHTMS$	BuLi, i-Bu_2AlX	A[g]	90
	BuLi, TiR_2X	A[g]	90
	-	S[g]	80
	-	-	81
$RCH{=}CH(OMOM)SnBu_3$	γ	A	82
$RCH{=}CH(OCH_2OMen)SnBu_3$[k]	Δ	A	83
$ROCH{=}CHCH_2SnBu_3$	-	S	84
$R_2NCO_2(TolSO_2)CCH{=}CHR$	BuLi, $Ti(OPr)_3Cl$	A	91
$TMSCH{=}CHCH_2B(OCMe_2)_2$	-	A	92
	-	A	93
$RCH{=}CHCXBR_2$			
$R_2 = (OCMe_2)_2$[l]	-	A	94
$[OCH(C_6H_{11})]_2$	-	-	95
$RCH{=}CHC(SiMe_3)[9\text{-BBN}]$	-	A	96
$R_2NCO_2CMe{=}CHCHMeSnBu_3$	$TiCl_4$	A	97

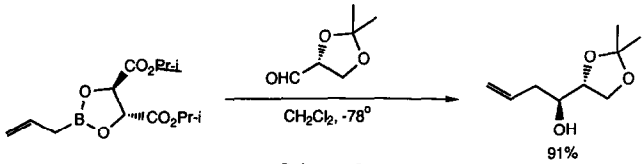
[a] The isomer can vary depending on the substrate, refer to the original citation. The abbreviations S = syncat (syn), and A = ancat (anti) have been used. [b] X = a halogen. [c] Not applicable or not given. [d] X = OH. [e] X = SPh. [f] Denotes γ-addition of the allyl anion is the major reaction pathway. [g] From the cis-alkene. [h] The trans-isomer is inferred, unless otherwise stated. [i] No specific base is quoted. [j] An Evans rearrangement also occurs under the reaction conditions. [k] Where Men denotes menthyl. [l] Where X is a halogen or methoxy.



Scheme 8.

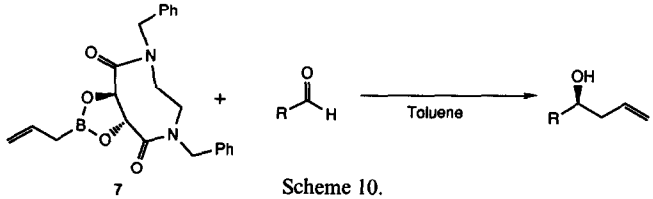
The additions can proceed through one of four likely possible cyclic transition states (Scheme 8).[38a] In these cases, the ligand, L, can determine the stereochemical outcome of the reaction. Diastereoselectivity decreases as the length of the metal–oxygen bond increases.[98] The selectivity is dependent upon the minimization of steric interactions within the chair transition state.[38d] However, it is not certain that a cyclic transition state is involved in every case; an S_E2' reaction pathway could be preferred, particularly when the heteroatom is silicon or tin.[99] The use of organosilanes and stannanes in the presence of a Lewis acid provides homoallylic alcohols.[52c]

The use of chiral allyl boranes allows transfer of the allyl group in an asymmetric manner (Scheme 9).[68,69,71a,74d,76a,76c,79,80,83,100]



Scheme 9.

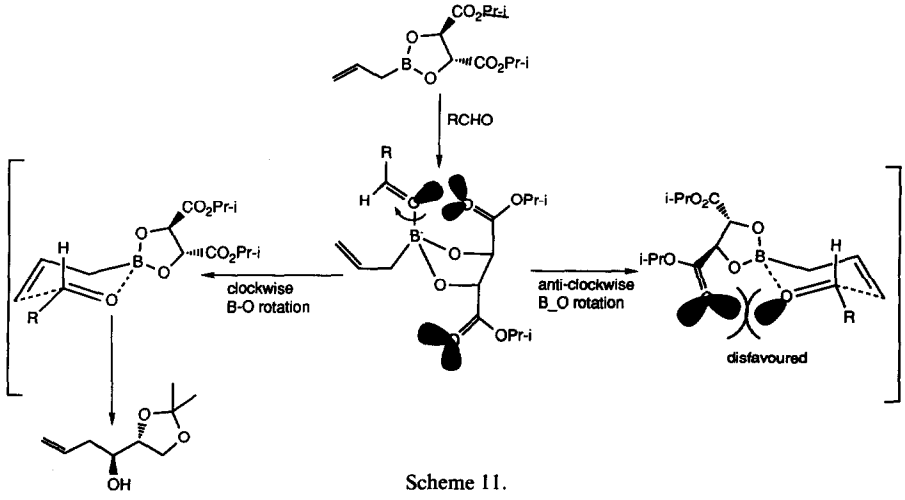
Indeed, the use of substituted allylboron systems, such as crotyl, with α-substituted aldehydes has been the subject of considerable investigation. The diastereoselectivity does not depend upon the size of the substituent in the reagent, but only on the alkene geometry (*vide infra*). These observations have been interpreted in terms of the minimization of strain energies for a chair transition state.[68c,101] The high selectivity could arise from n–n electronic repulsive interactions between the aldehyde oxygen atom and an ester carbonyl group. These interactions have been exploited by the use of the boron compound **7** (Scheme 10).[77]



7

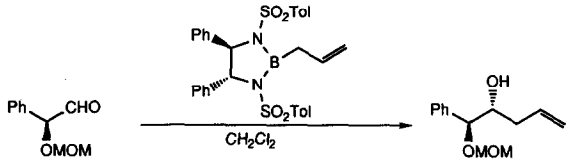
Scheme 10.

The tartrate esters, although they do not provide the highest diastereo- and enantio-selectivity, are very reactive and provide very short reaction times, certainly when compared to compound **7**.[102] A hypothesis which accounts for the effect of reaction variables (temperature, solvent, moisture), and based on lone pair interactions has been proposed (Scheme 11).[102a]



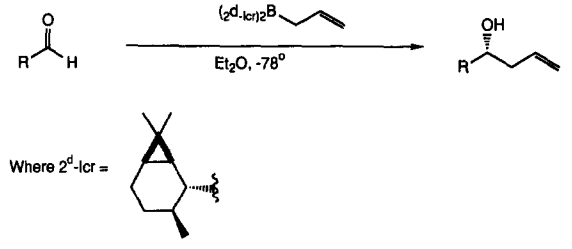
Scheme 11.

The use of the 'stien' control group allows recovery of the chiral reagent in an expeditious manner (Scheme 12). Substituted allyl anions can also be employed in this approach.[78a]



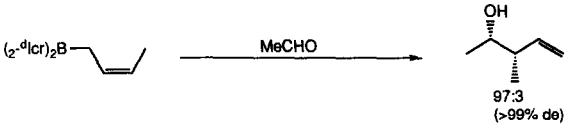
Scheme 12.

Isocaranylboranes have provided excellent selectivity for the control of a single chiral centre (Scheme 13), and compare extremely well to other boron reagents (Table 1). In addition, the homoallyl alcohol product has the opposite stereochemistry to that from the analogous reaction with *B*-allyldiisopinocamphenylborane or *B*-allylbis(4-isocaranyl)borane.[80,103]



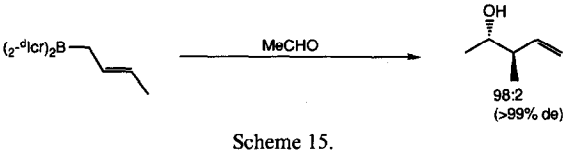
Scheme 13.

When a substituted allyl system is employed with 2-isocaranylboranes, a high degree of selectivity is observed (Schemes 14 and 15). Again, the resultant diastereoselectivities compare favourably to those obtained with other chiral auxiliaries on boron.[80,104]



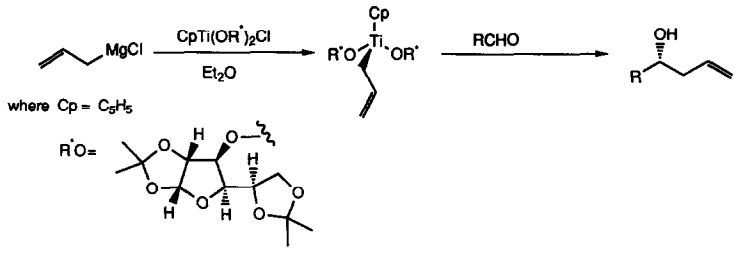
Scheme 14.

The use of metal carbonyl complexes of aromatic and propargylic aldehydes greatly enhances the enantioselectivity observed for reaction with allylboron reagents.[105]



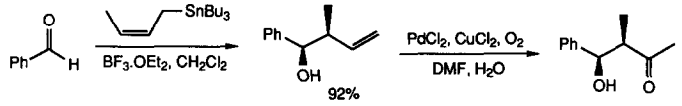
Scheme 15.

The use of a chiral titanium complex has allowed enantioselective alkylation (86–94% *ee*) (Scheme 16).[45a,45c,106] A similar result is observed with a molybdenum complex.[46,107]



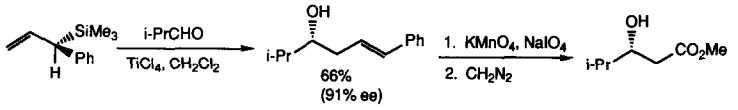
Scheme 16.

The alkene unit of the condensation product can be used for further modifications. In the first example (Scheme 17), an aldol-type product is obtained without the use of a strong base.[55] For the



Scheme 17.

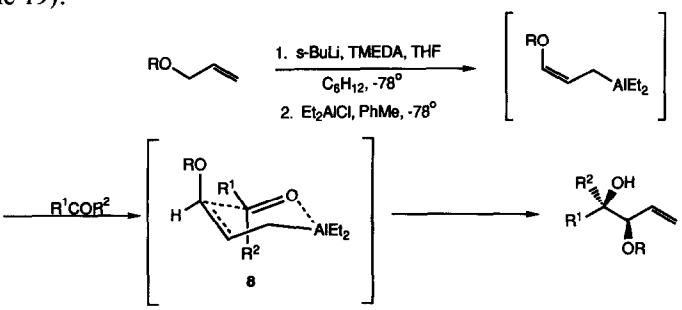
latter example (Scheme 18), a chiral silane is used which ultimately provides a β-hydroxy ester with good enantioselectivity.[51a] A chiral allylsilane based on an asymmetric silicon also affords enantioselectivity when reacted with an aldehyde.[99g]



Scheme 18.

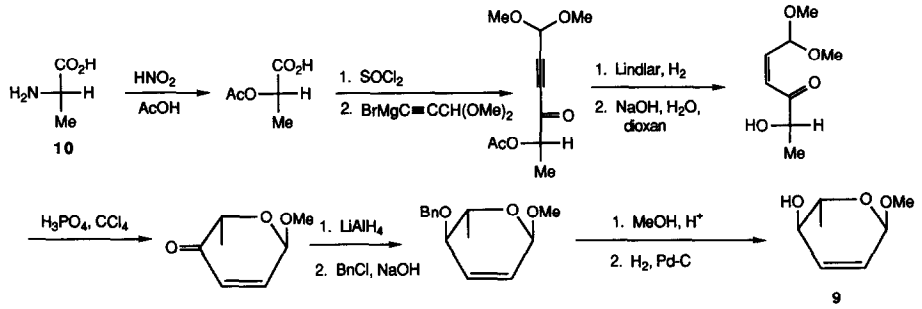
Chiral carbonyl moieties provide the opportunity for either Anh–Felkin or chelation-controlled addition.[108] Condensation of an allylstannane with an α-alkoxy aldehyde in the presence of magnesium bromide forms the chelation-controlled addition product.[109] The diastereofacial selectivity also increases with the size of the alkyl group in the aldehyde moiety. The preferred method of protection for the hydroxy group is benzyloxymethyl.[56c] Similar results are obtained for β-alkoxy aldehydes with allylstannanes.[56a] The exact mechanism of these stannane reactions is dependent upon the reaction conditions.[110] Of the many allylic nucleophiles investigated, allyltrimethylsilane provided the best selectivity (cf. Scheme 18); this outcome has been rationalized in terms of a strong chelation effect.[111]

As shown in Table 1, other functionality can be incorporated into the allyl anion. Examples are provided by the γ-alkoxyallylaluminium series, which show high diastereoselectivity through formation of a chair-like transition state (**8**) where the large group adopts a quasi-equatorial orientation (Scheme 19).[58b]



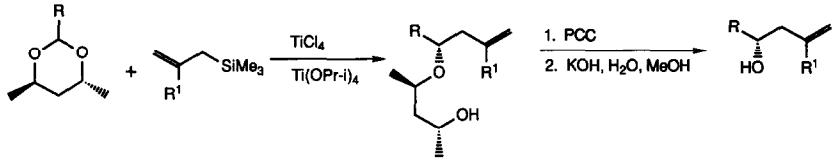
Scheme 19.

Employment of an acetylene anion removes the regiochemical problem associated with ambident allyl anions. Methyl-α-L-oleandroside (**9**) is available from L-alanine (**10**) by such a method (Scheme 20).[112]



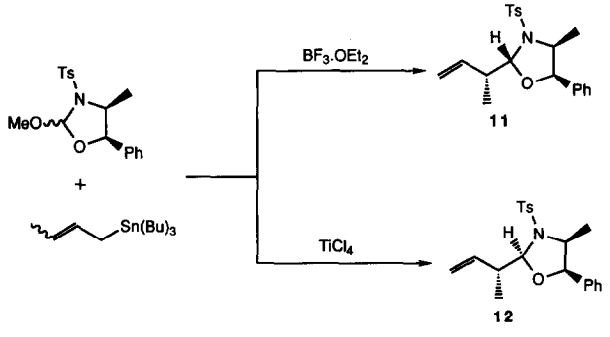
Scheme 20.

In the presence of a Lewis acid, an acetal can act as a carbonyl surrogate.[113] The use of these masked electrophiles also allows for the introduction of a chiral auxiliary (Scheme 21).[114]



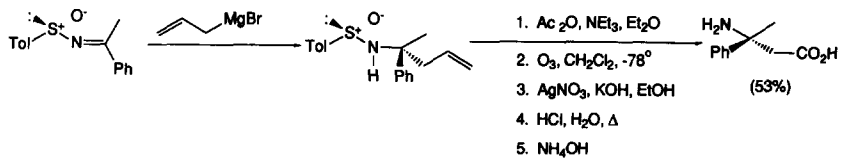
Scheme 21.

A varient is the use of 2-methoxyoxazolidines where the Lewis acid employed can control the stereochemical outcome of the reaction (Scheme 22). In this case, the addition could be selective, while the Lewis acid promotes an equilibration; treatment of **11** with titanium tetrachloride provided exclusively **12**.[115]



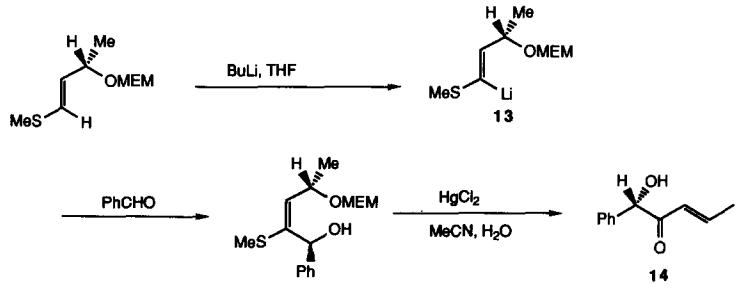
Scheme 22.

Anhydrides can function as electrophiles to afford ω-keto acids after reaction with the organometallic species.[116] The addition of allylorganometallic reagents to imines affords homoallyl amines.[117] The allyl unit can be difunctional; the imine nitrogen also allows for the introduction of a chiral auxiliary (Scheme 23).[118]



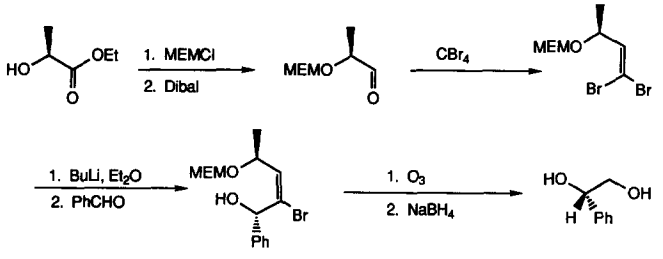
Scheme 23.

Vinyl anions have also been used in stereoselective additions to carbonyl compounds.[119] Reaction of the vinyllithium **13**, obtained from ethyl (*S*)-lactate, with benzaldehyde resulted in formation of the enone **14**, after hydrolysis (Scheme 24).[120]



Scheme 24.

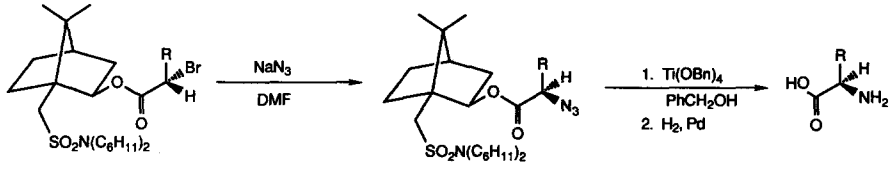
A related reaction allows for the preparation of diols (Scheme 25)[121] and triols.[122]



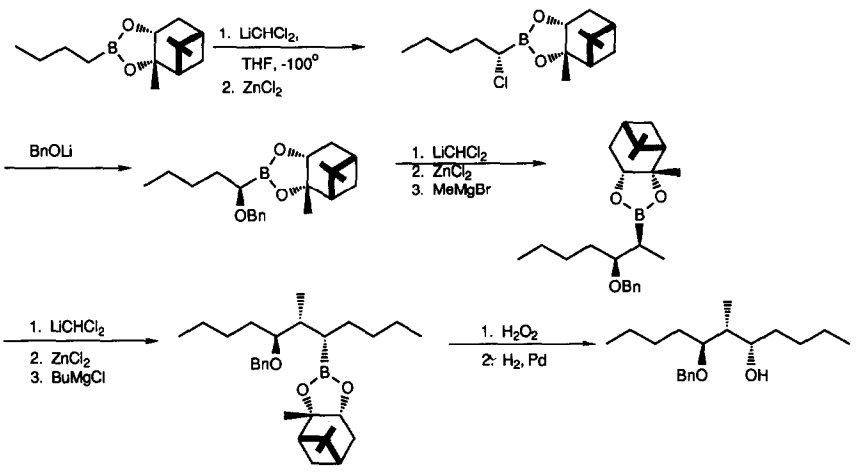
Scheme 25.

2.4. *Inversions at a single carbon centre*[123]

The classic S_N2 reaction is a useful, ubiquitous tool for the stereospecific introduction of a variety of functional groups at a specific carbon atom. As always, care must be exercised with the choice of reagent, solvent, and other reaction parameters.[124] Representative examples of this methodology are given in Schemes 26[125] and 27.[126]

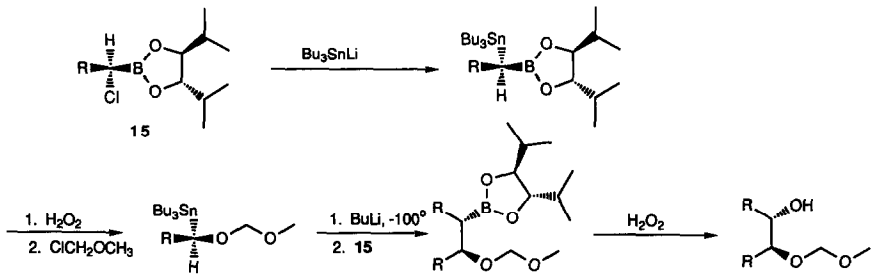


Scheme 26.



Scheme 27.

The former approach is particularly useful for the introduction of a nitrogen moiety adjacent to a carbonyl group.[127] The latter method has been extended to prepare 1,2-diols (Scheme 28)[128] and 1,2,3-triols.[129]



Scheme 28.

For the formation of a carbon–carbon bond, the use of an organocuprate, particularly with a tosylate, has been advocated as inversion at a secondary centre is clean, particularly when a heteroatom group is on an adjacent carbon atom.[130]

Retention of configuration at a specific centre is often best achieved by use of two inversions.[131]

Not all substitution reactions can be accomplished with a high degree of asymmetric induction. However, results continue to accumulate, as for the coupling of an organometallic reagent with an alkyl halide, and hold promise for future application.[132]

2.4.1. *Inversion of a hydroxyl group.* To transform stereochemistry, inversion of a hydroxy group can be an extremely useful tool in carbohydrate chemistry. Unfortunately, it is not always a straightforward procedure. Conversion of a specific D-sugar to the L-isomer does not involve inversion at just one centre and, therefore, requires a multistep procedure.[133]

Inversion can be achieved by conversion of the alcohol to a mesylate or tosylate followed by nucleophilic displacement with potassium superoxide or nitrite in dimethyl sulphoxide.[134] Caesium carboxylates in *N,N*-dimethylformamide, or in toluene with a crown ether, also give clean S_N2 reactions with mesylates.[135]

The Mitsunobu reaction allows substitution of a hydroxy group by a wide variety of nucleophiles with inversion of configuration.[136] This Mitsunobu protocol often provides very high yields for

unhindered alcohols.[136,137] A useful version involves the use of zinc tosylate, diethylazodicarboxylate and triphenylphospine.[138]

3. 1,2-FUNCTIONAL GROUPS

The backbone of a carbohydrate molecule may be considered as an array of 1,2-functional groups. Indeed, a linear synthesis of a carbohydrate through the addition of a series of one-carbon units onto an original building block is demonstrated by the Formose reaction.[1]

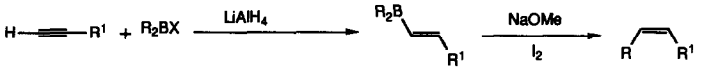
The principal methods for the introduction of juxtaposed functional groups rely on the stereoselective addition of an electrophile to an alkene. This addition can be either a one-step process, e.g. when a nucleophile is also present in the reaction medium or a metal oxide is employed as the reagent, or a two-step sequence proceeding, for example, through an epoxide.

A carbonyl group can be reduced to provide an alcohol or used to extend a carbon chain through addition of an organometallic reagent. A key methodology, which cannot be overlooked, therefore, concerns the stereoselective reactions of aldehydes, ketones and esters at the α-carbon atom (*vide infra*).

3.1. *Alkene synthesis*[124,139]

Many of the methods cited below rely on the addition of various reagents to an alkene in a stereoselective manner. To provide good stereoselection, only one isomer of the alkene must be present in the substrate. Indeed, many of these methods have been employed in the synthesis of the insect pheromones.[140] It is pertinent, therefore, to address methods that can be used to prepare alkenes stereospecifically. These methods fall into three main categories: reduction of an acetylene; condensation of an organometallic species with a carbonyl or vinyl compound;[141] and elimination reactions.

Acetylenes can provide *E*-alkenes by reduction with sodium in ammonia,[142] while hydrogenation and hydroboration provide access to *Z*-alkenes (Scheme 29).[143,144]



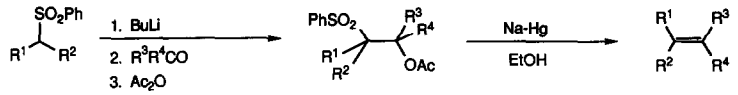
Scheme 29.

The *E*-alkene is available through use of a 1-bromo-1-alkyne as the substrate in a hydroboration approach.[143] Carbonyl compounds can be converted to either geometric isomer of the corresponding alkene by hydroboration of the enamine.[145]

Many metals are available to catalyze the condensation of vinyl anions with a wide variety of electrophiles, providing a versatile preparation of alkenes.[146] The vinyl anions are available by transmetallation procedures as well as from acetylenes.[147]

The Wittig reaction has been investigated extensively, and it is possible to control the stereochemical outcome of this condensation to a large degree through manipulation of the reaction parameters.[148] The silicon analogue of this reaction, the Peterson reaction, can also be used for the stereoselective preparation of alkenes, although separation of the diastereoisomeric intermediate β-hydroxysilanes may be necessary if a single alkene isomer is the desired product.[149]

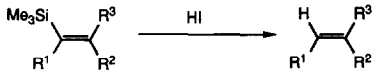
Olefins are available by the Julia method, where a sulphone is reacted with a carbonyl compound.[150] Subsequent conversion of the hydroxy formed to a better leaving group, such as acetate, followed by reductive elimination, usually affords the *E*-alkene (Scheme 30).[151] An analogous reaction with sulphides to provide *Z*-alkenes is known.[152] Selenium can also be a useful alternative to sulphur.[153]



Scheme 30.

