Carboxylic acids and esters

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Reviewing the literature published between 1 August 1995 and 31 July 1996.
Continuing the coverage in *Contemporary Organic Synthesis*, 1996, **3**, 243.

1 Introduction

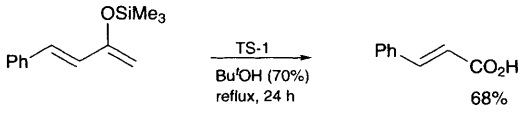
This review covers the literature pertaining to carboxylic acids and esters. Some chemistry of amino acids has also been included, although this area, as well as chemistries associated with amides and lactones, is covered in separate articles in *Contemporary Organic Synthesis*.

2 Carboxylic acids

2.1 General

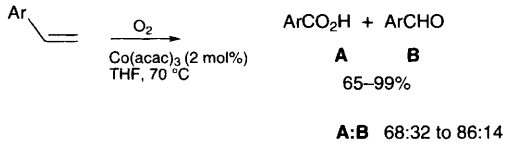
A number of new methods for obtaining carboxylic acids from esters have been reported. For instance, methyl and isopropyl carboxylates can be hydrolysed with organotin oxides and hydroxides, a significant increase in the speed of the reaction being observed upon microwave irradiation.[1] Solid superacid (sulfated SnO_2) is an efficient catalyst for the deprotection of allyl esters, even in the presence of methyl esters, under anhydrous conditions.[2] The products are isolated simply by filtration. Prop-2-ynyl esters can be cleaved selectively under extremely mild conditions, even in the presence of β-lactams, in good yields (61–97%) using triethylammonium tetrathiomolybdate.[3] In addition, magnesium methoxide can be used to cleave alkyl esters selectively.[4] The reactivity follows the order *p*-nitrobenzoate > acetate, benzoate > pivalate. Interestingly, magnesium in methanol does not react with esters. Diphenylmethyl esters, conveniently synthesised using a carboxylic acid and diphenylmethanol under Dean–Stark conditions, can be cleaved in refluxing toluene under acid catalysis.[5]

Novel methods for the conversion of other functional groups into carboxylic acids include the use of titanium silicates (TS-1 and TS-2) to catalyse the oxidation of simple ethers to the corresponding acids in moderate yields.[6] Hence benzoic acid is obtained from benzyl methyl ether in 65% yield. TS-1 has also been used, in the presence of *tert*-butyl hydroperoxide, as a remarkably selective system for the cleavage of silyl enol ethers to give carboxylic acids, even in the presence of ordinary double bonds (**Scheme 1**).[7]

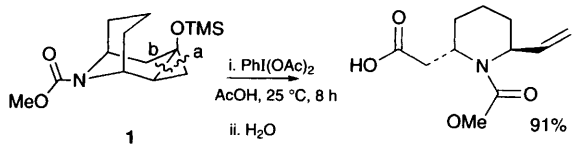


Scheme 1

Commercially available $Co(acac)_3$ catalyses the aerobic oxidation of vinyl aromatic compounds to the corresponding acids in the presence of THF (**Scheme 2**).[8] Here the THF initially forms a hydroperoxide which functions as the oxidant. Interestingly, sand or activated carbon has been found to catalyse the activity of $KMNO_4/NaIO_4$ or $KMnO_4$/NaOCl induced double cleavage in good yields (70–85%).[9] Iodobenzene diacetate has been found to be a superior reagent to lead tetraacetate in the cleavage of (trimethylsilyl)bicyclo[*n*.1.0]alkenes, giving alkenoic acids in high yield (62–96%) (**Scheme 3**).[10] Most reagents like ZnI_2, $Hg(OAc)_2$, and $SnCl_4$ cleave bond 'a' of the fused cyclopropane in **1**.

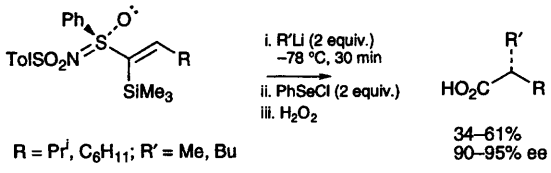


Scheme 2



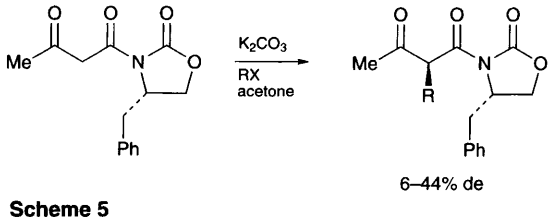
Scheme 3

The many methods reported for the preparation of enantiomerically enriched carboxylic acids include the one by Jackson *et al.* for the one-pot synthesis of homochiral α-substituted carboxylic acids using α-silyl sulfoximines.[11] These, unlike their non-silylated counterparts, undergo facile 1,4-addition with lithio anions, cuprates and Grignard agents (**Scheme 4**). *N*-Acetoacetyl derivatives of oxazolidinones, previously prepared by



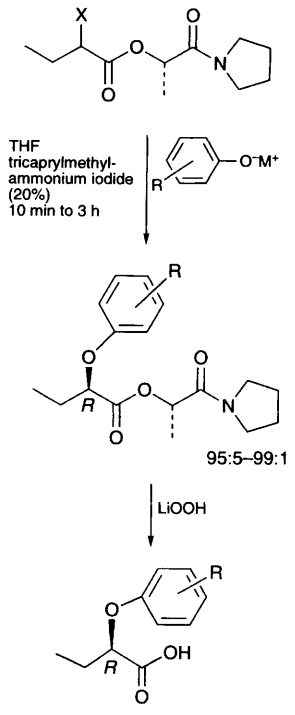
Scheme 4

Evans *et al.*, have now been shown to be much less successful than their *N*-propionyl analogues in diastereoselective alkylations (de 6–44%) (**Scheme 5**).[12] The *N*-acetoacetyl sultam derivative also shows similar low diastereoselectivities, although its alkylation with benzyl bromide alone is successful (>95% de). Flash chromatography, however, enables the facile separation of the diastereomers, hence enabling the synthesis of homochiral β-keto acids.



