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THE SYNTHESIS OF CARBOHYDRATE DERIVATIVES FROM ACYCLIC PRECURSORS

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CONTENTS

1. INTRODUCTION

In a previous Report, we described methodologies that lead to the establishment of 1,2- or 1,3-difunctionality with a further potential for the synthesis of carbohydrate derivatives.[1] This Report describes reactions which have been used to prepare carbohydrate derivatives and methodologies for the preparation of contiguous chiral centres. By this definition, a carbon atom with no functional group that is part of the backbone, yet is still an asymmetric centre because of an alkyl substituent, can be accommodated with ease.* The chemistry of sugars and the conversion of one carbohydrate to another have not been addressed.[2] Thus, many reactions which manipulate specific hydroxyl groups in a carbohydrate system have been omitted.[3]

Many of the methods described herein were developed, and have been employed successfully, in cyclic systems. These methodologies have been included, where appropriate, as many carbohydrates exist in a cyclic form. In addition, the Baeyer–Villiger reaction,[4] together with other oxidative cleavages,[5] are very powerful tools for the conversion of a carbocycle to a carbohydrate derivative. However, many methods that rely solely on the topological properties of a ring structure to bring about stereochemical induction have been omitted.

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.[6]†

2. ACYCLIC SYNTHETIC METHODOLOGY

2.1. 1,4- *and Higher functional groups*[8]

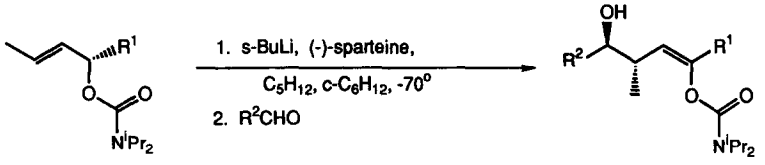
Some of the methods that have been developed to establish 1,2- and 1,3-difunctional compounds have been extended to prepare polyfunctional compounds, including carbohydrate derivatives. The simple applications of these methodologies have already been described,[1] but the relevant extensions are described below. In addition, methodology that has been specifically developed to prepare 1,4-, 1,5- and 1,ω-difunctional compounds from acyclic precursors is covered in this section.

The majority of methods used to achieve the stereoselective introduction of acyclic 1,4-difunctionality are based on those already discussed for 1,2- and 1,3-functionalisation.[1] An example of this is the hydrogenation of homoallyl alcohols.[9] Extended aldol methodologies[10] or organometallic reactions[11] can provide highly functionalized products (*vide infra*).

2.1.1. *Uses of allylorganometallic reagents.*[1,12] The addition of allylorganometallic reagents to a carbonyl compound results in the formation of a homoallyl alcohol;[13] epoxides can also be used as the electrophile to provide 4-en-1-ols.[14] If a chiral ligand is present on the metal, particularly with boranes,[15] asymmetric induction may be observed.[16] In addition, other functional groups can be tolerated in the nucleophilic species;[1,11,17] this then allows a rapid entry to highly functionalised compounds (Scheme 1).[17a]

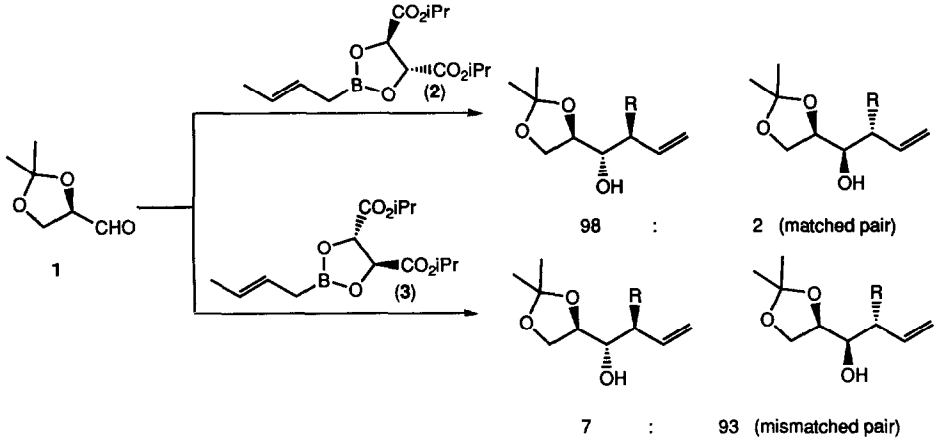
* Throughout this Report, in the interest of space, only the *major* isomer of a reaction product is shown. In addition, when a racemic mixture results, only one isomer is illustrated.

† Alternative nomenclature systems have also been proposed to avoid this dilemma (see reference 7, and citations contained therein).



Scheme 1.

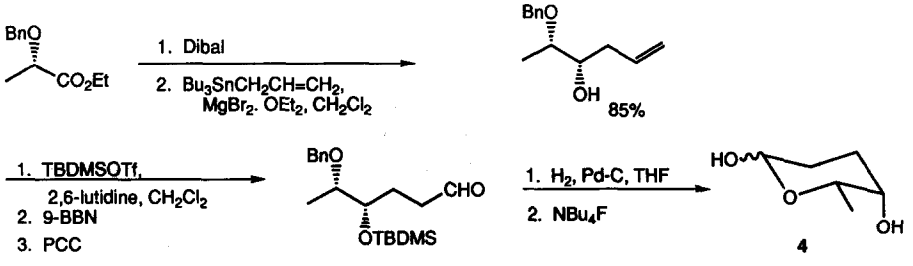
The presence of a chiral centre within the electrophilic moiety provides the possibility for double asymmetric induction (Scheme 2).[18] The selectivity observed with the mismatched pair (**1** and **3**) is lower than that for the corresponding matched pair (**1** and **2**). The induction observed has been rationalised by the interactions of the lone pairs within the transition state.[18a]



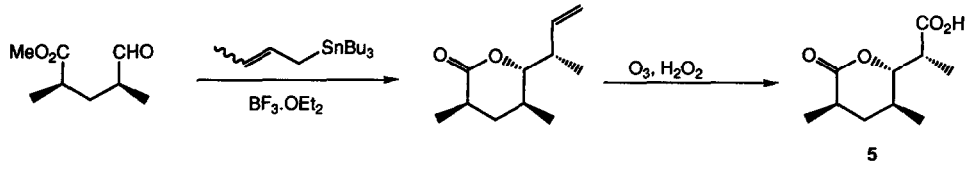
Scheme 2.

In addition, if the α-group contains a heteroatom, this can influence the stereochemical outcome of the reaction by chelate formation (*vide infra*).[19]

2.1.1.1. *Examples of carbohydrate synthesis through the use of allylorganometallic reagents.*[20] Allylstannanes have provided methodology to a number of carbohydrate derivatives as illustrated by the expeditious synthesis of L-rhodinose **4** (Scheme 3),[21] and the Prelog–Djerassi lactone **5** (Scheme 4).[22]

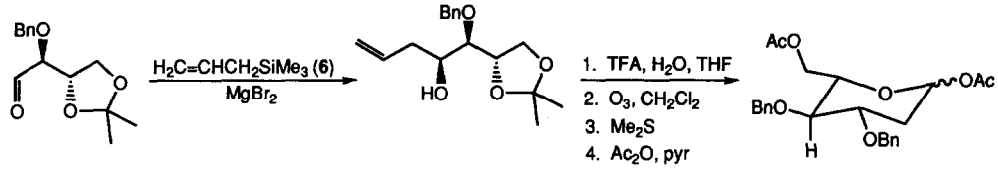


Scheme 3.



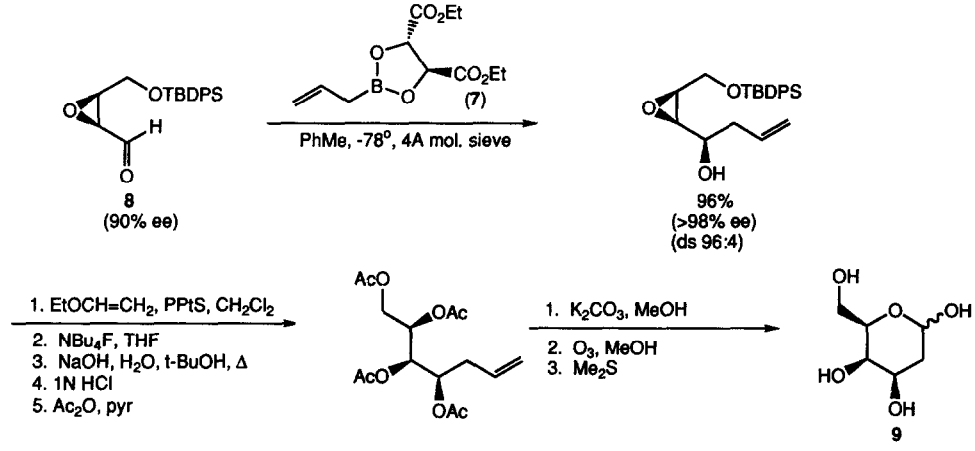
Scheme 4.

L-Hexose derivatives are available from the condensation of allyltrimethylsilane **6** with a chiral aldehyde in the presence of magnesium bromide (Scheme 5).[23]



Scheme 5.

The selective reaction of the allylborane **7** with the epoxyaldehyde **8**, as a matched pair, led to a preparation of 2-deoxy-D-galactose **9** (Scheme 6).[24] An allylborane approach also provided a D-oliose derivative.[25]



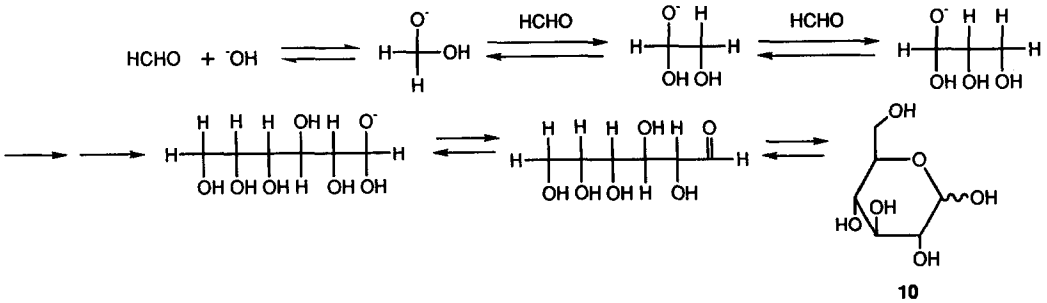
Scheme 6.

2.2. *Reactions of carbonyl compounds*[1]

The reactions of carbonyl compounds (nucleophilic attack at the carbonyl centre, α-alkylation, and aldol-type reactions) have all been extended to prepare polyfunctional compounds. In addition, conjugate additions to unsaturated carbonyl compounds can provide remote functionality. As the underlying principles are the same as for simple substrates, representative examples only have been included in the following sections.

2.2.1. *The formose reaction.*[26] The formose reaction affords a useful method for the formation of poly-1,2-diol units from formaldehyde.[27] The reaction occurs in the presence of a base,[28] such as calcium hydroxide.[29] Despite the large number of potential products, a single monosaccharide, such

as glucose,[30] can result through a careful choice of reaction conditions.[31] As the reaction is a series of equilibria, glucose **10** is the major product as all of the ring substituents are equatorial (Scheme 7). The condensation proceeds by way of a hydride transfer from the alcohol chain to formaldehyde.[26b,29c] The major competing pathway is the Cannizzaro reaction.[32]

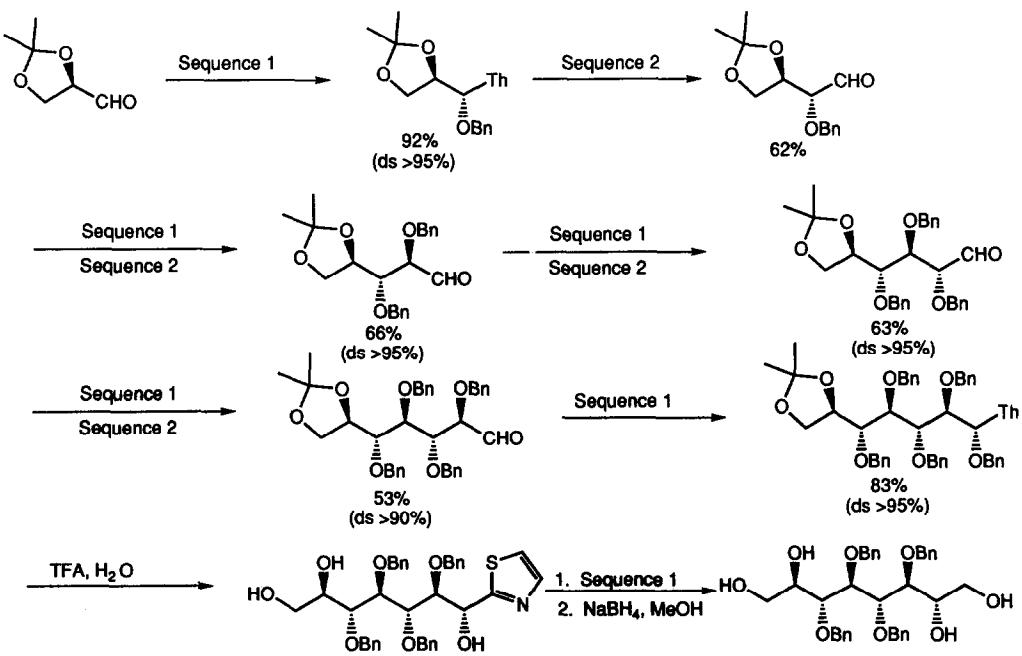


Scheme 7.

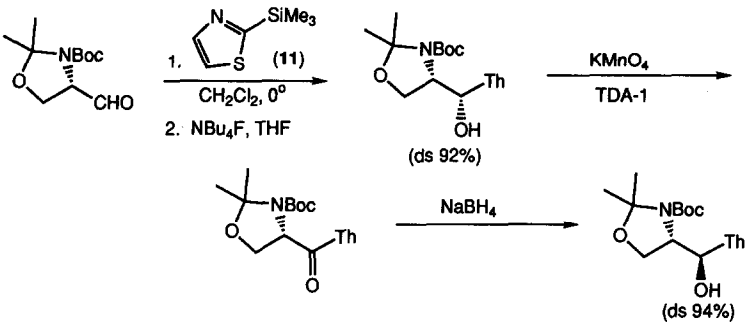
The use of this reaction, however, has practical problems of execution on a small scale, including isolation of the product,[33] and is more amenable to an industrial scale.[26]

The formose reaction is also catalysed by thiazolium salts, such as thiamin; these catalysts have provided a selective method for the conversion of formaldehyde to 1,3-dihydroxyacetone.[34]

An iterative process that adds a one carbon unit to a carbonyl compound is better suited in the laboratory to the use of a formyl anion equivalent.[35] The addition of the formyl anion equivalent has to be diastereoselective; 2-trimethylsilylthiazole (ThTMS) **11** has been advocated, as the addition provides the *ancat*-isomer.[36] The use of this iterative process is illustrated by the synthesis of the *meso*-octitol derivative **12** (Scheme 8).[37]



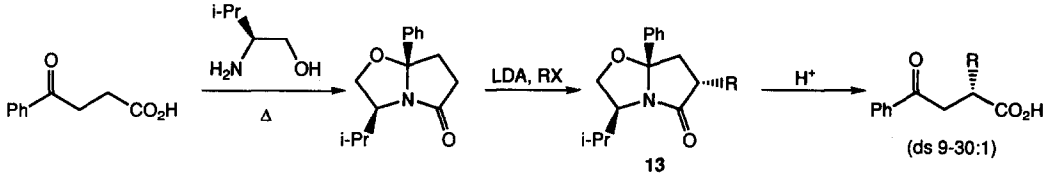
Scheme 8.



Scheme 9.

The limitations of this stereoselective addition can be overcome by an oxidation–reduction procedure (Scheme 9).[38]

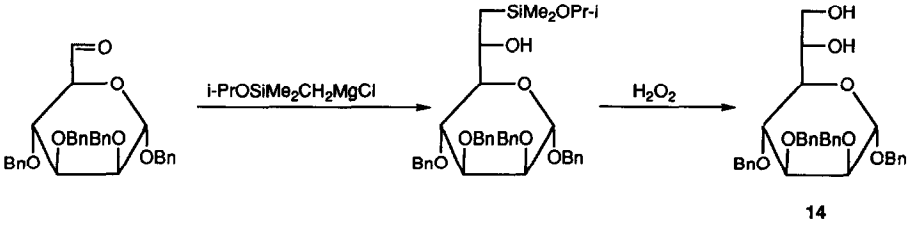
2.2.2. *Alkylations.*[39] Polyfunctional compounds can often be alkylated stereoselectively through the use of chelation and face selectivity,[1] as with, for example, the enolates of tartaric acid and 2-hydroxy-1,4-diesters.[40] In a similar vein, γ-ketoacids are available for an alkylation protocol (Scheme 10).[41] A second alkyl group can also be introduced into the amide **13**; again, the second alkyl group is also introduced from the bottom face.[42]



Scheme 10.

Other chiral auxiliaries have been used to bring about these regio- and stereoselective alkylations.[43]

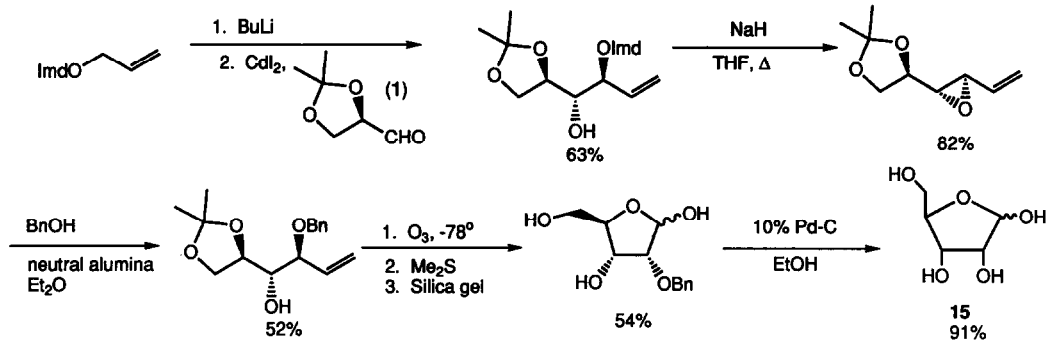
2.2.3. *Nucleophilic additions.*[44] As saccharides contain hydroxy groups, selective protection in turn allows for selective oxidation and subsequent homologation. This is illustrated by the chelation controlled addition in the synthesis of the L-*glycero*-D-*manno*heptose derivative **14** (Scheme 11).[45]



Scheme 11.

Further examples of functionalised nucleophiles are provided by the use of a vinyl anion (*vide infra*).[46]

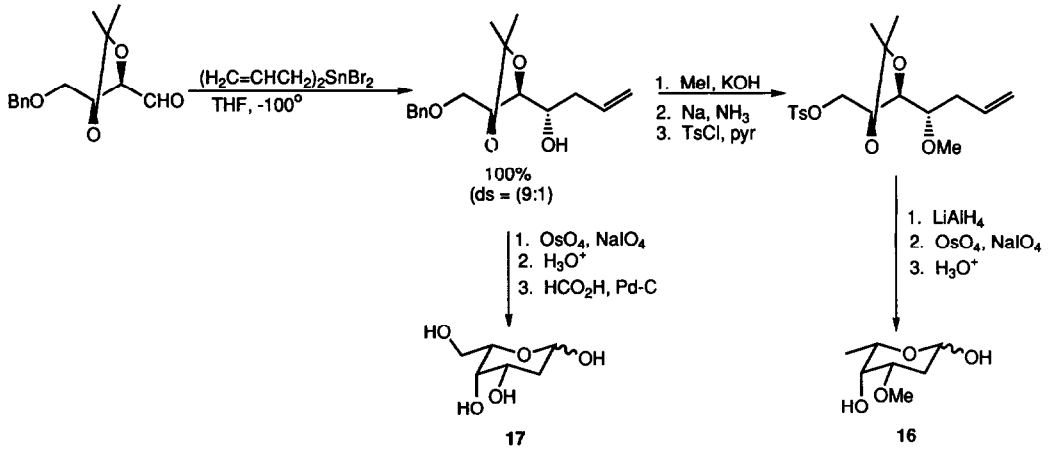
2.2.3.1. *Examples of carbohydrate synthesis through the use of nucleophilic addition reactions.* The acetonide of L-glyceraldehyde **1** has proved a useful entry to carbohydrate synthesis through



Scheme 12.

nucleophilic attack at the carbonyl group.[47] Compounds prepared by this strategy include L-diginose,[48] (+)-altholactone,[49] D-ribose **15** (Scheme 12),[50] and D-ribulose.[51]

Examples of other building blocks that have been used in a similar context are shown in the syntheses of thymine polyoxin C,[52] L-diginose **16**, and 2-deoxy-L-galactose **17** (Scheme 13).[53]



Scheme 13.

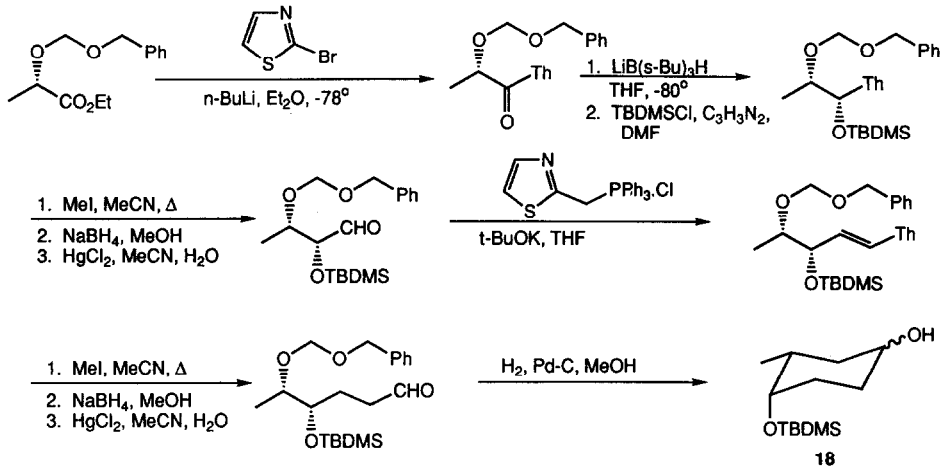
A formyl anion equivalent with an ester provides a methodology to an α-hydroxyaldehyde (cf. Scheme 8). Such a substrate has been used in a Wittig homologation to prepare a derivative of L-(−)-rhodinose **18** (Scheme 14).[54]

Pinnacol-type coupling of two aldehydes can provide high selection for the *syncat* diol. Such an approach has been used to prepare *N*-benzyl-D-3-*epi*-daunosamine **19** (Scheme 15).[55]

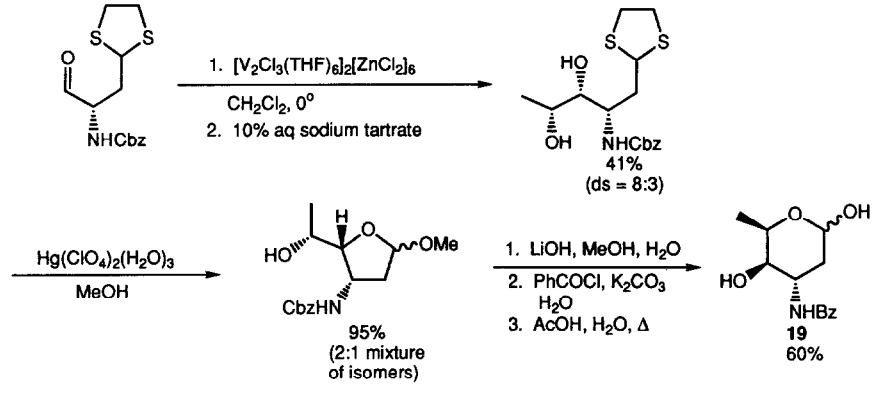
An example that involves a vinyl carbanion, **20**, is seen in a synthesis of the carbohydrate, 3-deoxy-D-manno-2-octulosonic acid (KDO) **21** (Scheme 16).[56]

2.2.4. *Aldol type reactions.*[39b,57] The use of functionalised enolates in an aldol type reaction with controlled addition allows for the construction of several centres with stereochemical control and a convergent approach.[10,58] Indeed, functionality or chiral auxiliaries can be incorporated into one or more of the substrates.[59] For high diastereoselection, however, matched pairs must be used.[60]

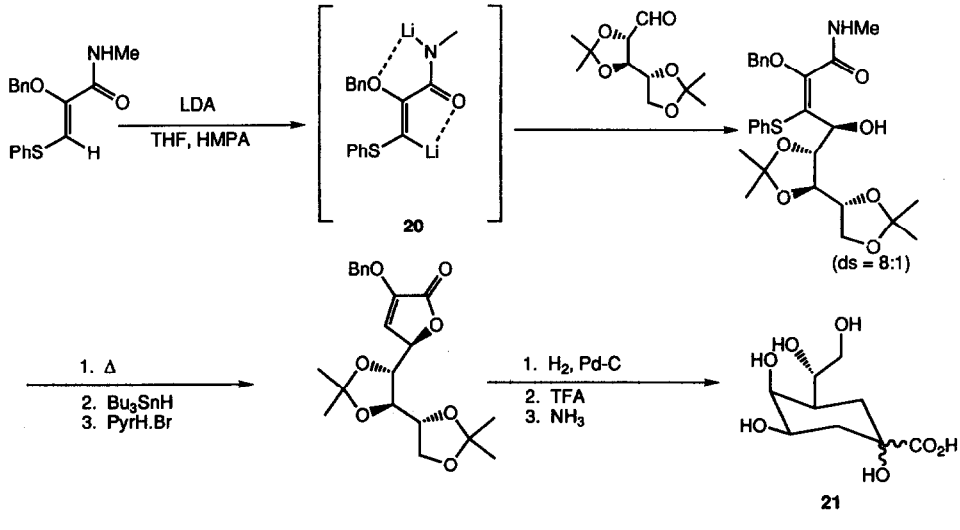
The use of a chiral boron enolate allows for a choice in the product stereochemistry (Scheme 17),[61] as does the β-keto imide **22** (Scheme 18).[62]



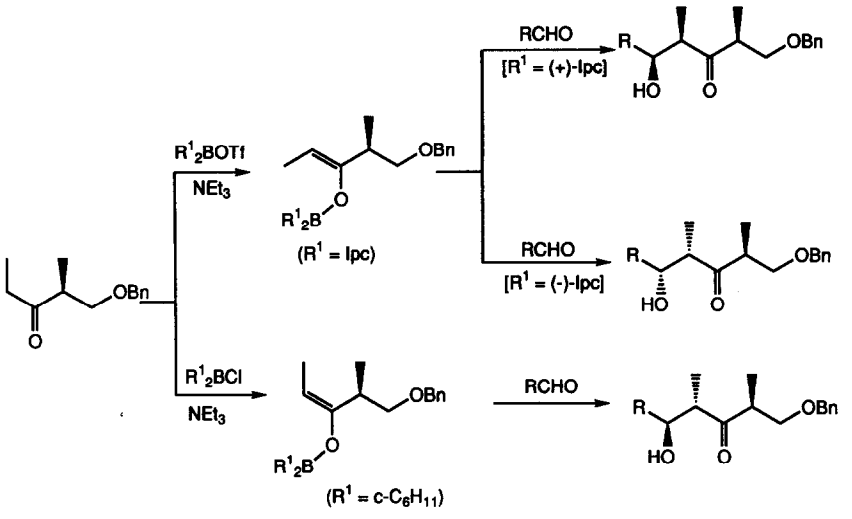
Scheme 14.



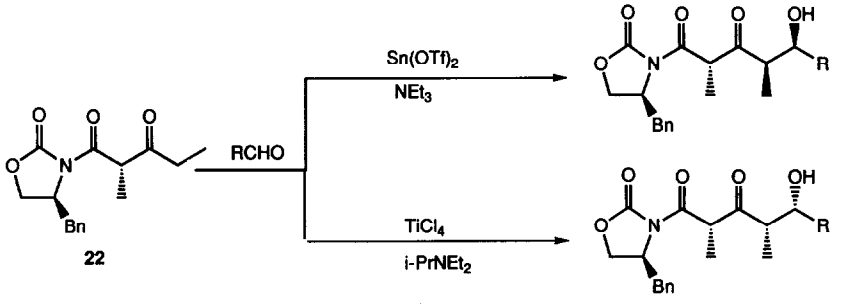
Scheme 15.



Scheme 16.

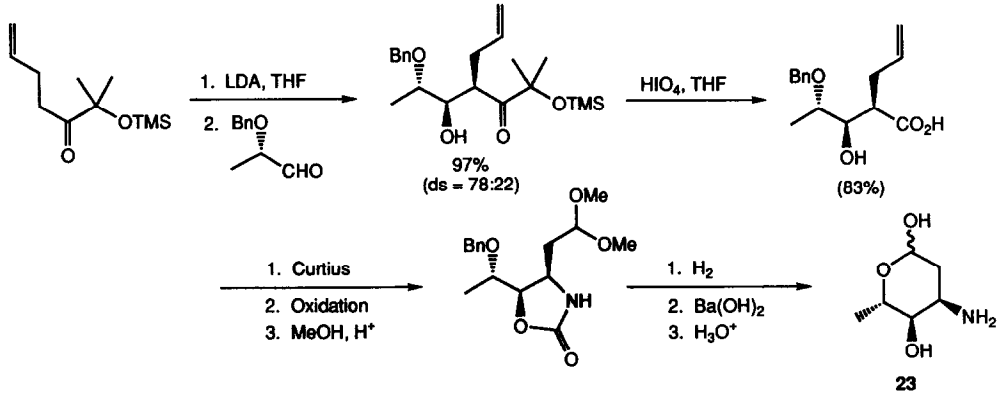


Scheme 17.

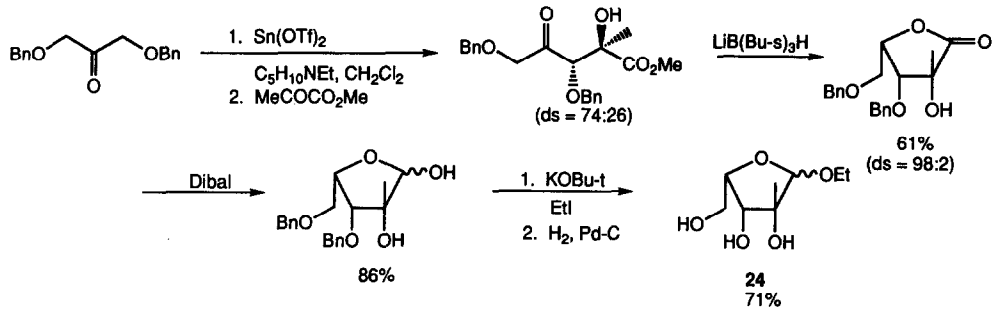


Scheme 18.