Allylic compounds can undergo substitution by organometallic species to provide alkenes (see Section 4.12.1).[154]

Vinylsilanes offer a variety of methods for the preparation of alkenes. The vinylsilanes are, in turn, available from a number of routes including the reduction of acetylenes, silylacetylenes, and carbonyl condensation reactions.[155] The silyl group can be displaced in a regioselective, and often stereoselective manner by a wide variety of electrophiles, including protiodesilylation (Scheme 31).[155e,156]



Scheme 31.

Elimination of a wide variety of functional groups either through an *E*2 reaction,[157] or by thermal elimination provides stereospecific routes to alkenes.[158] In general, the former reactions proceed with *anti*-stereochemistry, while the latter are *syn*.[14a,124a] However, both approaches destroy asymmetric centres to afford a single alkene isomer.[159]

Sulphoxide elimination, along with the selenoxide analogue, have been used to prepare alkenes,[160] but the stereoselectivity of these *syn*-eliminations can be compromised by the problems associated with the asymmetric introduction of the heteroatom.[160c,161]

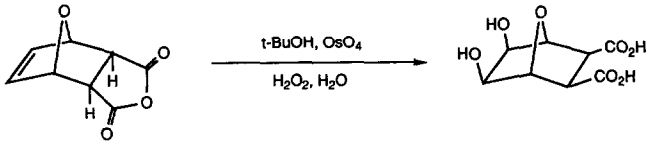
Alkenes are also available from epoxides[162] and diols.[163] Many methods also exist for the inversion of olefin stereochemistry.[162a]

3.2. 1,2-*Functional groups*

Many reagents add stereoselectively to alkenes, such as hydrogen halides[164] and halogens.[124a,165] Such an addition can be useful to control relative stereochemistry, especially if regiochemical control is accomplished through application (or violation!) of Markovnikov addition.[124,166] In contrast, very few methods are currently available to control absolute stereoselectivity;[167] however, advances in this area have been rapid (*vide infra*).[168]

3.2.1. *Metal oxide additions.* Many metal oxides have been employed to convert an alkene to a *cis*-1,2-diol.[169] This approach is complemented by nucleophilic opening of an epoxide, which invariably results in the net formation of a *trans*-1,2-diol.[170]

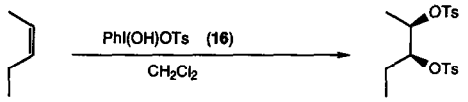
Oxidation of an alkene by osmium tetroxide,[171] or alkaline potassium permanganate[172] occurs by *syn*-addition from the less hindered face of the double bond.[173] This steric effect is amplified in cyclic substrates (Scheme 32).[1,174] Such an approach has been employed in the preparation of many natural products, including methyl elenoate[175] and mannose.[176]



Scheme 32.

In both the osmium and manganese oxidations an intermediate cyclic ester accounts for the *cis*-stereochemistry.[171d,177] Use of chromyl chloride can lead, by a *syn*-addition, to formation of a chlorohydrin or epoxide through appropriate choice of reaction conditions.[178]

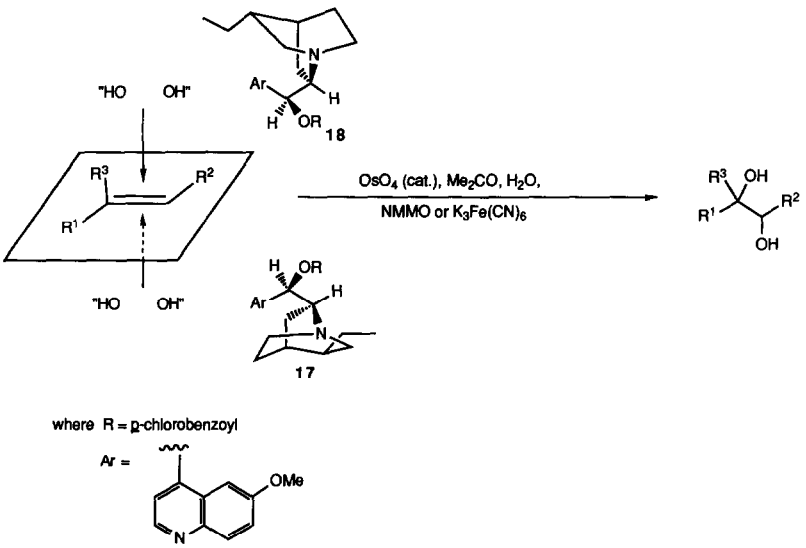
The hypervalent iodine reagent [hydroxy(tosyloxy)iodo]benzene (**16**) oxidizes alkenes to the *cis* tosylate by a *syn*-addition (Scheme 33),[179] although the exact mechanism has yet to be determined.



Scheme 33.

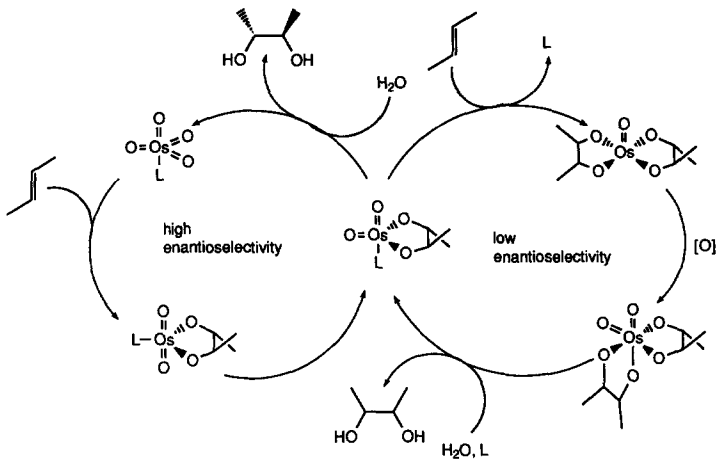
3.2.1.1. *Osmium reagents.* Osmium reagents can be used reliably to form *cis*-vicinal diols[171a,171b] from the less hindered face of a carbon–carbon double bond.[180] Cyclic examples can provide extremely selective conversions (Scheme 32).

Significant advances have been made towards an asymmetric transformation through the use of chiral ligands.[181] Early work on the oxidation of an alkene by osmium tetroxide in the presence of a chiral ligand, such as dihydroquinine acetate (**17**; R = Ac) or dihydroquinidine acetate (**18**; R = Ac), led to diol formation with some enantiomeric excess.[182] However, this asymmetric dihydroxylation problem has now been solved by the use of cinchona alkaloid esters (**17** and **18**; R = *p*-ClC_6H_4) together with a catalytic amount of osmium tetroxide. The alkaloid esters act as pseudoenantiomeric ligands (Scheme 34).[183] They can also be supported on a polymer.[184]



Scheme 34.

The original procedure has been modified by the use of a slow addition of the alkene to afford the diol in higher optical purity, and ironically this modification results in a faster reaction. This behaviour can be rationalized by consideration of two catalytic cycles operating for the alkene (Scheme 35), since the use of low alkene concentrations effectively removes the second, poorly enantioselective cycle.[183b,185] The use of potassium ferricyanide in place of *N*-methylmorpholine-*N*-oxide (NMMO) as the oxidant also improves the level of asymmetric induction.[186]

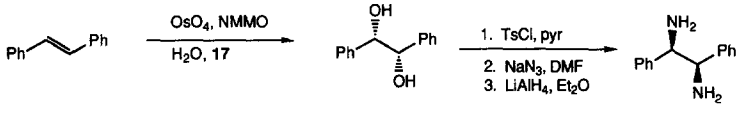


Scheme 35.

X-ray, nmr, kinetic analyses and theoretical approaches have provided insight into the mechanism of the oxidation.[181d,183b,187]

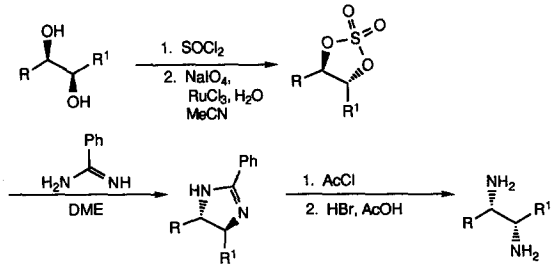
Although the use of cinchona alkaloids as chiral ligands does provide high asymmetric induction with a number of types of alkene, the search for better systems has continued.[188] Thus, this area promises to provide better methodology for the asymmetric oxidation of a wide variety of unfunctionalized alkenes.

The 1,2-diols formed by the asymmetric oxidation can be used as substrates in a wide variety of transformations. Conversion of the hydroxy groups to *p*-toluenesulphonates then allows nucleophilic displacement by azide at both centres with inversion of configuration (Scheme 36).[189]



Scheme 36.

The use of azide can be avoided by reaction of the cyclic sulphate (Section 3.2.2) with an amidine (Scheme 37).[190]

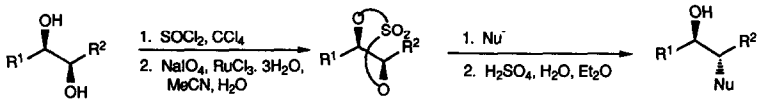


Scheme 37.

Allyl ethers can be used as substrates for this oxidative methodology providing alternative strategies to the epoxidation of allyl alcohols (Section 4.4).[191]

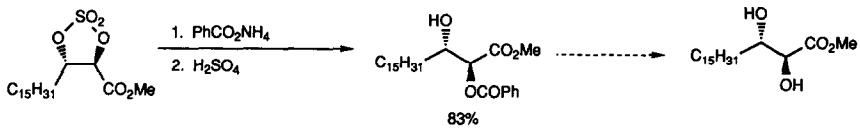
3.2.2. *Formation and reactions of cyclic sulphates.* Cyclic sulphates provide a useful alternative

to epoxides now that it is viable to produce a chiral diol from an alkene. These cyclic compounds are prepared by reaction of the diol with thionyl chloride, followed by ruthenium-catalyzed oxidation of the sulphur (Scheme 38).[192] This oxidation has an advantage over previous procedures, as it only uses a small amount of the transition metal catalyst.[193]



Scheme 38.

The cyclic sulphates undergo ring opening with a wide variety of nucleophiles, such as hydride, azide, fluoride, benzoate, amines and Grignard reagents. In the case of an ester ($R^2 = CO_2Me$) the addition occurs exclusively at C-2 (Scheme 39); however the analogous epoxide does not demonstrate such selectivity.[192,194] Terminal cyclic sulphates (Scheme 38; $R^2 = H$) open in a manner completely analogous to the corresponding epoxide.[194a]

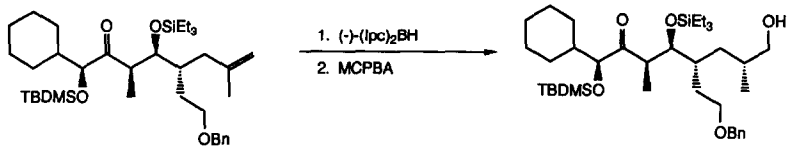


Scheme 39.

The resultant sulphate ester can be converted to the alcohol by acid hydrolysis. If an acid sensitive group is present, this hydrolysis is still successful through use of a catalytic amount of sulphuric acid in the presence of 0.5–1.0 equiv. of water with tetrahydrofuran as solvent. The use of base in the formation of the cyclic sulphates themselves can also alleviate problems associated with acid sensitive groups.[187a,195]

The sulphites, obtained by reaction of the 1,2-diol with thionyl chloride (cf. Scheme 38), also undergo facile ring opening with concurrent inversion at the reaction centre when treated with azide.[196]

3.2.3. *Hydroboration.*[197] Hydroboration has become an extremely powerful method for the transformation of an alkene into an alcohol, particularly since the advent of chiral reagents. In addition to this transformation (Scheme 40),[198] a borane can be converted into many other functional groups including amines, alkyl halides, aldehydes, carboxylic acids, ketones, esters, nitriles, acetylenes, alkenes and allenes.[197a,199]

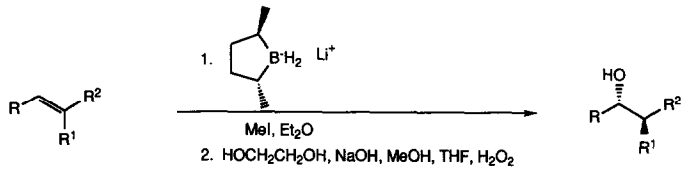


Scheme 40.

Good levels of 1,3-asymmetric induction are observed with terminal olefins (Section 4.1).[200] Diisopinocamphenylborane [$(Ipc)_2BH$] shows a high degree of selectivity toward *cis*-alkenes.[144c,201] The improvement of reagents continues,[202] not only through theoretical investigations into the reaction pathway and the factors influencing the outcome, but by synthetic approaches.[203] For allyl alcohol substrates, other factors can play an important role to provide excellent stereochemical control (Section 4.10).

Reaction of pinanediol alkylboronates with dichloromethyllithium can be followed by displacement of the chloride by a variety of nucleophiles (cf. Scheme 27) including alkoxides, Grignard reagents, ester enolates, hydroxide and azide. This methodology, coupled with the ability of the resultant boronic ester to act as the substrate for a further homologation sequence, is very powerful for the stereoselective introduction of a number of functional groups.[126a,204]

The use of borolanes has been advocated over the use of chiral boranes (Scheme 41) for the diastereoselective synthesis of homochiral compounds through double asymmetric synthesis.[205]



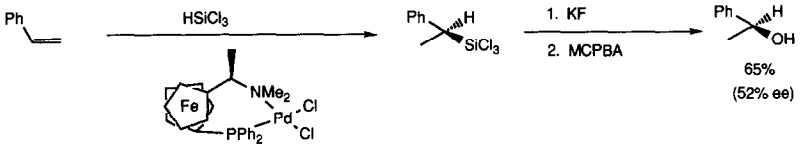
Scheme 41.

Some asymmetric induction has been observed for the addition of catecholborane to an alkene in the presence of a chiral rhodium(I) catalyst.[206]

In addition, boranes have been used for the chiral reduction of carbonyl compounds (Section 3.4.2.2).

3.2.4. *Hydrogenation.*[207] Despite the ubiquitous use of hydrogenation in organic synthetic methodology, asymmetric hydrogenation of simple alkenes still remains elusive.[208] Although the elegance of such an approach has spurred many attempts, the optical yields with unfunctionalized alkenes as substrates are invariably low.[209] In contrast, considerable success has been achieved when a functional group near to the alkene can act as a ligand for the metal catalyst (Section 4.11).[209c,210] Of course, hydrogenation usually provides *cis*-delivery of the hydrogen which is very useful.[211]

Hydrosilylation of an alkene usually provides a higher degree of asymmetric induction than hydrogenation.[212] The methodology introduces a silyl group into the substrate, which must be removed by subsequent manipulation (Scheme 42).[213]



Scheme 42.

Reduction of carbonyl compounds (Section 3.4.2.2) by hydrogenation or hydrosilylation suffers from the same limitations as olefin reduction. Enol ethers have been reduced, but again with only moderate asymmetric induction.[214]

3.3. *Epoxidations*

Epoxidation of an alkene can be achieved through a halohydrin, or by reaction with an oxidant which effects overall delivery of an oxygen atom,[215] such as a peroxy acid[216] or a porphyrin.[217] In the former situation, the chirality of the halohydrin must be controlled prior to epoxide formation.[218] The key to asymmetric induction with an oxygen donor is discrimination between the two alkene faces. This has been achieved by use of chiral peroxy acids and chiral oxaziridines, although the magnitude of the asymmetric induction is generally not high.

3.3.1. *Peroxy acid epoxidation.*[219,220] An alkene reacts with a peroxy acid to afford an epoxide in one step.[219,221] When prior association between the peroxy acid and alkene is possible, as in the case of an allyl alcohol (Section 4.4.1), stereoselection can be good. In the case of a simple alkene,

peroxy acid epoxidation is sensitive to steric effects caused by the degree of substitution on the alkene,[219,222] while for cyclic alkenes, the steric constraints of the ring system can impart facial selectivity.[219,221c,221e] The stereoselectivity series for the rate of epoxidation (Fig. 5) indicates that there is little selectivity in reaction rates between *cis*, *trans*, and 1,1-disubstituted alkenes.[223] Facial selectivity, therefore, is difficult to achieve with a simple alkene.

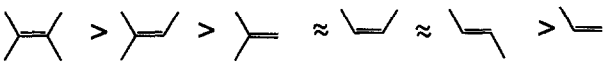
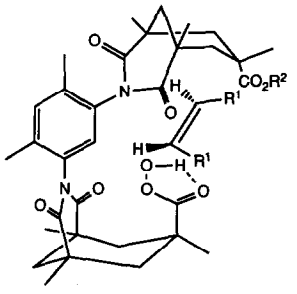


Fig. 5.

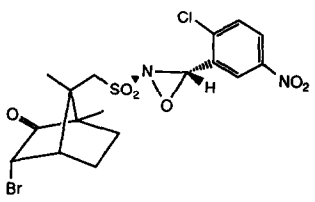
Some progress has been made toward geometrical differentiation for disubstituted alkenes. Reaction of the peroxy acid **19** with an alkene shows that as the size of the alkyl group of the ester increases, the *cis*-alkene reacts preferentially to the *trans*-isomer.[223,224]



19

Use of a chiral peroxy acid with alkenes results in very low asymmetric induction (<8% *ee*) with chirality transfer from the peroxy acid to the 'major' product enantiomer.[224a,225]

3.3.2. *Oxaziridine epoxidation.*[226] Chiral oxaziridines **20** and **21** have been used to oxidize alkenes, and showed much greater enantioselectivity than when a chiral peroxy acid was employed.[227]



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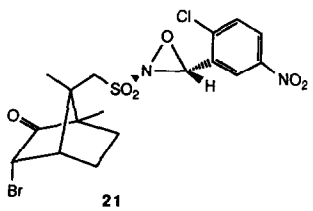


21

The configuration of the three-membered heterocycle determines the configuration of the epoxide product. Despite the increase in enantioselectivity over peroxy acids, the degree of asymmetric induction is not yet high enough for general synthetic application.[227,228] The transition state geometry has been calculated,[229] and is borne out by experimental observations, to be analogous (Fig. 6) to the parallel peroxy acid mechanism.[228,230]

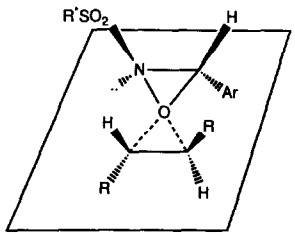
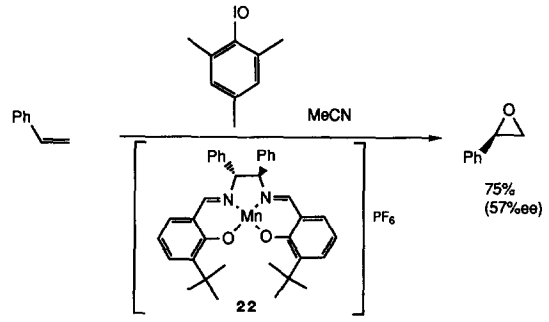


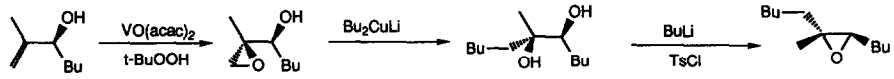
Fig. 6.

3.3.3. *Metal-catalyzed epoxidation.*[231] Some metals such as ruthenium, tungsten, vanadium and molybdenum catalyze epoxide formation in addition to diol formation from an alkene.[232] Use of a molybdenum(VI) catalyst in the presence of diisopropyl tartrate led to low (< 11% *ee*) asymmetric induction.[233] The use of (*S*)-*N*,*N*-dimethyllactamide as a ligand led to slightly better optical yields (16–35% *ee*),[233,234] which, in turn, has been improved upon by a platinum(II) complex (18–41% *ee*).[235] Although the facial selectivity has not been optimized, manganese complexes provide sufficient induction for synthetic utility (Scheme 43).[236] The manganese(III) salen complex **22** can also have bleach as the oxidant rather than an iodosylarene.[237]



Scheme 43.

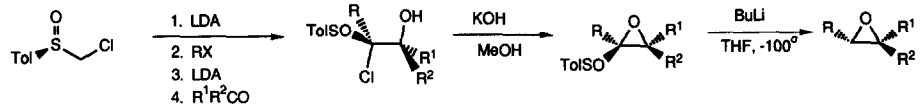
It should be noted that chiral epoxides are available by an allyl alcohol epoxidation protocol (cf. Section 4.5) (Scheme 44).[238]



Scheme 44.

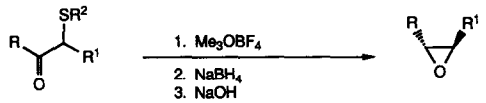
Studies have been conducted with iron porphyrins in the presence of iodosylbenzene or other oxidants. Enantiomeric excesses are moderate, although chemical yields are good.[217a,217b,239]

3.3.4. *Other methods.* Epoxides are available through condensation of various nucleophilic species which contain a heteroatom leaving group, such as sulphur,[240] selenium[241] and arsenic, with an aldehyde or ketone.[242] Chiral epoxides are available from chiral sulphoxides and their derivatives by a number of strategies (e.g. Scheme 45).[243] This methodology is an extension of the sulphide variant introduced by Corey.[240a]



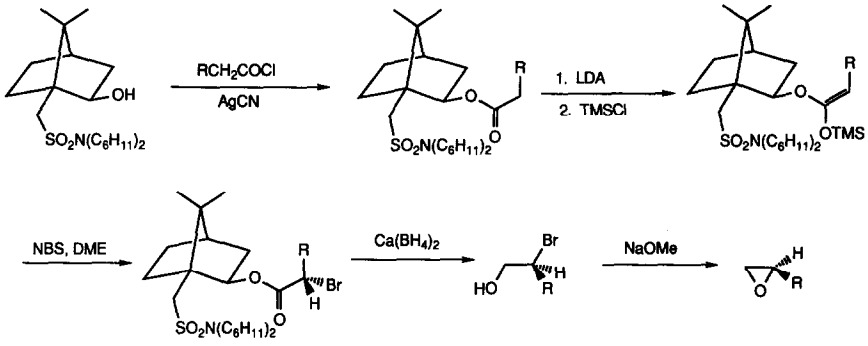
Scheme 45.

α-Thio ketones provide a useful approach to *trans*-epoxides through control of relative stereochemistry (Scheme 46).[240a]



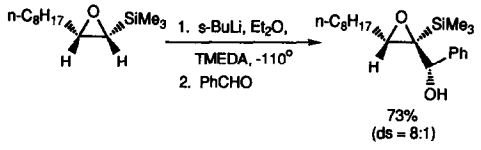
Scheme 46.

The use of a camphor chiral auxiliary allows for the asymmetric preparation of a halohydrin and, consequently, an epoxide (Scheme 47).[244] An alternative procedure relies on a cobalt-catalyzed asymmetric cyclization of chlorohydrins.[245] A kinetic resolution during epoxide formation from chlorohydrins under phase transfer conditions has been claimed.¶[246]



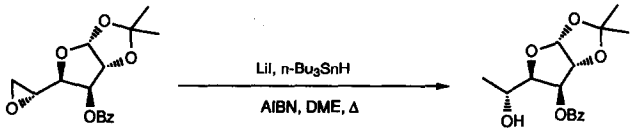
Scheme 47.

α-Trimethylsilylepoxides, available from vinylsilanes, can be used to prepare epoxides through fluoride ion displacement of the silyl group and subsequent reaction with an electrophile.[248] A tin group can be exchanged with an alkyllithium and then the resultant α-lithioepoxide reacted with an electrophile in a similar manner.[249] In addition to exchange reactions, groups that stabilize an α-carbanion, such as silyl, sulphoxide, sulphone, cyano, carbon–carbon unsaturation, aryl and esters, allow deprotonation to occur on the carbon atom of an epoxide that is bonded to one of these groups without disruption of the epoxide ring (Scheme 48).[248a,250]



Scheme 48.

3.3.5. *Reactions of epoxides.*[251] The regioselective control for the nucleophilic opening of an epoxide in an acyclic system is well known. Under basic conditions, the nucleophile usually attacks the sterically less encumbered site, while under acidic conditions, the sterically more hindered site is favoured.[252] The product invariably contains the functional groups in a *trans*-disposition, when and S_N2 pathway is followed.[252a,253] If the epoxide is chiral, then an optically active product can result from ring opening (e.g. Scheme 49).[254] The use of metal salts can provide useful catalysis for nitrogen amongst other nucelophiles to attack at the least hindered end of an epoxide.[255]



Scheme 49.