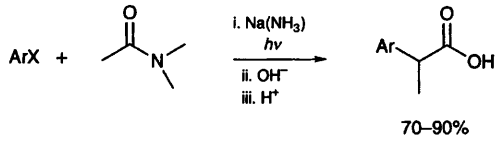
Scheme 5

(*S*)-Amide-bearing derivatives of racemic halo esters have been used successfully in reactions with aryl oxides in a dynamic kinetic resolution to give homochiral α-aryloxy acids in good yields, after hydrolysis (**Scheme 6**).[13] A convenient route for the resolution of norbornyl diacids involves the use of (*S*)-proline in an asymmetric ring opening of the corresponding *meso*-anhydride to give the amido acids in excellent enantiomeric excess.[14]



Scheme 6

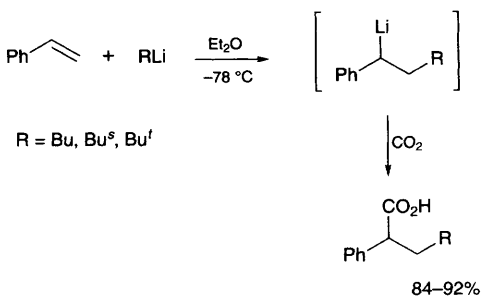
Methodology to enable the facile introduction of the carboxylate functionality into molecules continues to be sought. The area involving use of palladium and/or copper catalysis, in the presence of carbon monoxide, to carbonylate unactivated alkanes and arenes has been reviewed.[15] The *in situ* $S_{RN}1$ arylation–alkylation reaction using an aryl halide and *N*,*N*-dimethylacetamide under photostimulation in sodium in liquid ammonia, followed by hydrolysis, is an interesting route to arylpropanoic acids (**Scheme 7**).[16] Yet another novel synthesis of arylacetic acids involves the addition of alkyllithiums



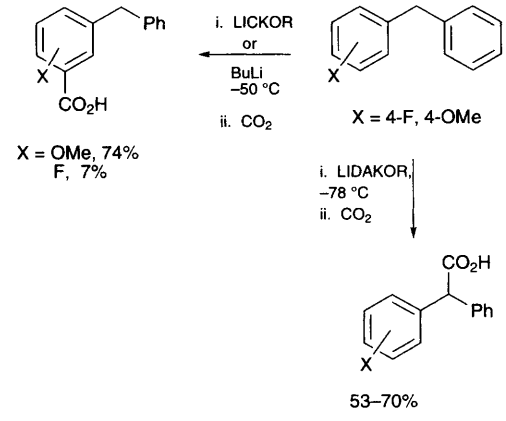
Scheme 7

in ether to styrene and subsequent trapping of the resulting anion with carbon dioxide to give α-alkylphenylacetic acid analogues (**Scheme 8**).[17] Diarylacetic acid analogues can be synthesised in good yields (53–70%) by deprotonating diphenylmethane exclusively at the benzylic position using LIDAKOR (Bu^nLi–Pr^i_2NH–$Bu^tO^-K^+$) and trapping with carbon dioxide.[18] Other bases such as BuLi,

and Schlosser's base (Bu^nLi–BuO^-K^+, LICKOR) result in alkylation on the aryl ring (**Scheme 9**).



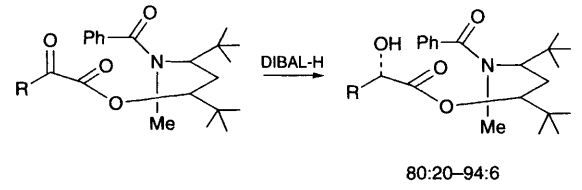
Scheme 8



Scheme 9

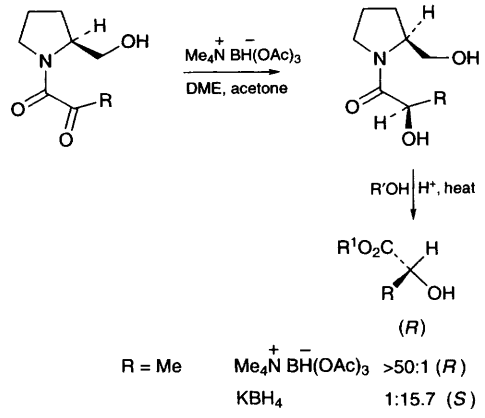
2.2 α-Hydroxy acids

α-Keto esters of 5-(*N*-methylbenzoylamino)-2,2,6,6-tetramethylheptan-3-ol can be reduced diastereoselectively when DIBAL-H is used (**Scheme 10**).[19] The chiral auxiliary can be recovered on base treatment to give α-hydroxycarboxylic acids in good yield and enantiomeric excess. The reaction may proceed through a chair type transition state where the amide and ester carbonyls are chelated to each other, although the fact that the diastereoselectivities are lower in the presence of zinc chloride is inconsistent with this hypothesis.