2.2.4.1. *Examples of carbohydrate synthesis through the use of aldol reactions.* A stereocontrolled aldol strategy has been employed in a synthesis of ristosamine **23** (Scheme 19),[63] cladinose,[64] and the branch chain sugar, 2-*C*-methyl-D,L-*lyxo*-furanoside **24** (Scheme 20).[65]

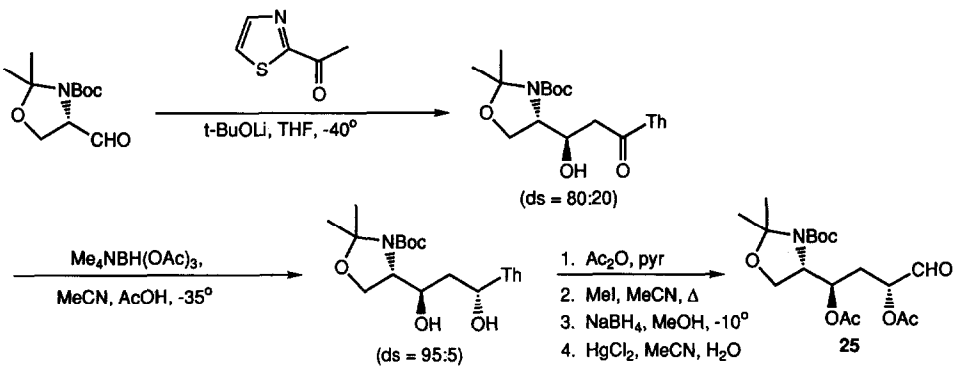


Scheme 19.



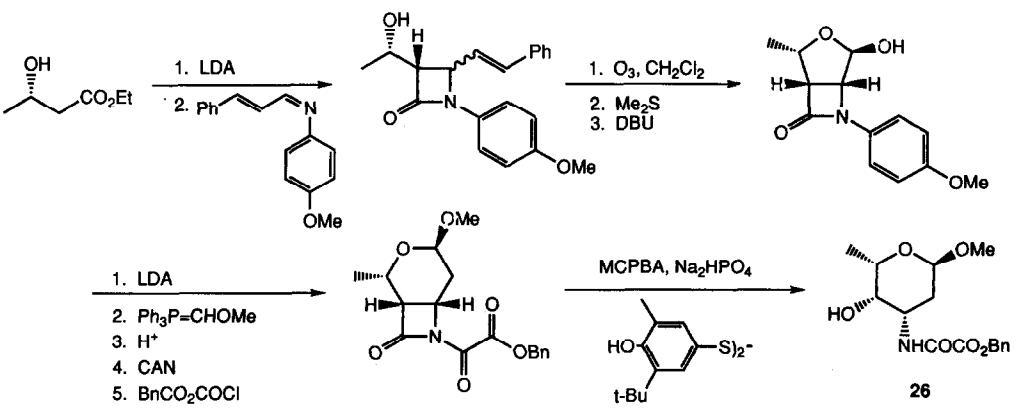
Scheme 20.

As with nucleophilic additions to carbonyl compounds (*vide supra*), derivatives of L-glyceraldehyde have proven to be useful building blocks in aldol methodology as illustrated by the syntheses of methyl D-glucosaminate,[47,66] 2-deoxyaldonates,[67] 2-deoxy-3-uloconates,[67] aminopentoses,[68] and protected aminohexoses, such as **25** (Scheme 21).[69]



Scheme 21.

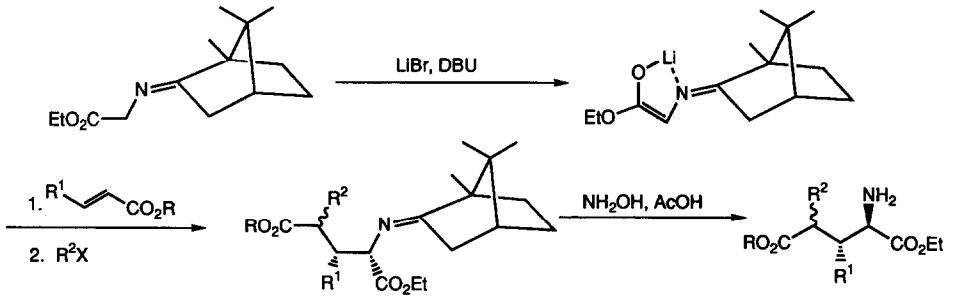
Reactions closely related to the aldol have also been used to prepare carbohydrate derivatives. Thus, reaction of an ester enolate with an imine to form a β-lactam has been used to prepare the daunosamine derivative **26** (Scheme 22).[70] Reaction of a nitrile with an ester enolate to form an oxazole provides another route to L-daunosamine.[71]



Scheme 22.

Carbohydrates are also useful templates for face selective aldol reactions.[72] They are also available from an enzyme catalysed aldol approach (see Section 5), while the methodology also provides an entry to higher sugars (see Section 6.1).

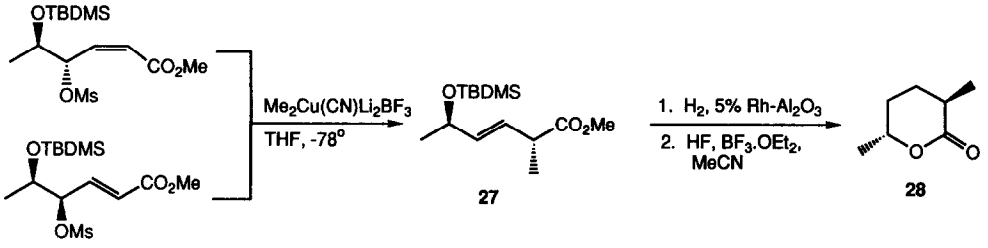
2.2.5. *Conjugate additions.*[73] The use of functionalised nucleophiles allows for the introduction of remote functionality through conjugate addition to an α,β-unsaturated carbonyl system (Scheme 23),[35,74] or other electrophilic species.[75] In addition, the electrophile can contain additional functionality.[76]



Scheme 23.

As with other reactions involving carbonyl groups, the degree of stereoselection observed is a function of solvent and counterion. Transition state models are being developed to explain the experimental observations.[77]

Allylic alkylations can also be achieved by an organocopper reagent; reduction of the product **27** and cyclisation provides the δ-lactone **28** (see Section 4.2 and Scheme 24).[78]

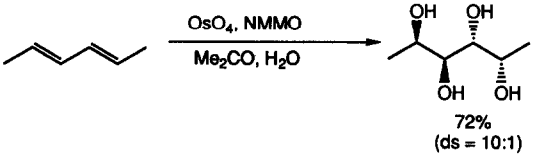


Scheme 24.

2.3. *Oxidations*

Many of the methods described for the stereoselective oxidation of isolated double bonds and allyl alcohols can be used with functionalised substrates.[1,79]

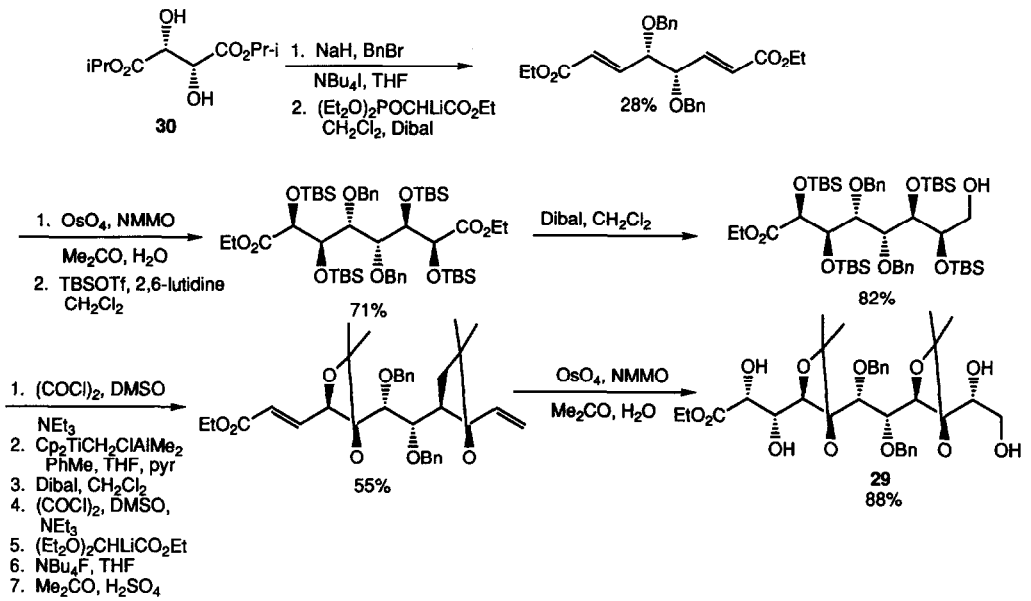
2.3.1. *Osmylation.* The osmylation of alkenes possessing an allylic oxygen centre is stereoselective with a predictable outcome.[80] High diastereoselectivity is also observed for the dihydroxylation of bis-allylic substrates,[81] even when no allylic oxygen group is present (Scheme 25).[82]



Scheme 25.

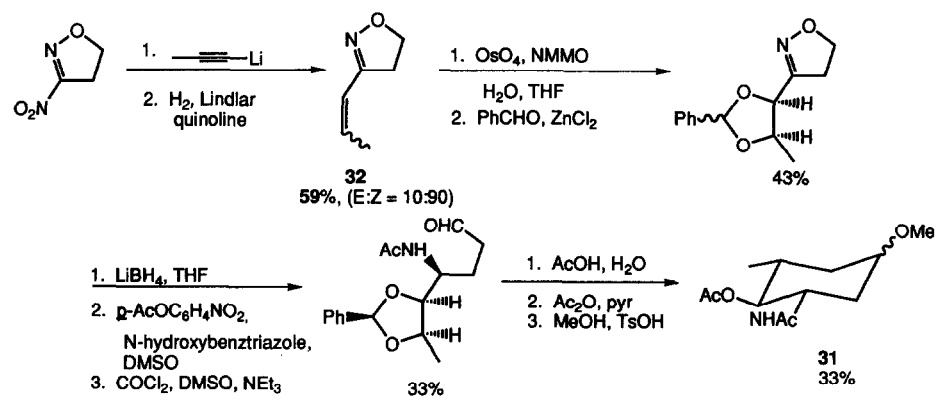
Cyclic substrates offer stereoselectivity through the inherent stereofacial requirements of the substrate.[1]

2.3.1.1. *Examples of osmylation in carbohydrate synthesis.* The undecose fragment of hikizimycin **29** has been prepared from L-(+)-diisopropyl tartrate **30** by a chain extension and osmylation strategy in a bisallylic system (Scheme 26).[81,83]



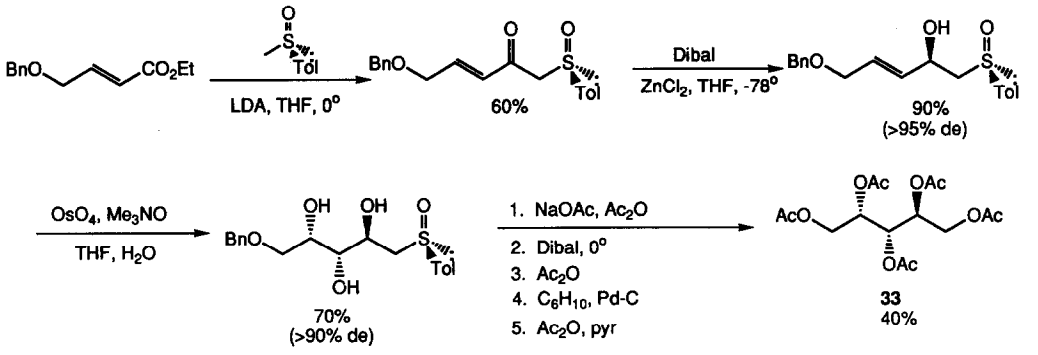
Scheme 26.

The 2,3,6-trideoxy-3-aminohexose **31** has been prepared by the oxidation of a dihydroisoxazole substrate **32** (Scheme 27).[84]



Scheme 27.

The reaction has been used to provide efficient syntheses of L-arabinitol pentaacetate **33** (Scheme 28),[80k] and 3,4-dideoxy-3-fluorohexoses where chiral sulphoxides were used to play a key role in stereochemical control.[80i,85]

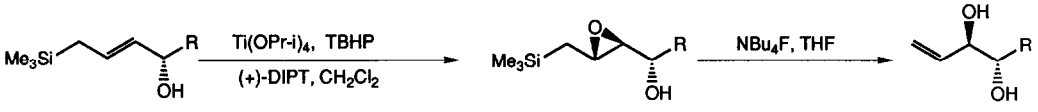


Scheme 28.

The introduction of hydroxy groups makes the methodology powerful in the synthesis of higher sugars (see Section 6.1).[86]

2.3.2. *Epoxidations.*[1] Allyl alcohols can be epoxidised with high stereoselectivity by Sharpless' method.[87] Peracids and other transition metals, such as vanadium, can also be used to accomplish this transformation. As a chelate is formed between the reagent and substrate's allylic oxygen group, the oxidation is not normally affected by other remote stereogenic centres within the substrate although exceptions have been observed.[88]

The Sharpless epoxidation of substituted allyl alcohols provides an entry for methods to functionalised diols (e.g. Scheme 29).[89]



Scheme 29.

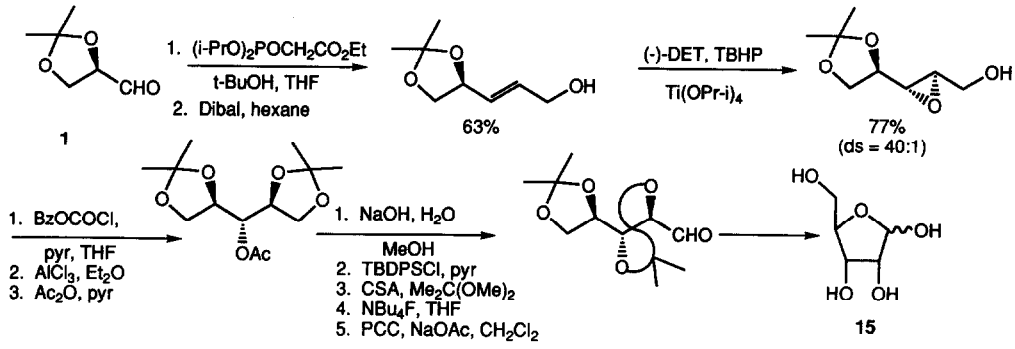
The protocol can also be used to epoxidise homoallyl alcohols, although the enantiofacial selection is opposite to that observed for allyl alcohols.[90] As an allyl alcohol usually reacts faster, the Sharpless epoxidation can be used to differentiate between two double bonds within a substrate molecule (*vide infra*).[91]

Homoallyl alcohols can also be epoxidised with high stereoselective control when vanadium is used as the catalyst.[92]

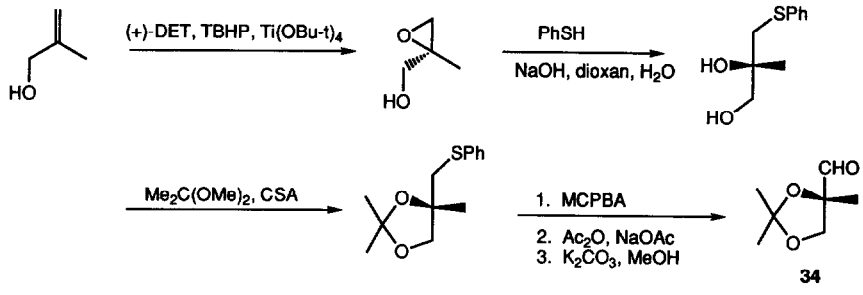
2.3.2.1. *Reactions of epoxyalcohols.*[93] Epoxyalcohols react in a regioselective manner with a wide variety of nucleophiles.[1] Often the regiochemistry is determined by the functional group within the substrate.[94–97] These reactions have already been discussed elsewhere,[1] and representative illustrations for the preparation of carbohydrate derivatives are given in the following section.

2.3.2.2. *Examples of carbohydrate syntheses from epoxides.* The Sharpless epoxidation has been exploited to synthesise a number of carbohydrate derivatives ranging from small molecules to higher sugars. D-Ribose **15** is available, along with other D-pentitols, from D-glyceraldehyde acetonide **1** (Scheme 30).[98]

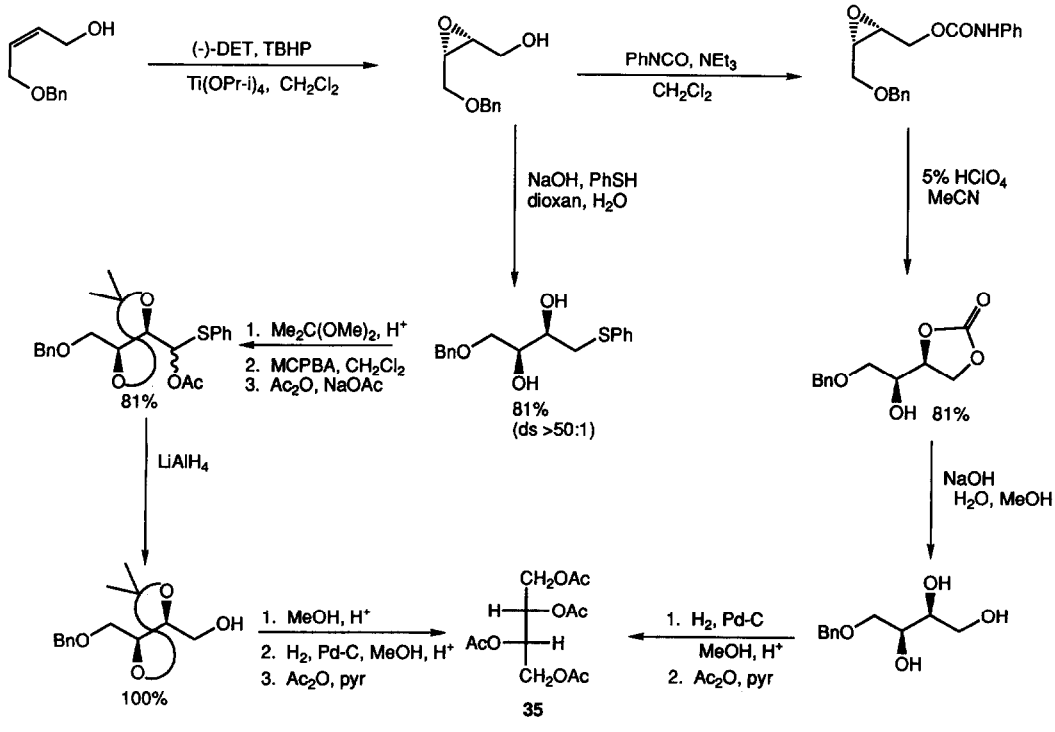
Use of a sulphur nucleophile has led to a general, systematic method for the synthesis of polyols. Thus, the useful building block, **34**, is available by a Sharpless protocol (Scheme 31).[99]
This methodology has been employed for the preparation of L-threitol **35** (Scheme 32) and erythri-



Scheme 30.



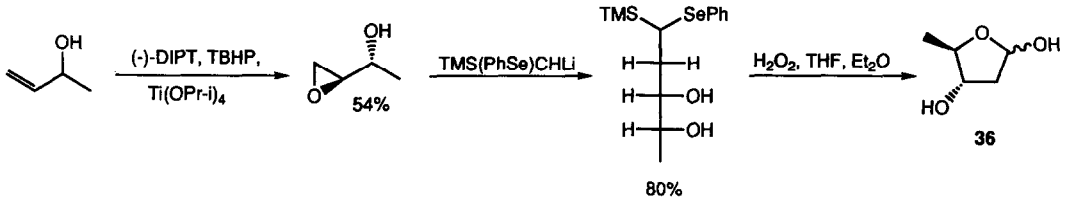
Scheme 31.



Scheme 32.

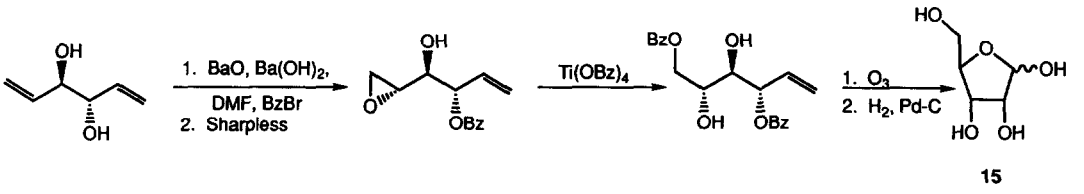
tol.[100] This simple iterative process has not only been used for the simple alditols,[100,101] deoxyalditols,[102] and aldoses,[100] but all of the L-hexoses.[103]

An *umpolung* homologation procedure results in a synthesis of 2,5-deoxyribose **36** (Scheme 33).[104]

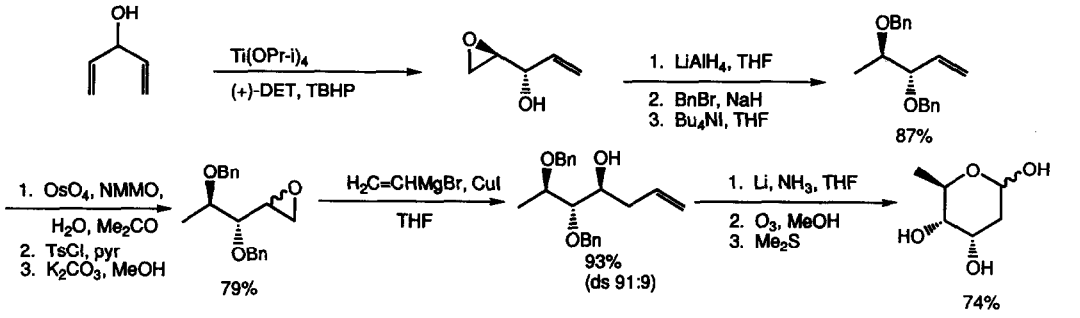


Scheme 33.

Oxidation of functionalised allyl alcohols provides alternative routes to D-ribose **15** (Scheme 34), and hexose derivatives (Scheme 35).[105,106]

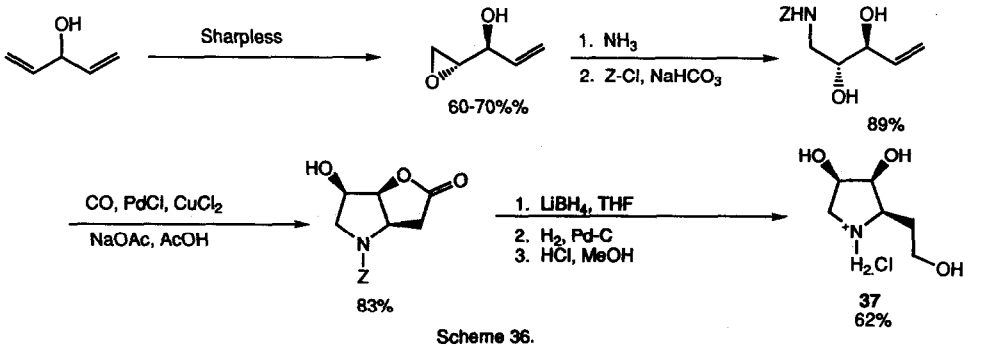


Scheme 34.



Scheme 35.

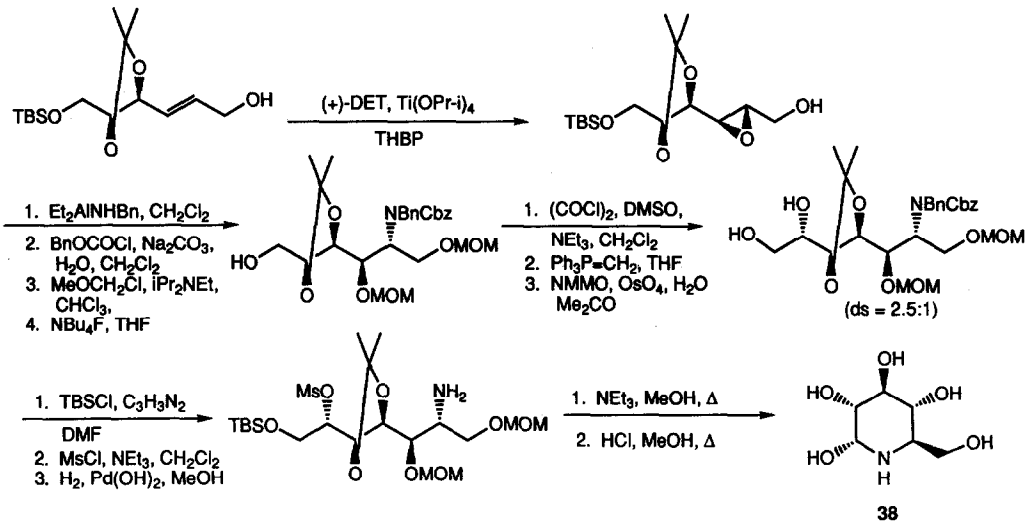
The use of a diene substrate has been used to prepare a variety of 4,6-dideoxy-D- and L-hexoses, including the imino-D-*lyxo*-hexitol **37** (Scheme 36).[107]



Scheme 36.

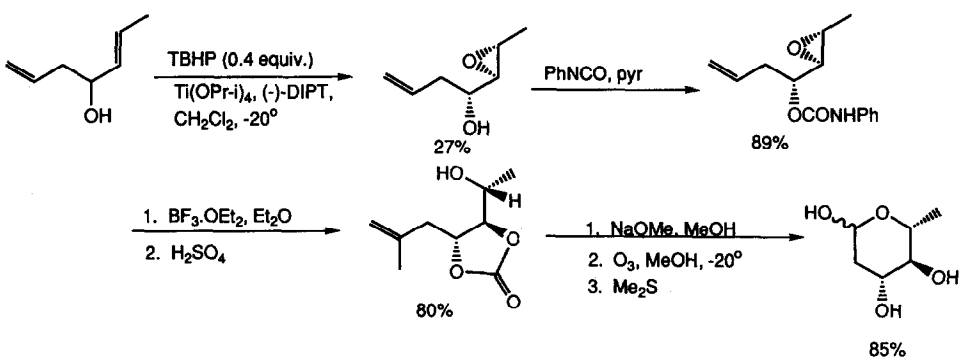
This procedure has also been used to provide higher carbon sugars by homologation methods,[108] to afford heptose,[109] octose,[110] and decitol derivatives.[111]

A synthesis of (+)-α-homonojirimycin **38** utilises an allyl alcohol oxidation and an osmylation reaction (Scheme 37).[112]



Scheme 37.

The Sharpless oxidation method can also be used for kinetic resolutions (Schemes 38 and 39).[1] This approach has been employed for the synthesis of 2,6-dideoxyhexoses; a 'chiral pool' methodology would have required many synthetic operations (Scheme 39).*[113]

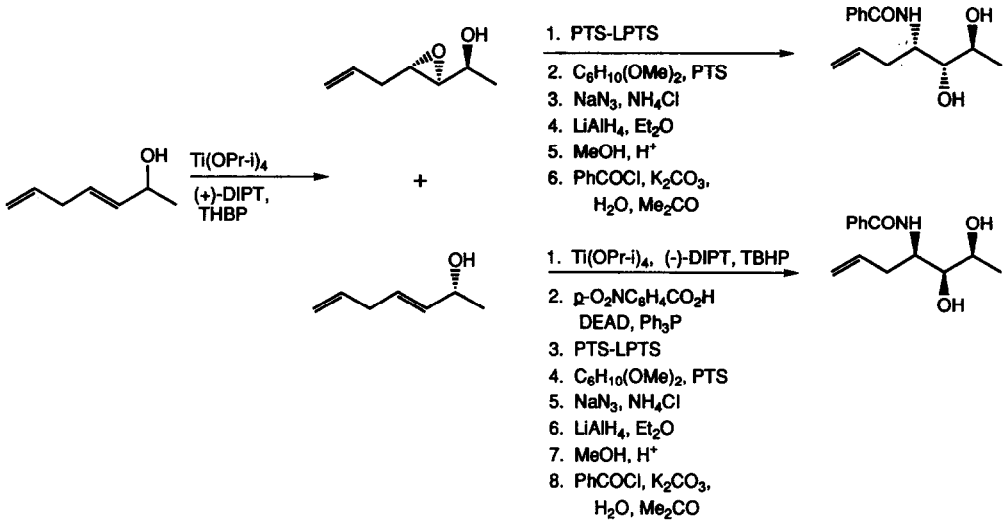


Scheme 38.

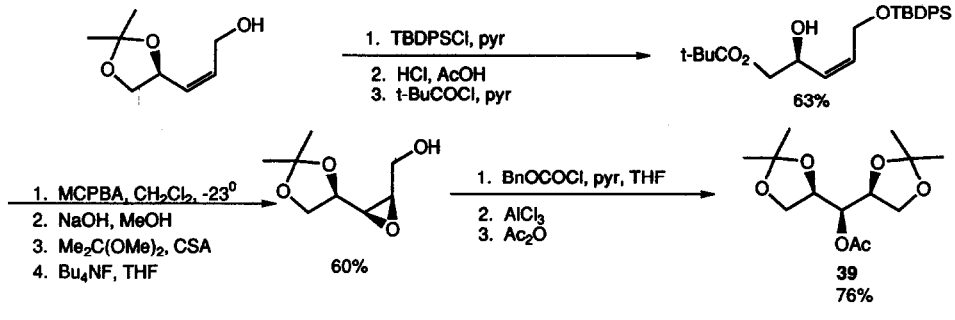
Amino sugars are available by a Sharpless approach (*cf.* Schemes 36 and 39).[115] The target sugars can be revealed by an oxidative cleavage of the alkene (*cf.* Scheme 34). In this case the alcohol left unreacted in the kinetic epoxidation is used as a synthetic resource.

A peracid oxidation can also be employed to prepare epoxyalcohols for carbohydrate synthesis, such as in the preparation of the xylitol derivative **39** (Scheme 40).[98]

* In some cases, the 'chiral pool' does provide the requisite starting material in an expeditious manner (see ref. 114).



Scheme 39.