¶ Reactions that involve chiral induction by chiral β-hydroxyammonium catalysts under basic conditions have been questioned with regard to the source of the optical activity observed (ref. 247).

Treatment of an epoxide with strong base provides a route to allyl alcohols (Section 4.3).[256] Kinetic resolutions of epoxides are also possible, giving access to 1,2-functionality.[257]

3.4. *Reactions with carbonyl compounds*

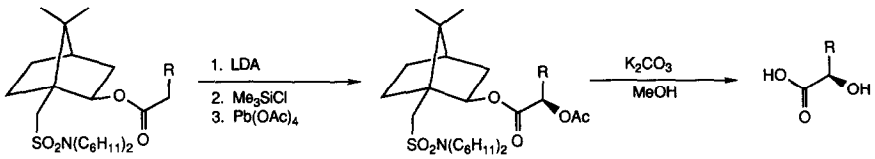
The carbonyl group is extremely versatile for the introduction of functionality beyond its role in the aldol reaction (Section 4.2). α-Alkylation can often be accomplished in a stereoselective manner, while α-hydroxylation is, of course, particularly important for carbohydrate synthesis.

The second powerful transformation of carbonyl compounds is nucleophilic addition to afford an alcohol derivative. For clarity, the discussion on the synthetic uses of nucelophilic additions to carbonyl systems has been included in this section.

Other reactions which have shown potential for asymmetric synthesis are facial selective reactions of carbonyl derivatives, including alkylations, and the use of chiral bases. Once again, the discussion of these methodologies has been included in this section for completeness.

3.4.1. *α-Hydroxylation of carbonyl compounds.* As carbohydrates are polyols, hydroxylation adjacent to a carbonyl group is an important transformation. Various methodologies have been developed to accomplish this goal, but as yet there has been little development of asymmetric methods except when the inherent properties of a cyclic substrate provide for selectivity.[258]

The introduction of an oxygen functional group juxtaposed to a carbonyl moiety can be accomplished through reaction of the derived enol acetate with a peroxy acid or dioxiranes.[259] The resultant epoxide usually rearranges to the α-acetoxy ketone upon chromatography or heat treatment.[176,219,260] The enolate derived from the corresponding carbonyl compound can also be oxidized with an oxygen donor, such as a molybdenum peroxide reagent or dimethyldioxirane.[261] Aldehydes and ketones are readily transformed to their silyl enol ethers (Section 3.4.3.3.). These ethers can, in turn, be oxidized by a peroxy acid to α-hydroxycarbonyl compounds.[262] Lead(IV) acetate, lead(IV) benzoate and manganese(III) acetate have been used in place of the peroxy acid.[263] Dimethyldioxirane can also be used as the oxidant.[264] The introduction of a chiral auxiliary allows excellent diastereoselectivity upon reaction with lead(IV) acetate (Scheme 50).[265]

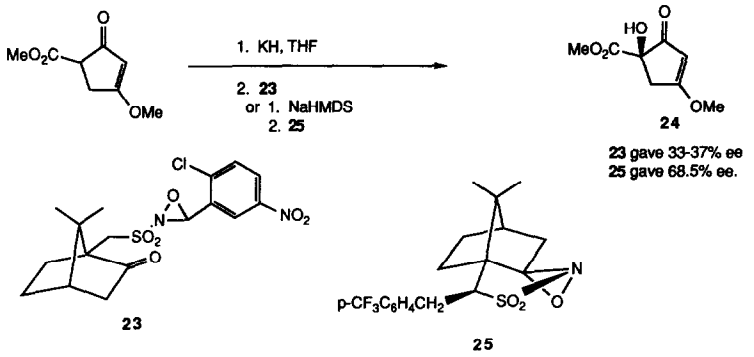


Scheme 50.

Osmium tetroxide in the presence of *N*-methylmorpholine-*N*-oxide has been used to effect this transformation,[266] while the use of a chiral diamine ligand derived from tartaric acid can lead to some chiral induction.[181b]

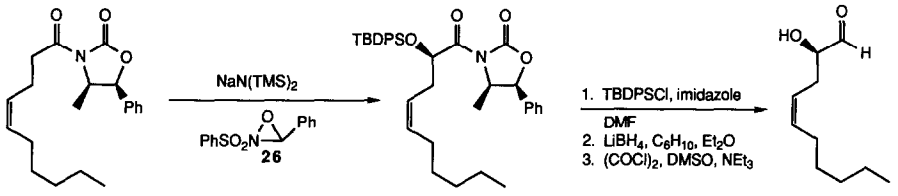
An alternative methodology is provided by hypervalent iodine compounds.[267] Some of these compounds, such as *o*-iodosylbenzoic acid,[268] react directly with ketones and alleviate the need to prepare the silyl enol ether.[269] Esters and lactones can also be used as substrates.[270] Variants of this methodology allow for the oxygen atom to be functionalized during its introduction.[271]

Treatment of a silyl enol ether with ozone usually results in oxidative cleavage of the unsaturation, although in some cases, an α-hydroxycarbonyl compound can result.[272] This oxidative cleavage problem can be overcome by use of a hydroboration–oxidation protocol,[273] or by use of a dioxirane.[259b] 2-Phenylsulfonyl-3-phenyloxaziridine reacts with ketone enolates to provide α-hydroxycarbonyl compounds.[226,239,258a,274] This latter methodology has been adopted, through the use of a chiral oxaziridine (**23**), to introduce the hydroxy functionality in a synthesis of kjellmanianone (**24**) with an enantiomeric excess of 33–37%.[275] The asymmetric induction was improved through use of the oxazirdine **25** (Scheme 51).[276]



Scheme 51.

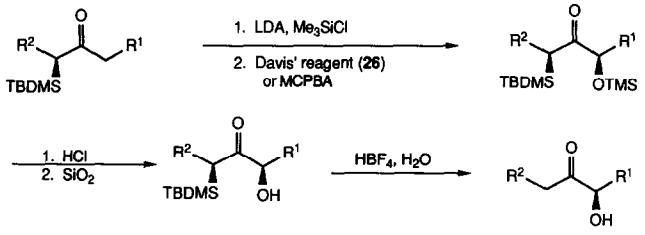
The enolate derived from a chiral oxazolidinone reacts with Davis' reagent **26** with high diastereoselectivity ($\geqslant 98:2$) (Scheme 52).[277]



Scheme 52.

The stereoselectivity is not only dependent upon the structure of the oxaziridine, but on the enolate substitution pattern and solution structure of the enolate, as well as, but to a lesser degree, the geometry of the enolate.[278]

High enantiomeric excesses are also possible when a hydrazone chiral auxiliary is employed to provide α-substituted ketones (*vide infra*).[279] This approach has been used to introduce a silyl group with regio- and enantio-selective control. The resultant α-silyl ketone was then transformed to the alternative regioisomeric α-hydroxy ketone (Scheme 53).[280] The α-silyl ketone can also be used to prepare 1,2-diols by reduction of the carbonyl group (Section 3.4.2.2) followed by oxidative conversion of the silyl moiety to hydroxy (Section 4.12.2).[281]



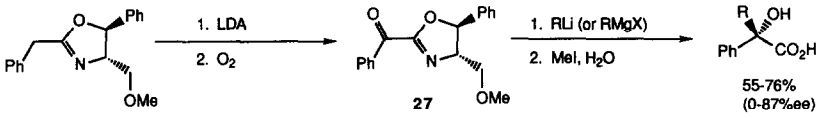
Scheme 53.

The α-hydroxylation of lactones and esters has been achieved by reaction of the corresponding enolate with an oxaziridine.[229,258a,282] Use of a chiral imide enolate with this protocol results in good diastereoselectivity.[283] Chiral esters also provide some diastereoselectivity when oxidized with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in acetic acid.[284]

α-Hydroxylation of an ester or carboxylic acid may be achieved by deprotonation followed by

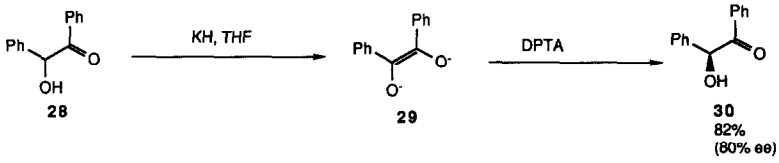
reaction with oxygen or an oxygen donor.[261a,285] A cyclic ketone in the presence of oxygen and a chiral phase transfer reagent did provide optically active α-hydroxy ketone.[255g]

An alternative strategy, which does allow asymmetric induction, is the reaction of an organolithium or Grignard reagent with the ketooxazoline **27** (Scheme 54) (cf. Section 3.4.2.1.).[286]



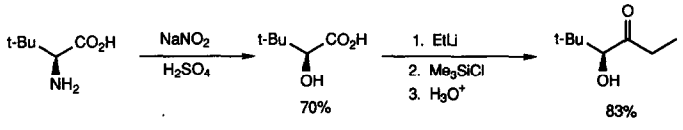
Scheme 54.

The racemic α-hydroxy ketone **28** has been transformed to the enolate by deprotonation with potassium hydride. Protonation of the symmetrical enediol **29** with (2*R*, 3*R*)-*O*,*O*-dipivaloyltartaric acid (DPTA) at low temperature afforded the optically active α-hydroxy ketone **30** in 80% *ee* (Scheme 55).[287]



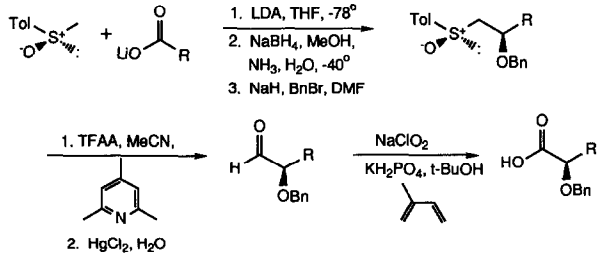
Scheme 55.

α-Hydroxycarbonyl compounds are also accessible by reduction of the corresponding α-ketocarbonyl substrate (Section 3.4.2.2). As α-amino acids are readily available, conversion of an amine to a hydroxy group with retention of configuration provides a simple entry to α-hydroxycarbonyl compounds (Scheme 56).[236a]



Scheme 56.

A chiral sulphoxide also provides access to α-alkoxy aldehydes and carboxylic acid derivatives (Scheme 57).[288]



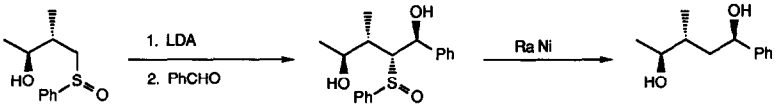
Scheme 57.

A conjugate addition of an oxygen nucleophile to an α,β-unsaturated nitro compound, followed by conversion of the nitro group to a carbonyl moiety through the Nef reaction also provides α-

hydroxycarbonyl compounds through umpolung methodology.[289] Other umpolung methodologies, such as the use of α-aminonitriles, can also lead to α-hydroxycarbonyl compounds.[289a,290]

3.4.2. *Additions of organometallic reagents to carbonyl compounds.*[291] The factors that control the addition of a nucleophile to a carbonyl group with an adjacent asymmetric centre have already been discussed (Sections 2.1 and 2.2). Indeed, many reagents have been investigated to improve Anh–Felkin selectivity in simple systems.[292] A similar scenario can be visualized if an asymmetric center is present in the nucleophilic moiety adjacent to the reaction site; examples of this type of addition are, however, not as common.[293]

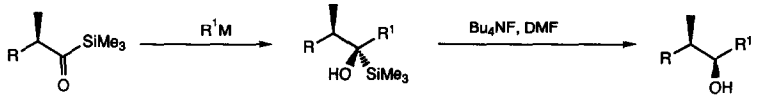
To circumvent some of the problems associated with the addition of functionalized organometallic reagents to complex carbonyl compounds, nucleophilic reagents are available that contain masked functionality (Section 2.3). Once the condensation has been performed, this functionality can be used for further elaboration (Scheme 58).[294]



Scheme 58.

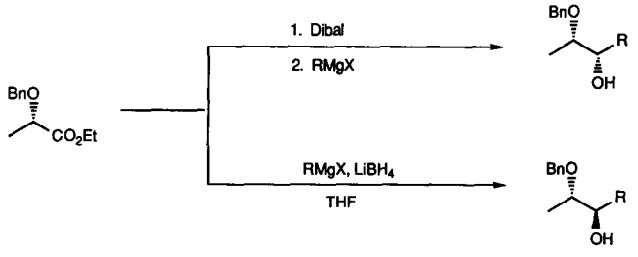
To circumvent some of the problems associated with the tendencies of organolithium or Grignard reagents to act as bases with carbonyl compounds, the use of organocerium reagents has been advocated.[295]

3.4.2.1. *Alkylating agents.* Chiral acylsilanes show high diastereofacial selectivity, which can be used to prepare alcohols in a highly stereoselective manner (Scheme 59).[296]



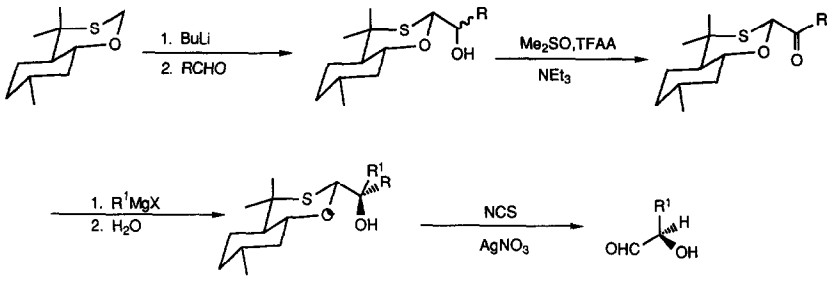
Scheme 59.

α-Alkoxy esters can react with nucleophiles in the presence of a reducing agent to provide either isomer of the protected diol (Scheme 60).[297]



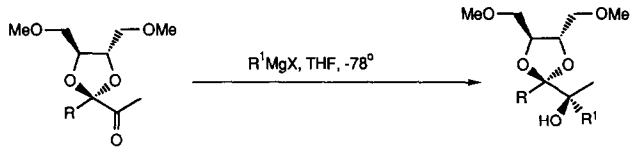
Scheme 60.

A 1,3-oxathiane chiral auxiliary allows excellent diastereoselective addition of Grignard reagents (Scheme 61).[298] The use of this reaction is extended further by the addition of ytterbium as this reverses the diastereoselectivity.[299]



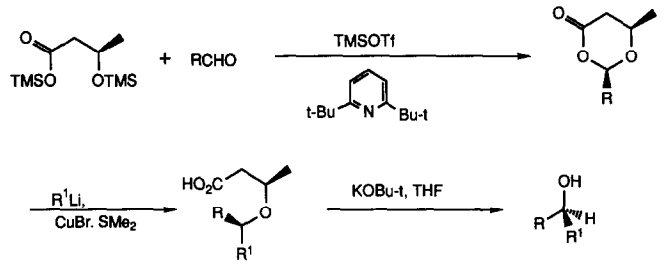
Scheme 61.

A variant of the methodology uses a proline-derived chiral building block,[300] while chiral α-keto acetals also show high selectivity in carbonyl alkylation reactions (Scheme 62).[301]



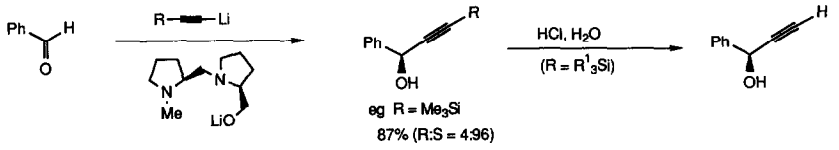
Scheme 62.

A further variation is provided by α-keto-1,3-dithiane-1-oxides.[302] An acetal functionalized within the auxiliary unit can act as a carbonyl equivalent to allow for stereoselective reactions (e.g. Scheme 63).[303]



Scheme 63.

Chiral ligands can be used to complex with a metal counterion.[304] Thus, addition of *n*-butyllithium to benzaldehyde in the presence of a chiral ligand derived from two proline molecules gives rise to moderate optical yields. Functionalized nucleophiles could also be used with this class of chiral ligand (Scheme 64).[304a,305] Similar findings are observed with chiral auxiliaries derived from tartaric acid,[306] carbohydrates,[307] and other sources.[308] However, a closely related reaction between

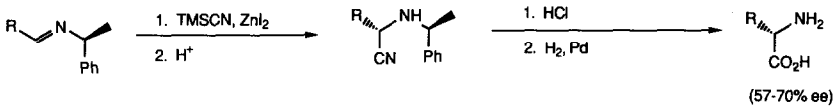


Scheme 64.

diethylzinc and benzaldehyde proceeds with high asymmetric induction.[309] Methyltitanium reagents also show high selectivity.[309n,310] With all of these chiral ligands, high optical yields are observed only with specific aldehydes;[311] this approach, as yet, does not seem to be general.[305d,308d,312] The use of titanium has, however, proven useful when a number of oxygen coordination sites are available within the substrate molecule (cf. Section 4.2).[313]

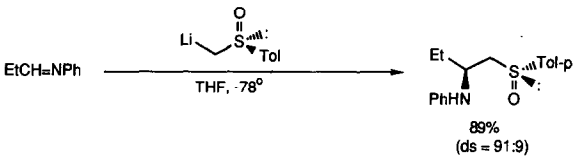
An asymmetric alkylation of a carbonyl compound has been achieved under phase transfer conditions.¶[314]

There are many variants that allow for the asymmetric addition of a nucleophilic species to a carbonyl group equivalent,[315] as illustrated by an approach to α-amino acids (Scheme 65).[316] The use of a nitrogen derivative of a carbonyl compound allows for the incorporation of asymmetry into the electrophilic moiety.[317]



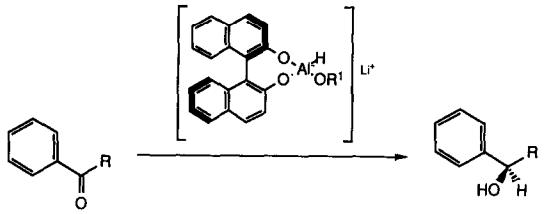
Scheme 65.

Conversely, the nucelophile can contain the asymmetry (Scheme 66),[29,318] and it should be possible to realize the potential of double asymmetric induction.



Scheme 66.

3.4.2.2. *Hydride donors.* Several examples of this reaction have already been given (Sections 2.1 and 2.2). Many ligands have been used for metal hydrides ranging from amino acids and sugars to clay.[37,305c,319] In some cases, optical yields are good (e.g. Scheme 67).[320] Unfortunately, the methodology is not generally applicable to a wide range of carbonyl compounds, which detracts from its synthetic utility. Besides classic metal hydrides, other organometallic species, such as Grignard reagents, can reduce carbonyl compounds with a degree of asymmetric induction.[6b,321]

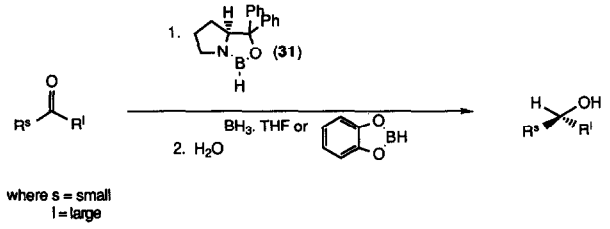


Scheme 67.

Carbonyl compounds can be reduced by hydrogenation. As with alkenes, asymmetric induction is usually not high.[6o,322] In contrast, hydrosilylation proceeds in good optical yield and affords silyl ethers, which are readily hydrolyzed to the alcohols.[6f,323] The approach can be used for the reduction of oximes to amines.[322c,324]

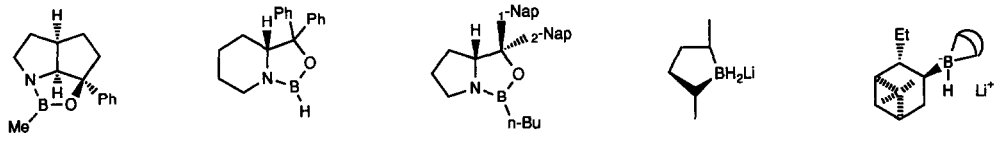
¶ Reactions that employ ephedrine phase transfer catalysts have proven difficult to repeat (ref. 247).

Reduction of carbonyl compounds by boranes, provides efficient access to alcohols.[37,197a,197c,325] Chiral boranes, such as the isocamphenyl derivatives, $(Ipc)_2BH$ and $IpcBH_2$, can provide asymmetric induction, but the levels may only be moderate.[326] The use of trialkylboranes does allow for the stereoselective reductions of aldehydes,[327] although the reduction of ketones is not as selective.[37,328] Diisopinocamphenylchloroborane can provide high induction in the reduction of aryl ketones,[329] while oxaborolidines **31** can provide high selectivity even in alkyl cases (Scheme 68).[330]



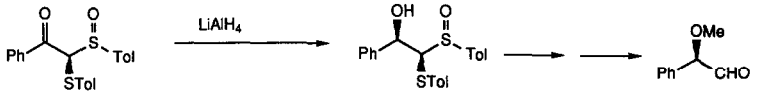
Scheme 68.

The oxazaborolidines **32–34** are also excellent catalysts for the asymmetric reduction of ketones to secondary alcohols.[331] Borolanes **35** also give high degrees of asymmetric reduction with dialkyl ketones,[332] as does lithium *B*-iso-2-ethylapopinocamphenyl-9-borabicyclo[3.3.1]nonyl hydride (Eapine hydride) (**36**).[333] The problem of asymmetric reduction of ketones can also be circumvented through the formation of an allyl alcohol intermediate.[258a]



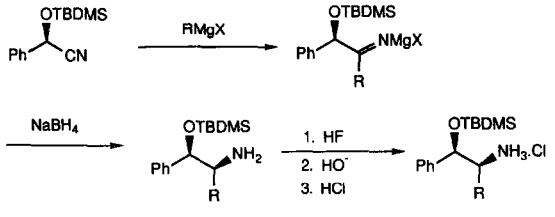
32 **33** **34** **35** **36**

As with alkylation reactions, the presence of another functional group, such as in α-keto esters (cf. Section 3.4.3.4), sulphoxides or sulphones, does increase selectivity (Scheme 69).[199b,243d,323d,334] while the nitrogen-based carbonyl equivalents allow for the introduction of chirality in an auxiliary unit and afford amines upon reduction.[335]



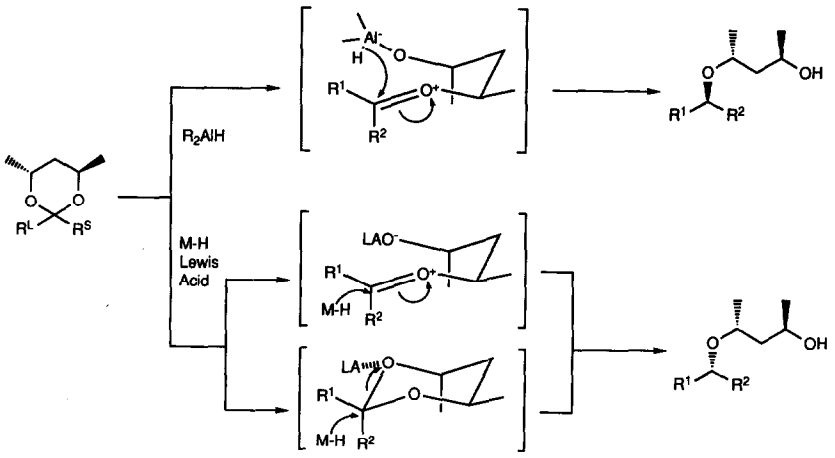
Scheme 69.

An alkylation–reduction procedure for cyanohydrins provides an asymmetric method to ethanolamines (Scheme 70).[336]



Scheme 70.

The reductive cleavage of chiral acetals derived from unsymmetrical ketones provides a means to control the absolute stereochemistry of the resultant alcohol through a choice of reaction conditions (Scheme 71).[337]



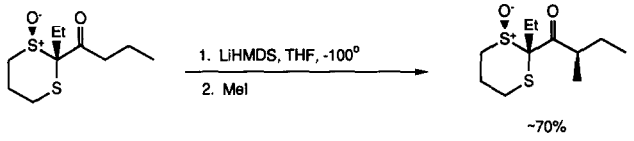
Scheme 71.

3.4.3. *Chiral α-alkylations.*[338] Carbonyl compounds are versatile in synthesis due to their inherent ability to undergo nucleophilic addition (see Section 2.4), but also to act as nucleophiles. The aldol reaction involves the combination of a nucleophilic carbonyl species with an electrophilic carbonyl compound (Section 4.2), and results in a 1,3-difunctional product. Similar methodology can be applied to other electrophiles, including alkyl halides, and again results in the introduction of 1,2-functionality.