Scheme 10

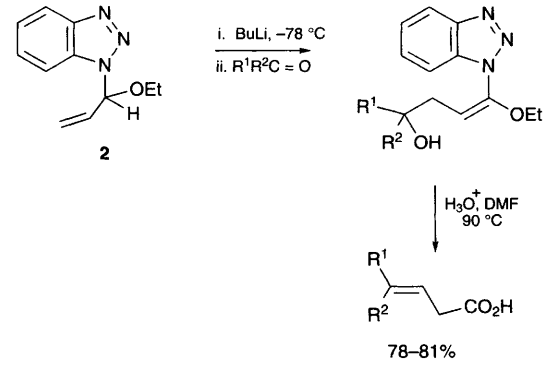
Prolinol derived α-keto esters have also been used for the enantioselective synthesis of α-hydroxy acids, giving the (*R*) enantiomer with tetramethylammonium triacetoxyborohydride, and the (*S*) enantiomer *via* a non chelated transition state with potassium borohydride (**Scheme 11**).[20]



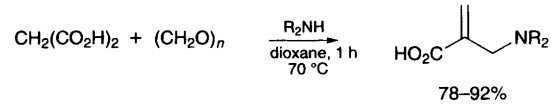
Scheme 11

2.3 Unsaturated carboxylic acids

The lithio anion of *N*-(α-ethoxyallyl)benzotriazole **2** is a homoenolate synthon for the synthesis of β,γ-unsaturated carboxylic acids (**Scheme 12**).[21] Allylic β-amino acids can be synthesised by the Mannich reaction of malonic acid in dioxane with various secondary amines in good yields. The reaction presumably occurs through the formation of α-methylenemalonic acid which, after the 1,4-addition of the amine, reacts with the Schiff base and subsequently undergoes eliminative decarboxylation (**Scheme 13**).[22]

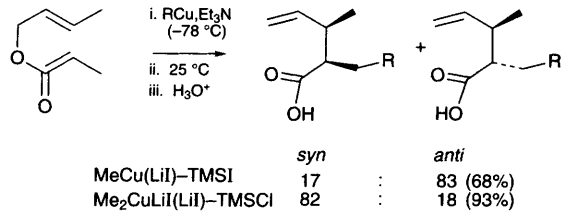


Scheme 12



Scheme 13

The diastereoselectivity in the conjugate addition–Claisen rearrangement of alkylcopper reagents and but-2-enyl acrylates depends on the nature of the copper reagent. Thus R_2CuLi–TMSCl leads predominantly to the *syn* product by adding to



Scheme 14

the starting ester in predominantly the s-*cis* conformation, while RCu(LiI)–TMSI adds to give the *anti* adducts through the s-*trans* conformation (**Scheme 14**).[23]

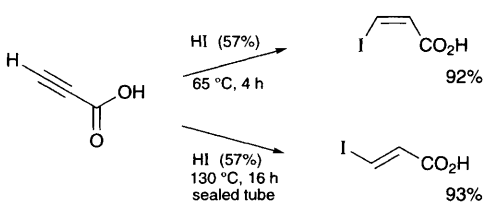
The addition of hydroiodic acid to propynoic acid occurs with *Z* stereoselectivity at lower temperatures, whereas at higher temperatures the *E* isomer is obtained as the only product (**Scheme 15**).[24] The reaction of the resulting vinyl iodides with organozinc or tin reagents allows the stereospecific synthesis of (*E*)- or (*Z*)-α,β-unsaturated acids.

2.4 Diacids

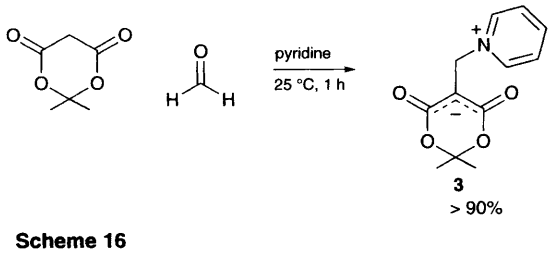
Literature methods for the synthesis of methylene Meldrum's acid, an unstable but versatile reagent that undergoes Diels–Alder and Michael reactions, gives only 37% yield of the product. The pyridiniumyl adduct **3** is a stable source of methylene Meldrum's acid which is formed in >90% yield from Meldrum's acid and formaldehyde in pyridine and, furthermore, can be stored at 0 °C for several months (**Scheme 16**).[25] The diethylaluminium cyanide promoted electrophilic conjugate addition of cyanide to enantiomerically pure α,β-unsaturated oxazolines **4** and **5** gives succinic acids of opposite configuration in moderate diastereomeric excess (**Scheme 17**).[26]

2.5 α-Halo acids

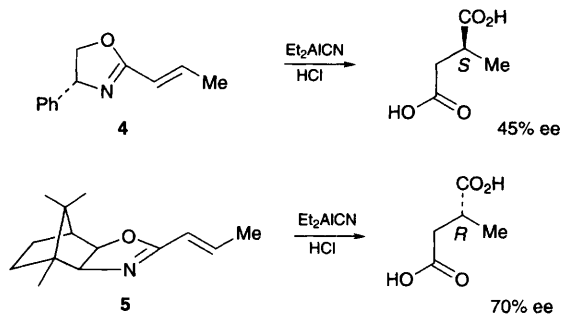
The silyl trifluoromethanesulfonate (triflate) mediated Claisen rearrangement of α-halo esters