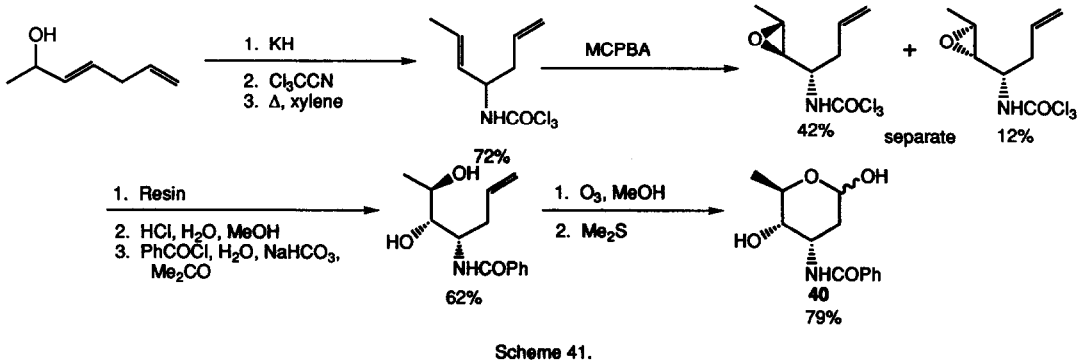


Scheme 40.

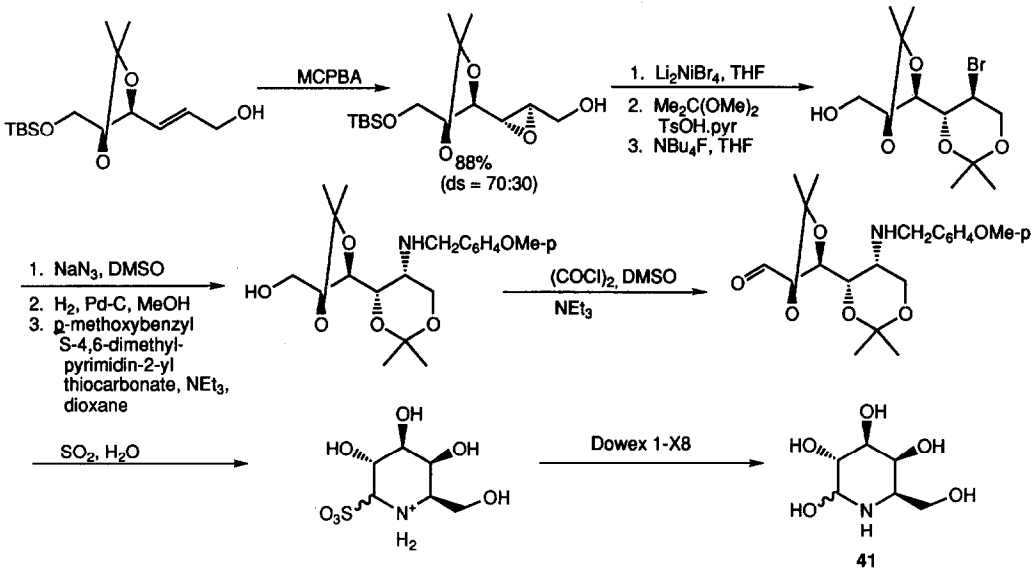
Stereoselectivity has been observed in the MCPBA oxidation of allylic amides. This result has been exploited in a synthesis of *N*-benzoylristosamine **40** (Scheme 41).[116]

A peracid oxidation has provided a route to (+)-galactostatin **41** (Scheme 42; see also Scheme 37).[117]

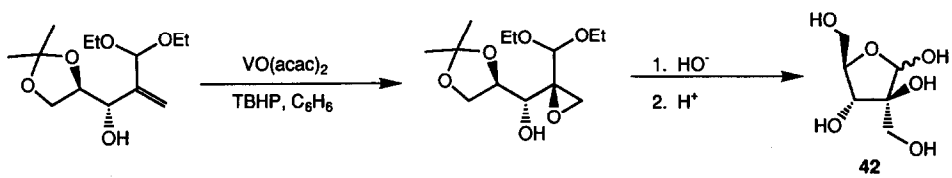
An example of a vanadium catalysed epoxidation is provided in the synthesis of 2-*epi*-hamamelose **42** (Scheme 43).[118]



Scheme 41.



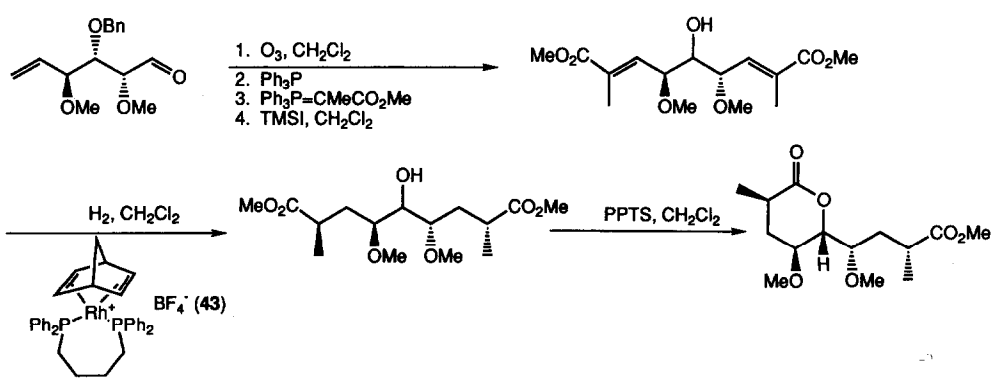
Scheme 42.



Scheme 43.

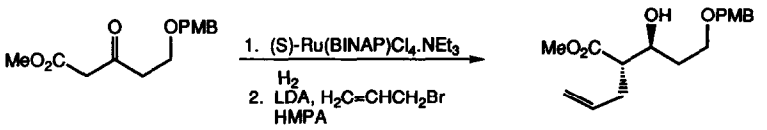
2.4. *Reductions*[1,119]

The stereoselective reduction of functionalised alkenes can allow the introduction of diastereoselectivity. The use of chiral ligands can provide asymmetric induction, as with simpler systems. Thus, rhodium catalysed reductions of substituted allyl alcohols can proceed with good selectivity,[120] as does the hydrogenation of homoallylic alcohols.[121] The catalyst **43** reduces dienes stereoselectively (Scheme 44),[120a,122] while ruthenium 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) com-



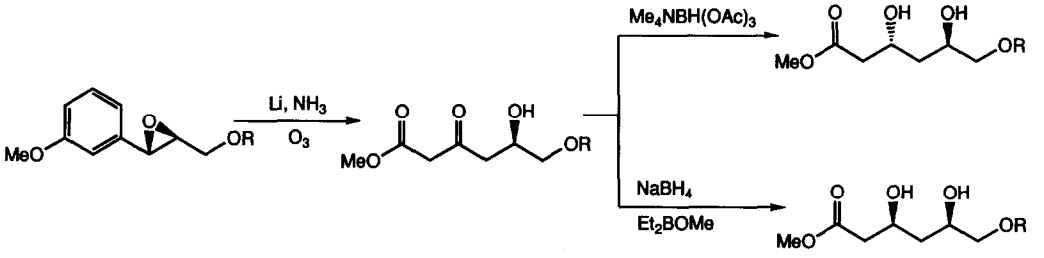
Scheme 44.

plexes catalyse the reduction of buta-1,3-diene-2,3-dicarboxylic acid to give the (*S,S*)-2,3-dimethylsuccinic acid.[123] β-Ketoesters can be reduced by ruthenium with high stereoselectivity,[1,124] to provide β-hydroxyesters (Scheme 45).[125]



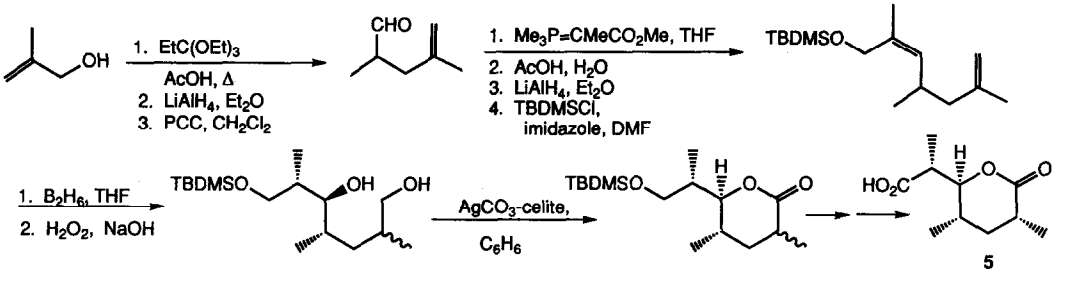
Scheme 45.

Hydrides can also reduce carbonyl compounds stereoselectively; either the *syncat* or *ancat* isomers are available (Scheme 46).[126]



Scheme 46.

Boranes can be used to reduce 1,4- or 1,5-dicarbonyl compounds or ω-enones.[127] A cyclic intermediate is formed. By the same type of intermediate, 1,4- to 1,7-triols are available from the respective dienes (Scheme 47).[127,128]



Scheme 47.

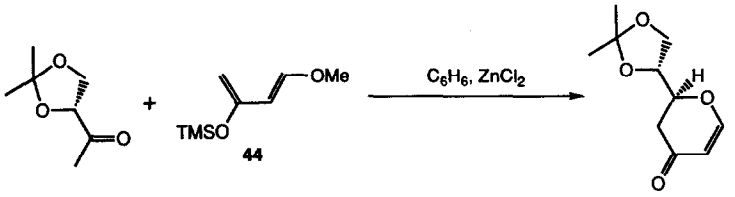
3. CYCLOADDITIONS AND RELATED APPROACHES

Pericyclic reactions have found widespread use in organic synthesis through their ability to control relative, and often absolute, stereochemistry.[129] Of this family, the Diels–Alder reaction has found the most favour.[129,130] In addition to the facial selectivity of this reaction,[131] considerable advances have been made to achieve an asymmetric transformation through the use of either chiral dienophiles,[130a,132] chiral catalysts,[133,134] or catalytic antibodies.[135] Indeed, carbohydrate derivatives have been used as substrates for this condensation reaction.[131d,136] The methodology certainly allows for a plethora of functionality to be introduced in a stereoselective and expeditious manner, particularly if an intramolecular strategy is adopted.[137]

3.1. *Reactions of dienes with carbonyl compounds*[129,130b,138]

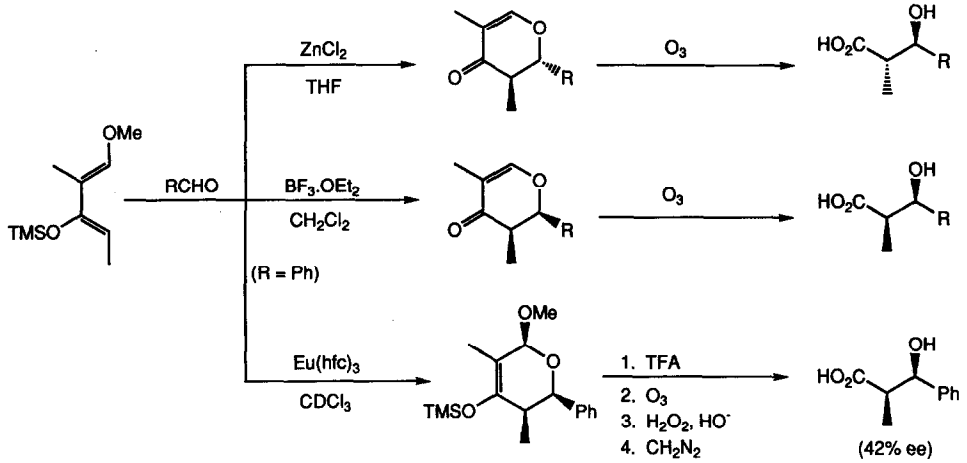
The reactions of carbonyl compounds with dienes have been included in the section on pericyclic reactions, as they were originally believed to be Diels–Alder reactions. The mechanism, however, has been established to proceed by a stepwise addition (*vide infra*), but the overall stereochemical outcome is the same whichever mechanistic pathway is followed. Early studies of the reaction of dienes with carbonyl compounds were thwarted by reactivity problems, although this was circumvented to a degree by the use of activated carbonyl components.[139]

Condensation of an aldehyde with oxygenated diene **44**[140] in the presence of zinc chloride provides high Anh–Felkin selectivity (Scheme 48).[141] Enals also act as dienophiles to afford 2,3-dihydro-4-pyridinone products.[142] Similar reactions can also be achieved with formaldehyde,[143] methoxybutadienes,[144] and α-alkoxy aldehydes.[145]



Scheme 48.

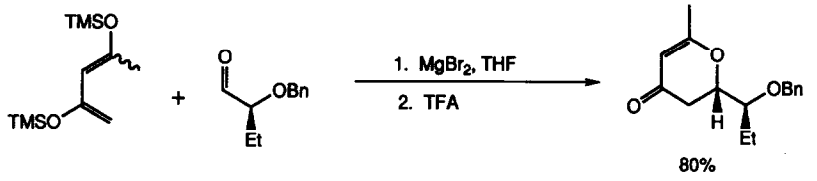
The nature of the Lewis acid can determine the relative stereochemical outcome of the reaction (Scheme 49).[141,146]



Scheme 49.

In addition to zinc or boron Lewis acids,[147] the reaction is catalysed by lanthanide metal complexes which allows fragile functionality to survive in the resultant adduct (Scheme 49).[148] The use of europium(III) complexes allows for high diastereoselectivity (>60:1),[145b,149] and a reasonable amount of asymmetric induction (18–58% *ee*).[148e,150] Homochiral pyranose derivatives have also been synthesised using a chiral auxiliary–chiral catalyst combination.[151] Chiral aluminium catalysts can also provide high levels of asymmetric induction,[152] while lower levels have been observed with chiral ruthenium complexes.[153]

Although the mechanism of the reaction can be described in terms of a pericyclic or aldol-cyclisation, the exact pathway followed can depend on the Lewis acid employed.[140c,154] Magnesium



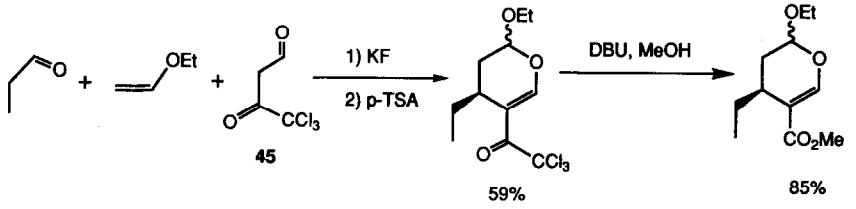
Scheme 50.

bromide exhibits high diastereofacial control (Scheme 50),[155] and favours the *endo*-topology.[146] The geometry of diene does control the relative geometry of substituents in the pyrone.[156]

The adducts from all of these reactions can be utilised as substrates for a wide variety of transformations,[157] as is evident from the range of products which have been prepared,[138a,144b,158] including higher sugars (*vide infra*).[159]

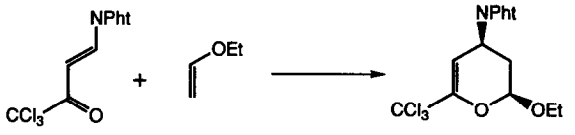
3.1.1. *Related cycloaddition reactions.* Other reactions that result in a pyranoside moiety exist, although as yet they have not been generally utilised for the synthesis of carbohydrates. Vinyl ethers and allenic ethers condense with enals to give dihydropyrans.[148b,160] Similarly, electron deficient acyl ketenes react with vinyl ethers.[161] This approach also provides methodology to spiroketals,[162] and spiroacetals.[158g]

Pyranose derivatives have also been synthesised by the tandem Knoevenagel hetero-Diels–Alder reaction of 4,4,4-trichloro-3-oxobutanal **45** with a number of aldehydes (Scheme 51).[163]



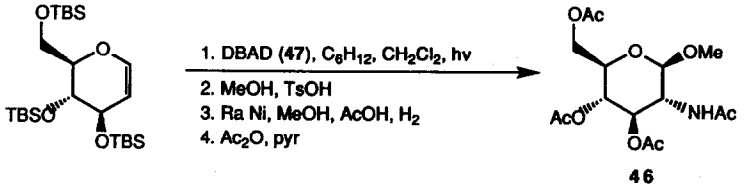
Scheme 51.

Electron deficient enamine carbaldehydes cyclise with vinyl ethers, and the resultant dihydropyrans can be converted to amino sugars (Scheme 52). When the reactions were conducted under high pressure there was a significant increase in diastereoselectivity for the resultant dihydropyran.[164]

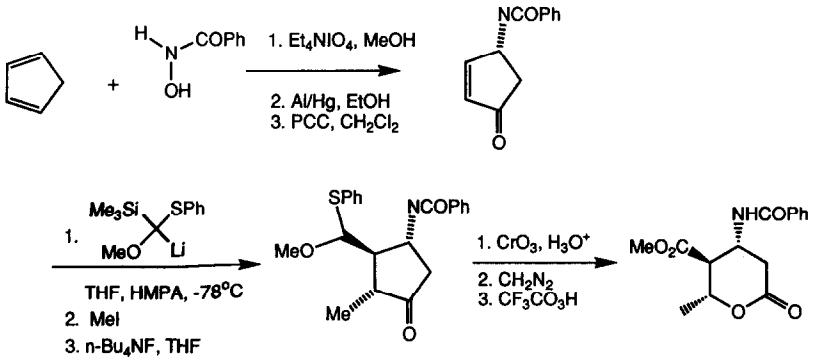


Scheme 52.

2-Aminoglycosides **46** have been synthesised by the reaction of dibenzyl azodicarboxylate **47** with a number of glycals (Scheme 53).[165]



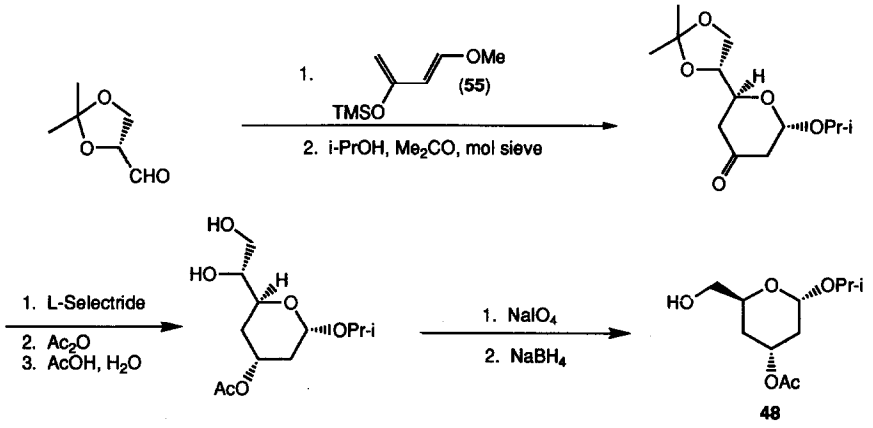
Scheme 53.



Scheme 54.

Cycloadditions of acyl-nitroso compounds with cyclopentadiene can ultimately lead to valerolactone derivatives (Scheme 54).[166]

3.1.2. *Examples in carbohydrate synthesis.* The chiral 2,4-deoxyglucose derivative **48** is available by use of the Anh–Felkin selectivity (Scheme 55).[147] Other examples are provided in the syntheses



48

Scheme 55.

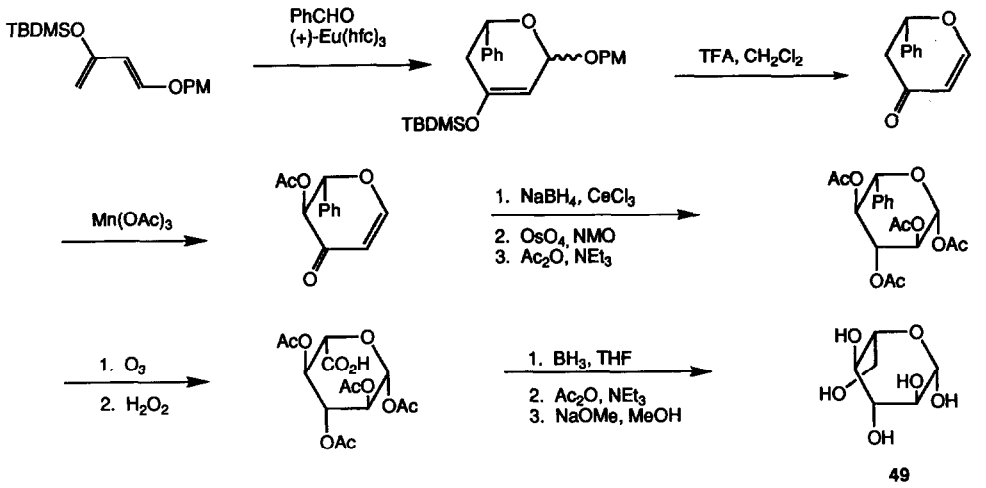
of *dl*-chalcose[167] and the use of a chiral auxiliary/chiral Lewis acid in the synthesis of L-glucose **49** (Scheme 56).[168]

The synthesis of a higher sugar, the lincosamine derivative **50**, illustrates the use of an enal as substrate and side chain transformations (Scheme 57).[169] The reaction of α-amino aldehydes has led to syntheses of lincosamine[170] and the 4-ethylamino sugar portion of calicheamicin.[171] In this series, the stereochemical outcome can be reversed through variation of the *N*-protection and whether chelation occurs (Scheme 58).[172] This reaction has also been shown to be influenced by high pressure and the nature of the Lewis acid.[170,172]

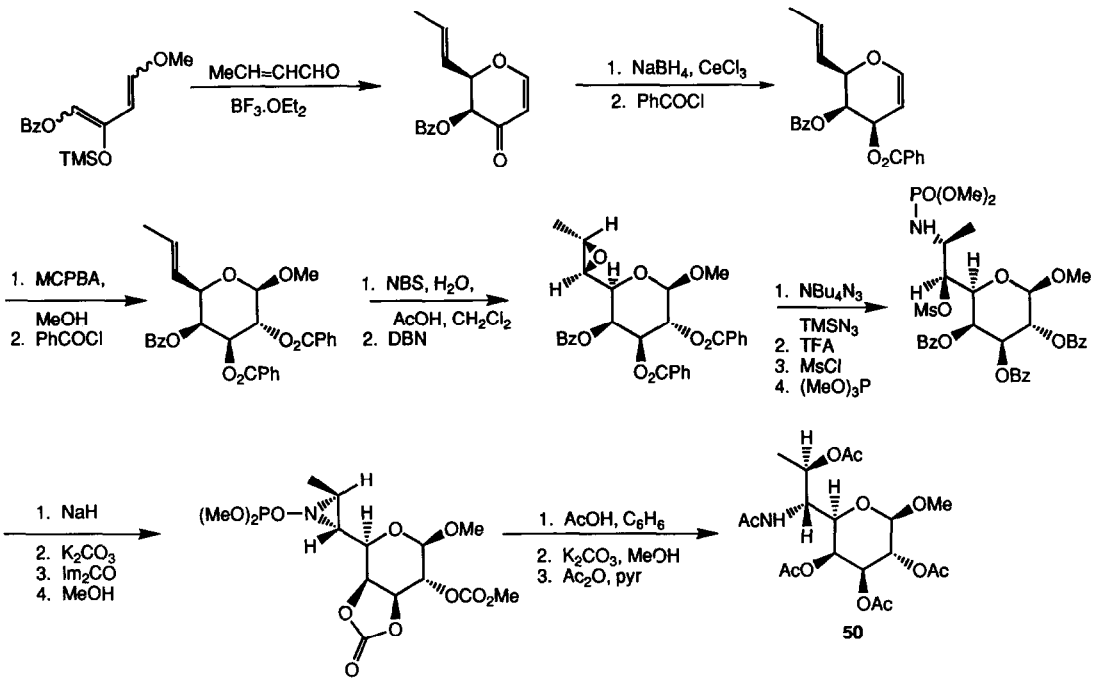
The use of a nitrogen-substituted diene is illustrated by the syntheses of a uracinine derivative,[173] and the desosamine derivative **51** (Scheme 59).[174] A nitrogen substituent can also be introduced later (Scheme 60).[175]

The preparation of 2-deoxy-L-glucose (**52**) illustrates the use of an activated diene, without the need for a Lewis acid (Scheme 61).[176]

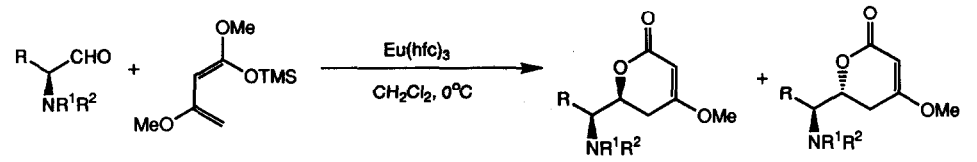
The methodology can also be used to prepare the higher sugars, such as the lincosamine derivative



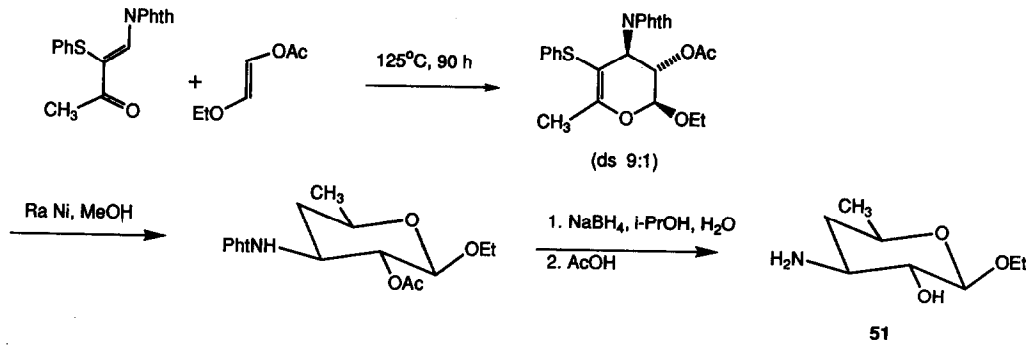
Scheme 56.



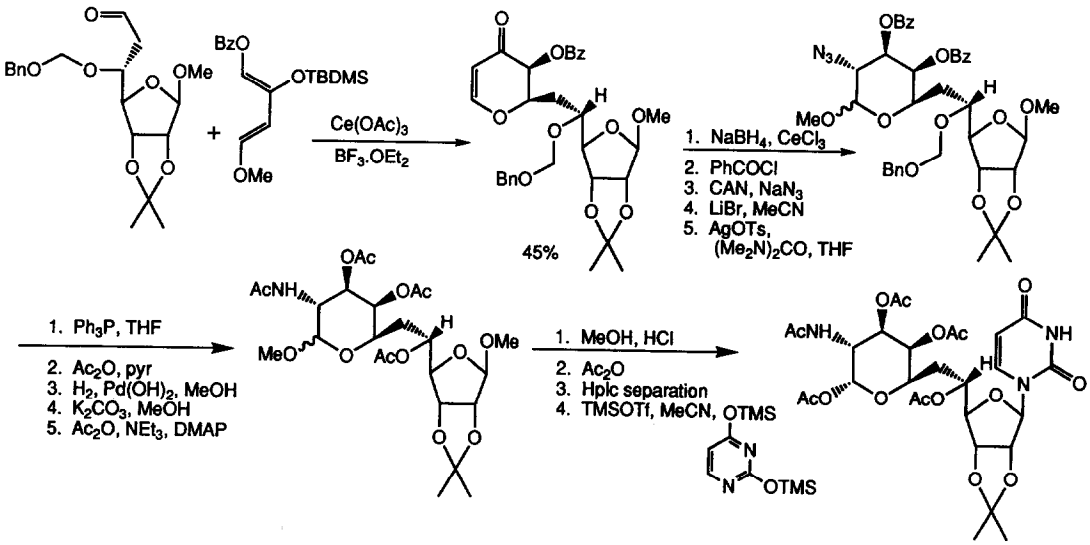
Scheme 57.



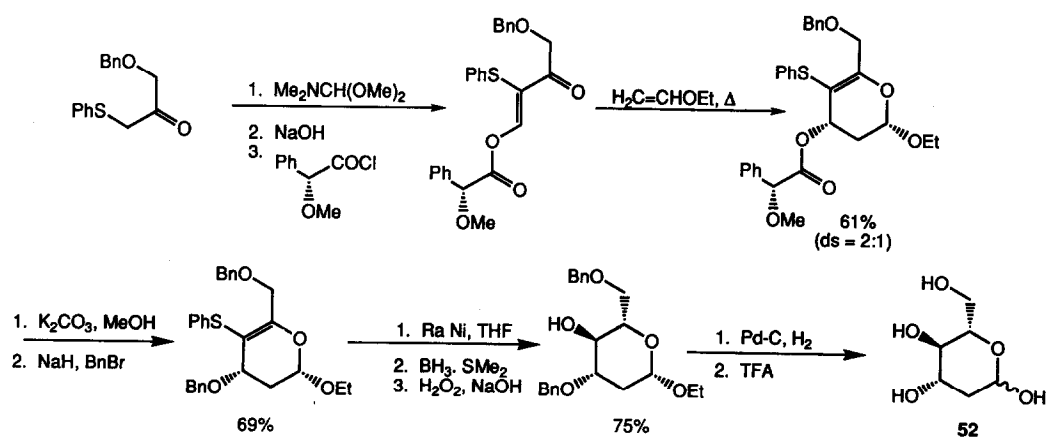
Scheme 58.



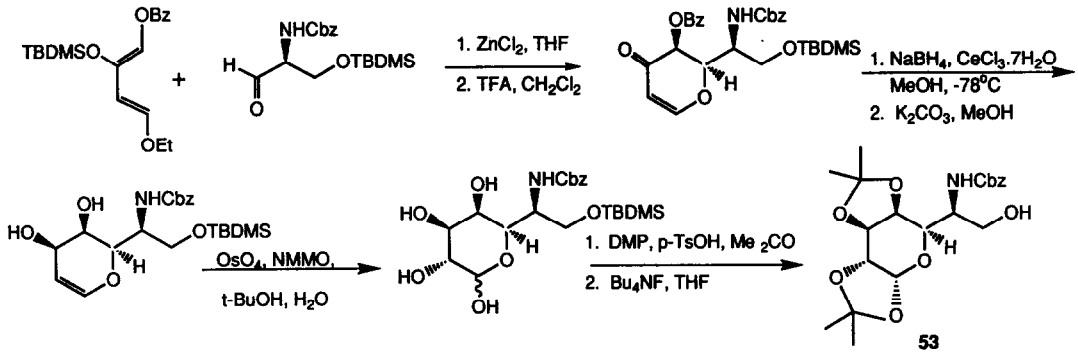
Scheme 59.



Scheme 60.



Scheme 61.



Scheme 62.