α-Alkylation of a carbonyl compound can be achieved by formation of an enolate, followed by condensation with an alkyl halide.[339] This methodology not only requires regioselective formation of the enolate,[340] but the need to minimize competing elimination reactions in the alkyl halide fragment. This latter problem can be circumvented, to a certain degree, by use of an enol ether and a Lewis acid catalyst.[341]

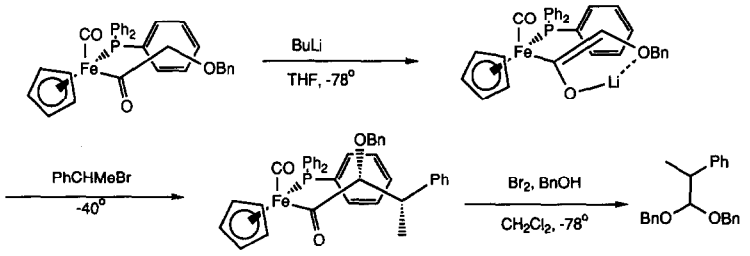
One aspect now beginning to come into fruition pertains to the structure determination of lithium enolates.[340a,342] The insight gained in this area should enable asymmetric induction to be increased.[343] Lithium enolates are the most commonly used species to perform functionalization of a carbon atom juxtaposed to a carbonyl moiety. They are generated by deprotonation from the parent carbonyl compound by a strong base, such as lithium diisopropylamide (LDA), which under standard conditions forms the kinetic enolate.[340c,341,342,344] An alternative general method uses the conjugate addition of an anion, often a cuprate, to an α,β-unsaturated carbonyl compound, and then reaction of the product enolate *in situ* (Section 4.8).[345] The formation of enolates and their geometry is discussed in detail in Section 3.4.3.3. This methodology overlaps with the chemistry of the aldol and related reactions (Section 4.2). Another area which is currently being exploited involves use of chiral phase transfer catalysts.[346] This has been exploited for the synthesis of α-amino acid derivatives, where many of the methods rely on the use of masked functionality.[347]

The problem of facial selectivity with a planar enolate has led to the incorporation of various chiral auxiliaries into the carbonyl precursor. The majority of these auxiliaries are nitrogen based (Section 3.4.3.1). However, sulphur-containing masking groups also allow for high diastereoselectivity (Scheme 72). The induction is rationalized in terms of a chelate between the enolate and sulphoxide oxygen atoms leading to a chair transition state.[348]



Scheme 72.

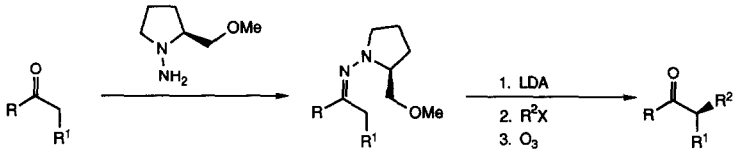
Alkylations of organotransition metal complexes can often be highly stereoselective (Scheme 73).[349] Asymmetric protonations (e.g. Scheme 55) perform the operational equivalent of an asymmetric alkylation.[350]



Scheme 73.

The substitution of functionality adjacent to a carbonyl group (cf. Section 2.4) can also be the equivalent of an alkylation.[351]

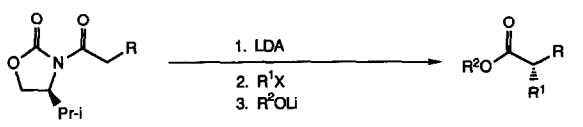
3.4.3.1. *Use of nitrogen derivatives.*[6c,352] The formation of an imine or another nitrogen analogue from a ketone allows incorporation of a chiral auxiliary which can be removed by hydrolysis after the alkylation. A wide variety of groups have been used in the amine moiety, including ones which chelate to the metal counterion during the alkylation procedure (cf. Section 4.2).[45b,353] However, many of the methods have been developed with cyclic ketones as substrates and have not been extended to acyclic cases.[354] Acyclic ketones can be alkylated by use of a hydrazone, although optical yields can be variable (Scheme 74).[352c,353a,355]



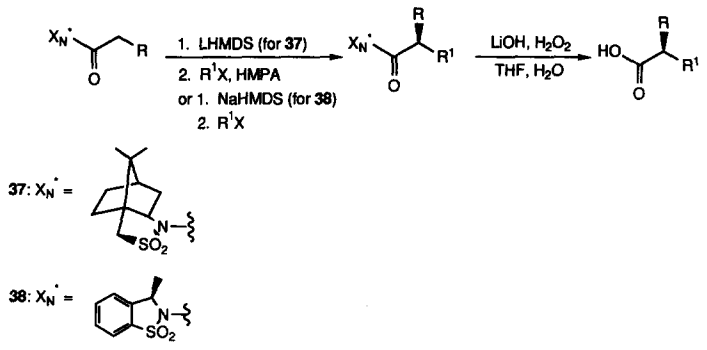
Scheme 74.

Imines have been used as a vehicle to transfer chirality from an α-amino acid, or similar precursor to an α-keto acid.[356] Some asymmetric induction has been observed during the hydrogenolysis of an enamine in the presence of a chiral acid;[357] an alternative is to use a chiral amine or other auxiliary for the formation of the imine.[358]

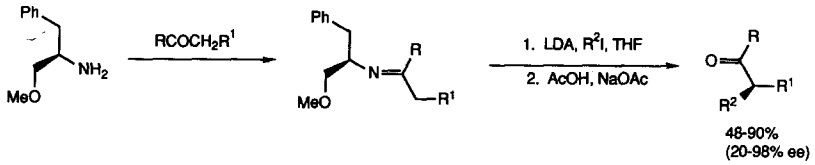
Chiral enolates derived from imines, imides, amides and sultams provide entry into α-substituted carboxylic acids (Schemes 75 and 76),[359] including α-amino acids (cf. Section 3.4.3),[360] aldehydes[353g,361] and ketones (Scheme 77).[362]



Scheme 75.

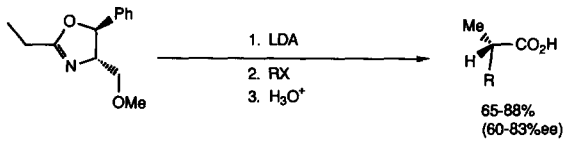


Scheme 76.



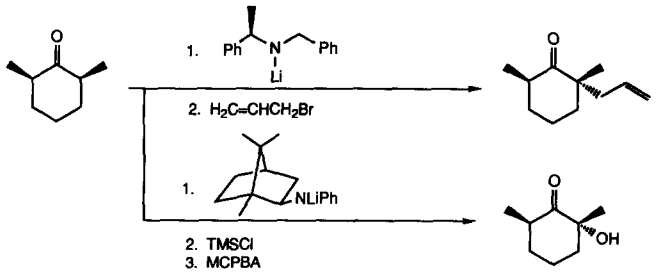
Scheme 77.

Oxazolines are useful intermediates for the asymmetric synthesis of many classes of compounds. They provide useful methods for the α-alkylation of a masked carbonyl derivative (Scheme 78).[363] Indeed this methodology can be used for kinetic resolution.[363d,364]



Scheme 78.

3.4.3.2. *Asymmetric deprotonations.*[365] A *meso*-ketone can be enantioselectively deprotonated by a chiral base.[6q] The enolate can then react at carbon with an electrophile such as an alkyl halide or carbon dioxide, or it can serve as a precursor to an enol ether (Scheme 79).[325b,366]



Scheme 79.

Chiral bases have also been used to promote eliminations[367] and to open epoxides.[368] Many of these reactions provide high regioselectivity.[366h,366i,369] To date, the use of chiral bases with asymmetric substrates has met with little general success for asymmetric transformations.[370]

Although these results have yet to be exploited, they hold much potential.

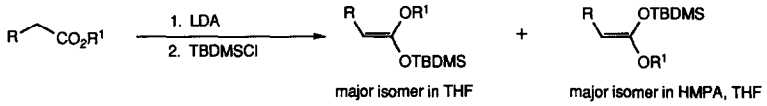
3.4.3.3. *Use of enol ethers.*[338d,371] Silyl enol ethers have found extensive application due to their ready availability. Furthermore, these ethers react with a wide variety of electrophiles, including tertiary halides, in the presence of a Lewis acid to afford the α-substituted carbonyl derivatives.[341,371,372]

As isomeric enol ethers can be separated, this class of compounds provides a powerful method to control the regiochemical outcome of many carbonyl reactions. Since these ethers are invariably derived from enolates, the discussion will therefore cover both of these species.

Deprotonation of the carbonyl substrate with a hindered base, such as LDA, usually ensures formation of the kinetic enolate.[338c,339a,340a,373] The use of low temperature eliminates problems due to self-condensation of the carbonyl compound.[374] The thermodynamic enolate is formed when sodium hydride is employed as base;[375] the silyl enol ether is available through reaction with chlorotrimethylsilane and triethylamine in DMF.[340a,374,376] Silyl enol ethers can be converted to the corresponding lithium enolate without loss of stereochemical integrity by reaction with methyllithium or fluoride ion.[375,377]

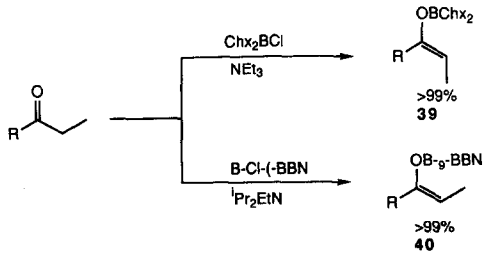
Many methods have now been proposed for the generation of regioselective enol ethers for a variety of carbonyl-containing functionalities.[371a,378] However, the geometry of the enolate may not be controlled during these preparations.[379] Vinyl anions can be oxidized to provide silyl enol ethers with retention of double bond geometry.[380] Alternative approaches rely on the thermal rearrangements of β-ketosilanes,[381] and β-keto esters.[382] In addition to physical separations,[375] isomeric silyl enol ethers can be separated by a kinetic resolution procedure that employs reaction with nitrosostyrene.[383] Chiral silicon moieties have been incorporated into silyl enol ethers;[384] however, the chemistry of these chiral compounds has yet to be exploited.[385]

Studies on the Claisen ester enolate rearrangement have shown that the ester *E*-enolate is formed in THF, while in HMPA–THF the *Z*-enolate predominates (Scheme 80).[386] *N,N'*-Dimethyl-*N,N'*-propyleneurea (DMPU) in THF also affords the *Z*-enolate with high diastereoselection, and provides an alternative to the use of HMPA.[387]



Scheme 80.

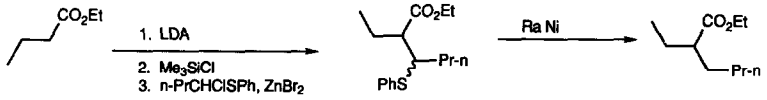
This observation, that HMPA can provide access to the alternative enolate geometry, has been applied to other systems including ketones,[388] hydrazones[355a] and oxazolines.[361b,363h] The formation of the *E*(*trans*)-enolate in THF has been the subject of various interpretations.[342c,379] The control of enolate geometry can be used to form silyl enol ethers with a high degree of stereoselection.[389] Some variations in formation of the enolate are observed when sodium hexamethyldisilazide is used as the base.[340b] Silyl keteneacetals can undergo thermodynamic equilibration in the presence of ammonium salts.[390]



Scheme 81.

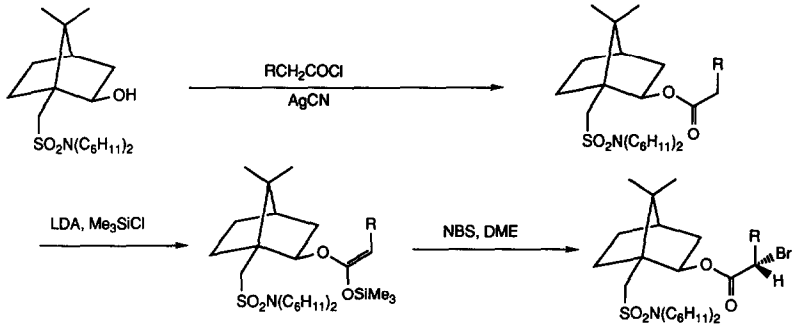
Ketones can be converted to either the corresponding (*E*)- or (*Z*)-boron enolate (**39** and **40**) by use of either dicyclohexylchloroborane (Chx_2BCl) or *B*-chloro-9-borabicyclo[3.3.1]nonane (*B*-Cl-9-BBN) (Scheme 81).[391] This stereospecificity is particularly useful for application with the aldol reaction (Section 4.2). Enolates undergo numerous reactions, including alkylations (*vide supra*).[340a] However, side reactions such as alkene formation from the alkyl halide can be minimized by use of an enol ether, and the opportunity is available to obtain the enol ether as a single stereoisomer. An additional advantage is that alkylation of a silyl enol ether is usually conducted in the presence of a Lewis acid, which allows use of functional groups not compatible with enolate chemistry.[371b,392]

A wide variety of alkyl side chains may be introduced through the use of α-chloro sulphides (Scheme 82).[371b,393]



Scheme 82.

Incorporation of a chiral auxiliary allows for the asymmetric preparation of a number of derivatives, including α-amino acids (cf. Schemes 26 and 83).[125,244]

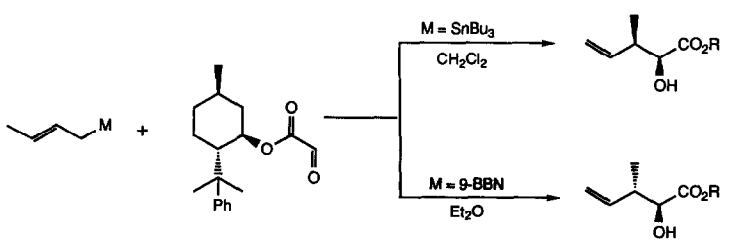


Scheme 83.

Although the majority of examples in this section have centred around silyl enol ethers, other elements, such as boron, can be used in a similar context.[360a]

3.4.3.4. *Alkylations of glycolates.* The asymmetric alkylation of a glycolate enolate provides a useful entry to α-hydroxycarboxylic acids.[394] The ketone moiety can be protected as a thioketal. This facilitates anion formation and subsequent reaction with a wide variety of electrophiles.[395] Of course, an alternative methodology is reaction of an α-keto ester with an organometallic reagent (Section 3.4.2.1).[396] Indeed, the additional functional group can afford increased stereoselectivity.[397]

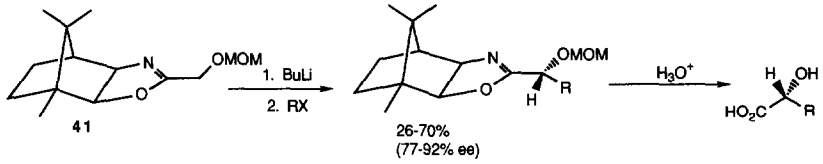
Addition of allylmetal compounds to a chiral glyoxylate affords the α-hydroxy esters. The selectivity is dependent upon the solvent and metal counterion (Scheme 84).[396b,396c,398]



Scheme 84.

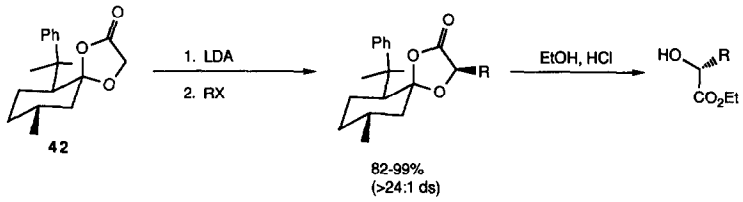
Organozinc reagents with chiral glyoxalate esters can also give good stereochemical yields of the resultant mandelic acid derivatives.[399]

The oxazoline **41** provided one such application of this methodology, but some difficulty was encountered in the hydrolytic removal of the chiral auxiliary (Scheme 85).[400]



Scheme 85.

An alternative approach is provided by the dioxolanone **42** but the preparation of the starting material does require a chromatographic separation (Scheme 86).[401]

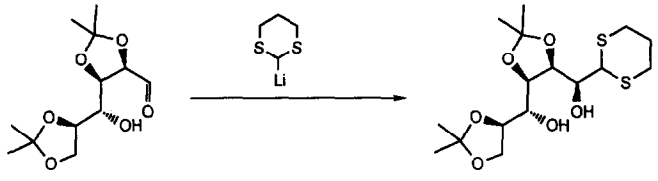


Scheme 86.

Indeed, many examples of the stereoselection available from this type of addition have already been discussed (e.g. Schemes 61 and 62).

3.4.4. *Homologation procedures.* Homologation of an aldehyde can produce a new chiral centre at the original carbonyl site. Many procedures accomplish this transformation and involve umpolung reagents.[13,289a,319a,402] Methodology has been developed which employs a metal-catalyzed addition of carbon monoxide.[403]

Stereochemical control for the addition of an umpolung formyl reagent can be achieved through chelate formation (Scheme 87),[404] or a similar strategy.[405]



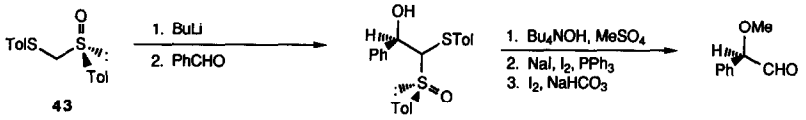
Scheme 87.

The use of 2-trimethylsilylthiazole has been advocated as a useful formyl anion reagent as additions to asymmetric aldehydes proceed with high diastereoselectivity.[1,406]

In many respects, the oxathiane is an asymmetric homologation reagent; although the original condensation tends not to be stereospecific, further manipulations allow a wide range of target compounds to be reached (Scheme 61).[298]

The chiral sulphoxide **43** has been used for a chiral homologation ($\geq 70\%$ *ee*) (Scheme 88).[407]

The Strecker-type synthesis of α-amino acids does provide some asymmetric induction when a chiral amine is employed.[408]



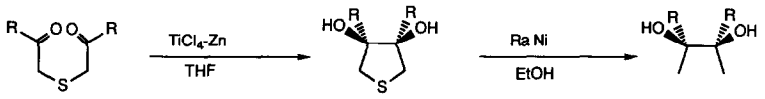
Scheme 88.

3.5. *Other reactions*

There are a number of reactions which establish 1,2-functionality yet do not conveniently fall into the categories described above.

α-Substituted carbonyl compounds can be prepared by the S_N2' addition of a nucleophile to an epoxy enol ether.[409]

A useful method for the preparation of *syncat*-1,2-diols relies on a ring closure, extrusion procedure (Scheme 89).[410]



Scheme 89.

Hydroformylation can be used to convert alkenes to carbonyl compounds. Asymmetric induction has been realized but the limitations of this approach parallel those of hydrogenation (Section 3.2.4 and 4.11).[411]

4. 1,3-FUNCTIONAL GROUPS

To keep in line with the carbohydrate theme, we have included in this section reactions that lead to functional groups at all three carbon atoms of a subunit.

A rule has been developed by Houk to predict the stereochemical outcome of a wide variety of reactions on allylic systems (Section 4.1); his rule also has some applications for simple alkenes (Section 3.2.3).

Two very powerful reactions exist to allow the introduction of 1,3-functional groups: the aldol reaction and Sharpless epoxidation. The ability within these methodologies to change relative stereochemistry through simple procedures has led to their widespread application in organic synthesis. Another approach which has found much use, particularly in cyclic systems, is the conjugate addition of a nucleophile to an α,β-unsaturated carbonyl system followed by trapping of the resultant anion with an electrophile. The final major reaction class relies on the stereoselective introduction of functionality at the α-position of a β-functionalized carbonyl compound.

4.1. *Houk's rule*

To control stereochemistry, the reactive species is 'guided' to a particular face of an unsaturated carbon atom through complex formation with an appendant functional group in the substrate – the Sharpless epoxidation is an excellent example. Asymmetric induction can still be extremely high even without prior complex formation between reactant and substrate as, for example, in the hydroboration of an alkene by a chiral borane. The induction in these latter cases has been rationalized in terms of the preferred angle of attack by a reagent on a multiple bond.¶[200b,412] These models are summarized in Fig. 7.[15e]

¶ These results can also be interpreted in terms of allylic 1,3-strain (ref. 413).

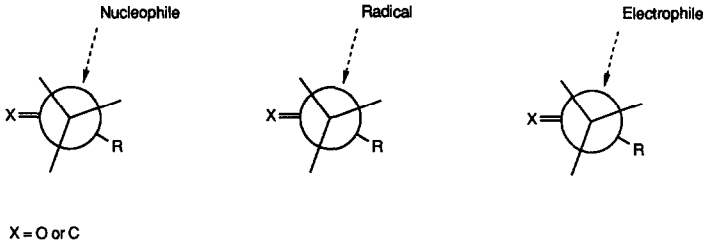


Fig. 7.

Under the assumption that a reagent will attack from the face opposite to a large substituent, nucleophilic addition becomes the Anh–Felkin model for X = O (Section 2.1). In a similar manner hydroboration, where the boron is an electrophile, resembles the empirical rule formulated by Kishi (Section 3.2.3.). Still another variant is provided by the alkylation of an ester enolate (Section 4.9.2).[414]

4.2. *The aldol reaction*¶[11,98,338b,349c,371a,371b,415]

The aldol reaction, condensation of a nucleophilic carbonyl species with an electrophilic carbonyl moiety, together with its many derivatives, has proven to be one of the most versatile methods for the formation of carbon–carbon bonds. The addition has, until recently, been plagued by dehydration of the initial aldol adduct and by regiochemical problems. Even with these problems circumvented, four different stereoisomers can be formed.[416] Most of the methods for stereochemical control of the aldol reaction rely on the use of chiral auxiliaries or the use of chiral organometallic reagents.[415b,417]

To circumvent the problems associated with the aldol reaction, alternative strategies have been employed, including the use of allyl anions (Section 2.3), the Claisen reaction[1] and reductions of β-dicarbonyl compounds (Section 4.9).

In carbohydrate synthesis, the aldol reaction has not found such widespread application as it has elsewhere due to inherent problems associated with an oxygen functional group juxtaposed to the carbonyl group in the nucleophilic moiety (see Section 3.4.1). However, the ketal of glyceraldehyde has proven an extremely useful aldehydic moiety for an aldol approach.[1,5c,35b]

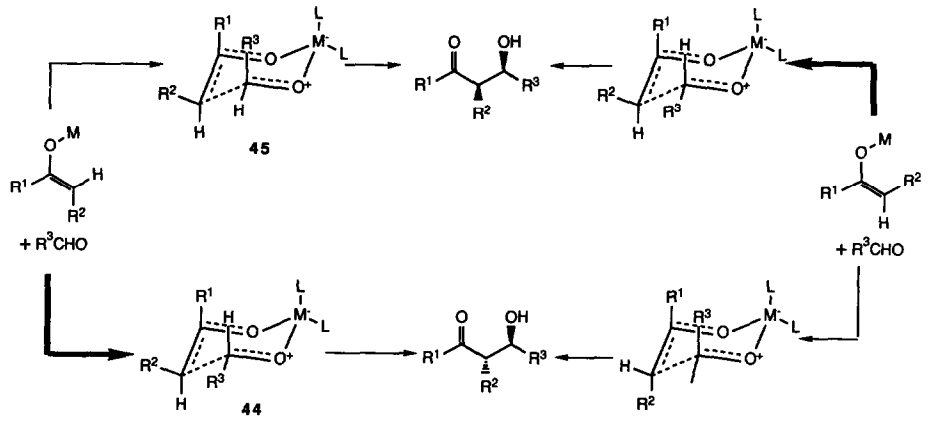
Many studies have addressed the issue of a stereoselective aldol reaction. The major variables are the metal counterion, together with its associated ligands, and the reaction conditions.¶[342a,418] High stereoselectivity correlates with the enolate geometry (Section 3.4.3.3), and the steric influences within this moiety, while the steric constraints associated with the electrophilic carbonyl moiety tend to play a minor role.[98,420] The observed stereochemistry can usually be interpreted in terms of a chair-like transition state. These principles are summarized in Scheme 90.[415f,421]

Thus, the *E*-enolate would be expected to give the *ancat* (*threo*) product as the transition state **44** has less serious steric interactions than **45**.[422] However, in many cases, the preferred transition state may not be a chair, or the energy difference between the two pathways is very small.[415f,423] The use of chiral auxiliaries allows 'double' asymmetric induction if a matched pair is utilized.[6n,424]

In some of the early studies it was found that a large alkyl group in the nucleophilic moiety

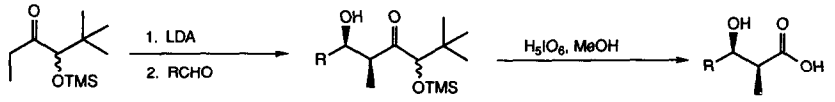
¶ The nomenclature of Carey has been used throughout this section. This includes *syncat* and *ancat*, where substituents are compared by steric bulk for a molecule written in the extended zigzag conformation. When like substituents are on the same side of the molecule, the relative configuration is *syncat*, and on the opposite side, *ancat* (ref. 13).