Scheme 15



Scheme 16



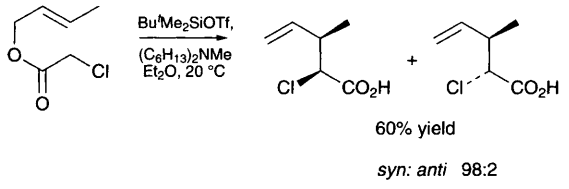
Scheme 17

can be performed at 25 °C to give halo acids with good *E* selectivity and distereoselectivity (**Scheme 18**).[27] (*R*)- or (*S*)-2-Fluorocarboxylic acids have been synthesised in good yield and with good enantioselectivity (50–60% yield, >92% ee) from the homochiral trichloromethyl alcohols, which in turn are derived *via* the oxazaborolidine mediated reduction of the corresponding trichloromethyl ketones (**Scheme 19**).[28]

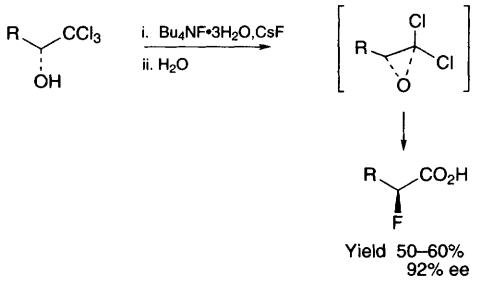
2.6 α-Amino acids

The enantioselective Strecker reaction involving inexpensive α-phenylglycinol has met with considerable success (**Scheme 20**). Trimethylsilyl cyanide adds to the imine **6** with good diastereoselectivity except in the case of the benzaldehyde derivative. The auxiliary is removed by oxidative cleavage to obtain the amino acid or its methyl ester directly.[29]

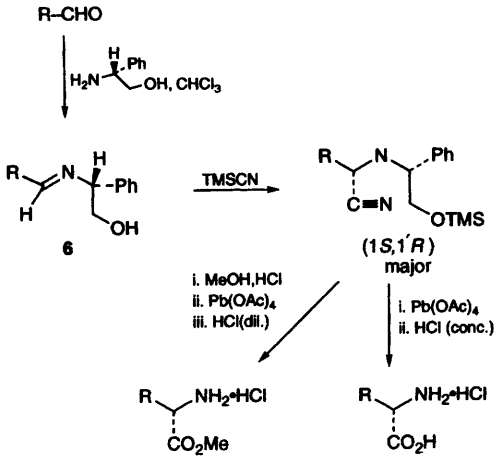
N-(*tert*-Butoxycarbonyl)-2-(*tert*-butyldimethylsiloxy) pyrrole can be substituted at the 5-position and used as a masked α-amino acid enolate synthon, giving rise to a variety of substituted amino acids *via* initial aldol reaction, subsequent scission of the lactam, followed by oxidative cleavage and hydrolysis (**Scheme 21**).[30] Serine, phenylalanine and threonine derivatives can be synthesised in racemic form using this methodology.



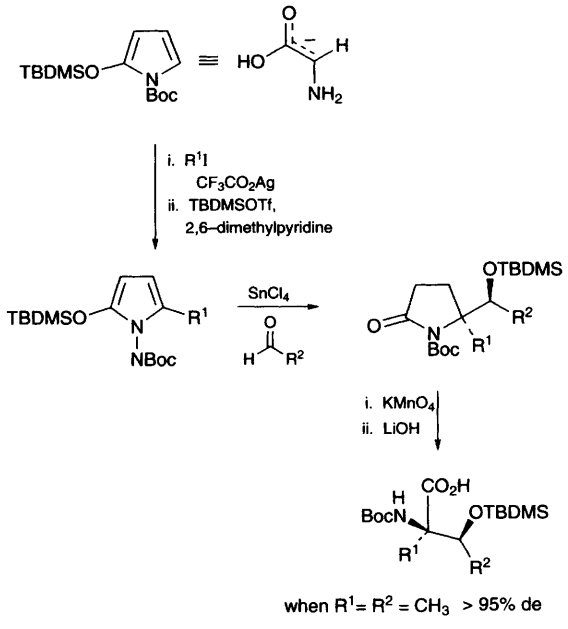
Scheme 18



Scheme 19

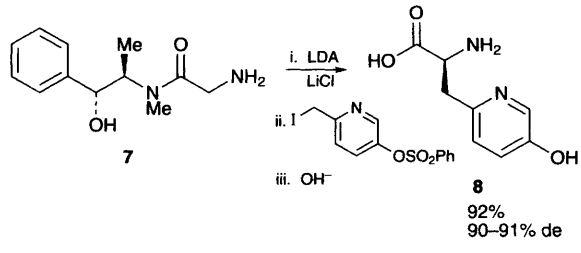


Scheme 20



Scheme 21

Glycine can be converted into the pseudoephedrine derivative **7** and alkylated diastereoselectively and in high yield. The auxiliary is readily cleaved under basic conditions to give the azatyrosine derivative **8** (**Scheme 22**).[31]

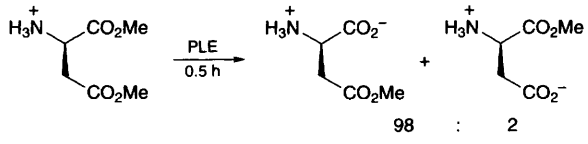


Scheme 22

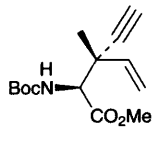
The addition of propan-2-ol to the enantiopure sulfinyl imine–Et_2AlCN mixture results in a dramatic improvement in the asymmetric Strecker reaction (**Scheme 23**).[32] The enhanced diastereoselectivity may be due to the *in situ* formation of an aluminium alkoxide with lower Lewis acidity than the original reagent.