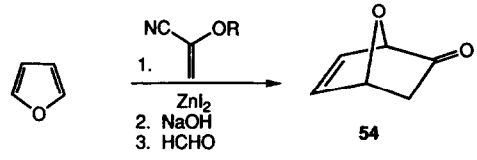
50 (Scheme 57),[169,171,177] 2-deoxy-L- and -D-galactoheptose,[176e] a hikosamine derivative,[178] and the destomic acid derivative **53** (Scheme 62).[159d]

3.2. *Diels–Alder reactions with furan derivatives*[179]

In spite of this reaction's inherent utility for carbohydrate synthesis and recent advances in Diels–Alder cycloaddition reactions—including the use of high pressure,[180] Lewis acid catalysts,[181] asymmetric induction by use of either chiral auxiliaries or chiral Lewis acids,[130a,182] and 'new' dienophiles, such as carbonyl compounds (*vide supra*)[183]—there have been relatively few advances in the case of furan.[184]

Although furan is notoriously unreactive in a Diels–Alder reaction, a large number of adducts derived from furan are known,[180a,181c,181e,185] especially from an intramolecular reaction.[137b,186]

The key to the synthesis of carbohydrate derivatives, by a furan Diels–Alder approach, is the use of 7-oxabicyclo[2.2.1]hept-5-en-2-one (**54**) as a 'chiron'; this molecule has been coined 'the naked sugar' (Scheme 63).[187] Either antipode of this ketone is available, in modest yield, from a Diels–Alder reaction; the use of a camphonate derivative allows resolution of the diastereoisomers.[181a,181b] Recently, some asymmetric induction has been noted using chiral dienophiles[188] or chiral auxiliaries (Section 3.2.2).[189]

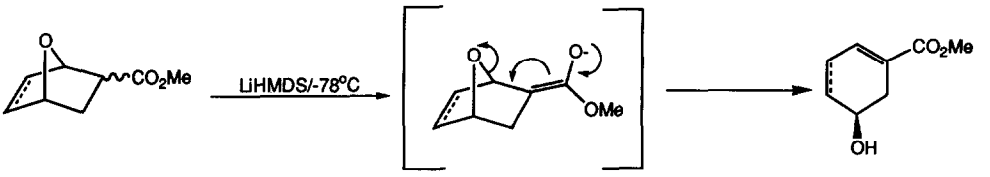


Scheme 63.

The development of an asymmetric Diels–Alder reaction with furan derivatives that alleviates the separation of diastereoisomers will greatly enhance the application of this bicyclic system for the preparation of carbohydrate derivatives.

3.2.1. *Chemistry of the 7-oxabicyclo*[2.2.1]*heptanyl system.* The cycloaddition product of furan, the 7-oxabicyclo[2.2.1]heptanyl system, has been used in the synthesis of a wide variety of natural products.[190] Examples include: nucleosides and C-nucleotides,[191,192] muscarine derivatives,[192,193] prostaglandins,[194] thromboxane analogues (*vide infra*), cyclooxygenase inhibitors,[195] antibiotics,[185f,196] cyclohexenol and cyclohexadienol derivatives (such as epishikimates),[181c,197] and more recently sugars, which may be prepared as either optical isomer.

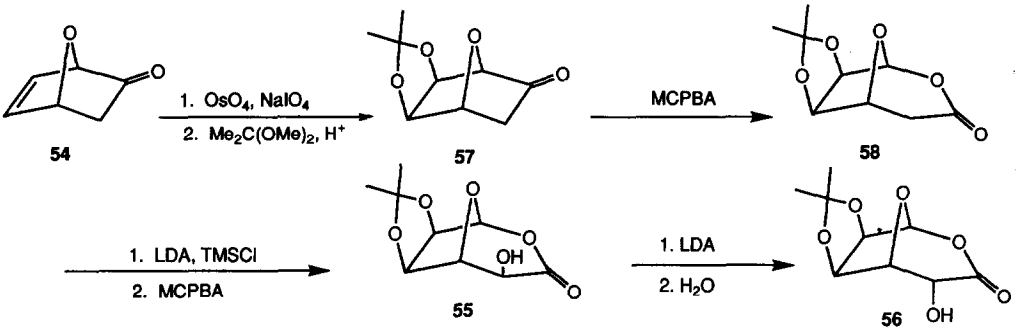
The chemistry of the 7-oxabicyclic system has been extensively investigated. The ridged skeleton allows for a number of regio- and stereoselective transformations. The chemistry parallels that of



Scheme 64.

the carbocyclic analogues bar two major exceptions: a favourable retro-Diels–Alder reaction,[185h,198] and an oxabicyclic system that is susceptible to ring opening (Scheme 64).[181c,185o,199] Ring opening occurs either via nucleophilic attack at the bridgehead position or by formation of an anion α- to the bridgehead. This latter ring opening tendency can be inhibited, allowing for the anion to be quenched with a number of electrophiles leading to a number of *exo*-substituted adducts.[199a]

The general protocol to carbohydrates relies on stereoselective oxidations of the ketone **54** and is summarised in Scheme 65.[185q,200] Regiochemical control may not be solely due to reagent approach from the least hindered face, as chelation is possible with the bridgehead oxygen.[181a,191b,200,201]



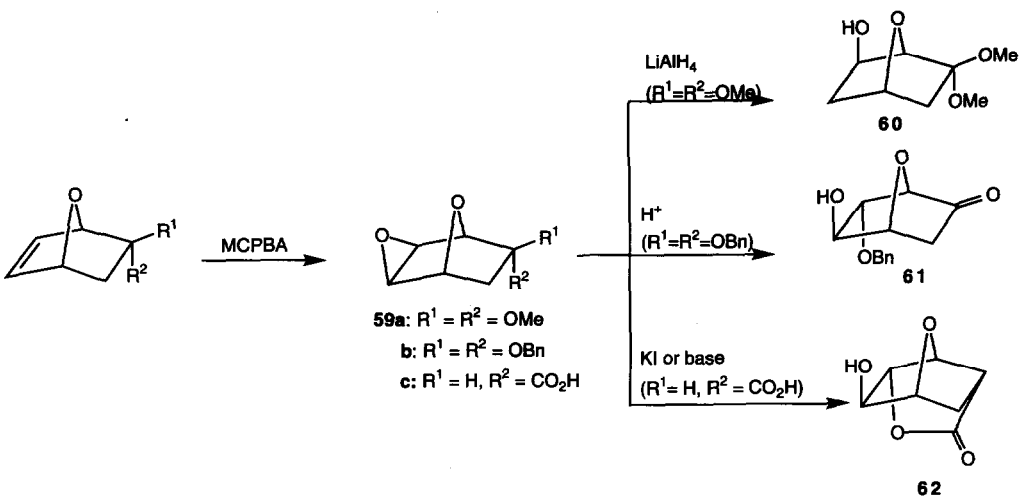
Scheme 65.

Treatment of the intermediate lactone enol ether with *m*-chloroperoxybenzoic acid affords the *exo*-α-hydroxylactone **55** stereospecifically again because of facial preference. The *exo*-α-hydroxylactone can be isomerised to the β-isomer **56** by treatment with base, as reprotonation of the enolate occurs from the least hindered side.[200] This isomerisation of the *exo* to *endo* isomer has also been noted with the analogous α-alkylated systems.[202] The ketone **54** is also a substrate for α-hydroxylation by a hypervalent iodine reagent.[203]

The double bond in the 7-oxabicyclo[2.2.1]hept-2-enyl system is readily hydrogenated with reaction taking place on the least hindered *exo*-face of the molecule.[180b,181c,185,190,204] Formation of an epoxide **59** is also regiospecific; again the reagent prefers to approach from the *exo*-face of the molecule (Scheme 66).[181a,199c,205]

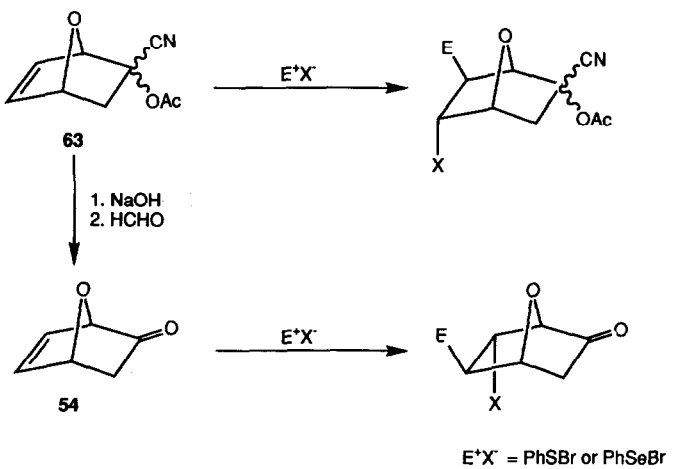
Subsequent epoxide opening is also regiospecific; not only are nucleophiles forced to attack from the *endo*-face, but attack can be controlled at either C-5 or C-6 by remote substituent effects. Reaction of the epoxide **59** with lithium aluminium hydride leads to the 5-deoxy-6-*exo*-hydroxy sugar precursor **60** exclusively.[205b] The selectivity has been attributed to the steric requirements of the remote methoxy substituent. This type of epoxide may also be opened under acidic conditions to form the hydroxyketone **61** (Scheme 66) with the opposite stereochemistry at C-6.[205a]

Epoxyacids, such as **59c**, may also be opened regiospecifically by neighbouring group participation of the carboxylic acid (Scheme 66).[185h] Hydrolysis of the lactone **62** would then lead to the 5-*endo*-6-*exo*-*trans*-diol derivative.



Scheme 66.

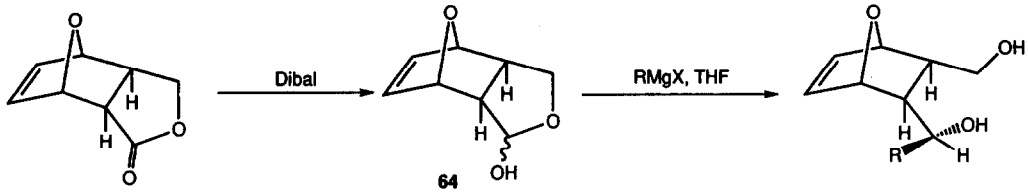
The effects of remote substituents can be seen in the electrophilic attack on the double bond of the bicyclic system.[204b,206] Nucleophilic attack at C-5 is influenced by the substituents at C-2; the ketone **54**, shows the opposite regioselectivity to the cyanohydrin derivative **63** (Scheme 67).[204b,206d,207]



Scheme 67.

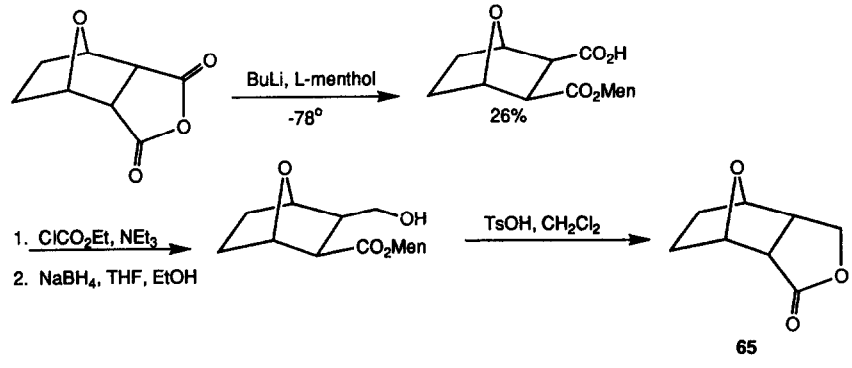
Azides can be used to prepare aziridines that have, in turn, been shown to rearrange stereoselectively.[205a,208] The ketone **54** reacts with organolithium and Grignard reagents as expected to afford the *endo*-alcohols. This selectivity can be reversed by use of lithium organocuprates.[209] Dichloroketene also adds to the *exo*-face of the carbonyl group of ketone **54**.[210]

The bridgehead oxygen atom can influence the stereochemical outcome of a reaction. Thus, reaction of lactol **64** with an organometallic reagent under chelation control shows strong facial selectivity (Scheme 68); the other isomer is produced when a chelate is not formed.[211]



Scheme 68.

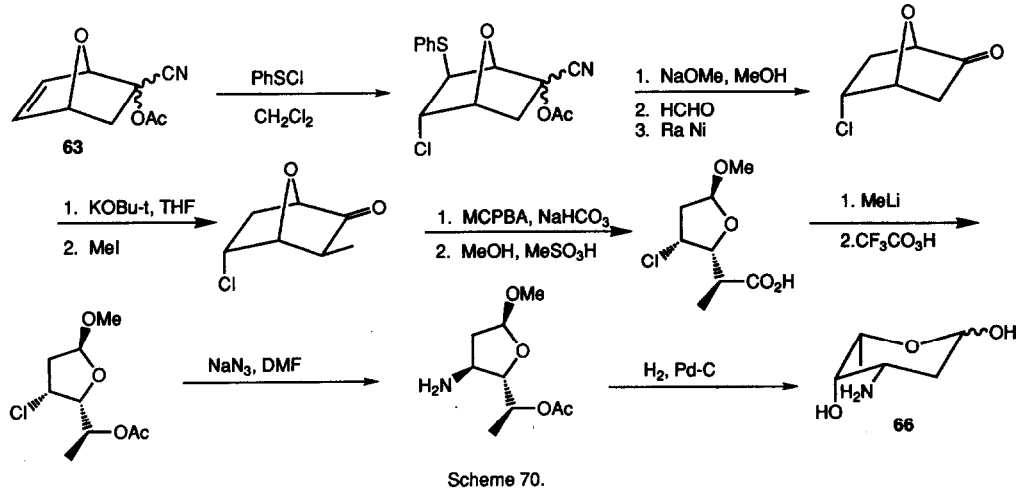
This effect has been exploited for the preparation of thromboxane analogues. The methodology is augmented by the use of an asymmetric anhydride opening which allows for the preparation of just one optical isomer of the intermediate lactone **65** (Scheme 69).[194,212]



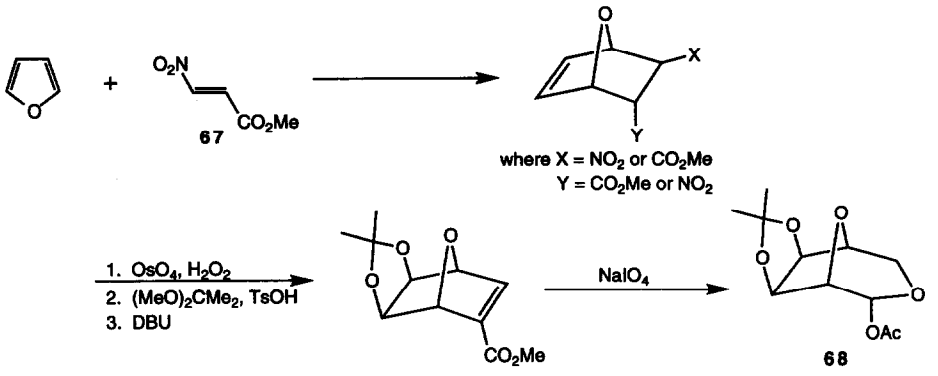
Scheme 69.

The 7-oxabicyclo[2.2.1]heptenyl system has been used as a substrate for 1,3-dipolar cycloadditions (Section 3.3).[213]

3.2.2. *Examples in carbohydrate synthesis.* The power of this approach is illustrated by the wide range of carbohydrate derivatives which have already been prepared. A selective electrophilic addition, followed by an alkylation procedure and nucleophilic nitrogen displacement provides a route to daunosamine (**66**) (Scheme 70),[204b] (+)-castanospermine,[214] and allonojirimycin.[207a]



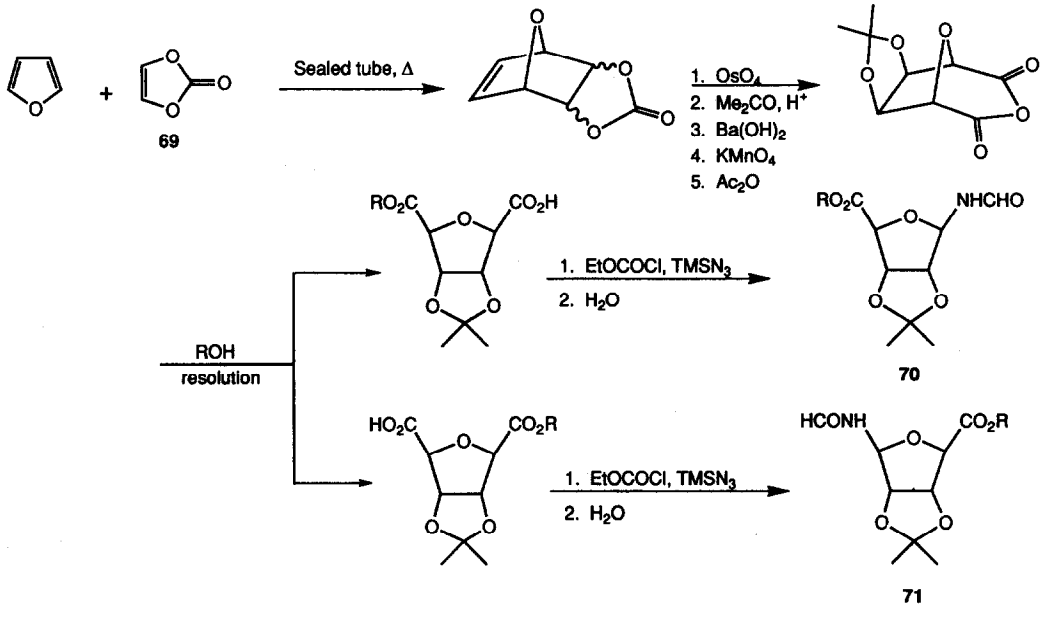
Scheme 70.



Scheme 71.

An oxidative cleavage protocol, coupled with the use of methyl nitroacrylate (**67**) as an acetylene dienophile equivalent provides a route to the protected 2,5-anhydroallose derivative **68** (Scheme 71).[191b,191k]

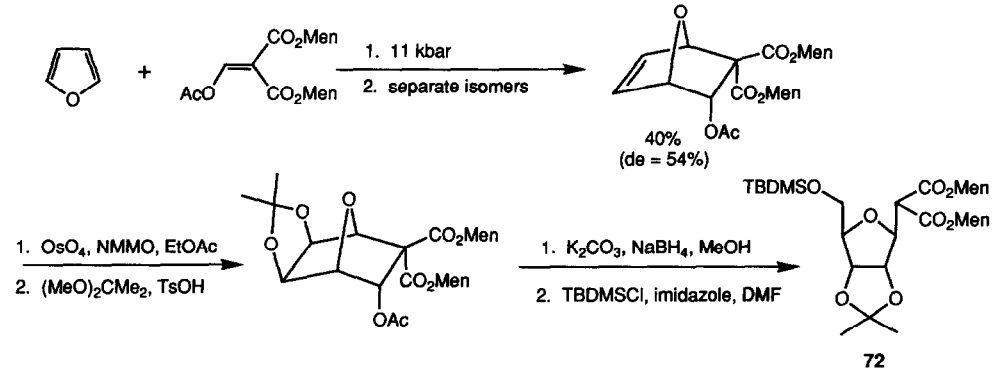
cis-Dihydroxy derivatives can also be synthesised by hydrolysis of the Diels–Alder adduct of furan and vinylene carbonate (**69**).[215] This methodology was used in the synthesis of D- and L-ribofuranuronate (**70** and **71**, respectively) (Scheme 72).[179,216]



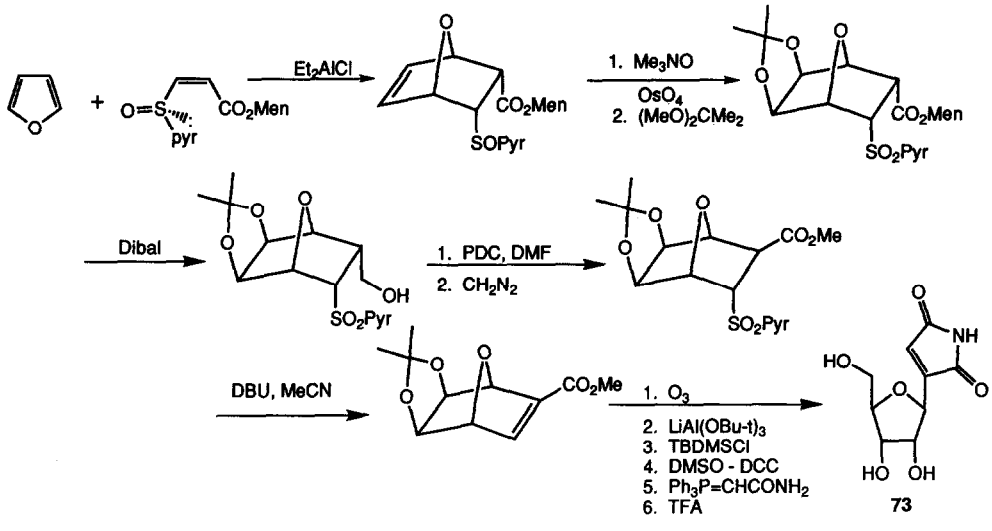
Scheme 72.

The use of a Baeyer–Villiger reaction to open the carbocyclic ring is illustrated by the synthesis of the 5-deoxy-*ribo*-hexofuranuranate (**58**) (Scheme 65).[185q]

A C-nucleoside precursor **72** is available through a high pressure Diels–Alder reaction (Scheme 73),[217] while a related approach to the C-nucleoside, D-showdomycin (**73**), depends on an asymmetric variant (Scheme 74).[181i,218]

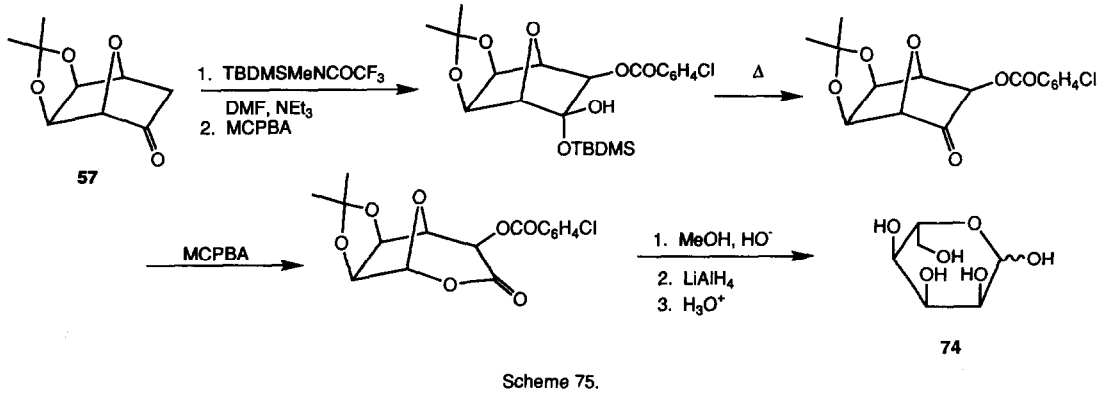


Scheme 73.

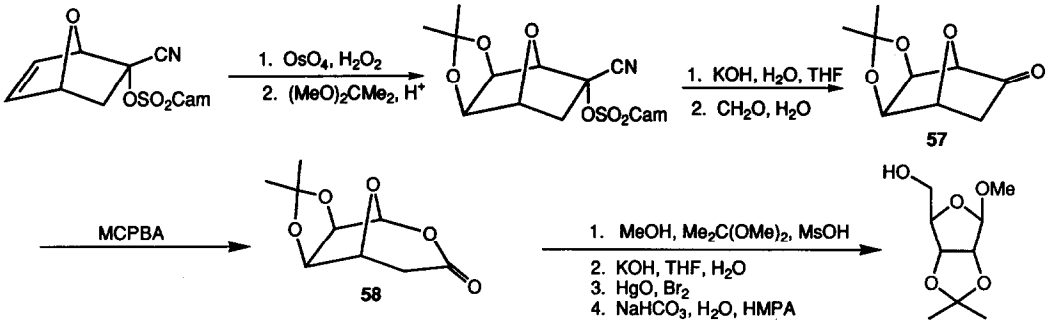


Scheme 74.

The synthesis of L-allose (**74**) illustrates the introduction of oxygen functional groups (Scheme 75),[219] while the preparation of D-ribose (**15**) shows a degradation procedure (Scheme 76; *cf.* Scheme 65).[220] Similar protocols to those described have been used in the syntheses of a number of carbohydrate derivatives, including allose,[207a,219] tallose,[219] and altrose.[205b,208,221]



Scheme 75.



Scheme 76.

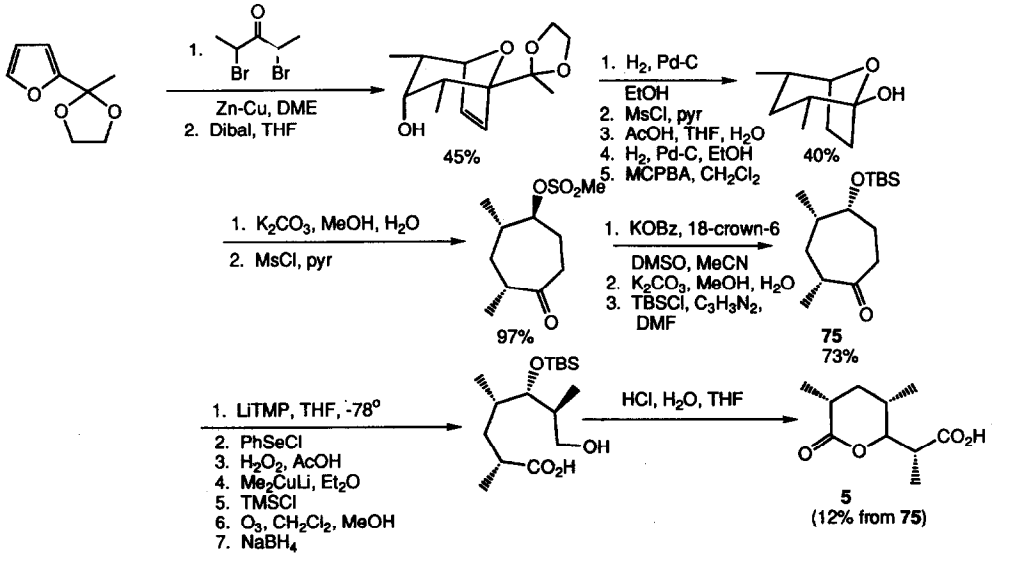
Regioselective functionalisation of the double bond was used in the synthesis of daunosamine (**66**) (Scheme 70), 2,5-anhydro-3-deoxy and -4-deoxy-D-hexonic acids including related deoxyadinosines, deoxy hexoses and lividosamine derivatives.[204b,207b,222]

Higher sugars such as octoses, caldose, calditol, 4-deoxy calditol, and 4-deoxycaldose have been synthesised via an aldol reaction of the bicyclic adduct with (*R*)-2,3-O-isopropylideneglyceraldehyde.[223] The addition of a glucopyranosyl radical to derivatives of the oxabicyclic system leads to α-1,3- and α-1,4-disaccharides.[207c]

3.3. *Dipolar cycloadditions*[129]

This class of reactions is closely related to the Diels–Alder reaction, but allows for the preparation of a five membered adduct.[224] Two major types of application for the preparation of carbohydrate derivatives are: use of a carbon–carbon dipole, and formation of isoxazolines.

Substituted furans readily undergo condensation with oxyallyl cations to form a bicyclo[3.2.1]oct-6-en-3-one system.[225] A variety of transformations can be performed on these adducts including alkylation adjacent to the carbonyl moiety.[201b,226] An example of the use of an adduct for the preparation of the Prelog–Djerassi lactone **5** is given in Scheme 77.[227] Note the excision of the acetyl appendage, ring cleavage and the relatively large number of functional group manipulations.



Scheme 77.

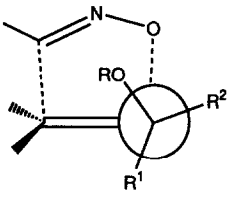
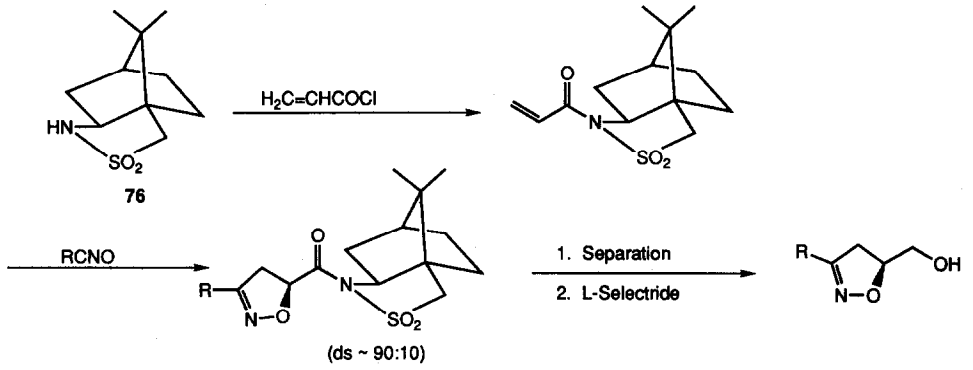


Figure 1.

Usually, reactions of carbon dipoles do not result in chemistry which is directly applicable to carbohydrate synthesis.[228]

Condensation of a nitrile oxide with a chiral allylic ether usually affords an isoxazoline with selectivity for the *pref*-isomer. This selectivity increases with the size of the alkyl substituent and is insensitive to the size of the allyl oxygen substituent. Allyl alcohols tend to form the *parf*-isomer preferentially, but the selectivity is low. These observations have been interpreted, through calculation, that allyl ethers prefer a transition state conformation with the alkoxy substituent inside and the alkyl substituent occupying the *anti* (R^1) position (Fig. 1).[229] In contrast, allyl alcohols react preferentially with the hydroxyl group outside (i.e. R^2 = OH). An alternative model with a Felkin type transition state has also been proposed.[230]

The condensation of chiral acrylate esters with nitrile oxides shows modest diastereoselectivity.[231] This problem has been circumvented by the use of a chiral sultam **76** (Scheme 78),[232] or by an intramolecular approach.[233] Vinyl sulphur compounds can also act as dipolarophiles,[234] even with unactivated alkenes.[235]

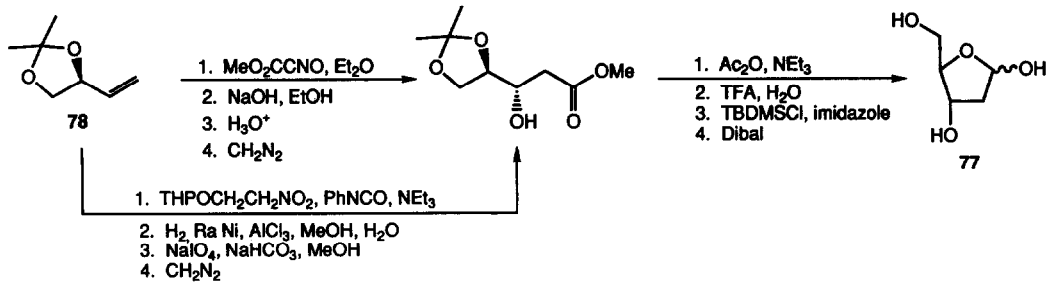


Scheme 78.