¶ Both theoretical and experimental studies to determine how these variables influence the stereochemical outcome of the reaction are being performed. See, for example, ref. 419.



Scheme 90.

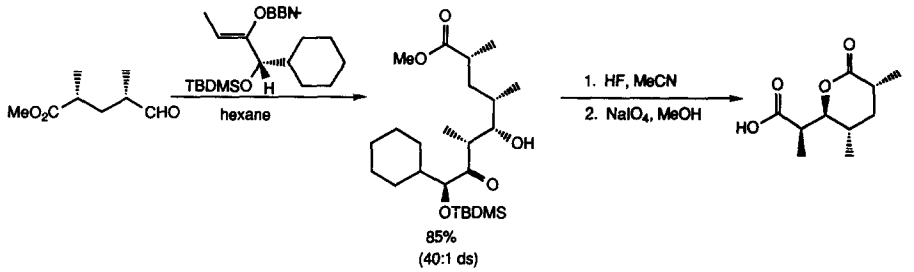
affords good stereoselection (Scheme 91).[422a,425] Silicon can also play the role of a large group, as in acylsilanes (cf. Scheme 59).[426]



Scheme 91.

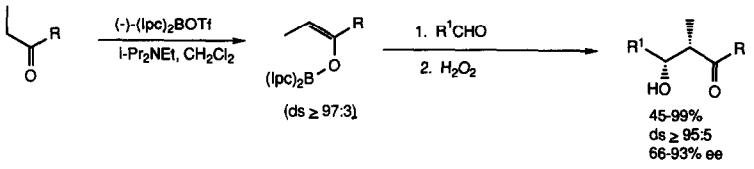
The use of a metal counterion, such as lithium or magnesium, which can form a chelate does offer selectivity through the use of either Anh–Felkin or chelation-controlled additions.[427] The use of titanium can also prove useful,[428] and if chiral ligands are present then an enantioselective transformation becomes available (*vide infra*).

Boron enolates have been used extensively to control the stereochemistry during an aldol reaction. Boron's small size does not allow coordination to other oxygen atoms present within the reaction parameters. In addition to high selectivity (Scheme 92),[422c,429] a reversal of that seen with a lithium counterion can also be observed.[98,422c,430]



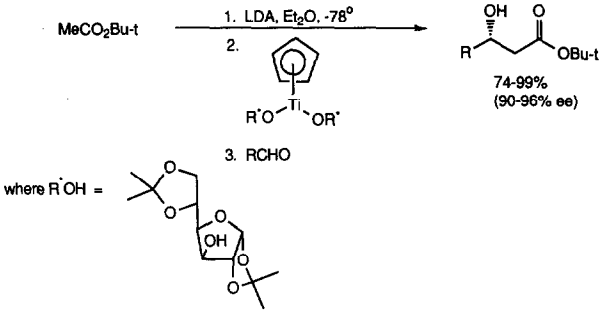
Scheme 92.

In early studies, alkylboranes were added to preformed lithium enolates to generate the boron enolate.[431] This technique has been superseded by treatment of the ketone with an appropriately substituted borane in the presence of base, as this allows the use of a chiral borane, but other approaches are available.[330e,422c,432] A suitable choice of chiral reagent overcomes the low selectivity associated with mismatched pairs.[432c] Indeed, some very high enantioselectivities have been observed (Scheme 93).[433]

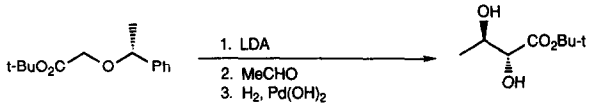


Scheme 93.

In addition to lithium and boron, many other metals have been proposed to control the stereoselection of the aldol reaction.[11,98,415d,415f] Titanium enolates are proving very successful, especially when used in conjunction with a chiral auxiliary.[434] High stereoselectivity can be achieved by use of a chiral auxiliary, which can then be removed by subsequent operations (e.g. Scheme 92).[338b,349b,435] Chiral auxiliaries can also be used as ligands (Scheme 94), or as part of the substrate (Scheme 95).[436]

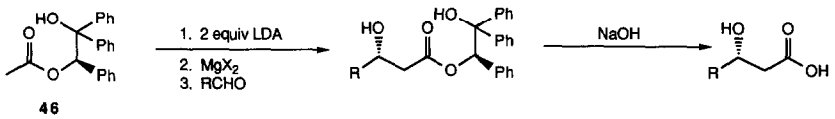


Scheme 94.



Scheme 95.

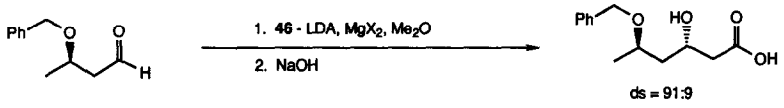
The addition of an acetic acid equivalent to aldehydes can be achieved with a high degree of stereoselection through the use of (*R*)-2-acetoxy-1,2,2-triphenylethyl acetate (**46**),[437] in turn available from (*R*)-mandelic acid (Scheme 96).[438] The (*R*)-reagent adds to the aldehyde predominately from the *Re*-face. The corresponding (*S*)-reagent gives *Si*-face attack.[415f]



46

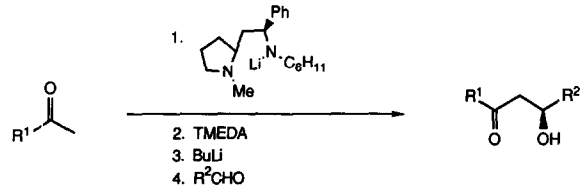
Scheme 96.

With aldehydes containing a chiral centre, the problem of mismatched pairs can arise; when the facial selectivity works in opposition, a smaller diastereomeric excess is obtained.[6n] The selectivity can still be high, however, with β-alkoxy aldehydes (Scheme 97).[415f] This chiral auxiliary has been used with α-amino aldehydes with respectable diastereoselectivity.[439]



Scheme 97.

The use of a chiral base (cf. Section 3.4.3.2) can provide reasonable enantioselectivity (Scheme 98).[440]

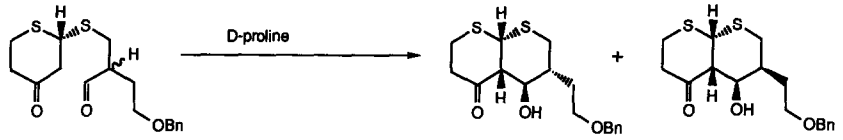


Scheme 98.

This type of approach allows for the preparation of contiguous asymmetric centres.[441]

Special mention must be made of 2-oxazolines, which provide routes to β-hydroxy and β-alkoxy acids. Although the enantiomeric excesses are usually not high (*ca* 20–25%),[442] the adducts are useful precursors to 1,4-addition methodology (Section 4.8).[363a,443] Indeed, many of the chiral auxiliaries used for the α-alkylation of carbonyl compounds, such as hydrazones, have been used to effect stereoselective aldol reactions to varying degrees of success.[444]

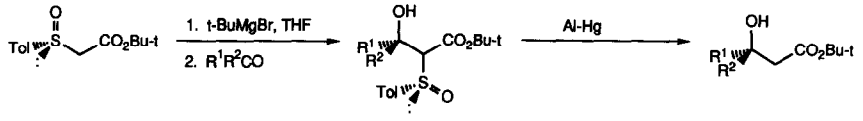
The use of chiral catalysts to bring about an asymmetric aldol reaction[210,445] was exploited in a synthesis of erythromycin (Scheme 99).[446] Use of L-proline gave racemic products, whereas D-proline led to good asymmetric induction, an example of double asymmetric induction.



Scheme 99.

Removal of the sulphur atoms provided the acyclic aldol product.[446a,446b,447]

Condensation of chiral esters with aldehydes usually results in low levels of asymmetric induction.[448] Incorporation of a chiral sulphoxide, however, as a chiral auxiliary allows for the synthesis of β-hydroxy acids in good chemical and optical yields (Scheme 100).[449]



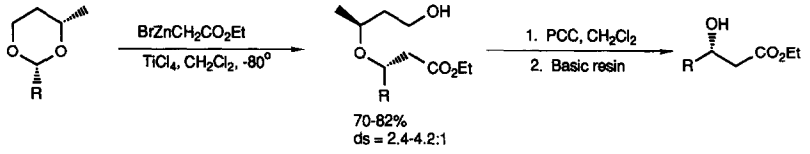
Scheme 100.

An alternative approach is to use an acetyl iron complex, as this provides for high induction (cf. Scheme 73).[450]

Nitrogen analogues of carbonyl compounds have been utilized to effect the equivalent of aldol reactions,[305a,451] as have thionium ions.[452]

The Reformatsky reaction is closely related to the aldol reaction.[453] Indeed, diastereoselectivity

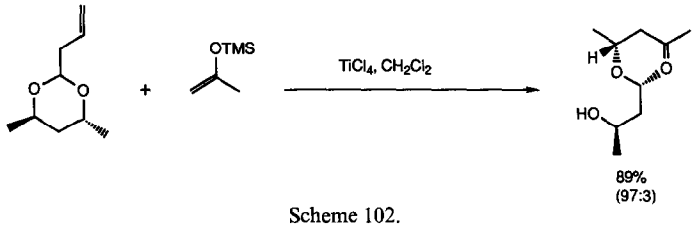
can also be observed with zinc enolate addition to carbonyl compounds.[421a,453d,454] The Reformatsky reaction with imines has been studied extensively as β-lactams are the result of this condensation.[455] Asymmetric induction occurs if the reaction is conducted with ketones or imines in the presence of a chelation agent, such as sparteine,[456] or if a chiral ester is incorporated.[457] The use of acetals with a Reformatsky reagent, in the presence of a Lewis acid catalyst, again allows for enantioselectivity (Scheme 101).[458]



Scheme 101.

In addition to zinc enolates, other metal enolates react with imines to provide β-aminocarbonyl compounds (cf. Section 3.4.3.1) or β-lactams.[455i,459] Samarium has been found to be useful for the intramolecular version of the Reformatsky reaction.[460]

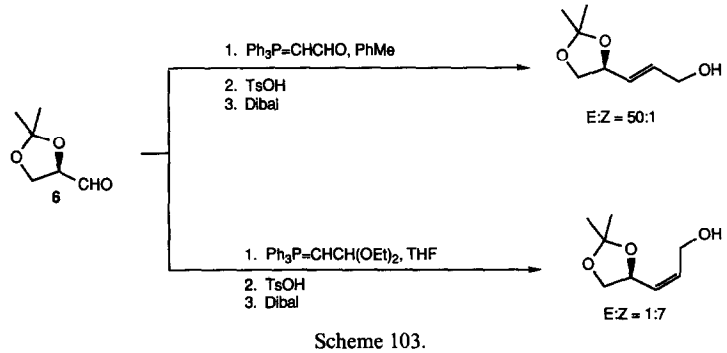
Silyl enol ethers react, with Lewis acid catalysis, with carbonyl compounds or acetals (the Mukaiyama reaction) to afford aldol-type products (Scheme 102).[303d,458a,461] Indeed, silyl enol ethers often provide excellent diastereofacial selectivity with aldehydes to afford the Anh–Felkin product.[427b,427c] Stereoselectivity can arise from the stereochemical requirements of one of the reactants, such as the acetal structure,[462] the silyl enol ether,[236d,463] or from the incorporation of a chiral ligand into the catalyst.[464] Oxazolidines provide an alternative to acetals for this type of approach.[465] The stereoselection is not, however, high across a broad range of substrates. The silyl enol ether approach can be extended to silyl ketene acetals where the additional alkoxy moiety is a useful handle for the incorporation of a chiral unit.[466]



Scheme 102.

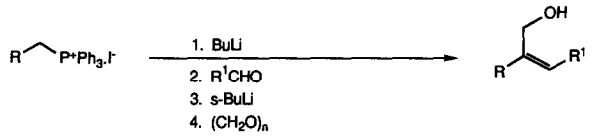
4.3. *Synthesis of allyl alcohols*

Many of the reactions discussed in the following sections rely on the availability of just one stereoisomer of an allyl alcohol.



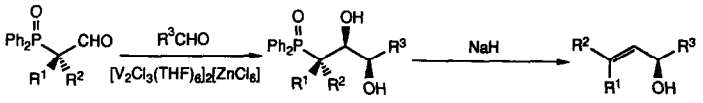
Scheme 103.

The use of a stabilized phosphorus ylid, followed by reduction of the carbonyl moiety has been a favoured approach for the preparation of precursors for the Sharpless epoxidation (Section 4.5) (Scheme 103).[467] The ester analogue of this reaction has also been used,[42a,468] while a Wittig reaction on an α-hydroxycarbonyl compound provides another variant.[469] The Wittig approach also allows for the introduction of a carbon atom prior to the elimination of the phosphorus (Scheme 104).[470]



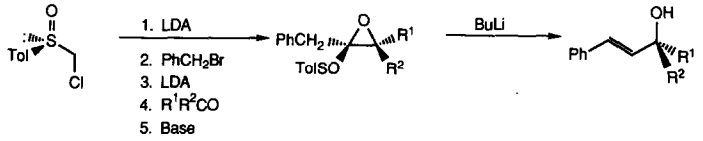
Scheme 104.

The condensation of a β-silylphosphorus ylid with an aldehyde provides a selective synthesis of allyl alcohols as a result of Anh–Felkin control.[105] The phosphorus moiety does not have to be eliminated in the initial condensation step (Scheme 105).[471]



Scheme 105.

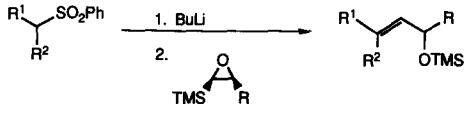
Many other strategies can be envisioned for the preparation of allyl alcohols,[140a] such as: the reduction of a propargyl alcohol;[472] addition of an organometallic species to an appropriately substituted acetylene;[473] a carbonyl condensation (Scheme 106);[243a,309a,474] or conversion of a silyl group to hydroxy (Section 4.12.2).[475] The Evans rearrangement also provides some useful methodology (Section 4.3.1).[476]



Scheme 106.

Reduction of an acetylene by a variety of metal hydrides generates a vinyl nucleophilic species, which can then be treated with a carbonyl compound.[477]

Epoxides can be converted to allyl alcohols by sequential treatment with an electrophilic silicon reagent then a non-nucleophilic base.[478] An appropriate nucleophile or base can also be used to open an epoxide to afford allyl alcohols (e.g. Scheme 107).[479]

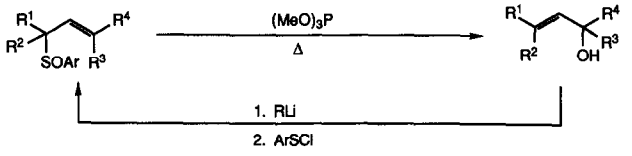


Scheme 107.

Chloromethyl epoxides provide allyl alcohols upon treatment with telluride ion.[480] Allyl alcohols are also available through reductive elimination of β,γ-epoxysulphones,[481] or palladium-catalyzed opening of a vinylepoxide.[482]

Allylic oxidation of an alkene provides a useful entry to allyl alcohols.[483] The most commonly used reagent is selenium dioxide.[484]

4.3.1. *Evans' rearrangement and related reactions.*[485] Treatment of an allyl alcohol with a base followed by arylsulphenyl chloride produces an allyl sulphoxide.[486] The overall reaction involves a [2,3]-sigmatropic rearrangement which can be driven in the opposite direction by the addition of a thiophile, such as trimethylphosphite (Scheme 108).[487] This strategy allows the chemistry of an allyl phenyl sulphoxide to be exploited before the allyl alcohol is unmasked.[470a,488] As the sigmatropic rearrangement is concerted, stereochemical transfer can be achieved.[489]



Scheme 108.

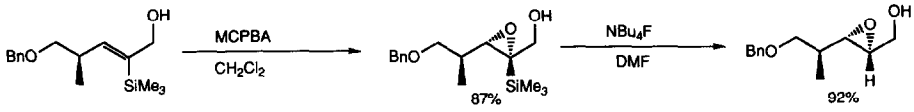
4.4. *Epoxidation of allyl alcohols*

The procedure for the asymmetric epoxidation of allyl alcohols has, in many respects, revolutionalized organic synthetic methodology. Very high asymmetric induction is observed with a wide range of substrates, allowing a chemical reaction to compete with an enzymatic process both in terms of chemical and optical yields. Several classes of reagents, mainly based on peroxy acids, vanadium and molybdenum, have been utilized to perform stereoselective oxidations of allyl alcohols in addition to the Sharpless titanium methodology.[220b,445]

4.4.1. *Peroxy acid oxidations of allyl alcohols.*[220a] Peroxy acids, such as *m*-chloroperoxybenzoic acid (MCPBA), when reacted with an allyl alcohol show a weak preference for formation of the *parf*-isomer of the product epoxide.[490] These observations have been interpreted in terms of complex formation between the peroxy acid and the allyl alcohol, in which a dihedral angle of 120° is preferred. In consequence, the rotamer **47** is preferred over the alternative **48** (Fig. 8).

Fig. 8.

When the α-substituent is large (e.g. $R^2 = SiMe_3$) then epoxidation with MCPBA can be stereospecific for the formation of the *pref*-isomer as the bulky substituent makes the rotamer **48** more favourable (Scheme 109).[491] As a silyl group can undergo protiodesilylation in the presence of the fluoride ion, this approach is an extremely powerful tool for the preparation of 2,3-epoxy alcohols of defined relative stereochemistry.



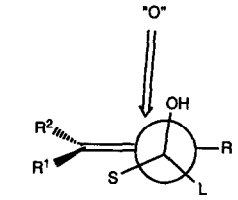
Scheme 109.

A systematic study for *p*-nitroperoxybenzoic acid with various allyl alcohols also showed that the hydroxy group had a strong directing effect. The effect was lost when the allyl acetate was used

in place of the alcohol. Stereoselectivity was compromised by the presence of a large group juxtaposed to the hydroxy group, or on the α-alkene carbon atom. β-Alkene substituents, however, allowed differentiation, particularly when that substituent was *cis* to the hydroxy moiety; these effects are very similar when MCPBA is the reagent.[490,491a,492] The use of silyl ethers promotes formation of the *ancat*-isomer.[493]

When a large substituent is present in the β-*Z*-position, then a large preference is shown for the rotamer **47**, and hence formation of the *parf*-product.[494]

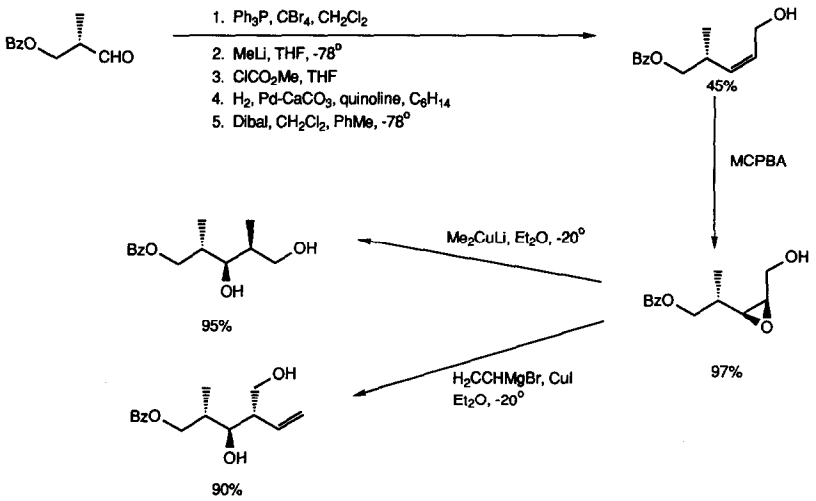
In addition to the model just described, others have been put forward to predict the stereochemical outcome of an oxidation.[220a,232d,492b,495] They are summarized in Fig. 9, which is consistent with *ab initio* calculations,[56] but none of these models differ significantly in their product prediction.



where S = a small substituent
L = a large substituent

Fig. 9.

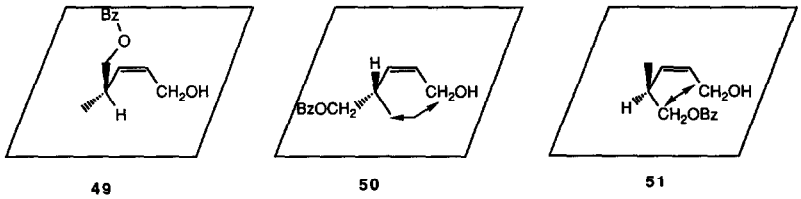
The heavy dependence of the resultant stereochemistry upon the substituents of an allyl alcohol have made metal-mediated oxidations preferable to the use of peroxy acids.[238a] Despite this drawback, peroxy acid oxidation of allyl alcohols can sometimes provide a workable alternative to give isomers of epoxy alcohols which are not readily available by a Sharpless epoxidation procedure (Scheme 110).[42a,496] Thus, the methodology has been used in the preparation of higher carbon sugar derivatives.[1,497] In cyclic cases, conformation considerations of the ring system usually results in high stereospecificity.[498]



Scheme 110.

Protection of the hydroxy group can still lead to selective oxidation through the *cis*-addition of the oxygen, as observed with simple alkenes (Section 3.3.1).[499]

Introduction of a second group which can also complex with the incoming peroxy acid can lead to high stereoselection (Scheme 110). The selectivity has been attributed to the preferred conformation **49**, as opposed to the conformers **50** and **51** (Fig. 10), thus this a variant of Houk's rule.[468e]



49 50 51

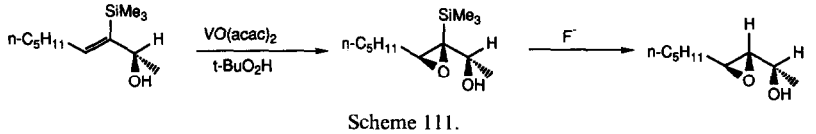
Fig. 10.

The stereoselection is good for peroxy acid oxidation with functionalized allyl alcohols.[495b]

4.4.2. *Other oxidations of allyl alcohols.* The problems associated with peroxy acid oxidation of an allyl alcohol and its susceptibility to substituent effects, have led to the development of other oxidation systems, particularly ones that involve metals.[231] This work has culminated in Sharpless' method, but other metals, such as vanadium, tungsten and molybdenum, do afford some selectivity.[232b,490,491a,492c,497,498,500] The preferred conformations for vanadium-catalyzed oxidations are shown in Fig. 11.[490,491a,495c]

Fig. 11.

As with peroxy acid oxidations, the use of the bulky trimethylsilyl group allows high selectivity (Scheme 111).[491a,494b,501]



Scheme 111.

The use of chiral ligands with molybdenum, vanadium or aluminium systems gave only modest asymmetric induction.[502] The ability to control relative stereochemistry does, however, provide an excellent method for asymmetric synthesis if a chiral allyl alcohol is the substrate (Scheme 44).[76b,238a]

In addition to allyl alcohols, allylic amides are suitable substrates for oxidation by molybdenum.[467c] Intramolecular epoxidations with hydroperoxides did not provide high asymmetric induction.[503]

Osmium oxidizes allyl alcohols to affords a triol. An empirical rule has been advanced, where the reagent approaches from the face opposite to the pre-existing oxygen functionality (Fig. 12).[504]

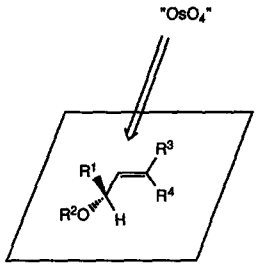


Fig. 12.

Although the hydroxy group may be protected, the presence of an acyl group reduces stereoselectivity; *cis*-olefins provide a better selection than do their *trans* counterparts.[504,505] It should be noted that this is one empirical rule and other variants exist,[506] which will no doubt be modified as our understanding of the osmylation reaction expands.