Scheme 23

Porcine liver esterase (PLE) regioselectively hydrolyses the α-ester of aspartate to give a differentially protected amino acid (**Scheme 24**).[33] Kazmaier *et al.* continue to develop the highly diastereoselective ester enolate Claisen rearrangement of *N*-protected amino acid allylic esters to synthesise a variety of substituted α-amino acids, including those with β-quaternary centres such as **9**.[34]



Scheme 24

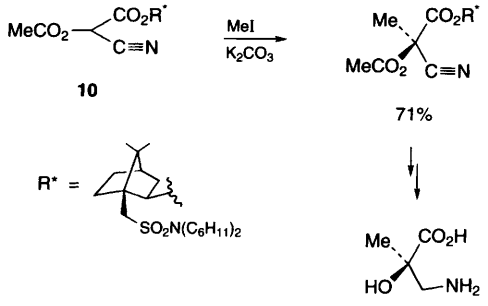


9

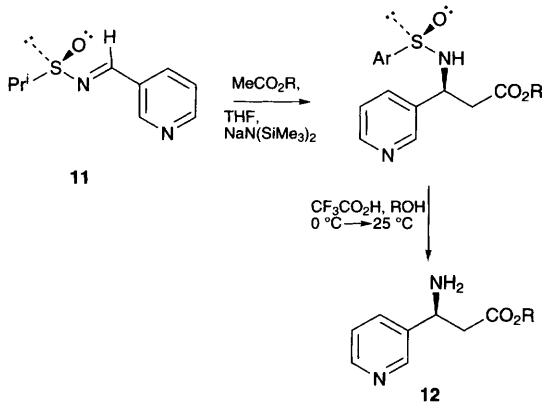
2.7 β-Amino acids

The efficient synthesis of α-hydroxy-β-amino acids derivatives involves the alkylation of the sulfamoyl isonorbornyl derivative **10** with potassium carbonate (**Scheme 25**).[35] A variety of other bases did not give any alkylated product. An efficient synthesis of the

pyridinepropanoate **12** involves the diastereoselective addition of the anion of ethyl acetate to the enantiopure sulfinyl imine **11** (**Scheme 26**).[36]

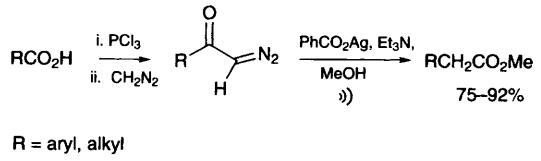


Scheme 25

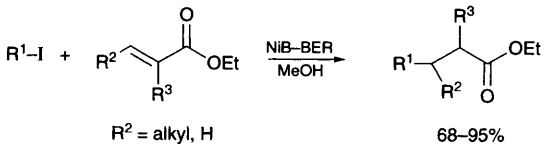


Scheme 26

α,β-unsaturated esters (**Scheme 28**).[39] The products again are simply isolated by filtration.

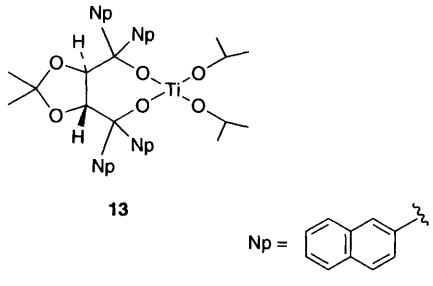


Scheme 27



Scheme 28

Hydrotalcites are neutral materials which contain positively charged layers with anionic compounds in the interlayer. They can be prepared according to literature methods and used to promote the Baeyer–Villiger oxidation of a variety of ketones to the corresponding esters.[40] Simple aldehydes can be directly oxidised to methyl esters in the presence of commercially available trichloroisocyanuric acid in methanol and pyridine.[41]

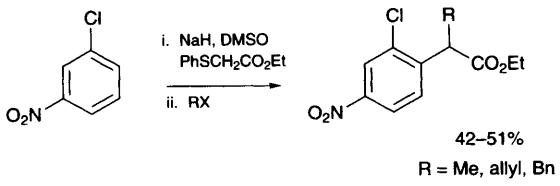


3 Carboxylic acid esters

3.1 General

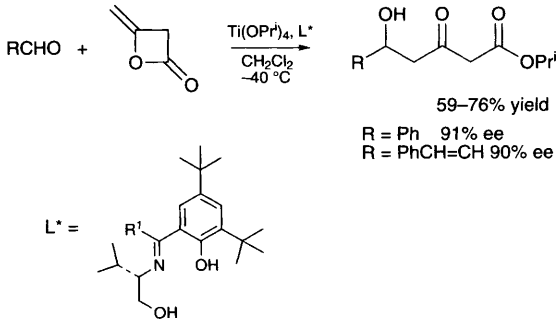
The use of ultrasonic activation in the silver benzoate induced Wolff rearrangement of diazoketones leads to homologated esters rapidly and in good yields (**Scheme 27**).[37] The homologation of aldehydes to α,β-unsaturated esters can be accomplished using an acid catalysed Wittig reaction involving methoxycarbonylmethylenetriphenyl phosphorane, in the presence of silica gel.[38] The triphenylphosphine formed in the reaction can simply be filtered off to give the products with reduced *E* selectivity compared to the conventional Wittig reaction. Nickel boride in the presence of borohydride exchange resin (BER) is an excellent reagent for the coupling of alkyl iodides with