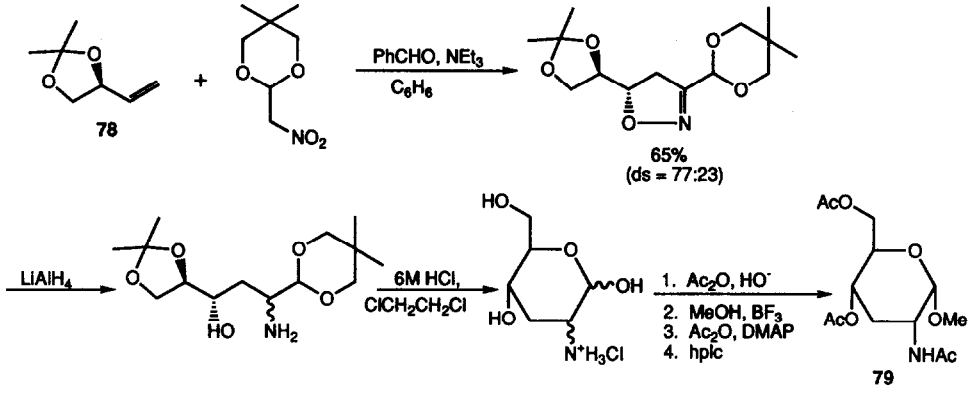
This reaction is very useful as the isoxazoline moiety can be converted into a wide variety of functional groups under relatively mild conditions.[236] The isoxazoline group can also be used as a method of protection, and can even influence relative stereochemistry through chelation control.[237]

2-Deoxy-D-ribose (**77**) has been prepared by condensation of an allyl ether **78** with a nitrile oxide (Scheme 79).[230,238] Other examples of carbohydrate synthesis are provided by derivatives of lividosamine (**79**) (Scheme 80),[239] D-allosamine hydrochloride,[239b] and daunosamine (*cf.* **80**) (Scheme 81).[240] The latter example illustrates that nitrones also participate in 1,3-dipolar cycloadditions,[241] which can be used to prepare alcohols with moderate asymmetric induction.[242]

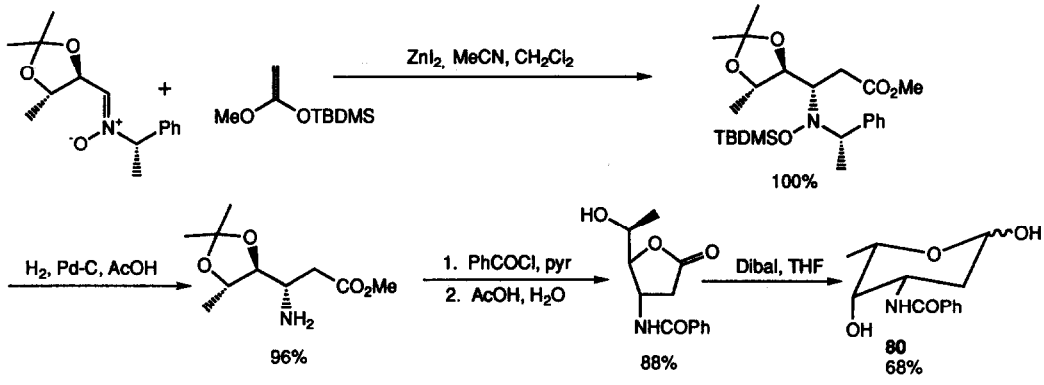
Carbohydrate derivatives are available through the use of furan as a dipolarophile. This methodology has been used to prepare an analogue of 5-*epi*-nojirimycin (**81**) (Scheme 82).[236l]



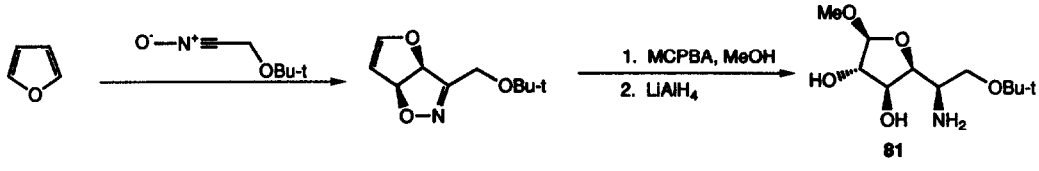
Scheme 79.



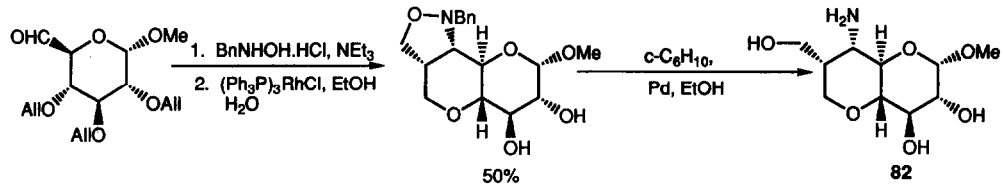
Scheme 80.



Scheme 81.



Scheme 82.



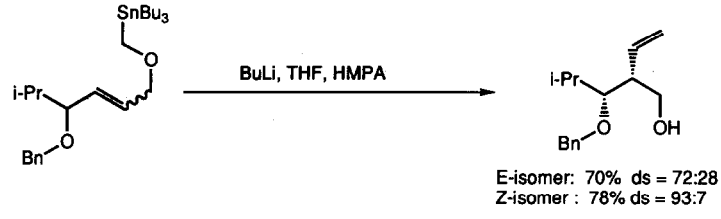
Scheme 83.

The high diastereoselectivity of the cycloaddition when the chiral substrate is derived from a carbohydrate allows for a simple entry to higher sugars (*cf.* Section 6.1) such as the pyranopyran **82** (Scheme 83).[243]

3.4. *Sigmatropic rearrangements*[244]

[2,3]-Sigmatropic rearrangements, of which the Wittig rearrangement is an example, allow for the transfer of stereochemistry.[90b,245] For carbohydrate applications, the oxygen series is the most important, although other heteroatoms have been used to stabilise the carbanion.

The rearrangement protocol can be employed to convert an allyl alcohol to a homoallyl alcohol (Scheme 84). The resultant stereochemistry of the double bond is, however, dependent upon the



Scheme 84.

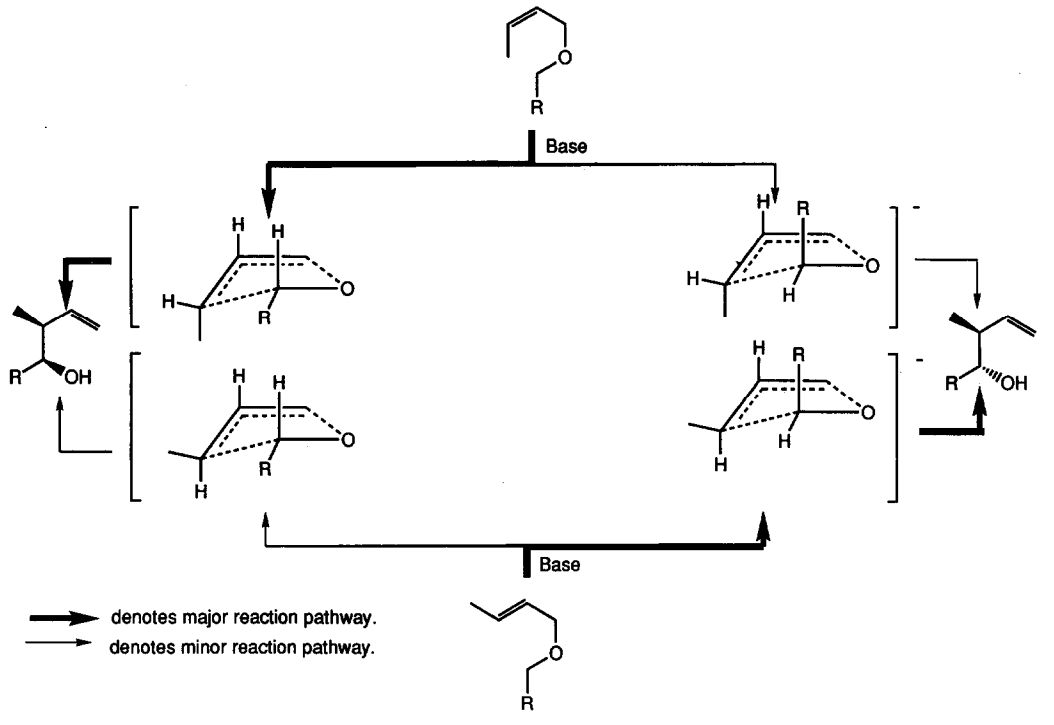
particular system, as the transition state geometry plays an important role to determine the reaction outcome (Scheme 85).[246]

The diastereoselectivity arises from the relative stabilities of possible transition state geometries. In general terms, use of a *Z*-alkene will result in the *parf*-isomer; *E*-alkenes show *pref*-selectivity but this does depend on the nature of the substituent. In addition, the substituent can play a role in stereoselection as it will influence the structure of the carbanion. The presence of a chiral substituent can lead to high asymmetric induction.[247]

Extension of the Wittig rearrangement to allyl ethers derived from secondary allyl alcohols, rather than primary, introduces a new stereochemical problem—the configuration of the resultant alkene.[248] The presence of allylic stereocentre usually results in the formation of the *pref* product isomer (Scheme 96). The use of the *Z*-isomer as substrate tends to allow higher selectivity for the *pref*-isomer than when the *E*-alkene is the reactant; these results have been rationalised by the transition state models **83** and **84** for the *Z*- and *E*-alkenes respectively (Fig. 2).[249]

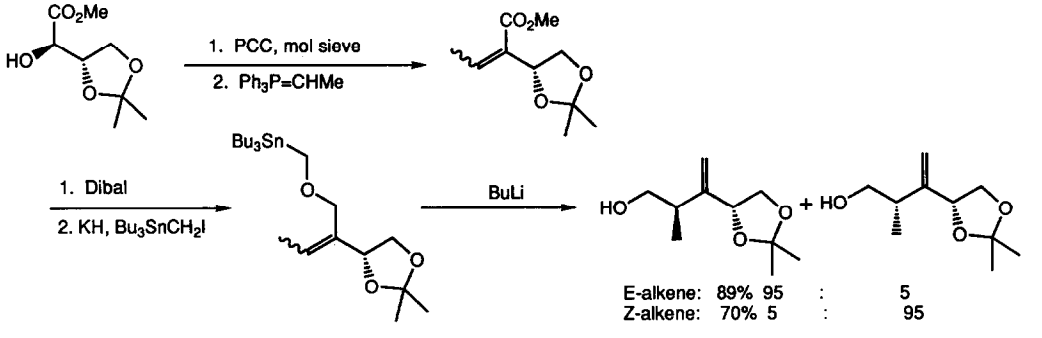
83 **84**

Figure 2.



Scheme 85.

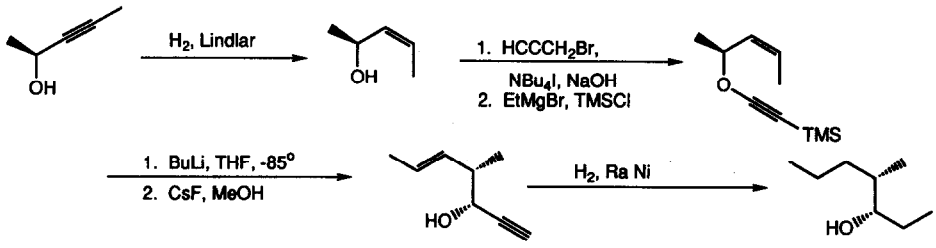
When a chiral substituent is present in the allyl moiety, 1,3-asymmetric induction is observed (Scheme 86).[250]



Scheme 86.

Although the rearrangement does not seem to be dependent on the metal counterion,[251] the stereochemical outcome is dependent upon the electronic and steric demands within the substrate itself.[249a,b,250,252] The use of a chiral base with acyclic substrates failed to give optically active [2,3]-sigmatropic rearrangement products,[253] although enantioselectivity has been observed with cyclic substrates.[254]

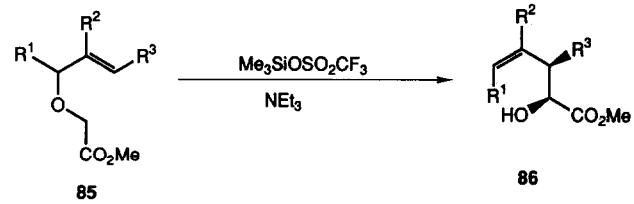
The rearrangement has also been extended to bis-allylic ethers, although a [1,2]-shift can compete.[255] This latter problem does not arise for allylic propargyl ethers.[244b,256] The relative stereochemistry at the saturated centres is unaffected (Scheme 87).[248a,257]



Scheme 87.

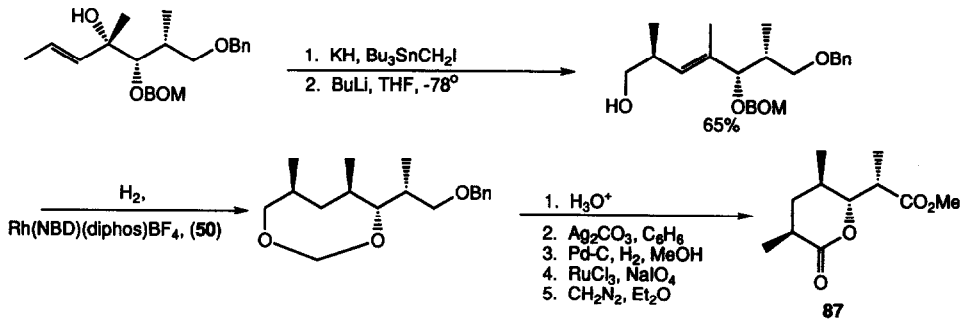
A further extension of the protocol provides a method to selectively protected 1,2-diols, but is limited by the necessity for an anion stabilising group to be present.[258] 1,3-Polyols are also available from a strategy that employs a Wittig rearrangement.[259]

Wittig rearrangement of allylic glycolic esters **85**, either in the presence of base or silyl triflate, allows for the stereoselective synthesis of γ,δ-unsaturated-α-hydroxyesters **86** (Scheme 88).[246d,e,256,260]



85 86

Scheme 88.



87

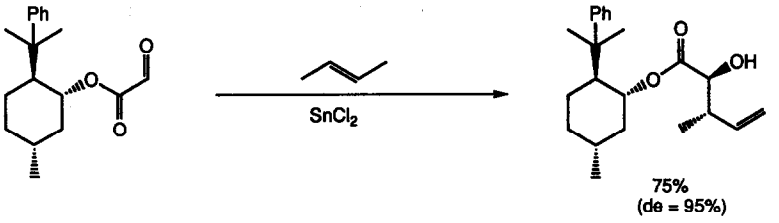
Scheme 89.

The utility of the Wittig rearrangement is readily demonstrated by the diversity of synthesis which rely on the methodology,[254,261] ranging from large antibiotics to dihydrofurans,[262] to the Prelog–Djerassi lactone ester (**87**) (Scheme 89).[261a,b]

In addition to the Wittig rearrangement, another [2,3]-reaction, the Evans rearrangement,[1,263] can be extended to prepare functionalised allyl alcohols.[264]

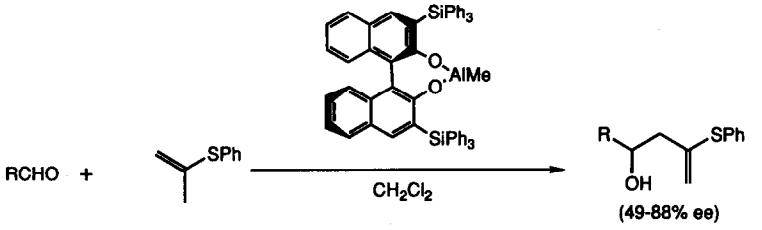
3.5. *Ene reactions*[130a,265]

The ene reaction, like the Wittig rearrangement, allows for chirality transfer.[266] In addition, relative stereochemistry can also be controlled (Scheme 90).[267]



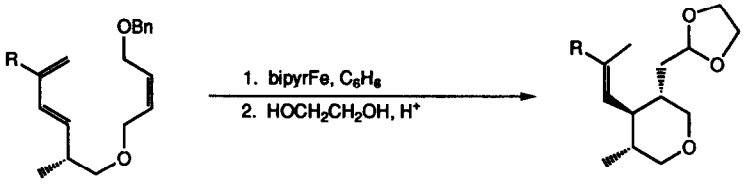
Scheme 90.

However, the majority of applications to date have centred around carbocyclic preparations.[268] Not only can alkenes be used in ene reactions, but masked functionality, such as latent carbonyl derivatives, can also be employed (Scheme 91).[269]



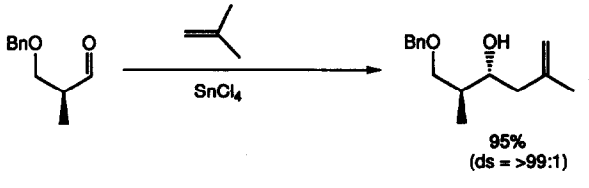
Scheme 91.

The methodology allows for a selective preparation of cyclic compounds, including tetrahydrofurans and pyrans (Scheme 92).[270]



Scheme 92.

Some acyclic applications provide useful stereochemical control when a cyclic primer is employed.[267,271] Chelation control can be used to obtain high stereoselectivity (Scheme 93),[272] while chirality can also be induced from the Lewis acid catalyst (*cf.* Scheme 91).[273]

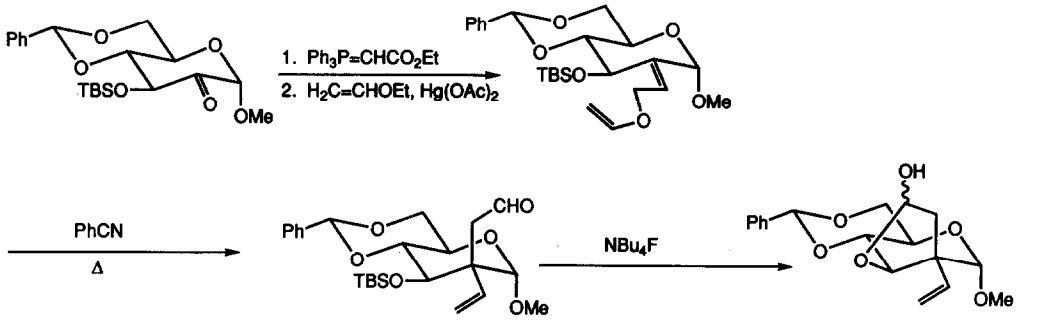


Scheme 93.

3.6. *Claisen rearrangements*[274]

The Claisen rearrangement has proven extremely useful in the synthesis of natural products.[274b,c,275] It has been adapted for a variety of derivatives including enol ethers,[276] amides,[277]

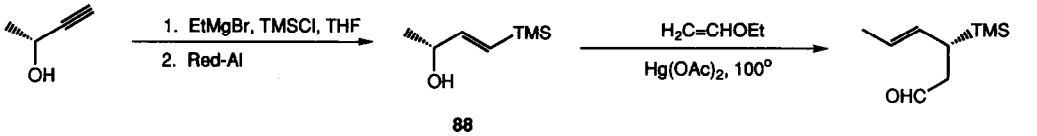
esters and orthoesters,[276e,278] acids,[279] oxazolines,[280] ketene acetals,[281] and thioesters.[282] Many of these variants rely on a cyclic primer to control stereochemistry, or to control only relative stereochemistry and alkene geometry. Thus, the use of a carbohydrate derivative allows *exo*-cyclic rearrangement to occur and afford geminal functionality at C-2 or C-3 of a hexapyranose system (e.g. Scheme 94).[283]



Scheme 94.

Carbohydrates have also been employed as chiral auxiliaries; they also allow the rearrangement to be performed in an aqueous medium.[284] Indeed, water has been used to accelerate the Claisen rearrangement without the need to use an auxiliary to solubilise the substrate.[285]

An example of an enol ether Claisen rearrangement is provided by the vinylsilane **88**, where the large silyl group adopts an equatorial position in the chair transition state (Scheme 95).[286]



88

Scheme 95.

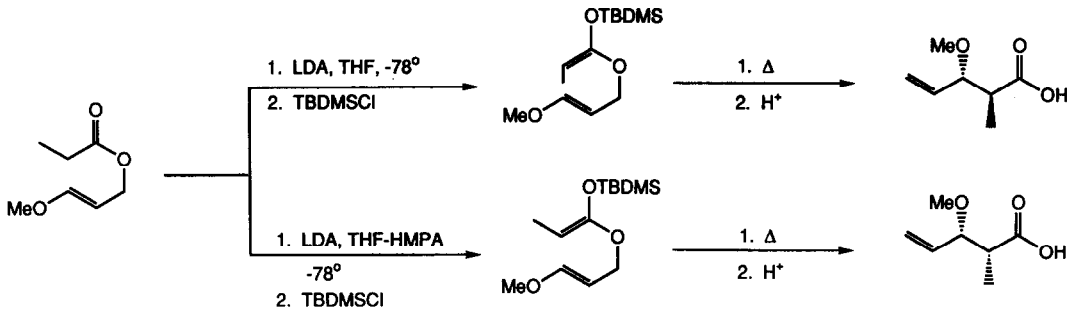
The reaction provides a useful entry into chiral butyrolactones (Section 4.1.1).[287]

The Claisen rearrangement can be accelerated through π-electron donating groups at the 2-position of the vinyl portion of the ether.[288] The aliphatic Claisen rearrangement does proceed in the presence of organoaluminium compounds,[275c,289] although other Lewis acids failed to bring about the same transformation.[275c,290,291]

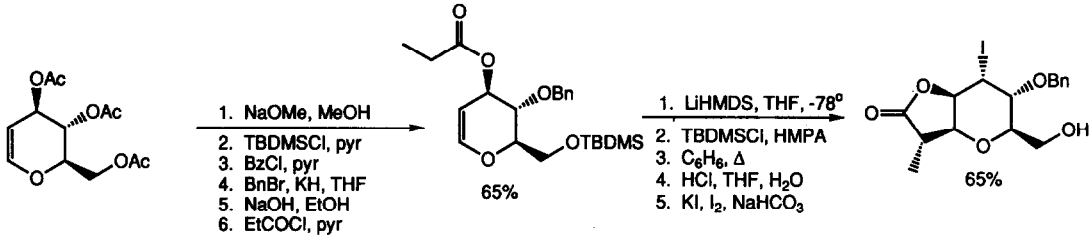
The current, major application of the Claisen reaction utilises allyl esters, as the overall reaction conditions are relatively mild.[279c] The geometry of the initially-formed enol ether substrate is controlled by the solvent (Scheme 96).[279a,292] Thus, the methodology provides a useful alternative to an aldol approach. The reaction even proceeds when a leaving group is β to the ester group.[293]

Examples of the application of this reaction[294] are provided by syntheses of nonactic acid,[295] the Prelog–Djerassi lactone,[296] prostanoids,[297] tirandamycic acid (*cf.* Scheme 97),[298] sesquiterpenes,[299] macrolides,[300] ionophores,[293,301] and bicyclic systems,[302] including steroids.[303]

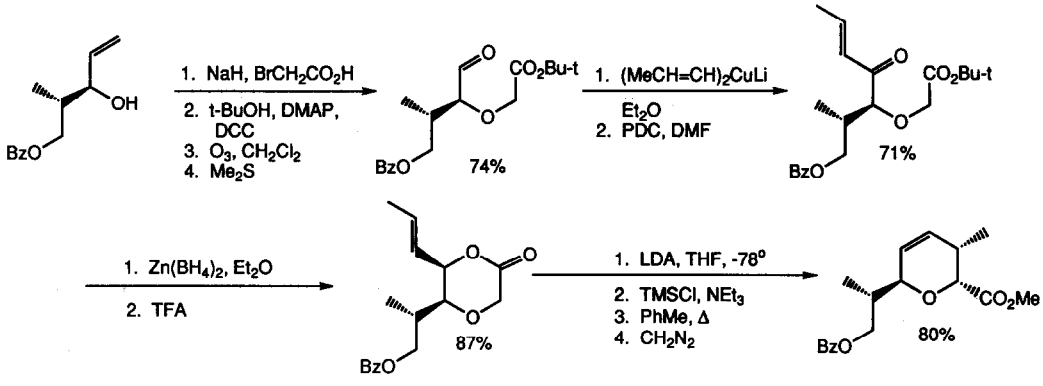
The methodology has been extended to allow the preparation of α-alkoxyesters, with diastereoselection,[304] α-phenylthioesters,[304d,305] α-amino acids,[306] α-fluoroesters,[307] cycloalkenes,[308] tetronic acids,[309] and dihydropyrans (Scheme 98).[298,310] The dioxanone to dihydropyran transformation allows a pyran nucleus to be built up rapidly with impressive stereochemical control.[300d,304f,311]



Scheme 96.



Scheme 97.

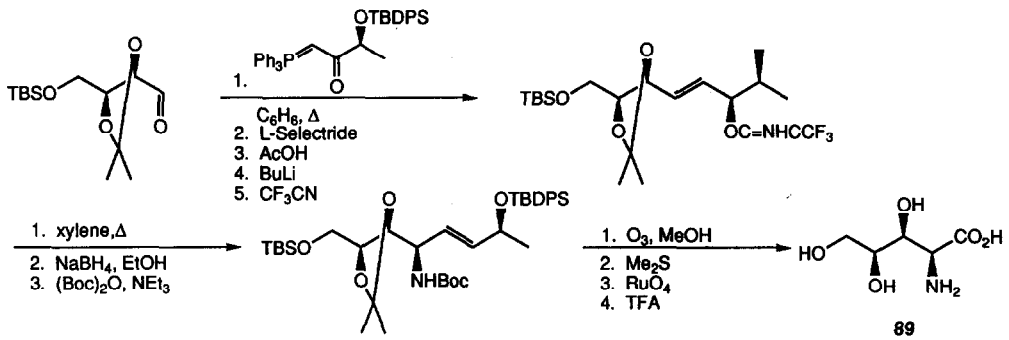


Scheme 98.

In a few cases an alternative, competing pathway which involves a retro-Diels–Alder reaction followed by a Diels–Alder addition has been observed rather than the Claisen rearrangement; the major product is the same, whichever mechanism is followed.[300e] Of course, the problems associated with a chair versus boat transition state are then alleviated.[312]

The thio-Claisen rearrangement can be used to provide substituted thioamides and β-hydroxydithioesters.[313] The ketal version of the rearrangement provides a regioselective method to γ,δ-enones from allyl alcohols.[314]

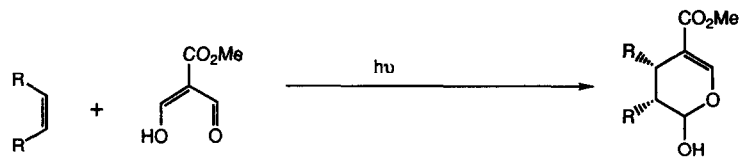
The closely related, ester enolate Carrol rearrangement affords entry into β-ketoacids or γ,δ-enones.[315] Another related reaction, the [3,3] thermal rearrangement of allylic imidates has been used in a synthesis of (+)-polyoxanic acid (**89**) (Scheme 99).[316]



Scheme 99.

3.7. *Photochemical reactions*

Photochemically induced annelation of an alkene with methyl diformylacetate (Scheme 100) allows for high stereoselectivity but poor regioselection.[317] This limitation has been overcome to a certain degree in a cyclic case, by use of an allylsilane.[318]



Scheme 100.

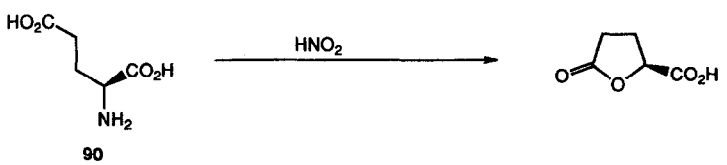
Photochemical addition of diethyl ketene acetal to a phenylglyoxylate ester affords good induction, although chemical yields are moderate at best.[319] Malic acid is available from an asymmetric [2+2] cycloaddition involving ketene and catalysed by quinidine.[320] Photocycloadditions of aldehydes to furans provide adducts with a plethera of functionality.[321]

4. APPROACHES BASED ON CYCLIC COMPOUNDS

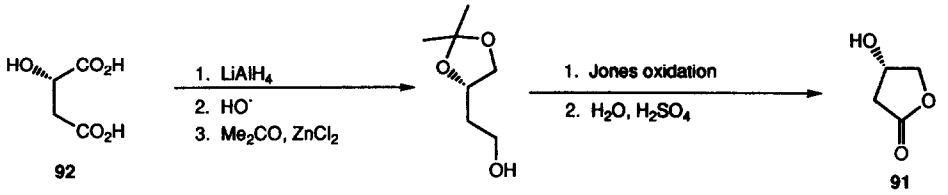
The majority of the reactions discussed in this section are based on oxygen heterocycles. Other approaches, that are not included, are the Baeyer–Villiger oxidation of a cyclic ketone to provide an ω-hydroxyacid lactone, or the use of a heterocycle, such as furan, to act as a masked functional group.

4.1. *Preparation of 5-membered ring compounds*

4.1.1. *Preparations of butyrolactones.*[39a,322] γ-Butyrolactones provide an extremely useful cyclic template for modification into a furanoside derivative. Cyclisation of a γ-hydroxyacid often occurs spontaneously to afford the butyrolactone.[309,323] One of the most direct entries into an asymmetric example of this class of compounds is from L-glutamic acid (**90**) (Scheme 101).[324]



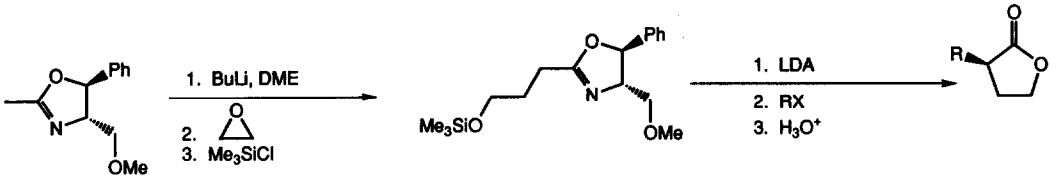
Scheme 101.