4.5. *Sharpless epoxidation*[220b,231,507]

One of the major advantages of the titanium asymmetric epoxidation is the simplicity with which the stereochemical outcome of the reaction can be predicted.[508] The other powerful feature is the ability to change this selectivity to the other isomer by simple means (see Fig. 13).[509]

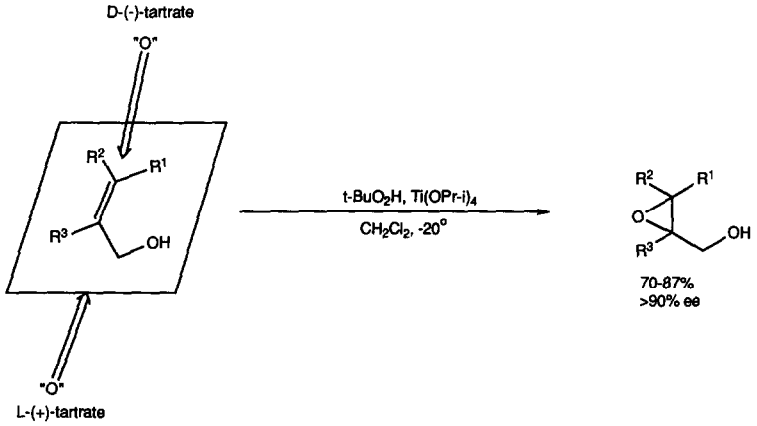


Fig. 13.

In addition to having commercially available ingredients, the reaction is promiscuous and proceeds in good chemical yield with excellent enantiomeric excesses. The reaction, however, does suffer when bulky substituents are *cis* to the hydroxymethyl functionality (R^1 in Fig. 13). For prochiral alcohols, the absolute stereochemistry of the transformation is predictable, while for a chiral alcohol, the diastereofacial selectivity of the reagent is often sufficient to override those preferences inherent in the substrate. When the chiral atom is in the *E*-β-position of the allyl alcohol (R^2 in Fig. 13), then the epoxidation can be controlled to access either diastereoface of the alkene. In contrast, when the chirality is at either the *Z*-β- or α-position (R^1 or R^3 in Fig. 13), the process is likely to give selective access of the reagent from only one of the two diastereotopic faces.[509a,510]

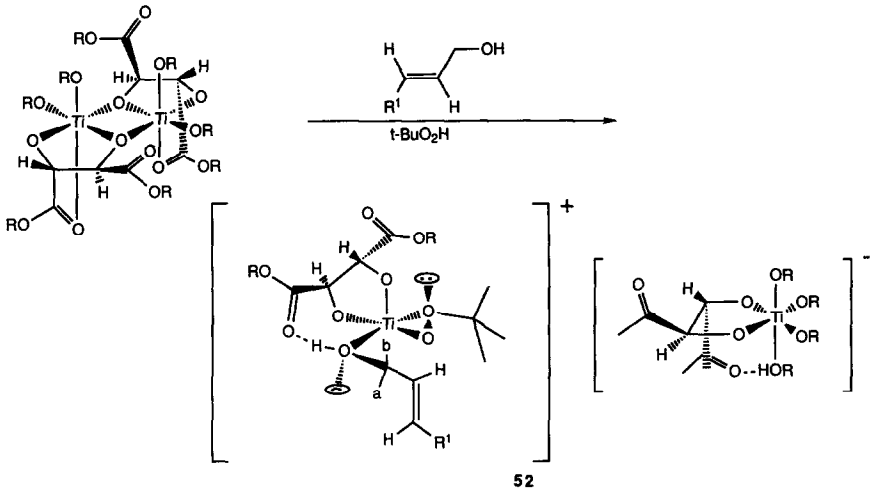
The introduction of a *tert*-butyl group at each of the possible positions in the allyl alcohols resulted in no deviation from the principles outlined in Table 2.[511] Many examples of substrates for the epoxidation protocol are known.[512] Even the prochiral divinylcarbinol undergoes epoxidation with high diastereo- and enantio-selectivity.[134e,513]

Table 2.

Selectivity of the Sharpless Epoxidation Procedure.

Bulky substituents Z-β to the CH_2OH group are deleterious.
High optical purities usually result.
Absolute stereochemistry is predictable for prochiral alcohols (see Figure 13).
The procedure can be used for the kinetic resolution of a secondary alcohol.
When a chiral atom is attached to the alkene moiety in the E-β-position, the epoxidation process can access either diastereoface selectively.
When a chiral atom is attached to the alkene moiety in either the Z-β-position or the α-position, then it is likely that only selective approach to one face will be observed (Scheme 112).

An improved work-up procedure increases the yield for allyl alcohols containing a small number of carbon atoms.[514] The reaction time has been reduced dramatically by the addition of calcium hydride, silica gel or montmorillonite catalysts.[515] Furthermore, less reactive substrates provide the epoxide readily.[516] The structure of the titanium–tartrate derivatives has been determined,[512,517] and is in accord with a frontier orbital interpretation.[518] Based on these observations, and the reaction selectivity, a mechanistic explanation has been proposed (Scheme 112).[519] The complex (**52**) contains a chiral titanium atom through the appendant tartrate ligands. The intramolecular hydrogen bond ensures that internal epoxidation is only favoured at one face of the allyl alcohol. This explanation is in accord with the experimental observations that substrates with an α-substituent (b = alkyl; a = alkyl or hydrogen) react much more slowly than when this position is not substituted (b = hydrogen).

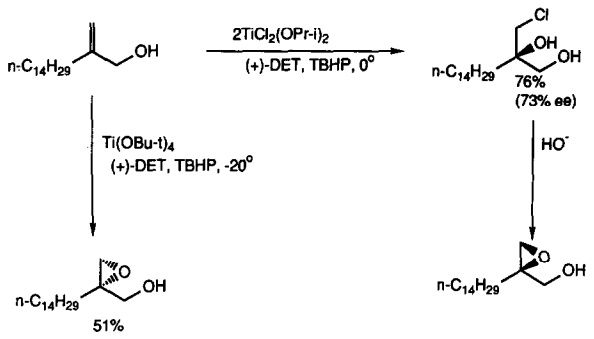


Scheme 112.

Use of dichlorotitanium diisopropoxide in a 2 : 1 ratio in place of the tetraisopropoxide reverses the enantioselectivity (Scheme 113). The use of the more hindered tetrabutoxide gives higher yields in this series.[520]

The use of tartamides can also reverse the observed selectivity.[512a] This has been rationalized in terms of the conformational disparity between the amides and esters.[521]

Despite the widespread use of this asymmetric epoxidation procedure, some care must still be exercised in the choice of substrate, and not only from the standpoint of ensuring good stereochemical selection. Subsequent reactions of the resultant epoxide, particularly intramolecular ones, must be considered.[522]



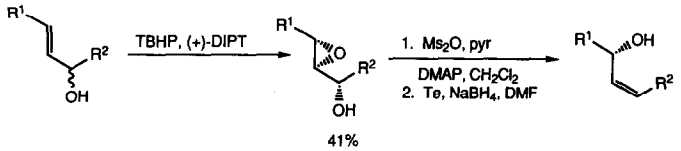
Scheme 113.

The power of the Sharpless epoxidation method is augmented by the versatility of the resultant 2,3-epoxy alcohols (Section 4.6).

4.5.1. *Kinetic resolution with the Sharpless epoxidation procedure.* The ability of the Sharpless epoxidation catalyst to differentiate between the two enantiomers of an asymmetric allyl alcohol affords a powerful synthetic tool to obtain optically pure materials through kinetic resolution.[523] As the procedure relies on one enantiomer of a secondary allyl alcohol undergoing epoxidation at a much faster rate than its antipode, reactions are usually run to 50–55% completion.[524] In this way, resolution can often be impressive.[511,512,525] An increase in steric bulk at the olefin terminus increases the rate of reaction.[525b,526]

This resolution method has been used to resolve furfuryl alcohols,[527] allyl propargyl alcohols[528] and silylallyl alcohols,[529] and has also been used to determine the absolute configuration of cyclic alkenes.[530] Racemic β-hydroxyamines and furfurylamines undergo kinetic resolution through *N*-oxide formation, by use of Sharpless' conditions.[531]

The resultant epoxy alcohols from this oxidation procedure can be used for a wide variety of transformations (Section 4.6), including an alcohol transposition (Scheme 114).[532]

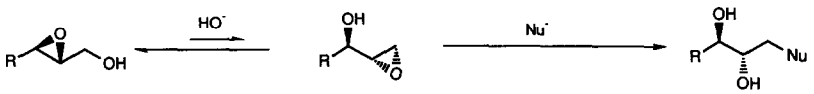


Scheme 114.

4.6. *Reactions of 2,3-epoxy alcohols*[509b,533]

As noted earlier, one reason for the powerful nature of the Sharpless epoxidation is the ability of the resultant epoxy alcohols to undergo regio- and stereo-selective reaction with nucleophiles.[509a] Methodologies have been developed to allow selective attack at any one of the three possible sites. Of course, epoxides derived from carbohydrates are also epoxy alcohol derivatives. However, the chemistry of these epoxides is often determined by their ring size and conformation, and the presence of participating neighbouring groups. Because of the large number of variables, discussion of these reactions has been omitted.[534]

A key reaction of 2,3-epoxy alcohols is the Payne rearrangement, an isomerization that produces an equilibrium mixture. This rearrangement then allows for the selective reaction with a nucleophile at the most reactive, primary position (Scheme 115).[509a,535] Reactions of a wide variety of nucleophiles with epoxy alcohols are summarized in Table 3.



Scheme 115.

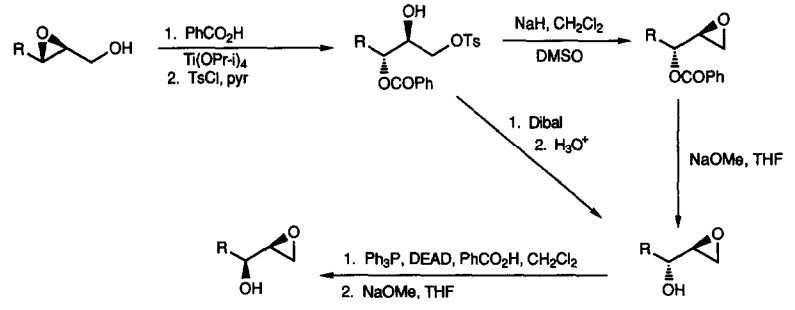
Table 3.

Examples of Reactions of Epoxyalcohols.[a]

Reactant	Primary Product[b]	References	Reactant	Primary Product[b]	References
PhSNa	1	467a,536	RMgBr,CuBr	1	550
	2	536b	R_2CuLi	2	42a,468e,551
PhSH	3	537		3	548b
KCN	3	536c	R_2Mg	3	548b
NH_3	3	536,538	$LiAlH_4$	2	552
NaN_3	1	136b,536b,539	Red-Al	2	102b,468c,552,
	3	536c,540			553
	2[c]	541	Dibal	3	548a,553
HONa	1	467a,513b,535	$LiBH_4$, Lewis acid	3	554
RCO_2H	3	536c,537,542	Li,NH_3,THF,t-BuOH[f]	2	555
NH_4Cl,Ti(OPr-i)$_4$[d]	3	543	$RuCl_3$,$NaIO_4$	1[g]	556
X_2,Ti(OPr-i)$_4$[d]	3	544	1. Swern, 2. $NaClO_2$	1[g]	557
RNCO[e]	1	545	CrO_3.2pyr	1[h]	558
TsCl[e]	1	546	Swern	1[h]	559
RX,base[e]	1	134e,547	Ph_3P,CCl_4[e]	1	560
R_3Al	3	548	Ph_3P,ZnI_2[e]	1	561
RLi	1	549			

[a] The variations in selectivity are due to changes in reaction conditions. [b] This Table indicates the major reaction pathway. The carbon atom (or oxygen atom) at which attack occurs is noted, the original hydroxyl group being labelled 1. [c] A silyl group must be present at C-2. [d] The halogen is the nucleophile. [e] The reagent is an electrophile, reaction occurs at oxygen. [f] The oxygen must be protected as the triisopropylsilyl ether. [g] The primary alcohol is oxidised to the corresponding carboxylic acid. [h] The primary alcohol is oxidised to the corresponding aldehyde.

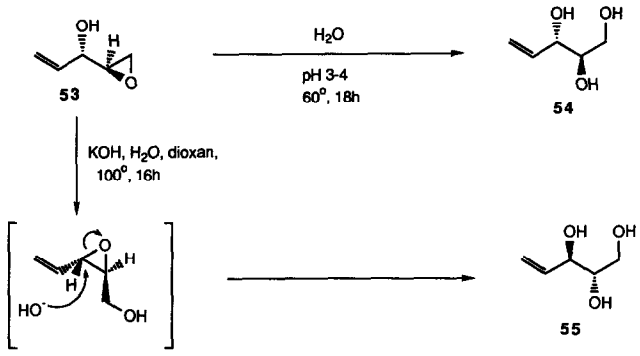
The configuration of the hydroxy group in a 2,3-epoxy alcohol can be inverted by use of Mitsunobu conditions (Section 2.4.1).[562] This approach has been exploited to provide the *parf*-2,3-epoxy alcohol, which is not readily available by a Sharpless protocol (Scheme 116).[542]



Scheme 116.

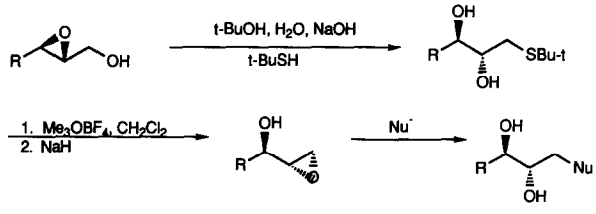
Reaction of divinylcarbinol with the (+)-diethyl tartrate version of the Sharpless reagent afforded the epoxide **53**. Ring opening at pH 3–4 provided the triol **54** selectively. In contrast,

treatment of the same epoxide with strong base provided the enantiomeric triol **55** as the major isomer by a double inversion (Scheme 117).[513b]



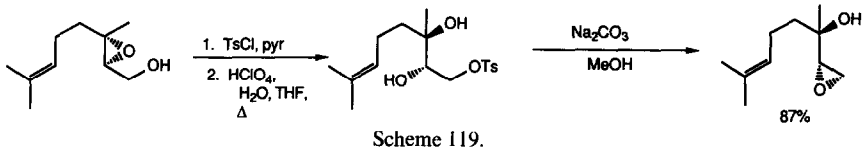
Scheme 117.

Under Payne rearrangement conditions, sodium *t*-butylthiolate provides 1-*t*-butylthio-2,3-diols with very high regioselectivity. The selectivity is, however, affected by many factors including reaction temperature, base concentration, and the rate of addition of the thiol. These sulphides can then be converted to the 2,3-epoxy alcohols, which in turn react with a wide variety of nucleophiles specifically at the 1-position (Scheme 118). This methodology circumvents the problems associated with the instability of many nucleophiles under 'Payne' conditions.[563]

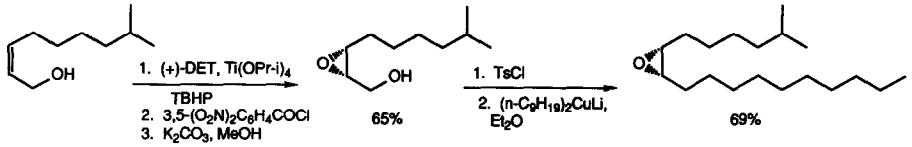


Scheme 118.

An alternative strategy to the 2,3-epoxy alcohols is illustrated in Scheme 119. Under basic conditions, the 2,3-epoxy-1-sulphonate esters usually react through selective displacement of the sulphonate moiety, rather than through epoxide opening (Scheme 120).[238b,546b,564] Under acidic conditions, the reaction is regioselective for ring opening at C-3. Mild base treatment then provides the terminal epoxide.[565]

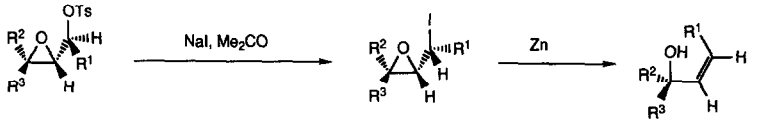


Scheme 119.

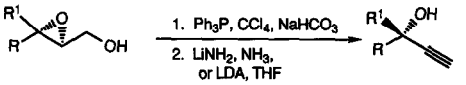


Scheme 120.

The tosylates derived from 2,3-epoxy alcohols can be displaced by halide with inversion of configuration at C-1. The allyl alcohol can then be generated by further treatment with zinc or trialkylstannate (Scheme 121) (cf. Scheme 114).[546a] The epoxychloride can also be used to give chiral propargyl alcohols (Scheme 122).[560c]



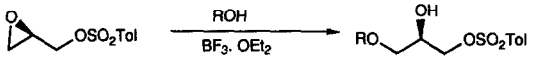
Scheme 121.



Scheme 122.

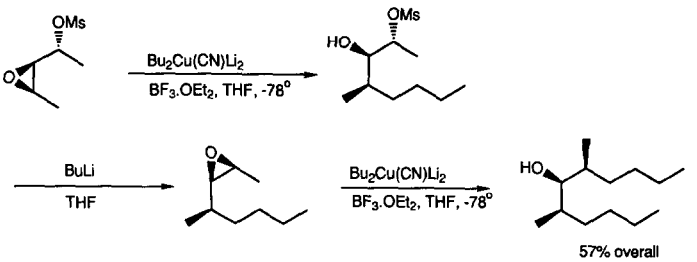
The Sharpless' kinetic resolution provides a number of other routes to optically active propargyl alcohols through γ-iodoallyl alcohols.[566]

Protected glycerol units are extremely useful for the preparation of many natural products. To achieve selective protection in glycerol nucleophilic substitution of sulphonate is a common approach, this is now augmented by the ring opening of an epoxysulphonate by an alcohol (Scheme 123).[567]



Scheme 123.

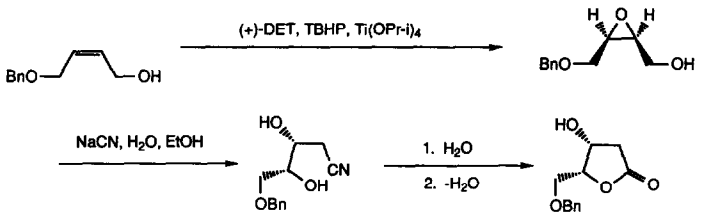
The mesylates or *m*-nitrobenzenesulphonates derived from 2,3-epoxy alcohols react with higher order cuprates at the least hindered epoxide centre.[565,568] The resultant alkoxymesylate does not ring close to the epoxide at −78°C, allowing stepwise reactions (Scheme 124).[568a]



Scheme 124.

An azide can be introduced at C-1 into a 2,3-epoxy alcohol under Payne rearrangement conditions.[539] Amines can be used as nucleophiles under Payne rearrangement conditions, provided excess is employed to overcome the regiochemical problems associated with the inherently slow reaction. However, attack at C-2 or C-3 can still be the preferred mode, and is dependent upon the substrate's structure.[540,565]

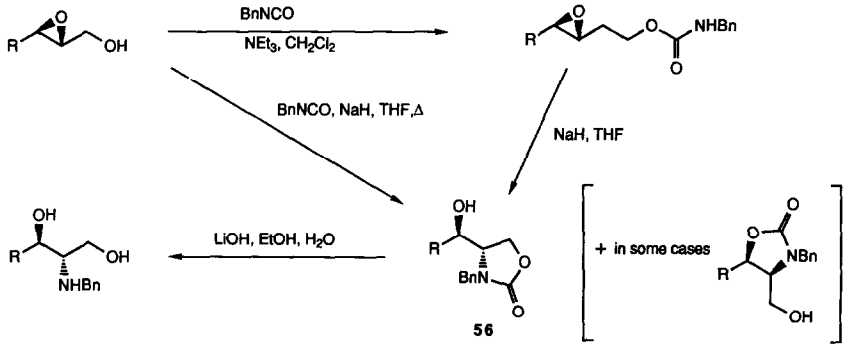
The use of cyanide as the nucleophile allows a variety of functional groups to be formed from the adduct (e.g. Scheme 125).[492a]



Scheme 125.

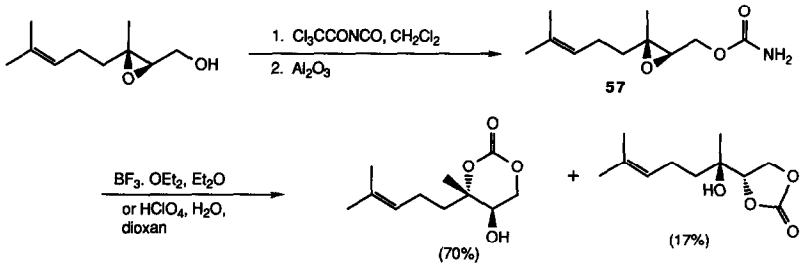
With good nucleophiles, under relatively mild conditions, 2,3-epoxy alcohols will undergo epoxide ring opening at C-2 or C-3. In simple cases, nucleophilic attack at C-3 is the preferred mode of reaction. However, as the steric congestion at C-3 is increased, or if substituents play a significant electronic role, attack at C-2 can predominate.[536b]

2,3-Epoxy alcohols react cleanly with isocyanates to provide the corresponding urethanes, which can then cyclize under basic conditions (Scheme 126). The same transformation could also be



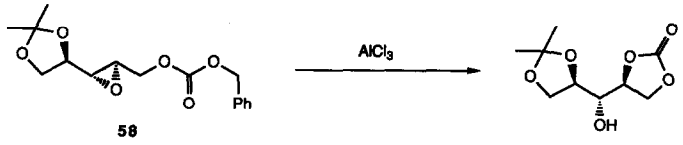
Scheme 126.

achieved as a one pot reaction. The resultant isoxazolidinones **56** are cleanly opened by lithium hydroxide to afford 2-amino-1,3-diols.[569] This methodology has been used for the preparation of β-hydroxy-α-*N*-methylamino acids.[545a] In contrast, acid treatment of the unsubstituted carbamate (**57**) afforded a mixture of cyclic carbonates (Scheme 127).[545b]



Scheme 127.

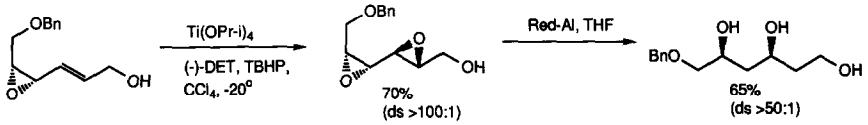
The intramolecular cyclization of the carbonate **58**, does proceed as expected (Scheme 128).[468c,570]



Scheme 128.

The presence of titanium tetraisopropoxide in the nucleophilic opening of 2,3-epoxy alcohols leads, not only to a marked increase in the reaction rate, but also to an increase in the regioselectivity for attack at C-3 with a wide range of nucleophiles.[536c,571]

In addition to the reactions with sulphur and nitrogen nucleophiles, regioselective reduction of an epoxy alcohol can be accomplished by sodium bis(methoxyethoxy)aluminium hydride (Red-Al).[553] Thus, this methodology can be used for a stereoselective synthesis of 1,3-diols, and has been extended to more complex systems (e.g. Scheme 129).[552,572]



Scheme 129.

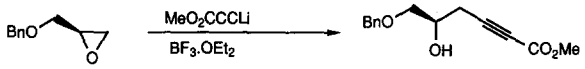
Complimentary to this methodology, epoxy alcohols undergo reaction at the 3-position with concomitant inversion of configuration when treated with organoaluminium reagents, including diisopropylaluminium hydride[553] and alkylaluminates.[548a] The reaction of trialkylaluminates is catalyzed by butyllithium or lithium methoxide and proceeds best in hydrocarbon solvents when the hydroxy group is protected as the benzyl ether.[573] This provides a method for the stereoselective synthesis of 1,2-diols (cf. Section 3.2).

Reduction of a 1,2-epoxy-3-ol protected as the ethoxyethyl ether, with lithium aluminium hydride proceeds by attack at C-1 and formation of a 2,3-diol,[562a] whereas attack at C-2 has been observed for a free alcohol.[468a]

An alternative method for the reduction of 2,3-epoxy alcohols to 1,2-diols through regioselective delivery of hydride at C-3 can be achieved by use of lithium borohydride in the presence of titanium tetraisopropoxide with benzene as solvent.[554a]

Epoxide opening with organocuprates is both regio- and stereo-selective, and affords the substituted 1,3-diol (Scheme 110).[42a,468e,551a,551b] However, when the 2,3-epoxy alcohol is not branched at C-4, cuprate epoxide ring opening may not be regioselective. This problem has been overcome, to a certain degree, by the use of higher order cuprates; the preferred mode of attack is once again at C-2.[551c]

The expected mode of attack, that is at the least substituted position of the epoxide, can be achieved with a wide range of nucleophiles if the hydroxy group of the epoxy alcohol is protected as an ether (Scheme 130).[574]



Scheme 130.