The diisopropoxytitanium TADDOLate **13** (TADDOL = α,α,α′,α′-tetraaryl-1,3-dioxolane-4,5-dimethanol) has been found to open a variety of bicyclic and monocyclic five-membered anhydrides to give the corresponding half-esters in excellent yield and ee (yield 73–92%, enantiomeric ratio 96:4–98:2).[42] Six-membered anhydrides give very low ees. In most cases the hemiesters are dextrorotary. The novel one-pot vicarious nucleophilic substitution–alkylation of nitrobenzoates with the enolate of ethyl thiophenoxyacetate or 2-chloropropionate, gives the nitrated α-alkyl-4-nitrophenyl esters directly (**Scheme 29**).[43]

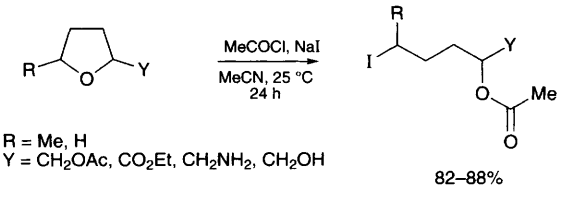


Scheme 29

Hayashi *et al.* have developed a new Schiff base for the titanium isopropoxide promoted reaction of diketene with aldehydes to give optically active 5-hydroxy-3-oxo esters in high enantiomeric excess (**Scheme 30**).[44] The cleavage of tetrahydrofurans substituted at the 2-position with electron withdrawing groups occurs at the 5-position regioselectively in the presence of an acyl halide and a nucleophile (**Scheme 31**).[45] Some selectivity is observed with 3-substituted tetrahydrofurans as well.

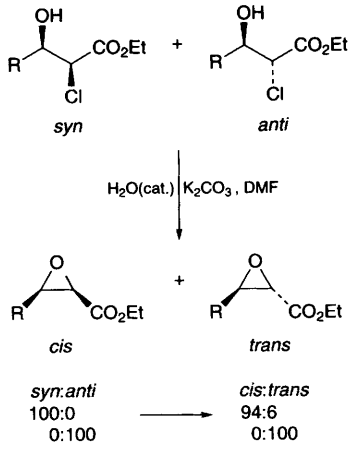


Scheme 30



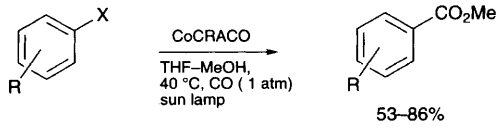
Scheme 31

cis and *trans* Glycidic esters can be synthesised from the corresponding 2-chloro-3-hydroxy esters, which in turn, are obtained by the microbial reduction of 2-chloro-3-oxo esters (**Scheme 32**).[46] Their treatment with potassium carbonate in DMF leads to the *cis* ester from the *syn* derivative and the *trans* from the *anti*. Sodium ethoxide, on the other hand, gives the *anti* derivative regardless of the stereochemistry of the starting ester.



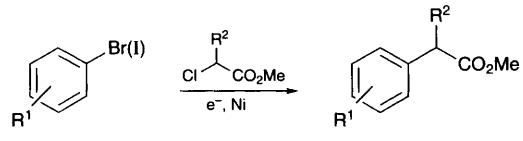
Scheme 32

The alkoxycarbonylation of aryl, heteroaryl and vinyl halides can be performed under atmospheric CO pressure, using a cobalt catalyst generated *in situ* from $Co(OAc)_2$ (**Scheme 33**).[47] This procedure is an improvement over an earlier version of this method which employed the use of $Co_2(CO)_8$ and excess methyl iodide. The electrochemical reduction of an aryl halide and an α-chloro ester in the presence of a catalytic amount of nickel bromide and bipyridyl leads to cross-coupled products in good to high yields (**Scheme 34**).[48] The reaction involves the use of a simple, undivided electrolytic cell and a sacrificial anode, thus making scale-up possible.



CoCRACO = NaH–^{t}C$_5$H$_{11}$ONa–Co(OAc)$_2$

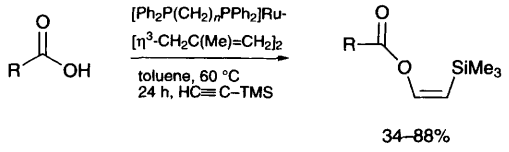
Scheme 33



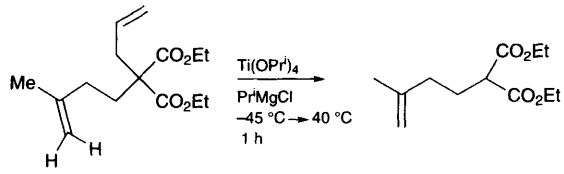
Scheme 34

Carboxylic acids, including amino acids, add to terminal alkynes in the presence of a ruthenium based catalyst in an anti-Markovnikov sense, to give *Z* enol esters regioselectively, under mild conditions (**Scheme 35**).[49] A useful method for the synthesis of monosubstituted malonates involves the utilisation of the allyl group as a protecting group.[50] This group can be removed using (η^2-propene)Ti(OPr^i)$_2$, readily generated *in situ* from titanium isopropoxide and isopropylmagnesium chloride (**Scheme 36**). A variety of 2-nitrocycloalkanones can be cleaved in a one-pot procedure which uses *N*-chlorosuccinimide.