Scheme 102.

(*S*)-3-Hydroxy-γ-butyrolactone (**91**) is available from (*S*)-(−)-malic acid (**92**) (Scheme 102).[325] Other natural products that afford butyrolactones are carbohydrates,[137a,326] such as mannose,[327] mannitol,[328] citramalic acid,[329] and tartaric acid.[330] Chiral α-hydroxyesters can be converted to 4-alkyl-2-hydroxytetronic acids by a Claisen rearrangement (Section 3.6).[331]

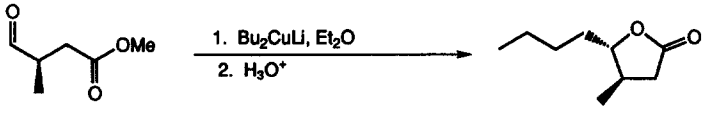
The above methods all rely on readily available natural products as starting materials. Some lactones can be resolved by an enantioselective kinetic protonation procedure.[332] The cyclic system is available by a variety of means including alkylative methods.[333] Chiral oxazolines provide methodology to γ-butyrolactones with moderate (64–73%) asymmetric induction (Scheme 103).[334]



Scheme 103.

Although ester enolates do not undergo a facile reaction with epoxides, the use of an aluminium enolate not only provides reasonable chemical yields, but high diastereoselection with the *cis*-isomer predominating.[335]

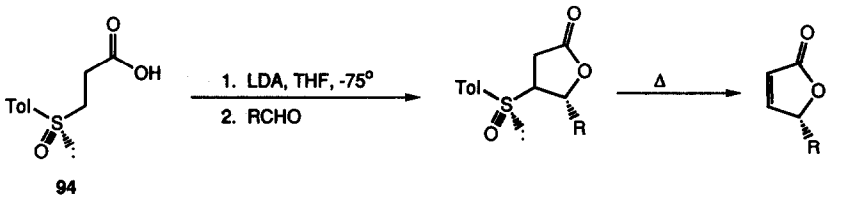
Reaction of a γ-aldehyde ester (**93**) with a cuprate results in chelation controlled addition (Scheme 104). The reaction is, however, very solvent dependent.[336]



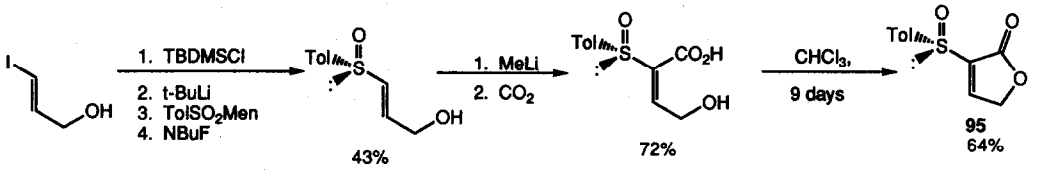
Scheme 104.

Reductions of γ-oxoesters under asymmetric hydrogenation conditions provide a powerful entry to 4-alkylbutyrolactones as either enantiomer becomes available.[337]

An alternative condensation approach uses a chiral sulphoxide **94** to control stereochemistry (Scheme 105).[338] A further variant utilises a chiral enolate derived from an organoiron compound.[339] A related methodology, that employs zirconium, can convert optically active propargyl alcohols to butenolides.[340] Indeed, propargyl alcohols, which can be obtained by asymmetric reduction, provide a number of useful synthetic methods to butyrolactones.[80f,341]



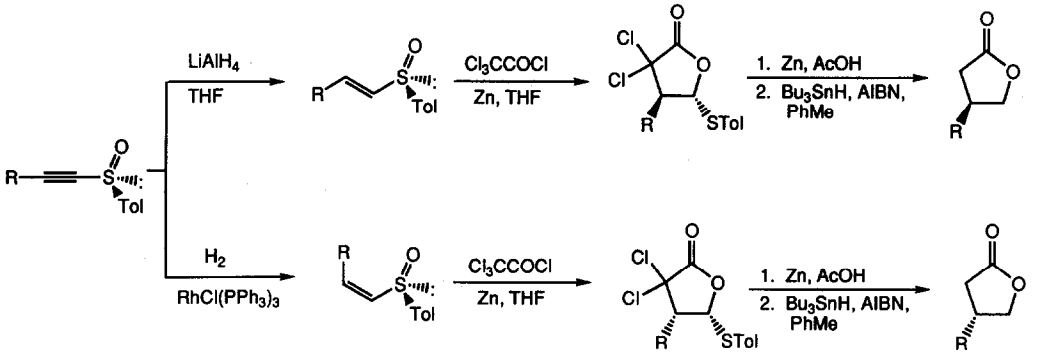
Scheme 105.



Scheme 106.

A chiral sulphoxide can be incorporated into a butyrolactone (Scheme 106).[342] The butenolide **95** can then be used as a Michael acceptor for further modification.[342,343]

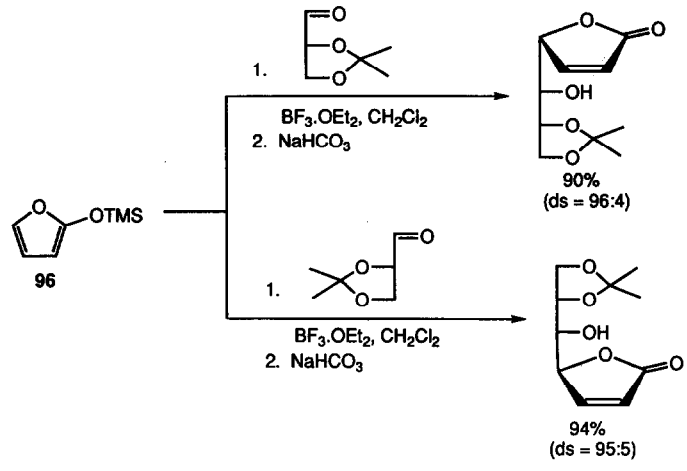
An approach that allows for the preparation of either isomer of a 4-substituted butyrolactone relies on the stereospecific addition of dichloroketene to an allyl sulphoxide (Scheme 107).[344]



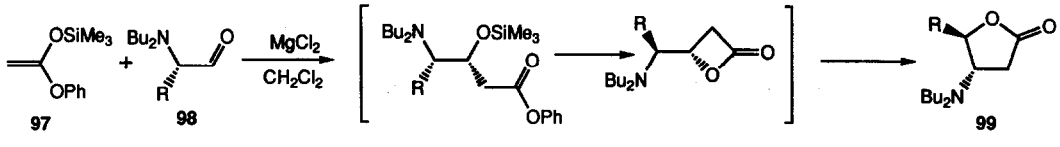
Scheme 107.

Furans can also provide a facile entry to butenolides.[345] 2-Trimethylsiloxyfuran (**96**) is a four carbon donor and a masked butenolide; it enters into stereoselective additions with carbonyl compounds. This provides a convergent approach to higher sugar derivatives (Scheme 108).[346] In a closely related approach, β-acylvinyl anions add to carbonyl compounds to yield 4-alkylbutyrolactones.[347] Substituted γ-butyrolactones are available from condensation of an allyl anion with a carbonyl compound (Section 2.1).[348] A similar approach is based on a Michael addition, but optical yields are low.[349] The use of α-alkoxyorganocuprates does allow the preparation of *cis*-substituted butyrolactones, but the approach is compromised by the relatively high amount of competing 1,2-addition.[350] α-Alkoxyorganolithium reagents react with α,β-unsaturated carbonyl derivatives to provide γ-hydroxycarboxylic acids and, hence, butyrolactone derivatives enantioselectively.[351]

Anh–Felkin addition of a silyl ketene acetal **97** to an α-aminoaldehyde **98** provides the lactone **99** (Scheme 109).[352]

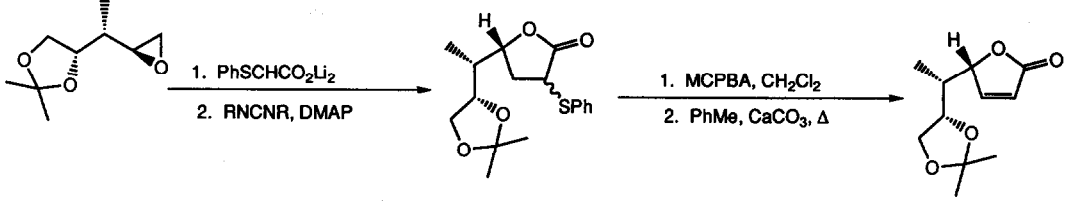


Scheme 108.



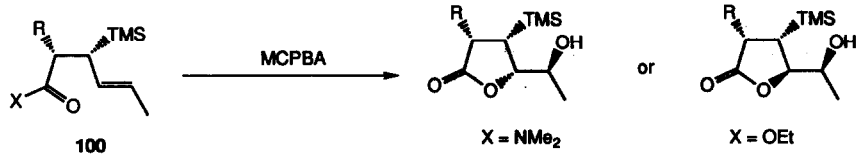
Scheme 109.

The larger number of asymmetric routes to chiral butyrolactones, however, rely on a 2,3-epoxyalcohol (Section 2.3.2), either derived by conversion of a carbohydrate,[353] or by a Sharpless protocol.[354] Opening of an epoxide by a carboxylate anion provides the basis for a general method to butyrolactones (Scheme 110).[137a,353,355]



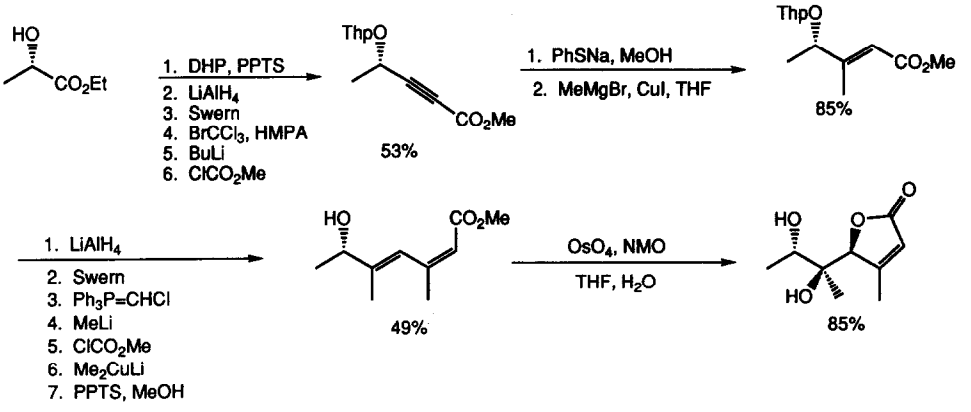
Scheme 110.

The use of an allylsilane substrate **100** for a peroxyacid oxidation allows access to butyrolactones with the stereochemistry of the cyclisation being controlled by the carboxylic acid derivative (Scheme 111).[356]



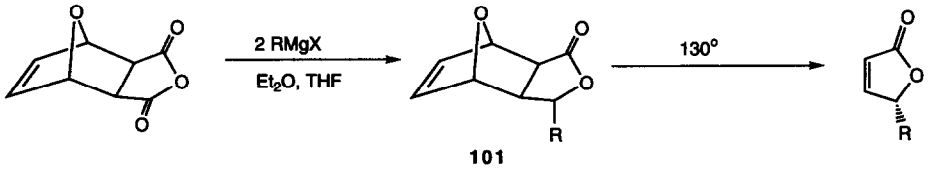
Scheme 111.

The stereochemistry of the lactone prepared by an acyclic method invariably results from stereochemical control during the synthesis of the precursor, as illustrated by the selective hydroxylation procedure (Scheme 112).[357]



Scheme 112.

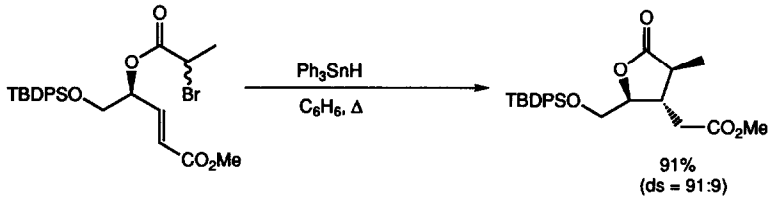
A bicyclic system framework that can then be removed provides a stereoselective route to butenolides with secondary Grignard reagents. The bicyclic adduct **101** can be separated from its diastereoisomer by simple recrystallisation (Scheme 113) (*cf.* Section 3.2.1).[358]



101

Scheme 113.

Lactones can be prepared by radical cyclisation.[359] The use of α-haloesters and a chiral substrate allows for asymmetric induction (Scheme 114).[360]

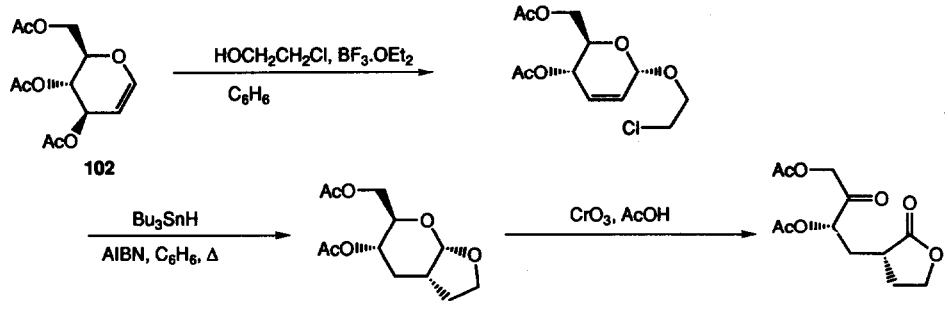


Scheme 114.

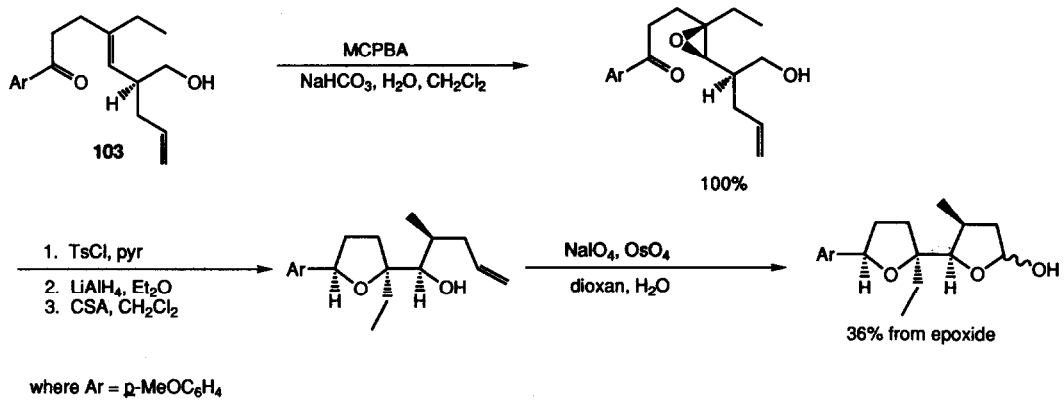
The use of an alkyl halide as a radical precursor, together with a glycal starting material, such as **102**, not only provides an entry to higher sugars, but a route to butyrolactones (Scheme 115).[361]

4.1.2. *Preparations of tetrahydrofuran derivatives.* Many methods have been developed to prepare tetrahydrofurans and tetrahydropyrans by a cyclisation protocol (e.g. Scheme 116).[362] Iodolactonisation is discussed in the following section.

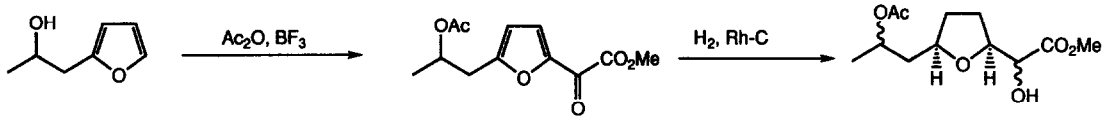
Reduction of a furan derivative provides a simple entry into *cis*-tetrahydrofuran derivatives. This approach has been capitalised upon for a variety of routes to nonactic acid (e.g. Scheme 117).[363]



Scheme 115.



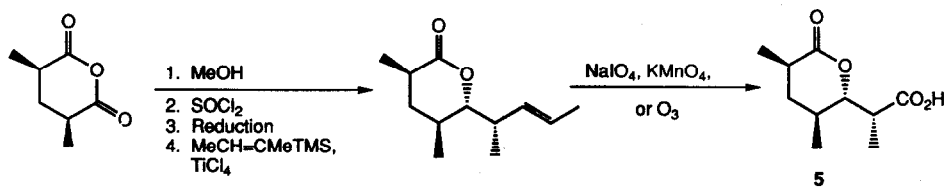
Scheme 116.



Scheme 117.

4.2. *Preparation of other cyclic oxygen compounds*[39a,322a,364]

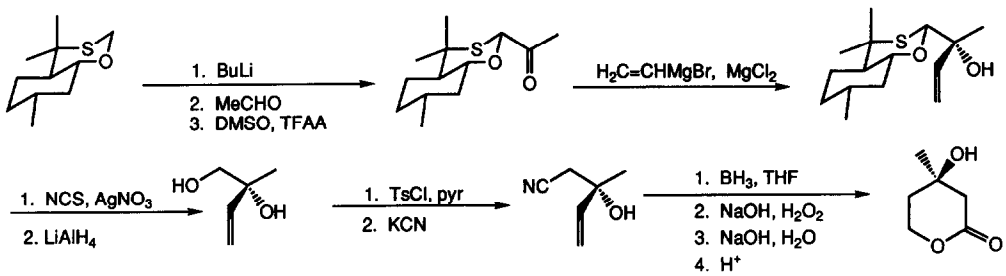
Many of the methods described for the preparation of butyrolactones can be modified to prepare valerolactones. There are many routes to valerolactone derivatives,[365] as evident by the various syntheses of the well-known Prelog–Djerrasi lactone (**5**) (e.g. Schemes 4, 89, and 118).[128a,366]



Scheme 118.

Similarly, saturated pyran synthesis can be modified from furan derivatives in an analogous manner. Tetrahydropyrans are formed preferentially by regioselective *endo-* or *exo*-epoxide opening.[367]

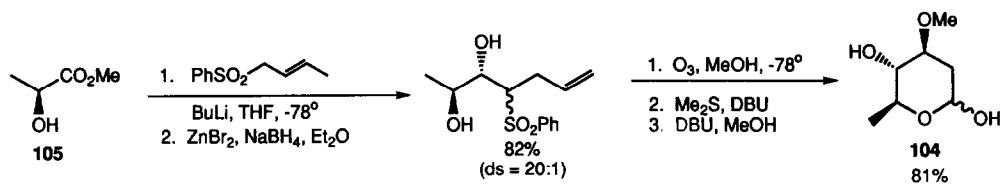
The use of chiral auxiliaries, such as oxazolines (Scheme 103),[368] oxathianes (Scheme 119),[369] and sulphoxides[338a,370] allow the preparation of butyro- or valerolactones.



Scheme 119.

The chiral centre for the preparation of a chiral valerolactone can be an integral part of the substrate molecule (Schemes 118 and 119).[371]

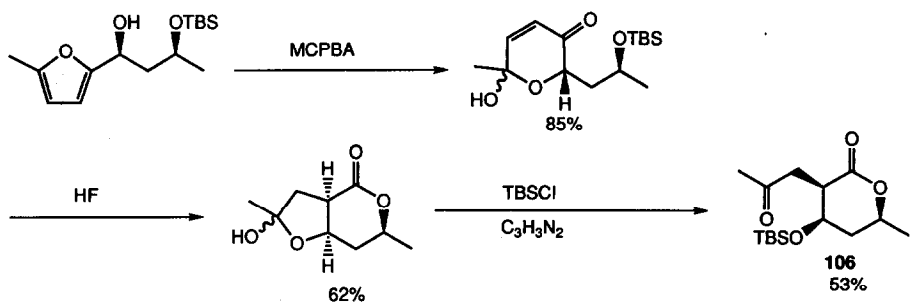
This philosophy has also been used for lactol synthesis as illustrated by a synthesis of L-(−)-oleandrose (**104**) from methyl lactate (**105**) (Scheme 120).[371d]



Scheme 120.

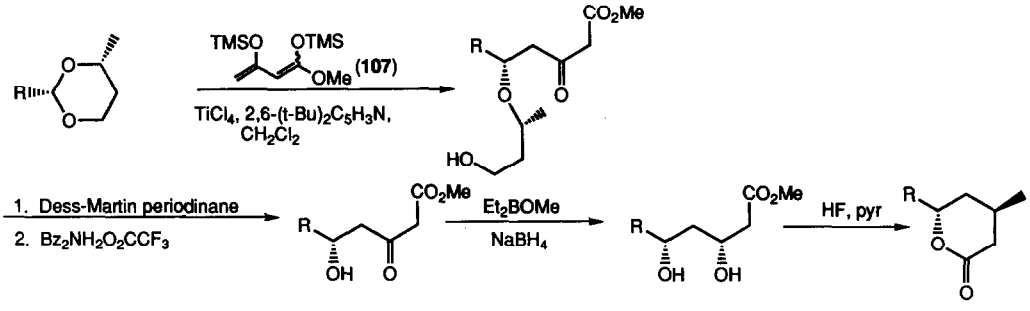
Another access to valerolactones relies on a Sharpless protocol to introduce the desired chirality.[372]

Oxidation of a furan derivative followed by rearrangement gives the functionalised valerolactone (**106**) (Scheme 121);[373] such an approach has been used to prepare (+)-KDO (3-deoxy-D-*manno*-2-octulosonic acid) (**21**).[374]



Scheme 121.

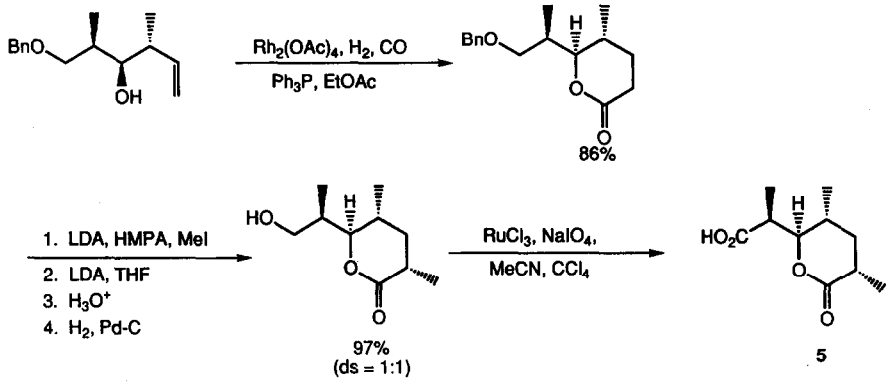
A Sharpless kinetic resolution can be performed on the 2-furylcarbinol; one isomer is converted to the functionalised valerolactone, while the other remains as the furan compound.[375]



Scheme 122.

Good stereochemical control for the preparation of valerolactones can also be obtained from an acetal opening approach (Scheme 122),[376] or an allyl addition (Section 2.1.1).[377]

The stereochemistry from a homoallyl alcohol can be retained in the product γ-lactone by use of a hydroformylation reaction. This is illustrated by another example of the synthesis of the Prelog–Djerassi lactone (**5**) (Scheme 123).[378]



Scheme 123.

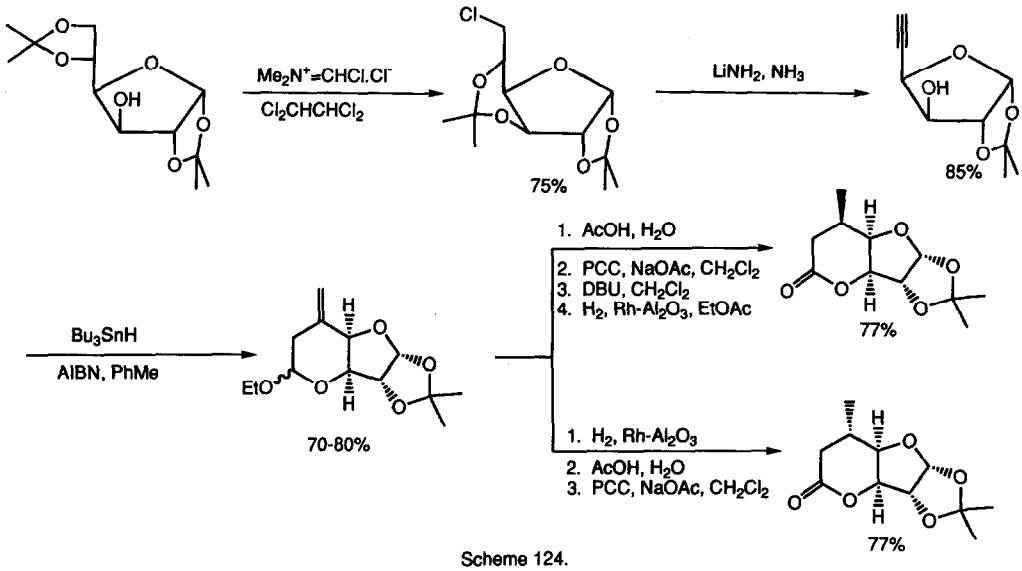
A radical cyclisation from a furanose template provides a method to a fused γ-lactone where either isomer at C-5 can be obtained through functional group manipulations (Scheme 124).[379] A radical cyclisation protocol allows for the preparation of *trans*-2,3-tetrahydropyrans; this methodology is complementary to the Claisen-type rearrangement of dioxanones to dihydropyrans (Section 3.6).[380]

Cyclisation of a 1-hydroxy-5-alkene with a palladium(II) catalyst and hydride elimination controlled by the solvent, DMSO, provides a route to *cis*-2,6-tetrahydropyrans (Scheme 125).[381]

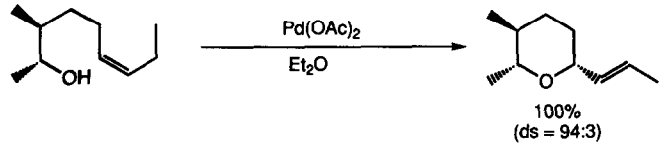
2,3-Dihydro-4*H*-pyran-4-ones are available by a Mukaiyama reaction of 2,4-bisilyl-1,3-pentadienes (**107**) with aldehydes or ketones. The reaction is under chelation control and, therefore, does provide some diastereoselection (*cf.* Scheme 122).[382]

cis-Dihydropyrones (**108**) are available by an aldol approach which also sets up the requisite stereochemistry (Scheme 126).[383]

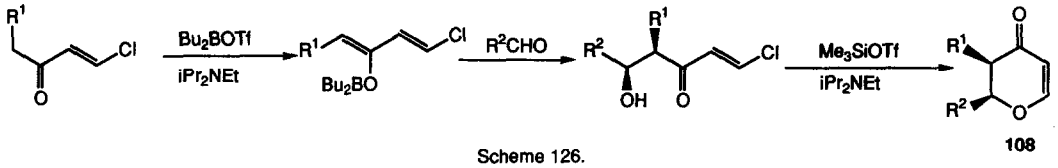
Of course, tetrahydropyrans can be prepared by cyclisation reactions that utilise stereogenic centres within the substrate. Thus, the pyrone (**109**) was prepared from the β-ketoester **110** (Scheme 127),[384] while tetrahydropyrans are available from chiral alkoxyallylsilanes (**111**) although optical yields are only moderate (Scheme 128).[385]



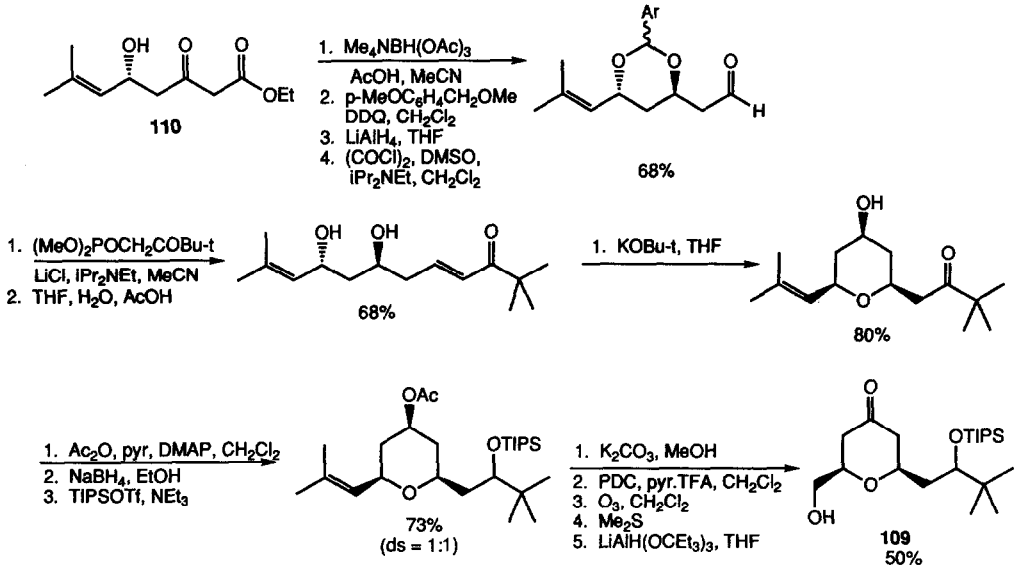
Scheme 124.



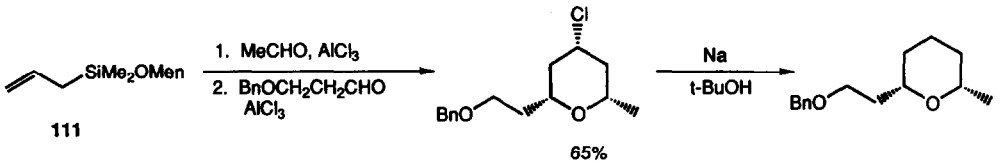
Scheme 125.



Scheme 126.



Scheme 127.

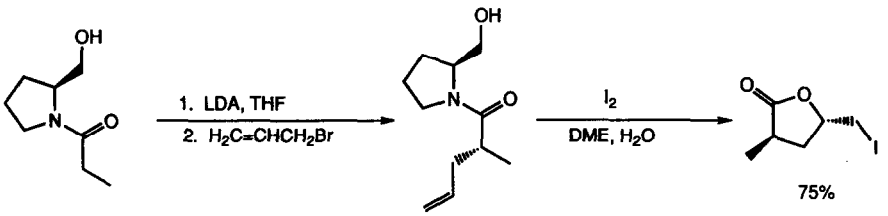


Scheme 128.