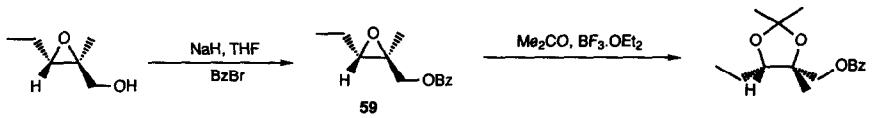
The 1,2-epoxy alcohols do react, as expected, with organometallic reagents at the primary position of the epoxide.[549] This aspect illustrates the importance of the isomerizations of epoxy alcohols (Schemes 118 and 119).

2,3-Epoxy alcohols can be oxidized to the corresponding epoxy acids by treatment with ruthenium chloride in the presence of sodium periodate.[556c] The analogous transformation to the aldehyde can be performed by use of Swern oxidation conditions.[559a]

The coupling of two reactions, namely the regioselective opening of a 2,3-epoxy alcohol by benzoate followed by ruthenium oxidation, allows for the enantioselective preparation of α-hydroxy acids.[525a]

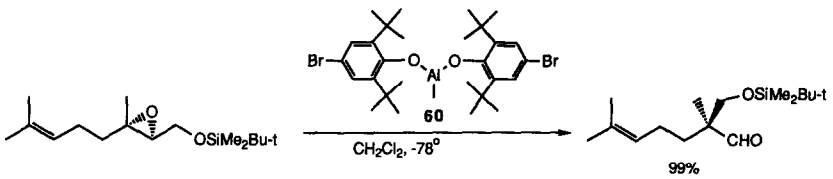
Protection of the hydroxy function in a 2,3-epoxy alcohol can have a significant effect on the

regiochemical outcome of a reaction. Acid catalysis during the ring opening of the α,β-epoxy ether **59** led to nucleophilic attack at the α-position, as evidenced by the inversion of stereochemistry at this centre (Scheme 131).[547,575]



Scheme 131.

Reaction of the silyl ether of an epoxy alcohol with the hindered aluminium reagent **60** leads to rearrangement and formation of the optically active β-siloxy aldehydes (Scheme 132).[576]



Scheme 132.

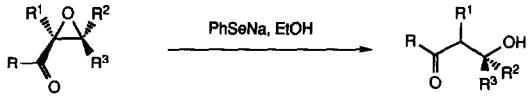
Finally, notwithstanding their amenability to ring opening, epoxides are relatively stable entities and, with care, can survive a number of synthetic sequences.[577]

4.7. *Oxidations and reactions of other unsaturated systems*

In addition to allyl alcohols, α,β-unsaturated carbonyl systems have also served as substrates for oxidation reactions. The products can undergo stereoselective reactions that often complement those observed for their allyl alcohol analogues;[251] some examples follow.

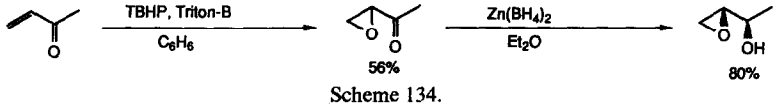
Epoxidation of enones in the presence of a *N*-benzylquinine salt may give optically active epoxides.¶[578] Enones have been converted to the corresponding α,β-epoxy ketones with a high degree of enantioselectivity by a triphasic system.[579] α,β-Epoxycarbonyl compounds are also available by a chromium-induced oxidative rearrangement of tertiary allyl alcohols.[580] An aldol-type condensation with α-halo ketones provides an alternative route to α,β-epoxy ketones.[581]

Treatment of an epoxy ketone with a selenide nucleophile provides an alternative route to an aldol-type product (Scheme 133).[582]



Scheme 133.

Although the stereochemistry for epoxidation may be difficult to control, relative stereochemistry can be controlled through reduction of the carbonyl group (Scheme 134).[583] The observed stereo-



Scheme 134.

¶ This result has been questioned.[247]

selection can be rationalized in terms of a chelate model,[492b] but the conformational model (as shown in Fig. 14) seems more likely, as the effect of α-substituents can be accounted for.[6i]

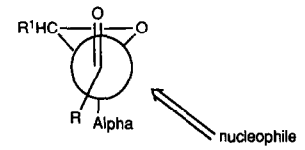
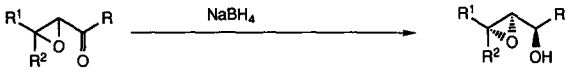


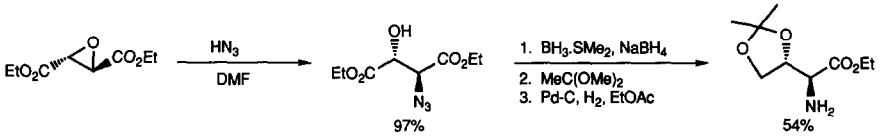
Fig. 14.

The carbonyl group of α,β-epoxy ketones can also be reduced with high stereoselectivity by sodium borohydride, as long as no α-substituent is present (Scheme 135).[492b,584] Use of zinc borohydride circumvents this limitation and results in the *pref*-isomer (cf. Scheme 134).[585]



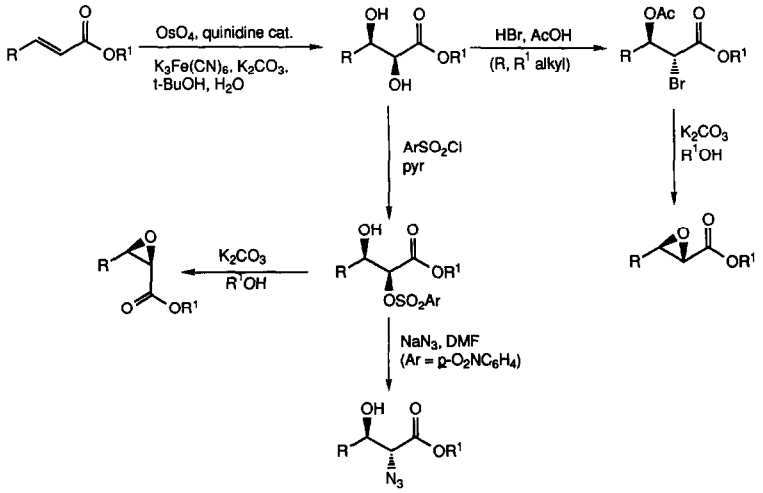
Scheme 135.

Oxidation of α,β-unsaturated esters may be achieved with peroxy acid[586] or dimethyldioxirane.[465b] Subsequent reaction with ammonia provides the β-amino-α-hydroxy acid.[586,587] In contrast, the epoxide can be opened with hydrazoic acid to provide β-hydroxy-α-amino acids (Scheme 136),[588] or treated with organoaluminates to provide α-hydroxy esters.[589]



Scheme 136.

α,β-Unsaturated esters are substrates for the asymmetric dihydroxylation methodology (Section 3.2.1.1) (Scheme 137).[590] The resultant diol can then be used to form a cyclic sulphite, which can undergo subsequent ring-opening reactions (Section 3.2.2). In addition, the 2,3-dihydroxy esters can be selectively reacted with arylsulphonyl chlorides at the 2-position. This then allows for epoxide formation or reaction with an external nucleophile (Scheme 137).[591]



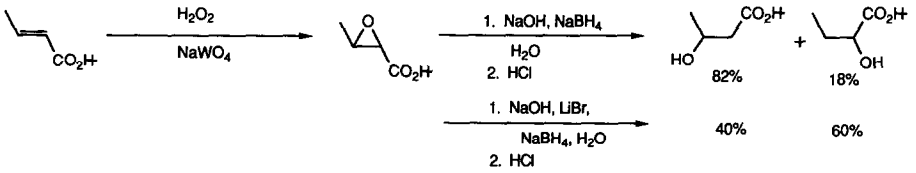
Scheme 137.

The Darzen condensation is a classical route to α,β-epoxy esters, but stereochemical control is difficult.[592] An alternative procedure is to react the dianion of a β-hydroxy ester with iodine, which provides the least hindered (*trans*) product due to control in the condensation step (cf. Section 4.9).[593]

α,β-Epoxy esters are attacked regioselectively by cuprates at C-2 to provide the β-hydroxy esters.[468b,593b] Reduction to β-hydroxy esters is available by a magnesium iodide catalyzed epoxide opening, followed by a tin reduction.[594]

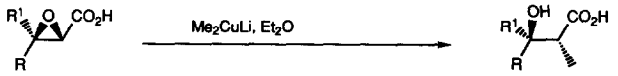
Lithium *t*-butylhydroperoxide oxidation of α,β-unsaturated esters which contain a chiral auxiliary in the ester portion can result in considerable asymmetric induction (20–100%).[595]

α,β-Epoxy acids are available by oxidation of the corresponding allyl alcohol with hydrogen peroxide in the presence of sodium tungstate; use of chiral amines then allows for resolution.[596] The reduction of these epoxides can be regioselective and is influenced by the counterion (Scheme 138).[597]



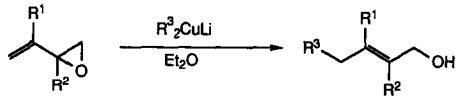
Scheme 138.

The epoxides of α,β-unsaturated acids are available from α-halo acids by a variant of the Darzen condensation.[598] 2,3-Epoxy acids are opened regioselectively by cuprates (Scheme 139).[599]



Scheme 139.

Conjugated dienes can be oxidized to monoepoxides in good chemical yields in the presence of molybdenum(VI), but the regioselectivity can be low.[232b] An alternative strategy, the Wittig condensation with an epoxy aldehyde, does provide the monoepoxide of a conjugated diene stereoselectively,[600] and telluride chemistry provides a further alternative.[601] These monoepoxides undergo S_N2' additions with organocopper reagents (Scheme 140) amongst other nucleophilic reagents.[602]



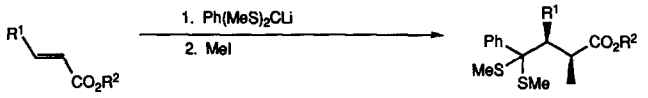
Scheme 140.

4.8. *Conjugate additions*[603]

The addition of a nucleophile to an α,β-unsaturated system involves a question of controlling facial selectivity.[604] Of course, the problem of 1,2- versus 1,4-addition must also be overcome,[17] and this aspect is often accomplished with a cuprate reagent,[605] although other metals, such as zinc, have been used.[606] Conjugate addition is usually observed when a 'soft', stabilized anion is employed as the nucleophile (*vide infra*).[607]

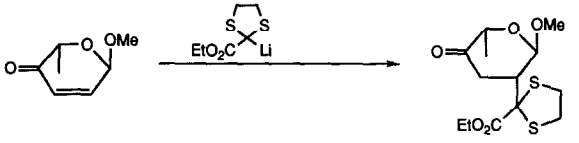
The resultant enolate is formed in a regioselective manner, and can undergo further elaboration, such as aldol condensations (Section 4.2), or silyl enol ether formation (Section 3.4.3.3).[339b,339f,340a] The methodology also allows for the introduction of functionality in both the nucleophilic and

electrophilic moieties.[40b,345,414a,608] In cyclic cases, the nucleophilic and electrophilic groups are introduced in a relative *trans*-configuration.[609] The methodology does translate to acyclic systems, provided that a large nucleophile is employed (Scheme 141).[610]



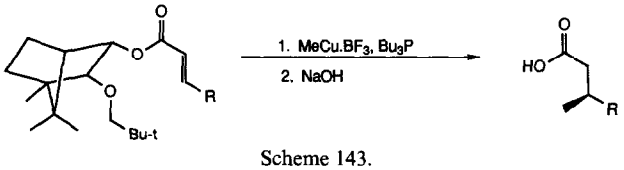
Scheme 141.

In cyclic systems, facial selectivity can be dictated by steric effects from appendant substituents (e.g. Scheme 142).[611]

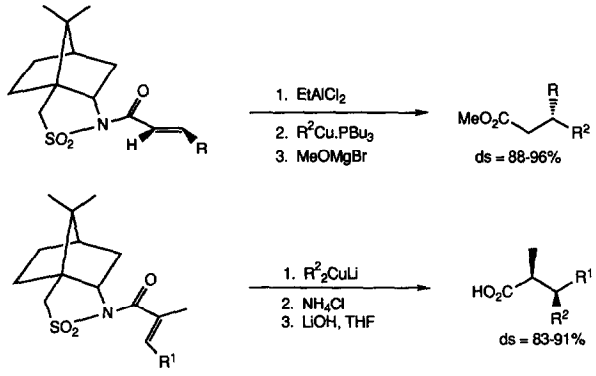


Scheme 142.

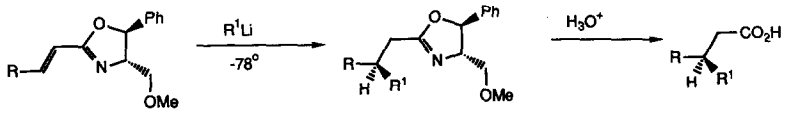
Control in acyclic systems has centred around the use of chiral auxiliaries, for example in esters (Scheme 143),[612] sultams (Scheme 144),[359i,612c,613] oxazolines (Scheme 145),[363e,443b,443c,614] imides,[615] imines,[615,616] amides,[617] enamines,[618] hydrazones,[619] oxazepines,[620] oxazionones,[621] aminals (Scheme 146)[622] and β-alkoxy sulphones (Scheme 147),[137c] amongst others.[349c,623]



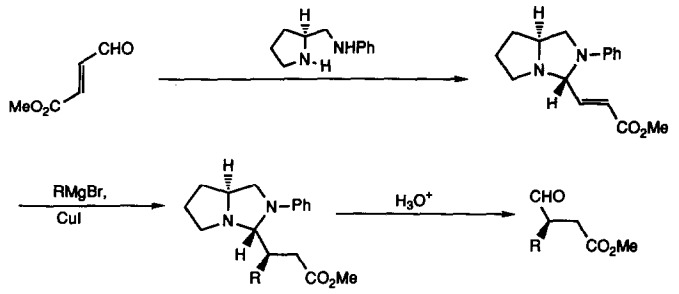
Scheme 143.



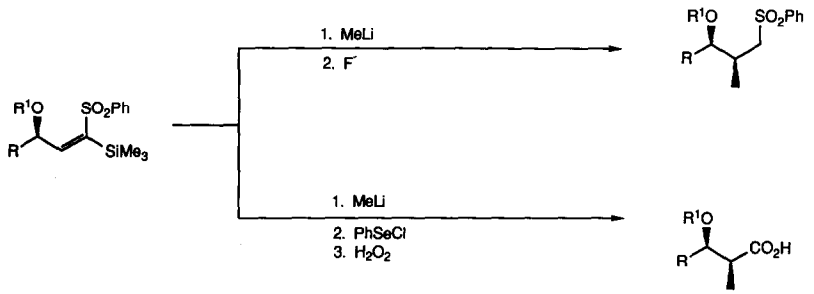
Scheme 144.



Scheme 145.

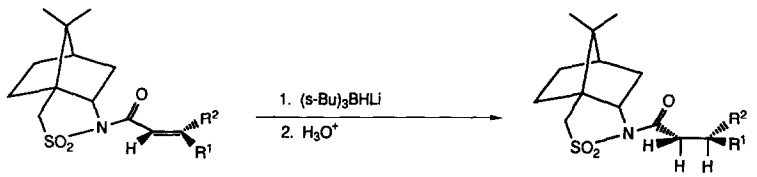


Scheme 146.



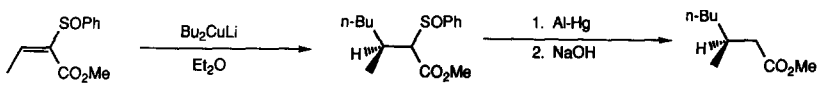
Scheme 147.

These systems not only allow for the stereoselective 1,4-addition of an alkyl group to an α,β-unsaturated system, but also conjugate reductions (Scheme 148).[624] This flexibility can allow for alternative stereochemistry to be available at the β-position.



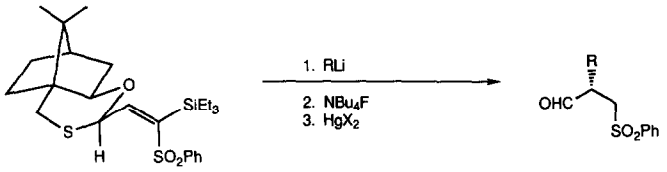
Scheme 148.

Asymmetric conjugate additions are observed when a chiral sulphoxide is present on the α-position of the enone. Although most of this work has focused on cyclopentenone derivatives,[625] examples are available in the acyclic (Scheme 149)[626] and lactone series.[627] Selectivity is also observed for simple chiral sulphoxides and sulphoximines.[628]



Scheme 149.

Conjugate addition to a vinyl sulphone in an asymmetric manner can be achieved in the presence of an adjacent chiral auxiliary (Scheme 150)[629] or asymmetric centre.[630]



Scheme 150.

With organocuprates, the addition of chiral chelation agents, such as sparteine, results in only low levels of asymmetric induction.[603,631] Higher optical yields were obtained with proline derivatives[632] and chiral copper complexes.[633] Chiral ligands for organozinc reagents also allow asymmetric 1,4-additions.[634]

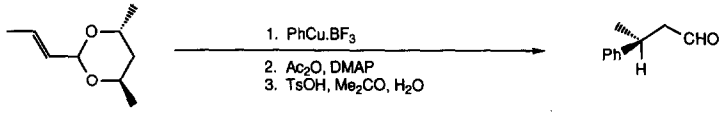
Michael additions can be catalyzed by chiral phase transfer catalysts, although optical yields are variable.[247,635]

Conjugate addition of enolate of methyl dithioacetate provides the *pref*-isomer, rather than that predicted by Houk's rule (Section 4.1). This selectivity has been interpreted in terms of an intramolecular proton transfer.[636]

A conjugate addition methodology allows functionalization at the α-position of an unsaturated system through use of a masking group to protect the unsaturation.[171d,637] Indeed, some enantioselectivity has been observed for the addition of thiols to anones.[635b,638] The nucleophile that partakes in a conjugate addition can be chiral, such as a sulphoxide,[354c,639] a β-hydroxy ester[640] or an oxazepine.[641] As an alternative, a chiral ligand can be used to provide induction (*vide supra*).[642]

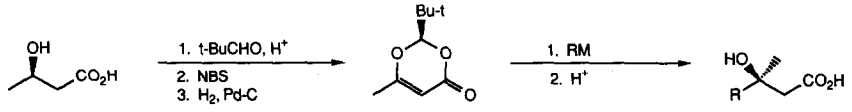
As yet, no universally applicable model has been found to predict the stereochemical outcome of a 1,4-addition, but significant advances are being made in this area.[643] The use of chiral ligands with cuprates has led to a transition state proposal for use with cyclic enones.[644] Michael addition is promoted by the presence of a Lewis acid,[645] or a silyl chloride,[646]and these experimental results are providing information about the transition state requirements.[647]

The use of an acetal allows for the introduction of a chiral moiety (e.g. Scheme 151).[648]



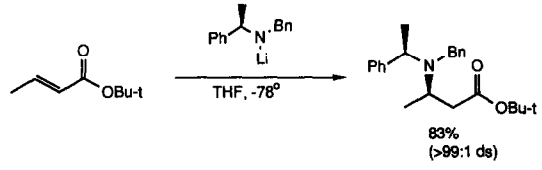
Scheme 151.

The self-regeneration of a stereogenic centre provides a powerful method for the preparation of β-hydroxy acids (Scheme 152).[646b,649]



Scheme 152.

The use of a nitrogen nucleophile in a Michael addition provides a rapid entry to β-amino acids (Scheme 153).[642a,650]

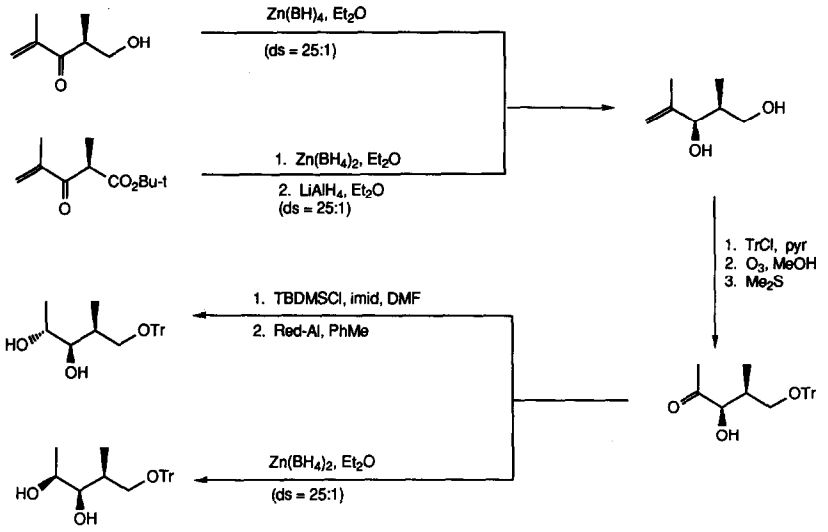


Scheme 153.

4.9. *Reactions of β-functionalized carbonyl systems*[338b]

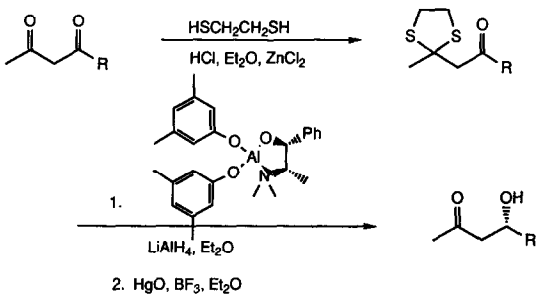
Aldol products, as well as β-dicarbonyl systems, can undergo stereoselective reductions or alkylations. Thus, these reactions augment those already described.

4.9.1. *Reductions.*[197c,651] α-Alkoxycarbonyl compounds are reduced stereoselectively by a careful choice of reductant and protective group (Scheme 154).[652] The observed stereoselection correlates directly to Anh–Felkin or chelation control, as governed by the relevant variables.[653]



Scheme 154.

β-Dicarbonyl compounds have been reduced selectively, allowing an alternative to stereoselective aldol reactions (Scheme 155).[1,654] Other dicarbonyl systems can also be reduced in an asymmetric manner,[655] such as by hydrogenation (Section 4.11).[656]

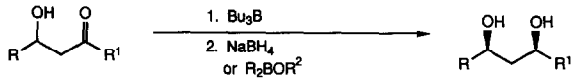


Scheme 155.

Reduction of an α,β-unsaturated carbonyl system can proceed in a 1,2- or 1,4-manner.[657] A number of metal hydride reagents have been developed that not only provide conjugate reduction, but achieve asymmetric reduction on the basis of their chiral auxiliaries.[6o,658] A chiral reducing agent has been developed for the 1,2-reduction of enones, and this methodology was paramount in a synthesis of ginkgolide.[258a,659]

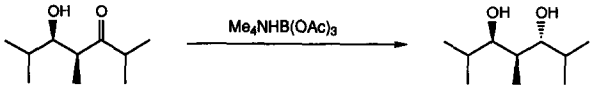
The use of binaphthol-derived aluminium hydrides allows for high asymmetric induction in the reduction of ynones.[320] The asymmetric reduction of enamines provides β-amino acids although optical yields are not high (cf. Section 4.11).[660]

β-Amino and β-hydroxy ketones have been reduced selectively (Scheme 156).[661]



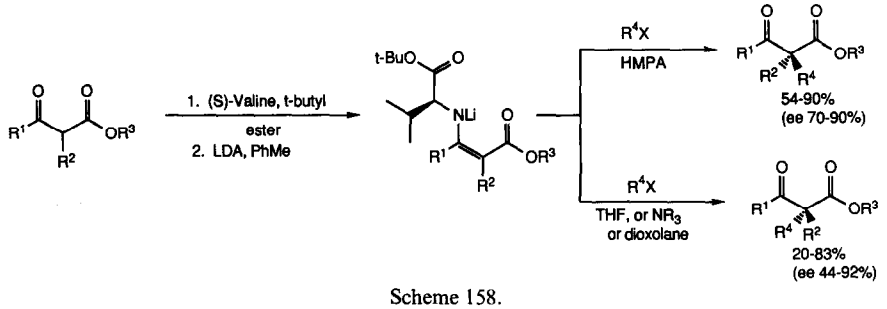
Scheme 156.