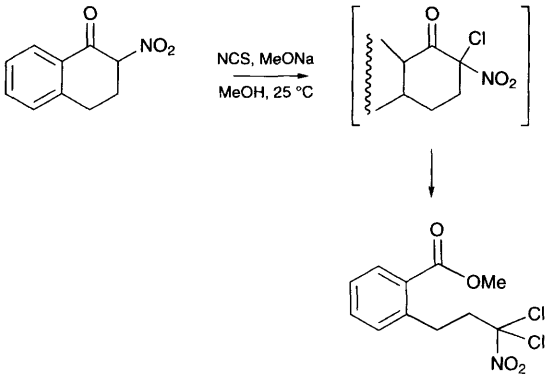
The reaction proceeds through an initial chlorination, followed by cleavage due to the enhanced lability of the α-chloronitro group (**Scheme 37**).[51]



Scheme 35

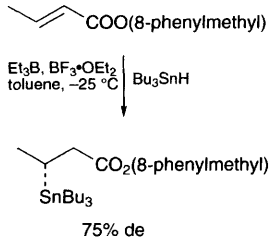


Scheme 36



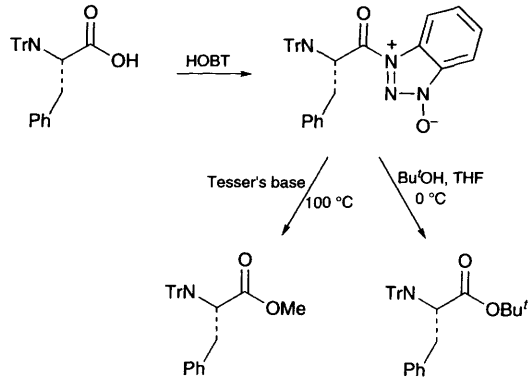
Scheme 37

The diastereoselective 1,4-addition of a stannyl radical to chiral α,β-unsaturated esters occurs in the presence of a Lewis acid (**Scheme 38**).[52] The 1,4-addition of nitroalkanes to α,β-unsaturated esters can be effectively catalysed by Amberlyst A-27.[53]



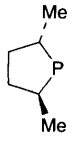
Scheme 38

The reaction of methyl (triphenylphosphoryl-idene)acetate in methanol with acids affords methyl esters in good yields.[54] An effective method for the esterification of *N*-trityl amino acids involves their initial reaction with hydroxybenzotriazole (HOBT) and treating the resulting amide with nucleophiles (**Scheme 39**).[55] *N*,*N*-dimethylformamide dineopentyl acetal can be used to synthesise *tert*-butyl esters, in particular from amino acids, directly.[56]



Scheme 39

The adsorption of carboxylic acids to silica gel [silica, H_2SO_4 (cat.)], followed by simply stirring the solid acid in dichloromethane with an alcohol, enables the esterification of a variety of simple alcohols in good (73–91%) yields.[57] Some limited success has been achieved in the first reported non-enzymatic enantioselective acylation[58] using an achiral anhydride and the chiral phosphine ligand **14** developed by Burk *et al.*

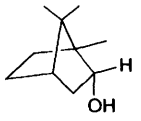


14

In the Mitsunobu inversion, for esterification to occur, a delicate balance must be established such that the carboxylic acid is a strong enough acid to initiate activation of the diazocarboxylate, but the resulting carboxylate is not strong enough a nucleophile to compete with the alcohol in the reaction with the triphenylphosphine–DEAD adduct. HOAc does not fulfil these criteria, whereas 4-nitrobenzoic acid and chloroacetic acid do. Menthol on the other hand can be esterified with HOAc in 67% yield in toluene, whereas the reaction yields none of the esterified product in benzene.[59] This discrepancy is apparently due to the fact that the insolubility of the triphenylphosphine–DEAD adduct in toluene ensures its slower reaction with the carboxylate anion.

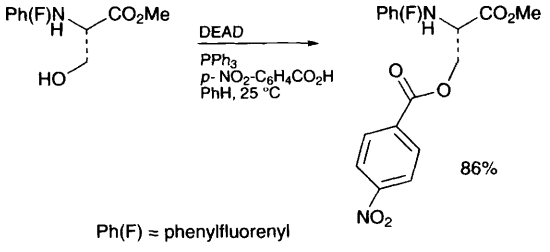
The commercially available superbase $P(MeNCH_2CH_2)_3N$† is a superior acylation promoter, even with hindered alcohols such as **15**.[60] The reaction works through an acylphosphoryl intermediate which can be detected by ^{31}P NMR.

†Available from Strem Chemicals, USA.