4.3. *Electrophilic cyclisations*[386]

Intramolecular cyclisation is a useful method for the preparation of lactones and cyclic ethers. The most common examples are iodolactonisation and iodoetherification, the difference being that the former uses a carboxylic acid derivative as the nucelophile, while the latter relies on a hydroxy group. Thus, butyrolactones are available from γ,δ-unsaturated carboxylic acid derivatives,[92b,387] while unsaturated alcohols lead to cyclic ethers.[388] Lactones are also available from a wide variety of nucleophiles such as carbonates,[389] orthoesters,[390] or carbamates, which can all be used in place of a carboxylate anion.[391]

The intermediate iodonium ion controls the relative stereochemistry of the cyclisation. An asymmetric centre present within the substrate, therefore, allows for enantioselectivity (*cf.* Scheme 129).[392] The reaction is very susceptible to the steric interactions within the transition state.[392,393]

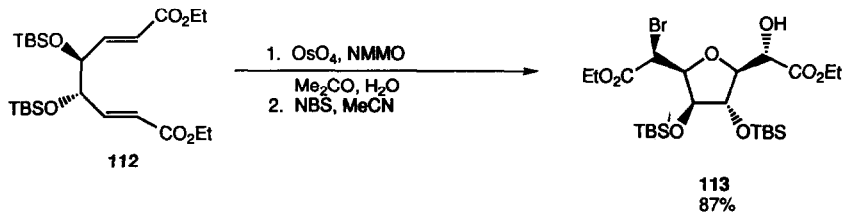


Scheme 129.

Variations on this methodology include the use of bromine, rather than iodine; again both lactones and ethers can be prepared.[362a,388f,389,390,391a,394]

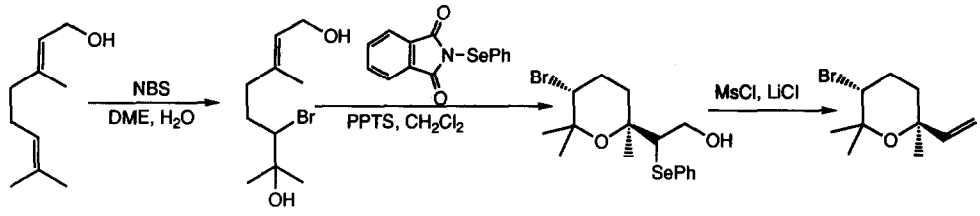
An asymmetric bromolactonisation procedure affords α-hydroxyacids with good asymmetric induction.[395] The procedure can be modified to prepare α,β-epoxyaldehydes.[396]

The selective oxidation of the diene **112**, followed by bromoetherification leads to the *cis*-tetrahydrofuran **113** (Scheme 130).[397]



Scheme 130.

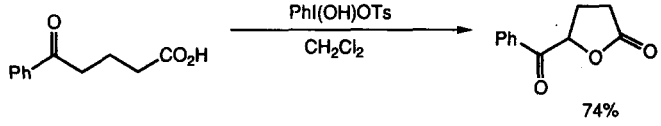
A further variation utilises selenium or sulphur as the electrophilic species to induce cyclisation. The diversity of organoselenium or organosulphur chemistry is then available for further modification of the product.[399] Both lactonisations with selenium,[399] and sulphur[400] are known. However, the majority of examples form cyclic ethers (Scheme 131).[401]



Scheme 131.

In addition to halogens and selenium compounds, transition metal salts such as those of titanium,[402] lead,[403] and mercury,[404] can be used to activate an alkene.

Oxidative methods can be used to induce cyclisation. Use of hypervalent iodine compounds provides an electrophilic centre adjacent to a carbonyl group (Scheme 132).[405] These reagents can also be used with carbon–carbon unsaturated compounds.[406]

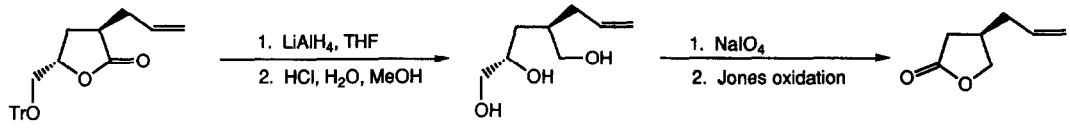


Scheme 132.

An alkene can also be converted to an epoxide; this then allows cyclisation to an ether or lactone.[407] Such an approach was used to establish four stereogenic centres from a single one, as in the allyl alcohol **103** (Scheme 116).[355a,362a,b,408] These reactions usually derive their stereoselectivity from the oxidation step as the epoxide opening occurs by an S_N2 mechanism.

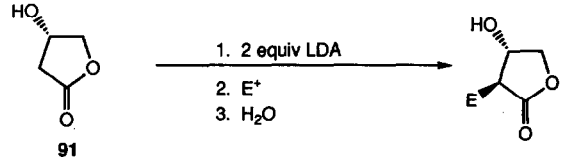
4.4. *Reactions of 5-membered ring compounds*

4.4.1. *Reactions of butyrolactones.*[322a] The steric constraints within the five-membered ring of a substituted butyrolactone allow for the stereoselective introduction of functional groups either by reaction juxtaposed to the carbonyl group, or at the β-position.[409] Functional group manipulation and extrusion of a carbon allow for the conversion of an α-substituent to a β-substituent (Scheme 133).[410]



Scheme 133.

Alkylation or aldol condensation of the dianion derived from lactone **91** results in stereoselective introduction of the electrophilic moiety (Scheme 134).[325,411]



91

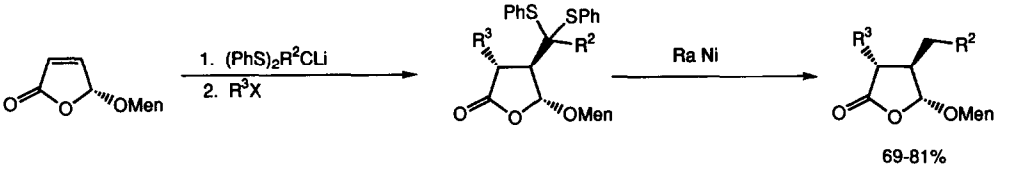
where E^+ = MeI or RCHO

Scheme 134.

Conversion of the hydroxy group of a 2-hydroxybutyrolactone to an *O*-trifluoromethanesulphonate ester followed by treatment with lithium iodide trihydrate in tetrahydrofuran provides the 2-deoxylactone.[412]

The use of 2-trimethylsiloxyfuran **96** in an aldol type addition provides the γ-substituted butyrolactone with good selectivity (Scheme 108).[413] This approach has been applied to the synthesis of higher sugar derivatives (*vide supra*).[346]

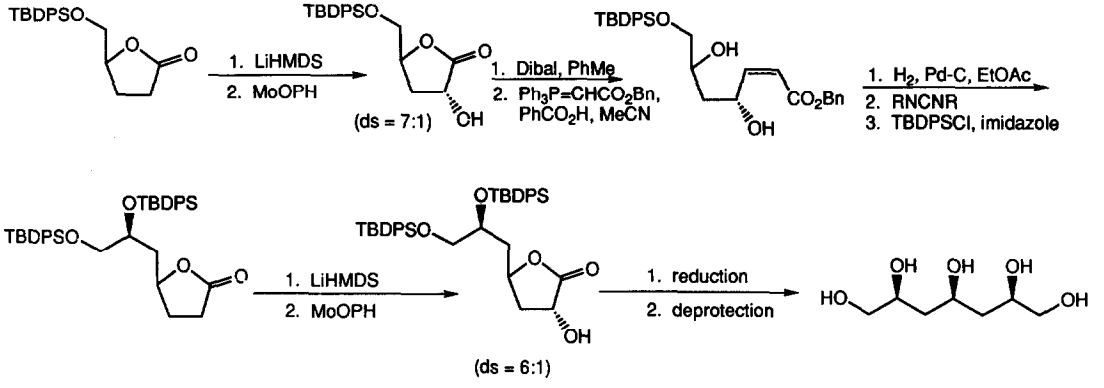
The side chain of a chiral butyrolactone can control the facial selectivity next to the carbonyl moiety (Scheme 110).[355i] The use of a chiral 5-alkoxy substituent on a butenolide also allows for asymmetric induction (Scheme 135).[414]



Scheme 135.

The facial selectivity imparted by a 5-substituent also allows for the consecutive, stereoselective introduction of two alkyl groups at C-2 in a butyrolactone.[415] Indeed, protonation of the lithium enolate of a butyrolactone bearing substituents at the α and γ-positions provides the *syn*-isomer selectively.[416] A β-substituent allows for the introduction of an electrophile at the α-position with the two resultant substituents being *trans*.[417]

Similar methodology can be used to introduce a hydroxy group, although the facial selectivity is slightly reduced (Scheme 136).[355h,418]



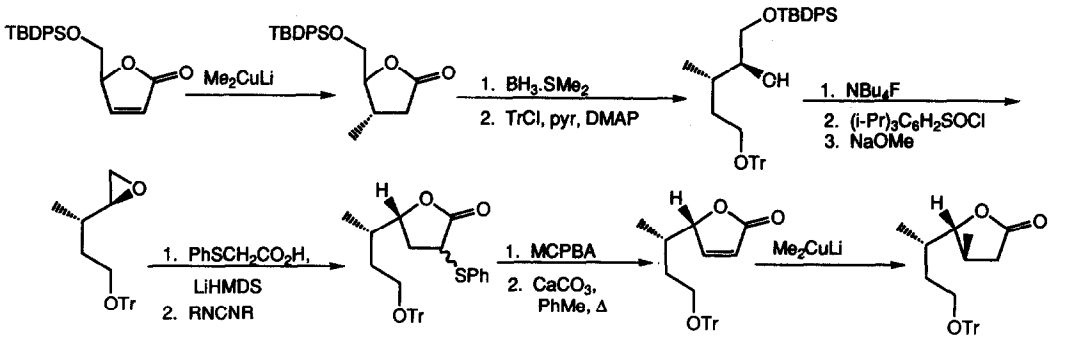
Scheme 136.

An enolate protocol can be useful for the conversion of a butyrolactone to a butenolide.[324b,419]

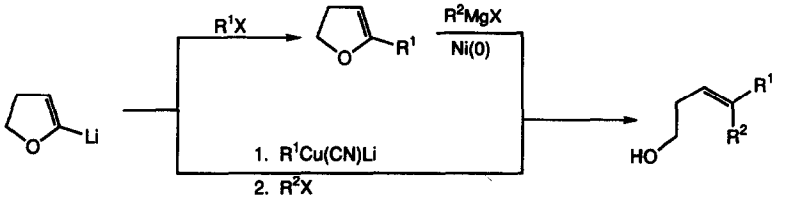
Conjugate additions can also be controlled by the stereochemistry of a γ-substituent (Scheme 137).[420] These two methods, conjugate additions and alkylations, can be utilised to introduce two groups in one operation (Scheme 135).[327a,418,421]

4.4.2. *Reactions of tetrahydrofuran derivatives.* The chemistry of 2-lithiofuranosides follows that of the pyranoside analogues (Section 4.5). The stereochemical control, however, is often not as good.

Dihydrofuran lithiation provides methodology to prepare homoallylic alcohols (Scheme 138).[422]



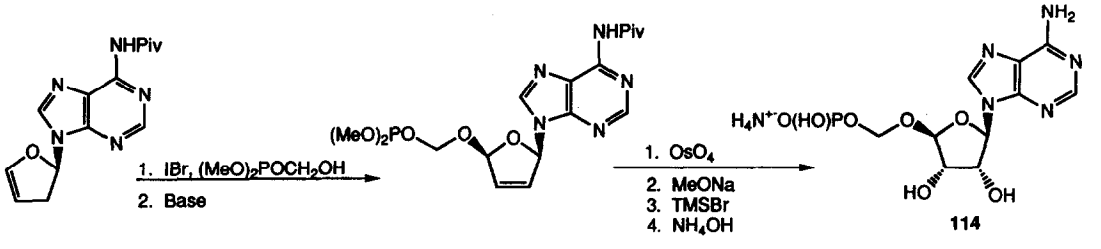
Scheme 137.



Scheme 138.

Lactol ethers can be converted to 2-bromotetrahydrofurans by treatment with bromotrimethylsilane.[423] The reaction of a dihydrofuran or dihydropyran and an α-hydroxyester allows for the resolution of the resultant acetal.[424]

The stereochemical requirements of a substituent have been used to prepare the phosphonate isotere of adenosine monophosphate **114** (Scheme 139).[425]



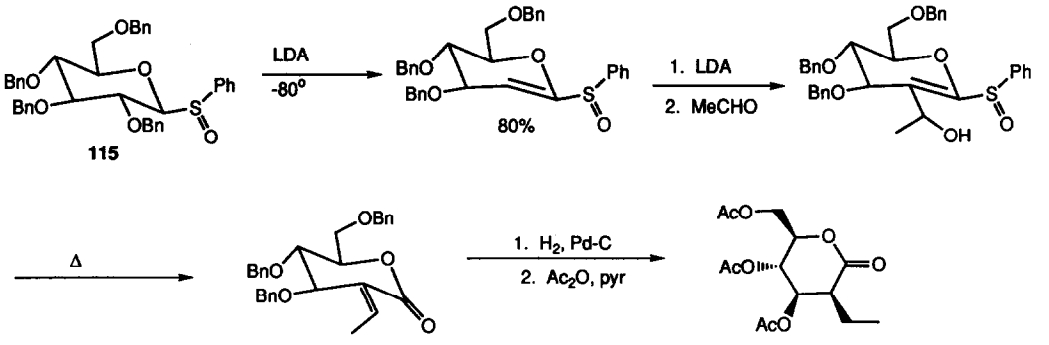
Scheme 139.

Nucleophilic addition to α-chiral lactols provides 1,4-diols with a high control of diastereoselection.[426] Lactols and their esters provide 2-substituted tetrahydrofurans with Reformatsky and other nucleophilic agents.[427]

4.5. *Reactions of 6-membered and other cyclic compounds*

A number of the methods developed for 5-membered ring compounds can be used with 6-membered rings. These methodologies include the chemistry of lactol ethers and vinyl ethers.

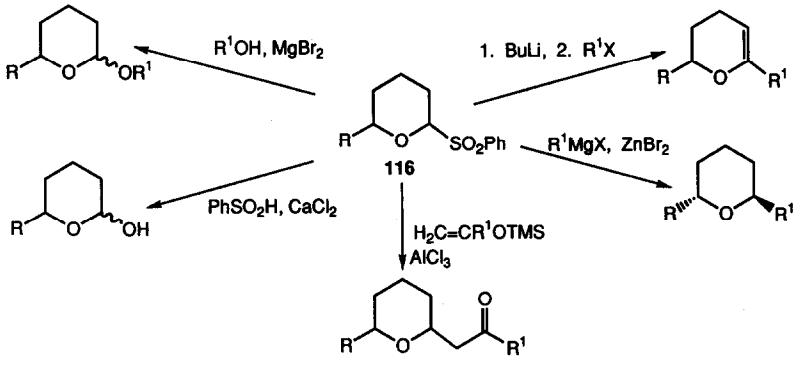
Several methods have been developed for the preparation of cyclic vinyl ether anions, which allow for the introduction of a wide range of functionality,[362d,422c,428] and are available in chiral form.[429] The approach has been extended to other dihydropyran derivatives.[430]



Scheme 140.

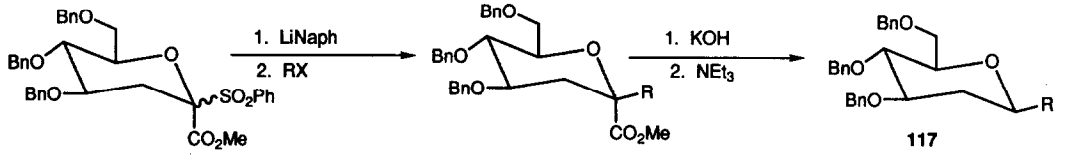
The use of a thioglucal **115** (*cf.* Section 6) not only allows carbanion formation at C-2, but deoxygenation of the parent monosaccharide occurs at C-2 (Scheme 140).[431]

2-(Benzenesulphonyl)tetrahydro-2*H*-pyrans (**116**), available by reaction of benzenesulfinic acid with dihydropyrans, lactols, or lactol ethers,[432] can be used with a wide variety of carbon nucleophiles to provide tetrahydropyrans, dihydropyrans, and even lactols (Scheme 141).[432b,433]



Scheme 141.

A variation to provide 2-deoxy-β-*C*-glycosides **117** is summarised in Scheme 142.[434]

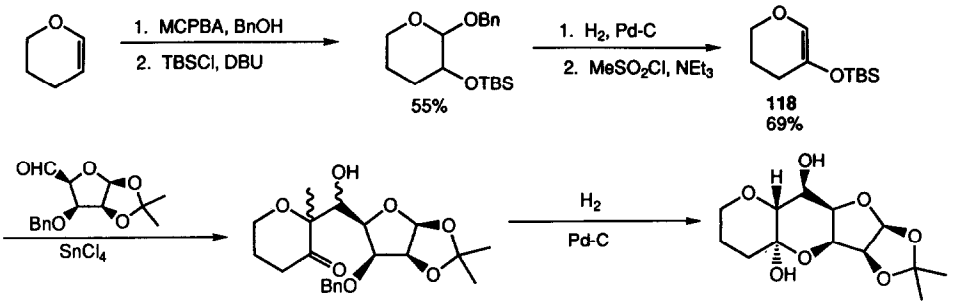


Scheme 142.

Employment of a silyl enol ether of tetrahydropyran-3-one (**118**), available from dihydropyran, allows for regiospecific reactions at C-2 (Scheme 143).[436]

Dihydrofurans and pyrans can be hydroborated by chiral boranes to provide β-hydroxyethers with high asymmetric induction.[1,436]

Of course, six-membered lactones undergo nucleophilic reaction at the carbonyl centre as expected;[4b,437] the use of cerium reagents has been advocated to prevent ring opening.[438] As with



Scheme 143.

butyrolactones, alkylations adjacent to the carbonyl group can be controlled by a β-substituent.[417,439] An alkyl group can be introduced at C-4 of an enolone by a radical reaction.[440]

A large amount of work has been performed with regard to the preparation and reactions of medium and large ring lactones,[441] including conformation effects;[442] however, as furanosides and pyranosides are invariably formed, the application of the larger ring chemistry is very rare for the preparation of carbohydrate derivatives.

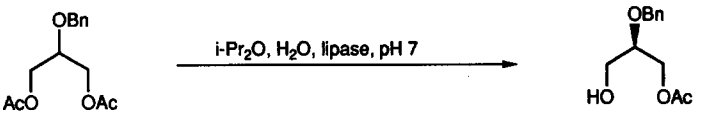
5. ENZYME REACTIONS

The use of enzymes in organic synthesis has become one of the fastest growing areas for the development of new methodology, and has been comprehensively reviewed.[443] The approach has been applied to the synthesis of carbohydrates.[443a,444] The aim of this section, however, is to highlight some enzyme reactions that could be useful in a chemical approach to carbohydrate derivatives. It must be remembered that some enzymes are promiscuous, while others are very specific to a particular functional group, or even compound.

The use of lipases has provided means to resolve alcohols, acids, and esters. *Meso*-substrates provide a powerful entry to a single enantiomer as all of the substrate is converted to the desired product.[445] If this approach is not available, racemisation of the undesired isomer and a recycle become a necessity as the scale of the reaction increases.[446] As lipase enzymes catalyse equilibria, esters can be prepared from alcohols, particularly if an activated ester, such as vinyl acetate, is used as the donor ester in a transesterification.[447]

Despite the relatively large number of substrates used with lipases, in particular pig liver esterase (PLE), it is not always possible to predict the stereospecificity of a particular lipase with a substrate.[448] This is one of the reasons that enzymes have not found complete acceptance in the repertoire of chiral reagents for chemical reactions. This problem is being addressed through the development of easy to use active site models. Some of these models predict selectivity, as for PLE[449] and *Candida rugosa* lipase,[450] while others give an estimation of the active site size so that they can be used for more general, predictive applications.[451] Many of the models are empirical, as for the reduction of ketones (*vide infra*),[452] and, hence, are not completely reliable. The ability to predict the isomer that is most easily hydrolysed by a lipase has led to a number of similar models.[453] In addition to predicting the stereochemical outcome, correlation of the model's stereochemical requirements to those of the substrate can be used to increase efficiency through substrate modification prior to the enzymatic step.

As well as enantioselective reactions, regio- and stereoselective reactions are also possibilities with enzyme catalysis, but often the limitations imposed by the structural requirements of the substrate are greatly increased.[454] The enzymatic approach has been expanded by the use of enzymes in non-aqueous media; this allows for the use of water insoluble substrates.[455]



Scheme 144.

Enzymes used for selective hydrolyses can provide kinetic resolutions.[456] Such selectivity allows differentiation within *meso* esters and the preparation of selectively protected glycerol (Scheme 144).[445,457]

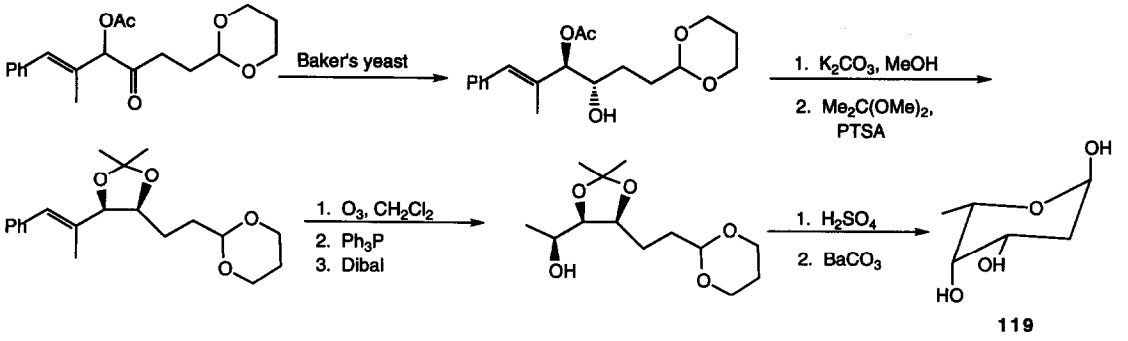
Of course, the desired product from a lipase reaction may be a carboxylic acid or an alcohol. Enzymes are also available to selectively hydrolyse esters of monosaccharides,[474] or esterify specific hydroxy groups.[458]

The use of catalytical antibodies now allows for the design and product of an enzyme-like system that can catalyse specific ester hydrolyses.[459] It is also possible to mutate an enzyme to increase stability, particularly in organic solvent systems, without affecting stereospecificity.[460] Indeed, the use of an organic solvent can effect the outcome of an enzymatic reaction.[461]

The reduction of carbonyl compounds by yeast allows for the direct introduction of a chiral centre. A number of classes of compounds have been reduced by this tolerant system.[462]

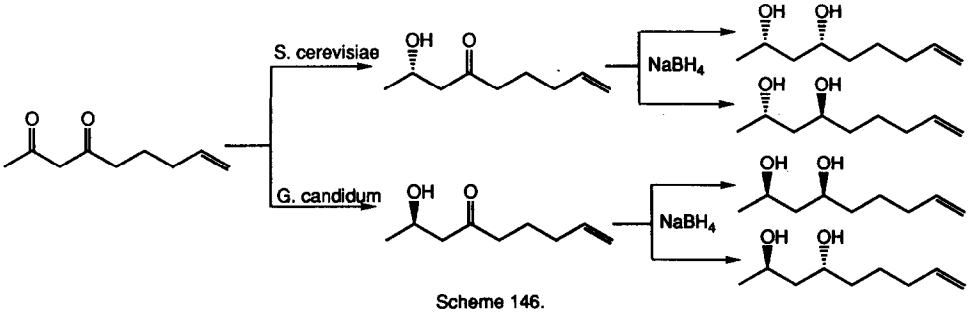
Reductions when performed by an enzymatic system usually require a cofactor; this is why organisms are invariably used rather than purified enzymes. Isolation of the product from the reaction media may become a significant cost and convenience factor; formation of the analogous methyl ester from a carboxylic acid through use of diazomethane is a common technique.[463]

A yeast reduction methodology has been used to prepare L-deoxy sugars (e.g. **119**) (Scheme 145).[464]



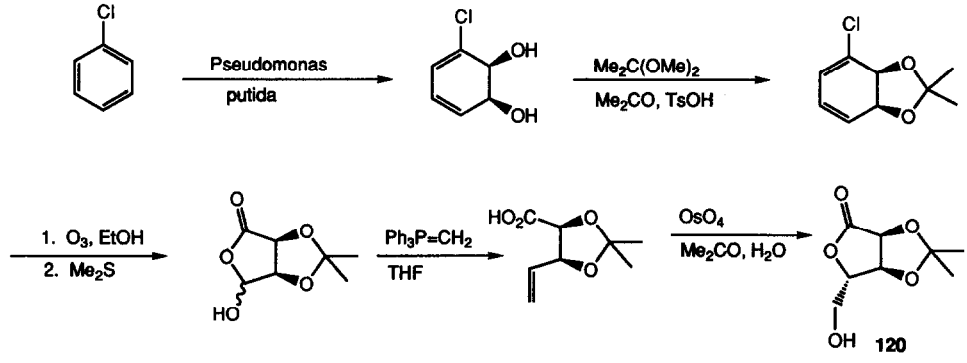
Scheme 145.

In some cases, enzymatic systems are available that allow for the production of one of two possible isomers, while another system provides the other isomer (Scheme 146).[465]



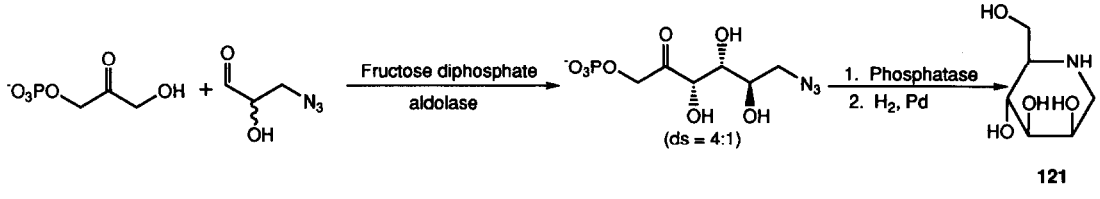
Scheme 146.

Enzymes can catalyse a wide range of chemical reactions, and some have been applied to the preparation of carbohydrate derivatives, such as the oxidation of an aromatic substrate which has provided a synthesis of 2,3-isopropylidene L-ribonic γ-lactone (**120**) (Scheme 147).[466]



Scheme 147.

As many carbohydrate derivatives are available by an aldol-type approach, the enzymes that catalyse this carbon–carbon bond forming reaction are of particular interest.[467] The power of these aldol enzymatic procedures for organic synthesis is illustrated by a route to 1-deoxymannojirimycin (**138**) (Scheme 148).[467,468]

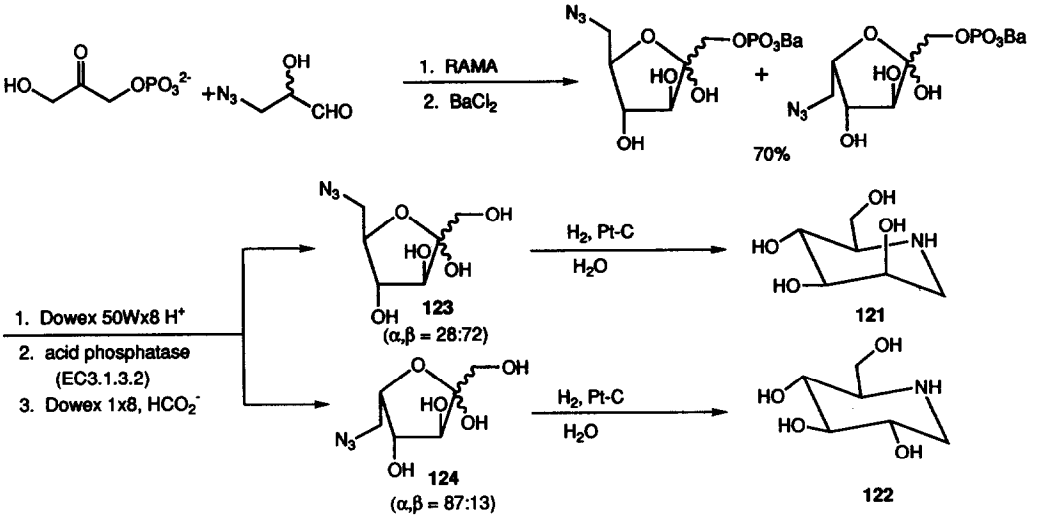


Scheme 148.

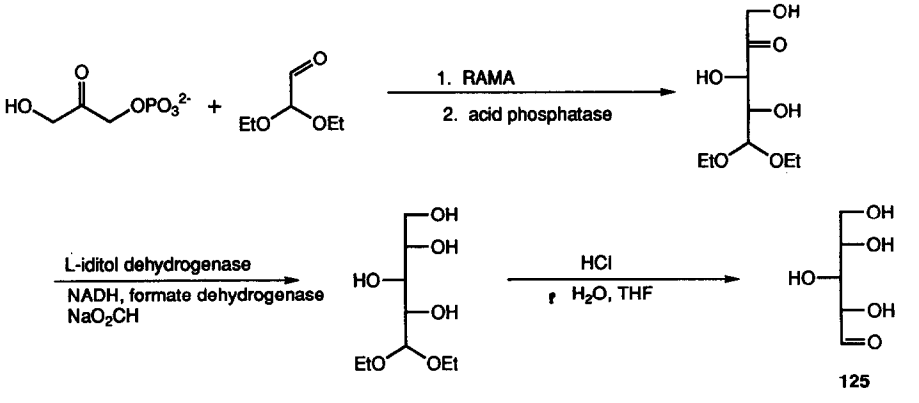
Rabbit muscle aldolase (RAMA) [D-fructose-1,6-bisphosphate aldolase] is proving to be a very powerful catalyst for an aldol approach to monosaccharides.[443a,454a,467,468,469] The preparation of 1-deoxymannojirimycin (**121**) and 1-deoxynojirimycin (**122**) are illustrated in Scheme 149; anion exchange chromatography was used to separate the azides (**123**) and (**124**).[469] The use of RAMA as a catalyst has these advantages: the hydroxy groups need no protection; the stereochemistry generated is D-*threo* (*parf*); and a wide variety of aldehydes can be employed as substrate.[443a,469,470] In contrast, dihydroxyacetone phosphate is required as substrate, and ketoses are the product (*cf.* Scheme 149). The use of a half-protected dialdehyde substrate allows for an aldose synthesis as illustrated by the preparation of L-xylose (**125**) (Scheme 150).[469]

The limitations of RAMA have led to the search for alternative enzymes. A bacterial fuculose-1-phosphate aldolase provides *pref*-isomer product stereochemistry,[471] as does a 2-deoxyribose-5-phosphate aldolase (DERA) (Scheme 151).[472] For aminosugars, acylneuraminate pyruvate lyase catalyses an aldol condensation (Scheme 152) and has a broad specificity. This allows the enzyme to be used with non-amino monosaccharides.[467,473]

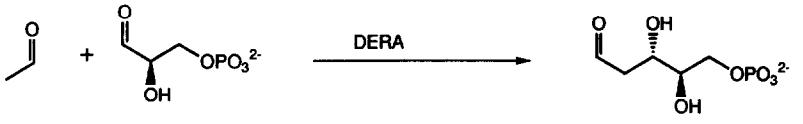
In addition to the preparation of monosaccharides, enzymes are available for the selective manipulation of functional groups within these units.[474]



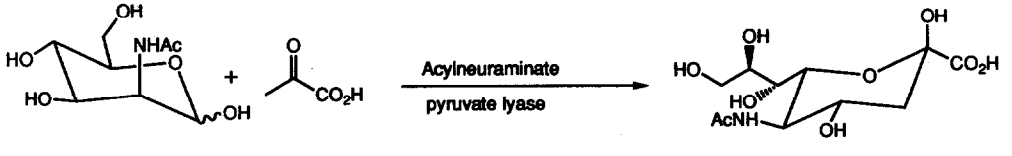
Scheme 149.