The *syn*-diols are available by a borane, Dibal or tin hydride reduction,[662] but the size of an α-(C-2)-substituent can have a significant stereochemical effect.[663] The mild reagent, tetramethylammonium triacetoxyborohydride, provides the *ancat*-diol with high selectivity (Scheme 157).[664]



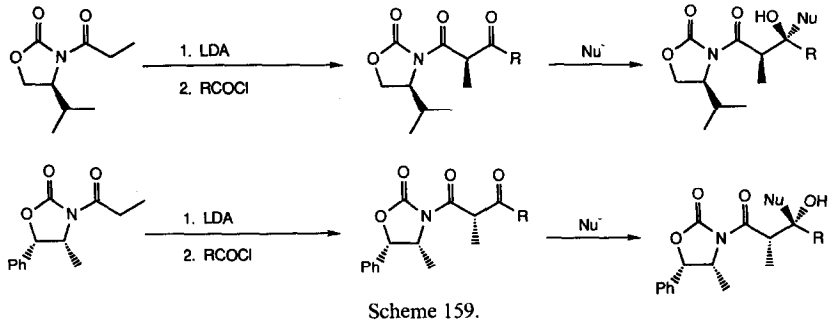
Scheme 157.

4.9.2. *Alkylations.* The regioselective alkylation of β-dicarbonyl compounds can be controlled through the use of the mono- or di-anion. The dianion usually undergoes reaction at the distal carbon atom,[484a,665] while the monoanion provides substitution at the central carbon atom; diastereoselection is usually poor.[666] Asymmetric induction can be achieved through incorporation of a chiral auxiliary. Use of different conditions for the alkylation of the enamine derived from valine allows for facial selectivity; top face attack is preferred in toluene in the presence of hexamethylphosphoric triamide, whereas bottom face attack takes place in the presence of THF, dioxane or an amine (Scheme 158).[475]



Scheme 158.

Asymmetric induction has been observed for the alkylation of a cyclic β-dicarbonyl compound in the presence of a chiral phase transfer catalyst[667] or an amino acid chiral auxiliary (cf. Section 4.8).[618c] Malonic acid derivatives have been successfully alkylated in an asymmetric manner through the incorporation of a chiral auxiliary in a monoester.[668]

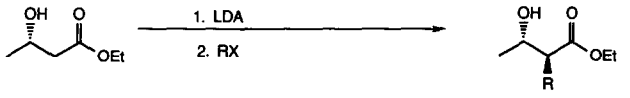


Scheme 159.

An alternative strategy to chiral β-dicarbonyl systems is through acylation of an enolate. The adducts can then undergo nucleophilic addition, including reduction (Scheme 159).[669]

The use of pyrrolidine chiral auxiliary allows for the asymmetric alkylation of α-cyanoacetic acid.[670]

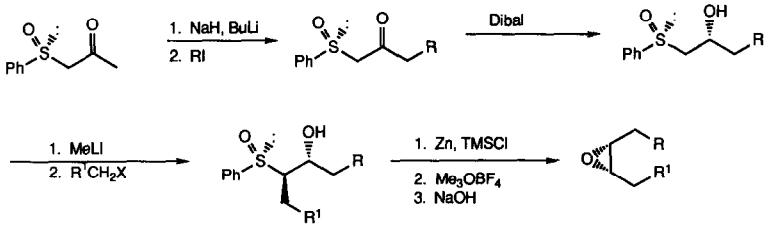
β-Hydroxy esters can be alkylated with a high degree of selectivity.[593b] β-Alkoxycarbonyl compounds, available by an aldol protocol, provide a better opportunity for asymmetric alkylations as a chiral centre is already present within the substrate (Scheme 160).[671] The affect is attributed to the chelation effect which shields one face of the enolate.[672]



Scheme 160.

A silyl group can be used as a latent hydroxy group to provide the equivalent transformation (Section 4.12.1).[673]

Sulphoxides provide a convenient method for performing stereoselective alkylations (Schemes 100 and 161).[674] The products can be converted into a wide variety of other compounds including epoxides, β-hydroxy esters and lactones.[675]

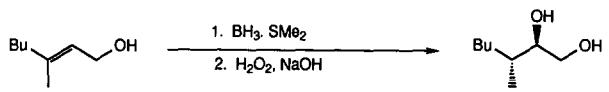


Scheme 161.

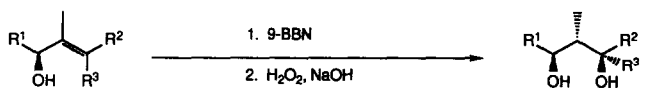
β-Amino esters can be alkylated with a wide degree of diastereoselection. The products can be used to prepare a wide range of compounds.[676] Enone alkylation can be achieved by a protection methodology (Section 4.8).[393a,677]

4.10. *Hydroborations of allyl systems*[197c,678]

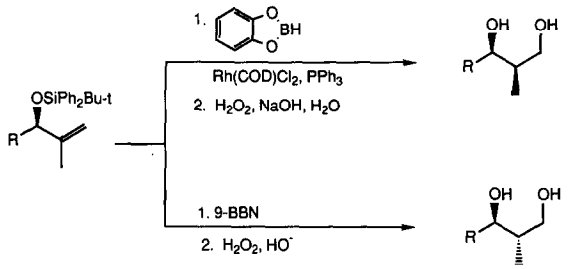
In addition to the power of hydroboration with chiral reagents (Section 3.2.3), the reaction of a borane with an allyl alcohol or derivative can provide control over relative stereochemistry (Scheme 162).[548a] The outcome does depend on the degree of substitution; indeed, in most reactions the *ancat* isomer of the 1,3-diol predominates (Scheme 163).[468e,679] The most sterically demanding



Scheme 162.

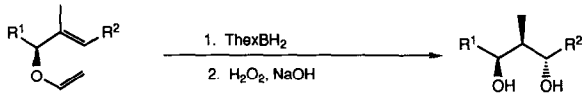


Scheme 163.



Scheme 164.

boranes afford better stereoselectivity, so the outcome is then consistent with Houk's rule.[15e,200b] The selectivity may be reversed by the use of a rhodium catalyst (Scheme 164),[680] or by use of a vinyl ether (Scheme 165).[624c,681] If the hydroxy group of the allyl alcohol is protected, anti-Markovnikov addition is observed with *syn*-addition control of relative stereochemistry.[682] For the rhodium-catalyzed additions, the larger the protection, the better the induction observed, and the oxygen acceptor group then adopts the *anti*-position.[680a] Clearly, an oxygen atom is not a prerequisite for Houk-type addition; indeed, allylsilanes provide a useful entry to 1,3-diols (Section 4.12.1).[683] Hydroboration of allylamines with, or in the absence of, a rhodium catalyst to give 1,3-amino alcohols parallels the reactions of allyl alcohols and ethers.[684]

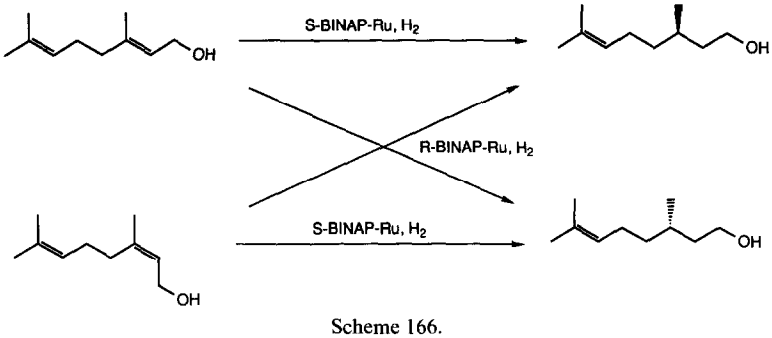


Scheme 165.

4.11. *Hydrogenations*[207,208d,209b,209c,685]

Unlike the situation for isolated double bonds, considerable success has been realized for the reductions of functionalized alkenes. For example, α,β-unsaturated esters and acids undergo stereoselective reductions (see also Section 4.9.1).[6f,6o,686] Introduction of an amide group then allows for the asymmetric synthesis of α-amino acids.[6f,6o,209b,687] The amide ligand is essential for selectivity. Kinetic resolution in an asymmetric reduction of an α-amidoalkyl acrylate has been observed.[523]

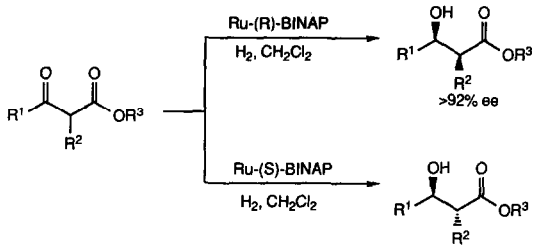
Allyl alcohols can be reduced to either antipode (Scheme 166).[688]



Scheme 166.

Unfortunately, the stringent requirements of functional group arrangement within the substrate detract greatly from the general application of asymmetric hydrogenations, although a plethora of ligands have been investigated to overcome this limitation.[6o,689] However, it is possible to reduce

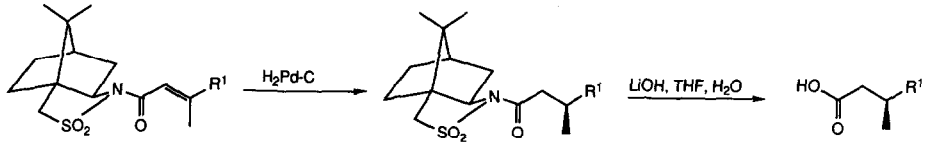
appropriately substituted α,β-unsaturated acids with good optical yields.[690] β-Keto esters can also be reduced by an asymmetric hydrogenation (Section 4.9.1).[691] This methodology is extremely powerful when a kinetic resolution occurs and the β-keto ester can equilibrate (Scheme 167).[692]



Scheme 167.

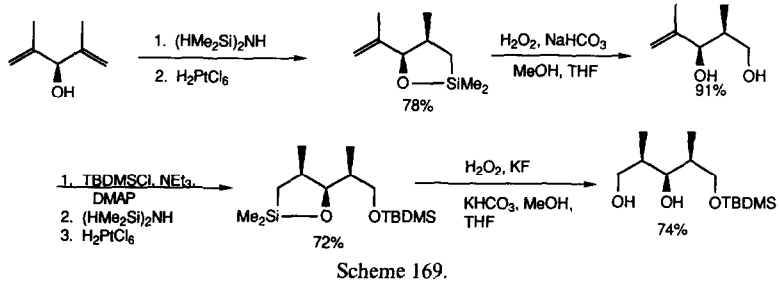
Substituted allyl alcohols bearing a chiral auxiliary are reduced selectively. However, the extent of diastereoselection depends upon the catalyst to substrate stoichiometry.[693]

α,β-Unsaturated amides with a chiral nitrogen moiety provide an efficient asymmetric hydrogenation protocol to carboxylic acids (Scheme 168).[694]



Scheme 168.

Hydrosilylation has been used to reduce a number of conjugated functional groups;[212e,695] the use of allyl alcohols allows a stereoselective synthesis of 1,3-diols (Scheme 169).[696]

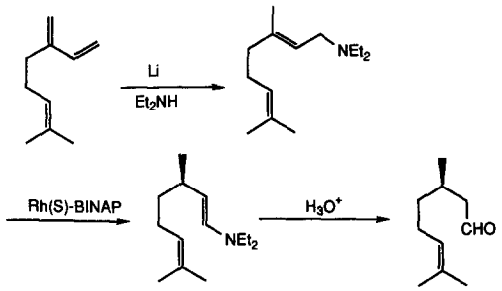


Scheme 169.

In many cases, the constraints of a cyclic system allow for facial selectivity during the reduction. This effect has allowed for the asymmetric synthesis of amino acid derivatives.[697]

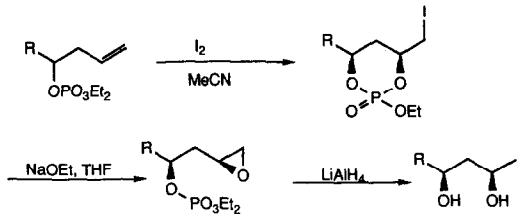
4.12. *Other reactions*

In addition to the general reactions cited above, others have proven useful for the preparation of 1,3-functionality. Rhodium BINAP catalyzes the asymmetric isomerization of an allylamine to an enamine (Scheme 170).[698]



Scheme 170.

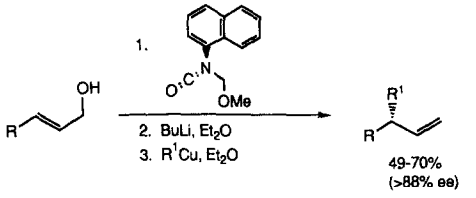
Homoallyl alcohols provide an entry into 1,3-diols (Scheme 171);[699] the analogous reaction with allylamines provides 1,2-amino alcohols as the four-membered cyclic intermediate is formed.[700] The two hydroxy groups of a *meso*-1,3-diol can be differentiated by Lewis acid promoted ring opening of the corresponding spiroketal derived from menthone.[701]



Scheme 171.

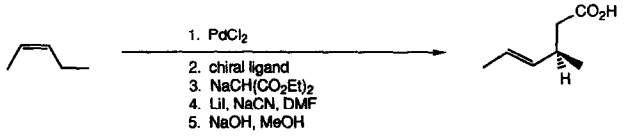
The pivotal role of glycerol has led to the development of many synthetic methods to control both relative and regiochemical problems associated with hydroxy group protection.[702]

4.12.1. *Allylic alkylations.*[38c,703] Allylic systems can undergo nucleophilic substitution in the S_N2 or S_N2' reactions.[704] Regiochemistry can often be controlled, such as by the use of cuprates.[130b,141b,154,705] This methodology has been employed for the regioselective synthesis of allylsilanes, where the urethane gives better selectivity than the corresponding acetate.[706] Use of carbamate as a chiral auxiliary does allow for some asymmetric induction (Scheme 172).[707]



Scheme 172.

The use of a metal catalyst, such as palladium, does allow for some asymmetric induction when an allylic system is treated with a stabilized ester anion (Scheme 173),[708] or with other nucleophiles.[148f,681a,708c,709] This approach also allows for the kinetic resolution of allyl acetates.[710]



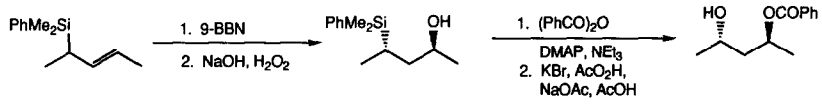
Scheme 173.

The methodology suffers from competition between *syn* and *anti* mechanisms in acyclic cases. Indeed, the pathway may depend on the nature of nucleophile and substrate.[703a,711]

4.12.2. *Reactions of functionalized silanes.*[330e,712] Organosilicon chemistry allows for a wide variety of transformations, often in a stereoselective manner. The use of this chemistry has expanded greatly by the development of methods for conversion of a silyl group to an alcohol.[713] Many of the reactions in this section comply with Houk's rule (Section 4.1)[15e] – the silyl group acts as the large substituent.

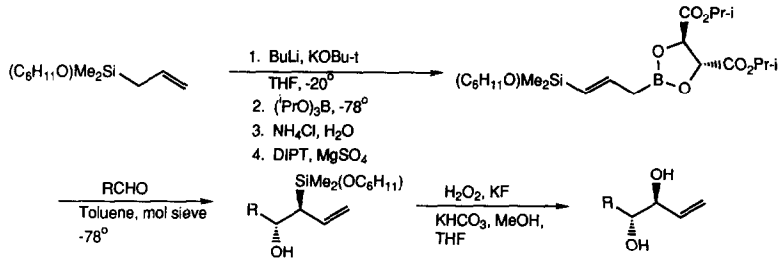
Allylsilanes allows for the regiochemical introduction of a wide variety of electrophilic species.[111,155e,371b,714] An intramolecular proton transfer can provide good asymmetric induction.[715] Conversion of the silyl group to hydroxy then provides an allyl alcohol.[716]

Reaction of a chiral allylsilane with an aldehyde provides the homoallyl alcohol with good asymmetric induction (Section 2.3). Oxidative cleavage of the unsaturation affords the β-hydroxy acid (Scheme 18).[51a,717] The selectivity arises from the *anti*-SE′ mode of the reaction. Indeed, condensation of a chiral allylsilane with a wide variety of electrophiles proceeds with high asymmetric induction.[718] Allylsilanes undergo hydroboration with good regio- and stereo-chemical control. The resultant alcohols can be converted to 1,3-diols (Scheme 174).[683,719]



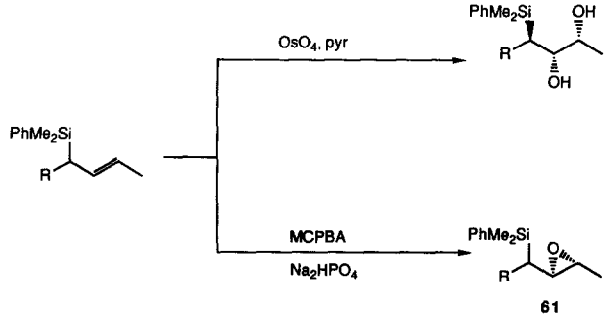
Scheme 174.

Ancat-1,2-diols are available by reaction of an allylborane with an aldehyde followed by oxidative substitution of a silyl group. The use of a chiral tartrate ligand on the boron also allows for enantioselectivity (Scheme 175).[93a]



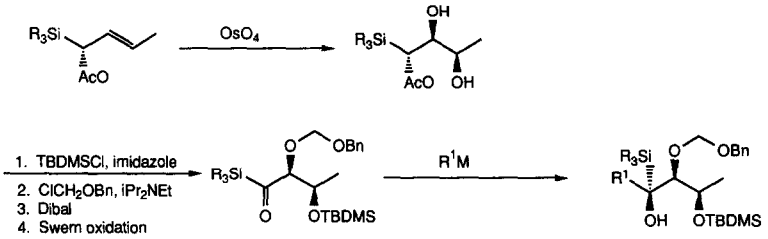
Scheme 175.

Phenyldimethylallylsilanes react with osmium tetroxide and MCPBA according to Houk's rule; the stereoselection, however, can be low for the methyl series (R = Me) (Scheme 176).[720] Reaction of the epoxysilane **61** with fluoride ion then yields an allyl alcohol.[721]



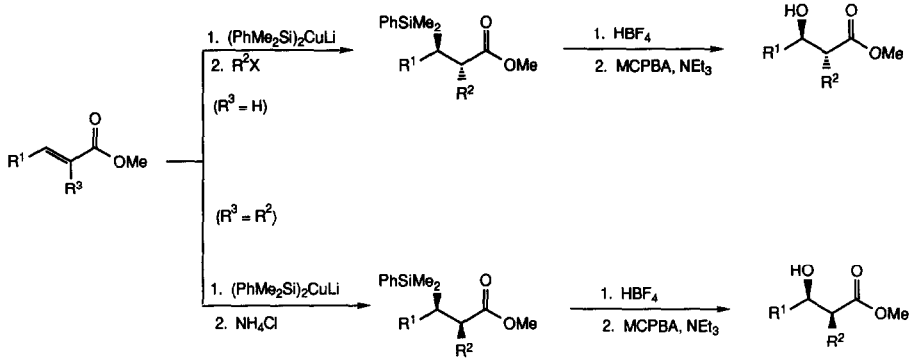
Scheme 176.

A related sequence uses an α-alkoxysilane and Anh–Felkin controlled addition of an acylsilane (Section 3.4.2.1) (Scheme 177).[722]

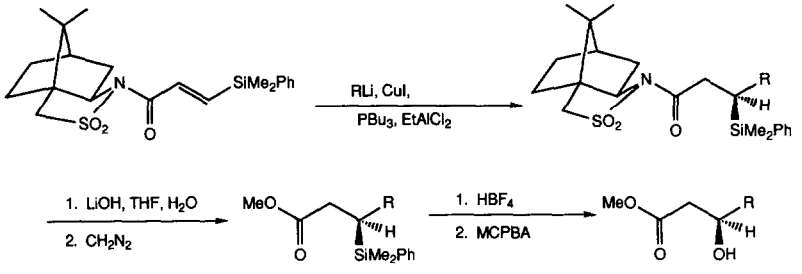


Scheme 177.

β-Hydroxy esters are available through conjugate addition of a silyl cuprate and then alkylation, the sequence of addition controlling the relative stereochemistry (Scheme 178).[413a,612c,673,723] The selectivity observed is attributed to electronic factors.[673] The scheme can be extended to aldol reactions,[724] and has been made asymmetric through employment of a chiral auxiliary (Scheme 179).[612c]



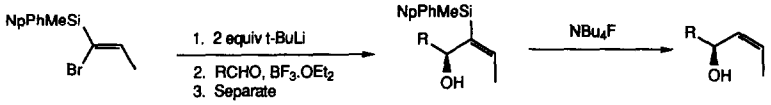
Scheme 178.



Scheme 179.

Conjugate introduction of a silyl group to an enone provides an approach to β-hydroxy ketones.[725] Vinyl sulphoxides can also serve as Michael acceptors for silylcuprates.[630b]

The use of a chiral vinylsilane does allow for the preparation of chiral allyl alcohols, although a separation of the intermediate diastereoisomers is required (Scheme 180).[726]



Scheme 180.

Hydrosilylations of allyl alcohols provide a stereoselective approach to 1,3-diols (Scheme 169).[696a]

5. CONCLUSIONS

Many methodologies have been developed for, and applied to, the synthesis of carbohydrate derivatives. The application of some of these methods, and the use of approaches that establish stereochemistry at multiple centres will be discussed elsewhere.[1]

An understanding of some reactions that have been available for a considerable period of time, such as epoxidation, hydroboration and the aldol reaction, has allowed the subsequent development of asymmetric methods. Other methodologies, such as hydrogenation, still require the development of a general reagent system which can be used on a broad range of substrates. Despite these shortcomings, there are still a large number of transformations available that can be used for the synthesis of carbohydrate derivatives.

Table 4.

List of abbreviations and acronyms used in this review.

AIBN	2,2'-azobis(2-methylpropionitrile)	LiHMDS	lithium hexamethldisilazide
ancat	like substituents on opposite side of zig-zag chain	MCPBA	m-chloroperoxybenzoic acid
		Ms	mesyl
9-BBN	9-borabicyclo[3.3.1]nonyl	NaHMDS	sodium hexamethyldisilazide
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl	Nap	naphthenyl
		NBS	N-bromosuccinimide
Bn	benzyl	NCS	N-chlorosuccinimide
Chx	cyclohexyl	NMMO	N-methylmorpholine-N-oxide
Cp	cyclopentadienyl	Np	naphthenyl
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone	parf	priority anti-reflective
		pref	priority reflective
de	diastereoisomeric excess	pyr	pyridine
DEAD	diethyl azodicarboxylate	Ra Ni	Raney nickel
DET	diethyl tartrate	Red-Al	sodium bis(2-methoxyethoxy)-aluminium hydride
DIPT	diisopropyl tartrate		
DME	1,2-dimethoxyethane	salen	N,N'-bis(salicylideneamino)-1,2-dipenylethane
DMF	N,N-dimethylformamide		
DMAP	4-dimethylaminopyridine	syncat	like substitutents on same side of zig-zag chain
DMPU	N,N'-dimethyl-N,N'propyleneurea		
DMSO	dimethylsulphoxide	TBDMS	t-butyldimethylsilyl
DPTA	(2R,3R)-dipivaloyltartaric acid	TBDPS	t-butyldiphenylsilyl
ds	diastereoselectivity	TBHP	t-butyl hydroperoxide
Eapine	B-iso-2-ethylapopinocampheyl-9-borabicyclo[3.3.1]nonyl	Tf	triflate
		TFA	trifluoroacetyl (or trifluoroacetic acid)
ee	enantiomeric excess		
es	enantioselectivity	thexyl	2-(2,3-dimethylbutyl)
HMPA	hexamethylphosphoric triamide	THF	tetrahydrofuran
2^d-Icr	2-isocaranyl	tol	p-tolyl
Imid	imidazole	TMEDA	N,N,N',N'-tetramethylethylene-diamine
Ipc	isopinocamphenyl		
$(Ipc)_2BH$	diisopinocamphenylborane	TMS	trimethylsilyl
$KN(TMS)_2$	potassium hexamethyldisilazide	Ts	tosyl (p-toluenesulphonyl)
LDA	lithium diisopropylamide	umpolung	reversal of a functional group's natural polarity

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