Scheme 150.



Scheme 151.



Scheme 152.

The selective coupling of monosaccharide units still presents a major hurdle (Section 6).[475] Enzymes are available to perform these couplings both with retention or inversion of configuration at the anomeric carbon.[476] In addition to carbohydrate based nucleophiles, other alcohols can be used to prepare a wide variety of glycosides.[477] The preparation of bacterial cell wall polysaccharides has been allowed through the use of enzymes to couple the aminosugar monomers.[478]

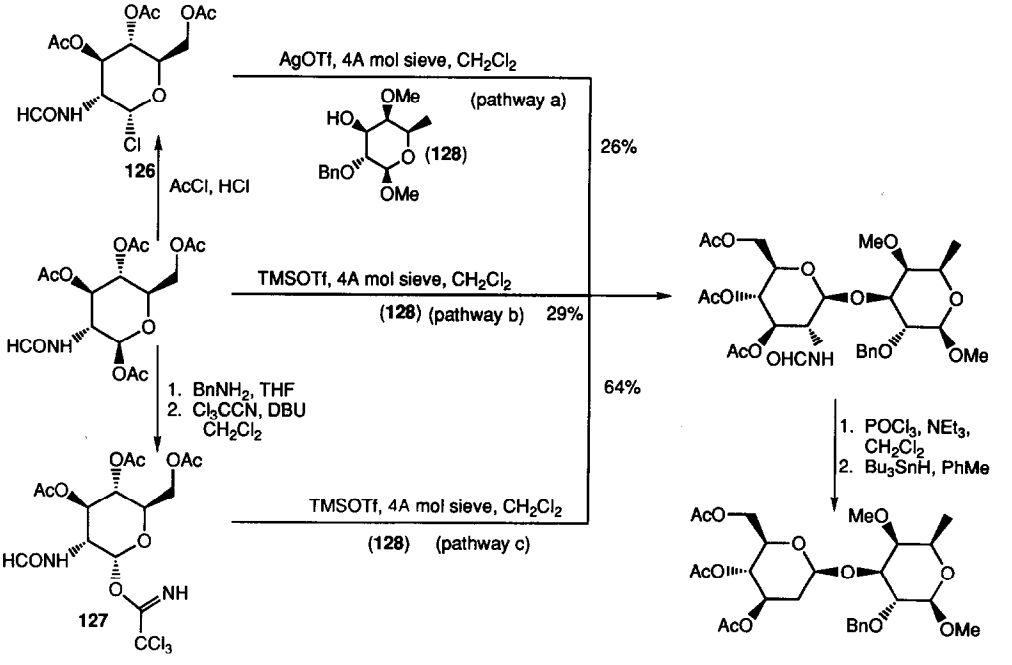
The constraints of enzymatic systems, substrate specificity in particular, have led to the development of catalytic antibodies or abzymes. A wide variety of transformations have now been catalysed by abzymes, and with the incorporation of surrogate cofactor moieties, the potential of these systems continues to expand. Abzymes can be used to perform stereoselective reactions with a large degree of substrate specificity.[479]

6. POLYSACCHARIDES AND HIGHER SUGARS

Unlike the situation for peptides and nucleotides, there are no simple, general methods for the synthesis of polysaccharides; the sugar units must be protected, and often mixtures of the α- and β-glycosides result.[480] However, some significant advances have been made that now allow disaccharides to be prepared with stereochemical control.[481]

Glycosidation of alcohols provides the problems of selective protection, reactivity enhancement, and stereochemical control so that only one of the two possible glycosides is formed.[317,482]

The classical approach is to activate the anomeric position by conversion to the chloride, or other halides, followed by reaction with a silver or mercury salt to provide the glycosyl donor (Scheme 153; pathway a).[483] Activation can also be achieved by the use of a hindered amine, high pressure,[484] or heat.[485]



Scheme 153.

An anomeric hydroxy group can be activated for a glycosylation coupling reaction by formation of a trichloroacetimidate through reaction with trichloroacetonitrile (Scheme 153; pathway c).[486]

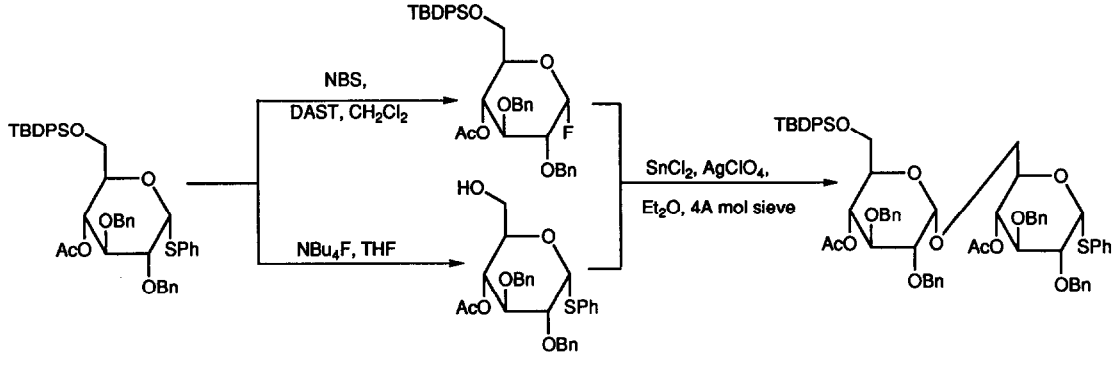
The choice of whether to use a glycosyl chloride (e.g. **126**) as opposed to a trichloroacetimidate (e.g. **127**) often can only be determined by experiment (Scheme 153).[486] In this example, the β-stereocontrol in the coupling is attributed to the *N*-formyl moiety, which can be removed.[486,487]

The stereochemical outcome of a trichloroacetimidate coupling reaction can be changed to form a β-disaccharide through use of a nitrile solvent which converts the mechanism from S_N2 to S_N1.[488]

A phosphate ester, or similar phosphorus derivative, can also be used to make the anomeric hydroxy a good leaving group.[489] Silicon agents can also be used to activate the anomeric group and provide a method to β-oligosaccharides (Scheme 153; pathway b).[490] The presence of a 2-amido group allows for intramolecular activation.[491] Indeed, 2′-deoxy-β-disaccharides are available by use of an acetyl group at C-2 that controls the coupling reaction, followed by a deoxygenation procedure.[492]

A Mitsunobu method has also been used for glycosylations and results in inversion at the anomeric centre,[482,493] while the *in situ* preparation of (1-imidazoylcarbonyl) glycosides usually result in the formation of the α-glycoside.[494]

Another α-selective glycosidation approach involves the coupling of an appropriate fluoride with thio or other derivatives (Scheme 154).[486,495] Zirconium and other metals can also be used as an activation agent.[496]

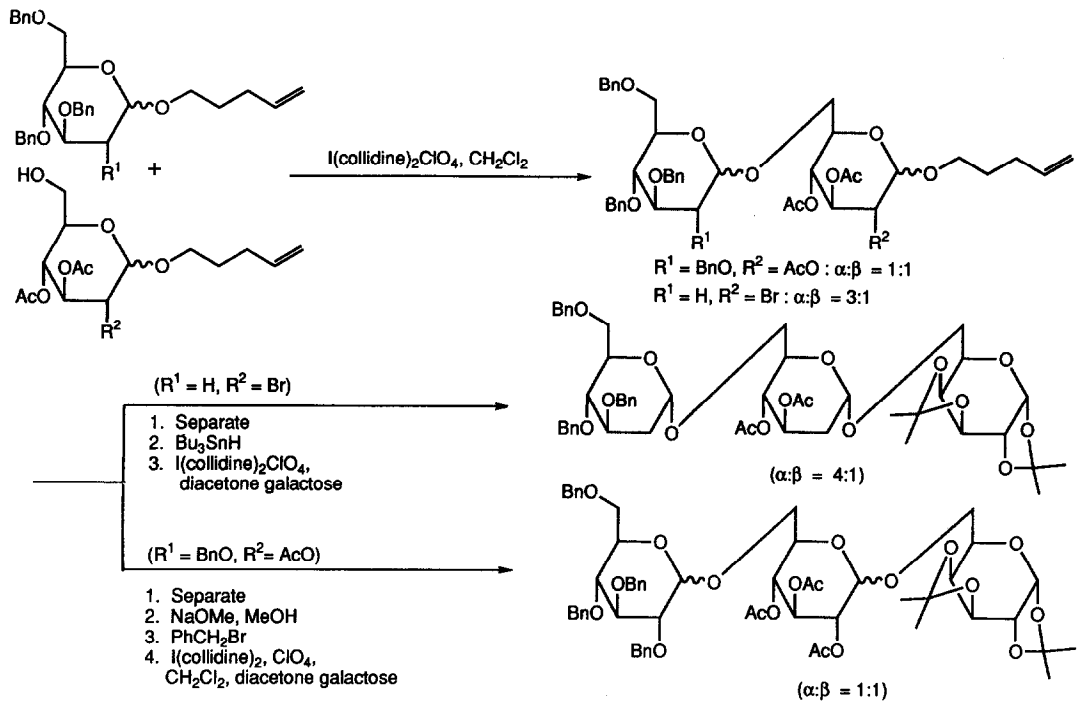


Scheme 154.

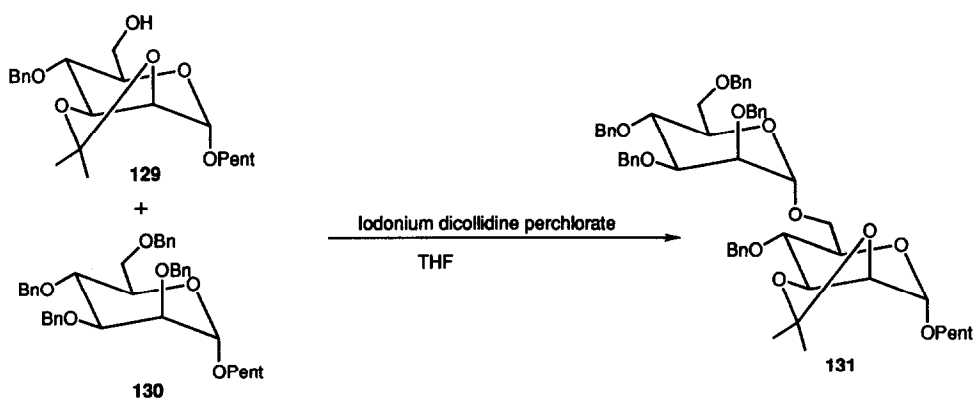
The use of phenylselenyl chloride also allows for the preparation of α-glycosides.[497] Another method, which can be employed with hindered alcohols, employs a sulphoxide at the anomeric position. The α : β ratio is solvent dependent; β-glycosides are favoured in more polar solvents, such as methylene chloride.[498]

The use of sulphur reagents allows formation of an intermediate episulphonium salt,[499] although some reagents just provide a good leaving group with no intramolecular participation.[500]

An elegant method to couple saccharide units employs pentenyl glycoside, activated by an electrophilic halogen (Scheme 155).[501] Ester protection at C-2 allows this saccharide to act as the nucleophilic unit completely unmolested at the anomeric position. When the C-2 hydroxy group is protected as an ether, the saccharide unit will react in an electrophilic manner.[501,502] Thus, in a reaction sequence a saccharide unit that was the nucleophile in one step can become the electrophilic unit in a subsequent step through a simple change of protecting group at C-2. The terms armed and disarmed glycosyl donors has been given to ethereal and ester protected *n*-pentenyl glycosides respectively. Thus, the alcohol donor **129** can be coupled with the glycosyl donor **130** to afford **131** in 41% yield (Scheme 156).[503] Pentenyl glycosides can be converted to the α-glycosyl bromides under mild conditions. The product bromides can then be used to form oligosaccharides without purification.[504] Pentenyl glycosides in either the armed or disarmed mode, that is with either ethereal or ester protection at C-2, can be converted to glycosyl donors by treatment with *N*-iodosuccinimide



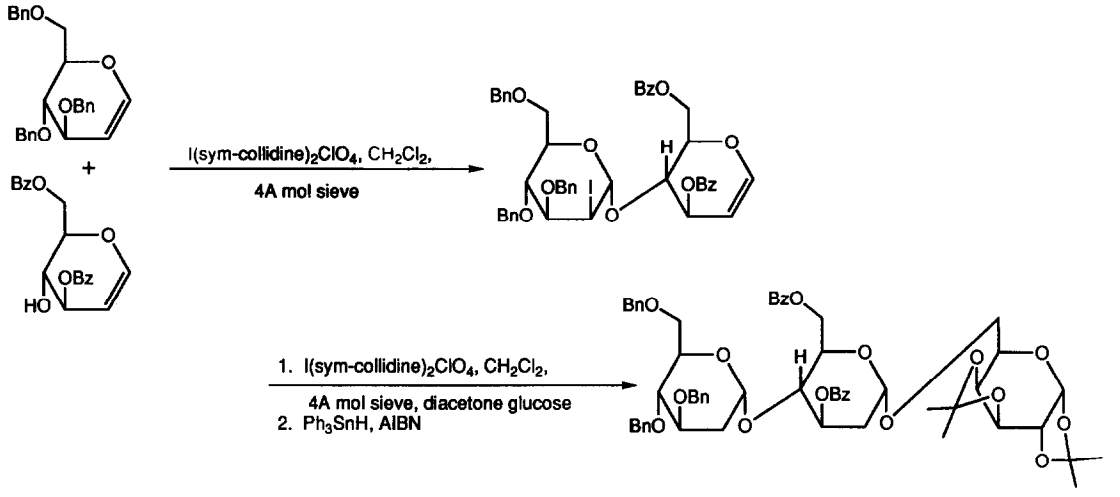
Scheme 155.



Scheme 156.

in the presence of trifluoromethanesulphonic acid.[499] The pentenyl glycoside approach can also be used for the preparation of *N*-α-linked glycoproteins.[505]

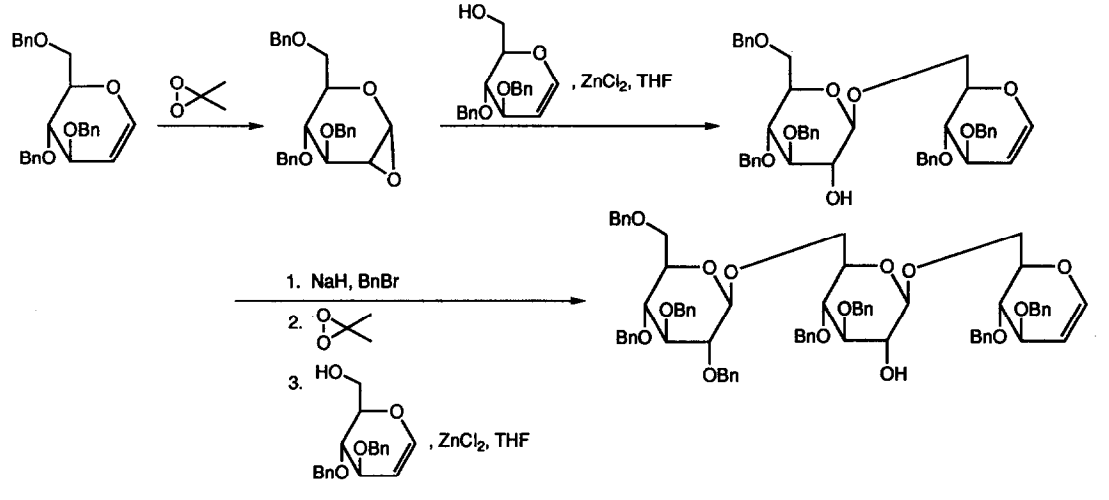
The use of an iodonium reagent again provides α-glycosides (Scheme 157).[506] This reagent also allows both saccharide units to be present within the reaction mixture and couple selectively without the formation of many by-products. The nucleophilic saccharide does not react at the anomeric position if the hydroxy groups are protected as esters. This coupling procedure can be repeated by changing the ester protection for ether, or by use of a non-competing saccharide as the nucleophile.[158d,506,507]



Scheme 157.

This iodine method is a variation of the traditional Koenigs–Knorr methodology,[508] and has other derivatives.[509] The use of a nitrogen nucleophile allows the formation of an iodosulphonamide which, in turn, leads to 2-aminosugars.[510]

β-Glycosides are available through use of dimethyldioxirane as the activation reagent (Scheme 158). Once again the choice of protection is important; ethers provide the best selectivity.[511]

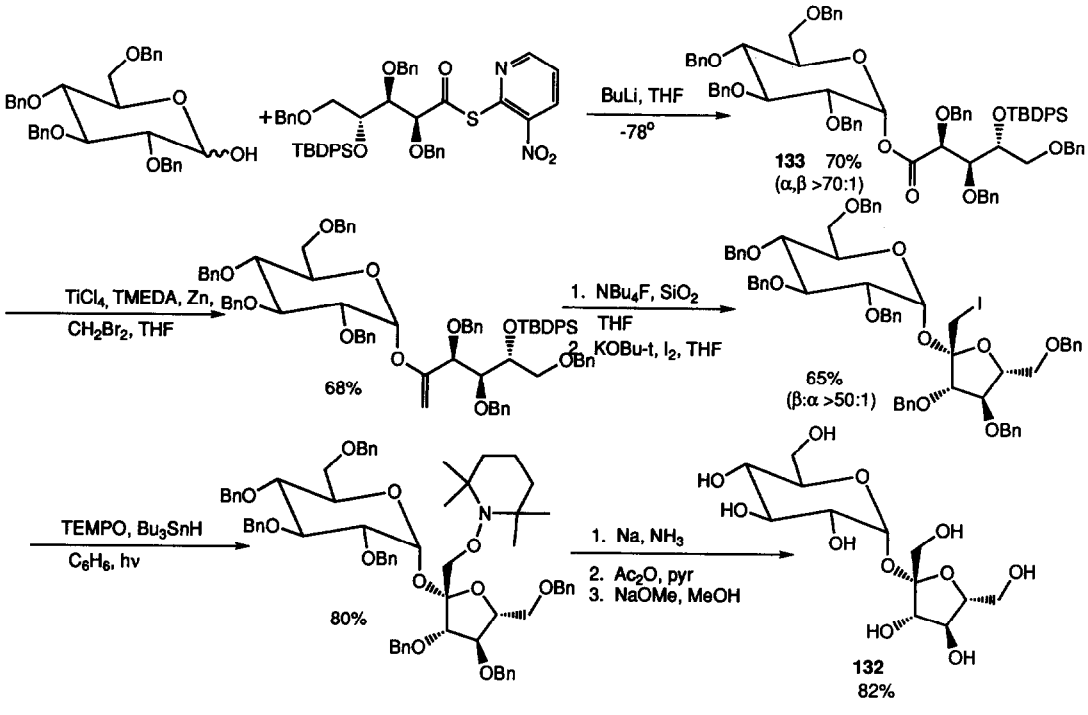


Scheme 158.

Other nucleophiles, such as nitrogen heterocycles, can be used with this approach.[512] This onium approach is a member of a number of reactions where an electrophilic species is established at C-1, often by use of an oxygen or sulphur reagent. The product stereochemistry is then a consequence of this intermediate.[499,513]

Rather than follow an alkylation procedure for the formation of a glycoside bond, an acylation methodology has been developed; the second ring is then formed by an iodoetherification (*cf.* Section 4.3).[514] This alternative to ether formation has been used in a synthesis of sucrose (**132**).

Formation of the ester **133** proceeded with $>50:1$ $\alpha:\beta$ selectivity. The stereochemistry at the fructofuranoside anomeric centre was again established with high kinetic stereoselectivity by an iodoetherification approach (Scheme 159).[515]



Scheme 159.

Another ester based strategy utilises thionoesters and an intramolecular cyclisation.[516] *n*-Pentenyl esters have also been used in glycosidation reactions. These esters are not as prone to the armed–disarmed phenomenon (*vide supra*).[517]

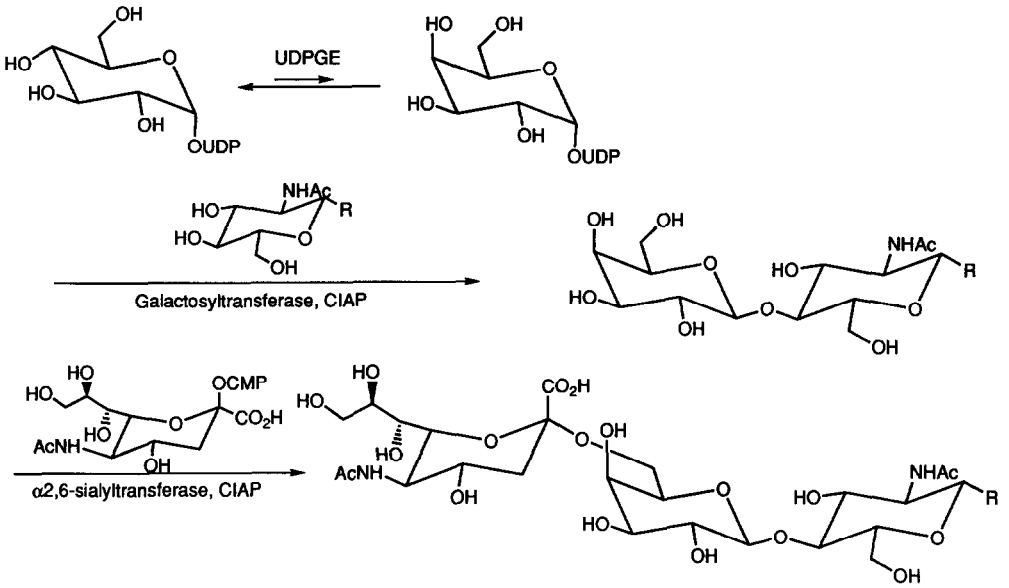
Enzymatic couplings allow for the stereoselective formation of glycoside bonds (Section 5).[443a] This approach is still somewhat limited due to the expense of the enzymes and, in many instances, the problems associated with selectivity between starting materials and products. The approach does, however, have applications when these limitations are lifted, such as through the use of cloning techniques,[518] use of recycle loops,[519] or coupling enzyme systems to drive equilibria in the required direction (Scheme 160).[520]

6.1. *Higher sugars*

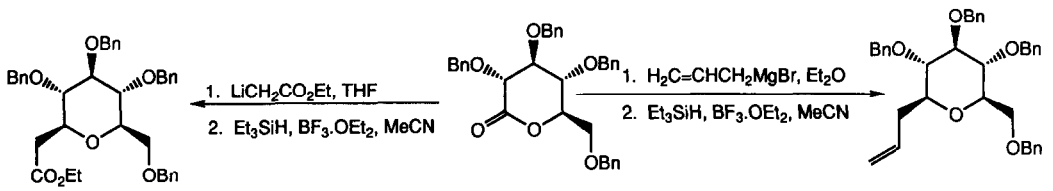
The preparation of higher sugars has already been addressed by Sharpless oxidative methods (Section 2.3.2),[108] osmylation (Section 2.3.1), dipolar additions (Section 3.3), and hetero-Diels–Alder reactions (Sections 3.1 and 3.2).[521]

Many of the synthetic methodologies already outlined[1,522] can be adapted for the preparation of higher or C-linked saccharides. For example, the nitroaldol reaction has been used to couple two saccharides,[523] and prepare higher sugars,[524] while allylsilanes condense with glycosides; the allyl unit then allows for further elaboration to higher sugars.[157b,525]

Monosaccharides contain a protected form of a carbonyl group. These can be reacted with organometallic or electrophilic reagents to provide higher sugar derivatives.[526] This procedure is augmented by use of other oxidation levels of the saccharide unit and nucleophilic reagents (Scheme 161).[527]



Scheme 160.



Scheme 161.

Radical reactions provide a plethora of synthetic methods for the preparation, and modification of higher sugars.[528] The glucal can also be made nucleophilic (*cf.* Section 4.5) and coupled with electrophiles,[529] to introduce extra carbon atoms.

7. CONCLUSIONS

A large number of reactions have been outlined above and in the previous Report.[1] Some have already been employed in syntheses of carbohydrate derivatives. Others, however, have yet to be applied, and we hope that through their inclusion in this Report and its predecessor,[1] they will prove fruitful.

In recent years, asymmetric synthesis has progressed to the point where relatively complex molecules can be built up by elegant enantio- or diastereoselective methodologies. The use of stereoselective reactions to control relative stereochemistry is of increasing importance as chiral starting materials are available not only from the chiral pool but from enantioselective reactions. The use of enzymes and other biological agents to either perform a kinetic resolution or an asymmetric transformation is becoming more common as chemists begin to capitalise on these types of agent.

Examples of all types of asymmetric reactions have been cited in this Report and, no doubt, other methods will soon join this arsenal. Some of these reactions have been scaled up and are performed on an industrial scale.[530] The synthesis of carbohydrate derivatives will continue to become simpler, whatever the target structure or scale of reaction.

Table
List of abbreviations and acronyms used in this review.

Ac	acetyl	MCPBA	m-chloroperoxybenzoic acid
acac	acetylacetonate	Men	menthyl
AIBN	azobis(isobutronitrile)	MOM	methoxymethyl
All	allyl	MoOPH	oxodiperoxymolybdenum(pyridine)hexamethylphosphoramide
An	anisyl	Ms	mesyl
ANL	*Aspergillus niger* lipase	NADH	nicotinamide adenine dinucleotide phosphate, reduced
9-BBN	9-borabicyclo[3.3.1]nonane	Naph	naphthyl
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl	NBD	norbornadiene
bipyr	bipyridyl	NBS	N-bromosuccinimide
Bn	benzyl	NCS	N-chlorosuccinimide
Boc	tert-butoxycarbonyl	NIS	N-iodosuccininimide
BOM	benzyloxymethyl	NMMO	see NMO
Bz	benzoyl	NMO	N-methylmorpholine N-oxide
Cam	camphanoyl	p-TSA	p-toluenesulphonic acid
CAN	ceric ammonium nitrate	PCC	pyridinium chlorochromate
Cbz	benzyloxycarbonyl	PDC	pyridinium dichromate
CCL	*Candida cylindracea* lipase	Pent	pentenyl
CIAP	calf intestinal alkaline phosphatase	PFL	*Pseudomonas fluorescens* lipase
Cp	cyclopentadienyl	Phth	phthalyl
CVL	*Chromobacterium viscosum* lipase	Piv	pivaloyl
CSA	camphorsulphonic acid	PLE	pig liver esterase
DAST	diethylaminosulphur trifluoride	PM	phenylmenthyl
DBN	1,5-diazabicyclo[4.3.0]non-5-ene	PN	protease N.
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene	PPL	porcine panreatic lipase
DCC	dicyclohexylcarbodiimide	PPTS	3-[5-(sulphophenyl)-2-pyridyl]-1,2,4-triazin-5-ylbenzenesulphonic acid, disodium salt
DCE	dichloroethane	PTS	see p-TSA
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone	PTSA	see p-TSA
DEAD	diethyl azodicarboxylate	Pyr	pyridine
DERA	2-deoxyribose-5-phosphate aldolase	Ra Ni	Raney nickel
DET	diethyl tartrate	RAMA	rabbit muscle aldolase, D-fructose-1,6-bisphosphate aldolase
DHP	dihydropyran	Red-Al	sodium bis(2-methoxyethoxy)aluminum hydride
Dibal	diisobutylaluminium hydride	SC	subtilisin carlsberg
diphos	1,2-bis(diphenylphosphino)ethane	TBDMS	t-butyldimethylsilyl
DIPT	diisopropyl tartrate	TBDPS	t-butyldiphenylsilyl
DMAP	4-dimethylaminopyridine	TBHP	t-butyl hydroperoxide
DME	1,2-dimethoxyethane	TBS	see TBDMS
DMF	dimethylformamide	TDA-1	Tris[2-(2-methoxyethoxy)ethyl]amine
DMP	2,2-dimethoxypropane	TEMPO	2,2,6,6-tetramethylpiperidinooxy, free radical
DMSO	dimethyl sulphoxide	Tf	trifluoromethylsulphonyl
$Eu(hfc)_3$	3-tris[3-(heptafluorohydroxymethylene)-d-camphorato]-europium(III).	TFA	trifluoroacetic acid
HMDS	hexamethyldisilazane	TFAA	trifluoroacetic anhydride
HMPA	hexamethylphosphoramide	Th	thiazole
Im_2CO	carbonyldimidazole	THF	tetrahydrofuran
Imd		TIPS	triisopropysilyl
Ipc	isopinocampheyl	TMEDA	N,N,N',N'-tetramethylethylenediamine
KDO	3-deoxy-D-manno-2-octulosonic acid	TMP	2,2,6,6-tetramethylpiperidine
L-Selectride	lithium tri-sec-butylborohydride	TMS	trimethylsilyl
LDA	lithium diisopropylamide	Tol	tolyl
Lev	levulinoyl	Tr	trityl
LiHMDS	lithium hexamethyldisilazide	Ts	tosyl
LiNaph	lithium naphthalenide	UDPGE	uridine diphosphategalactose 4'epimerase
LPTS	2,6-luidinium p-toluenesulphonate	Z	benzyloxycarbonyl

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