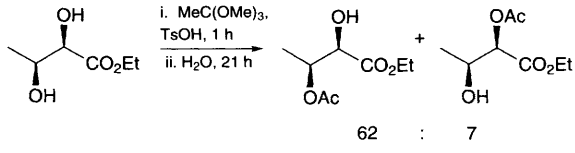
15

Interestingly, *N*-phenylfluorenyl or *N*-trityl protected serine undergoes the Mitsunobu reaction efficiently, whereas the corresponding *N*-Z protected analogue only affords the dehydrated product (**Scheme 40**).[61]

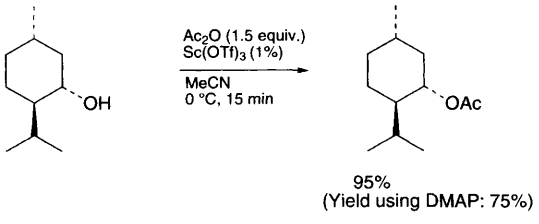


Scheme 40

The monoacylation of vicinal diols can be achieved under acidic conditions by initial conversion to the cyclic orthoester, followed by the addition of a stoichiometric amount of water (**Scheme 41**).[62] The reaction is often, but not always, regioselective. Commercially available scandium triflate is superior to DMAP in some acylation reactions (**Scheme 42**).[63]

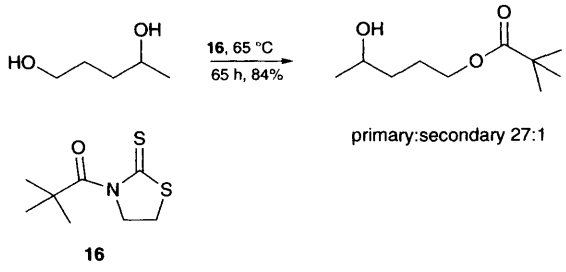


Scheme 41



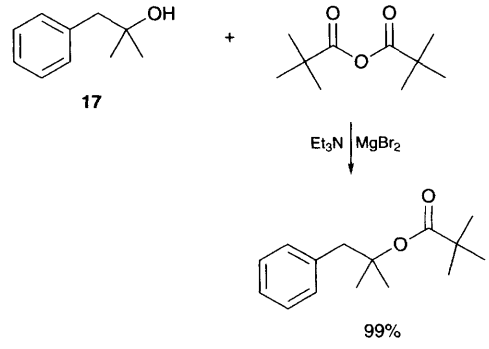
Scheme 42

Acylations with the activated amide **16** proceed under neutral conditions due to the strain around the C(O)–N bond (**Scheme 43**).[64] This reagent is also complementary to acyl halides and anhydrides in the acylation of diols containing both alcoholic and phenolic groups since the alcohols react selectively. The combination of magnesium bromide and a hindered amine, through double activation, produces remarkable rate accelerations in the acylation of alcohols with anhydrides.[65] Acetic anhydride does not work under these conditions. This reagent is superior to DMAP, being two orders of magnitude faster, and superior to the recently reported $Sc(OTf)_3$ which results only in producing eliminated products in the acylation of the hindered alcohol **17** (**Scheme 44**).[66]



16

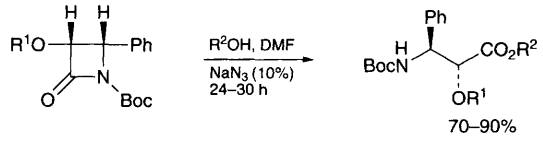
Scheme 43



Scheme 44

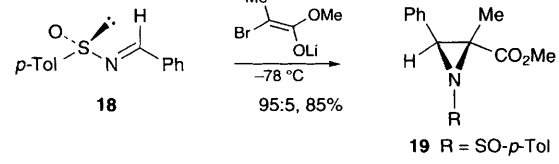
3.2 Amino esters

The ring opening of *N*-Boc-azetidinones with alcohols is greatly enhanced in the presence of NaN_3 or KCN (**Scheme 45**).[67] The reaction is amenable to the use of hindered alcohols which do not participate in the ring opening reaction without sodium azide being present. The anion of α-bromopropionate adds to the sulfinyl imine **18** to give the aziridine **19** diastereoselectively, which in turn can be ring opened in a variety of ways (**Scheme 46**).[68]



R^2 = Me, Bn, Pr^i, Cy

Scheme 45



18

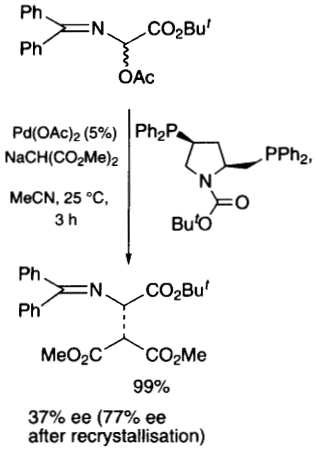
19 R = SO-*p*-Tol

Scheme 46

The treatment of *N*-benzyloxycarbonyl α-methyl esters of L-glutamine or L-asparagine with *tert*-butyl

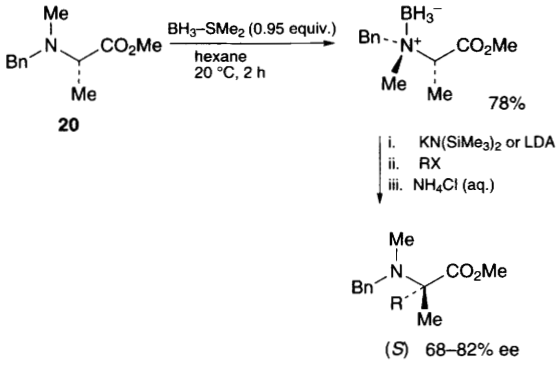
nitrite in refluxing acetonitrile results in the selective hydrolysis of the amide group to give optically pure Z-Glu-OMe (74%) or Z-Asp-OMe (88%) (**Scheme 47**).[69] Some limited success has been found in the coupling of a Schiff base with dimethyl sodiomalonate in the presence of a palladium catalyst and a commercially available chiral bisphosphine ligand (**Scheme 48**).[70]

Scheme 47



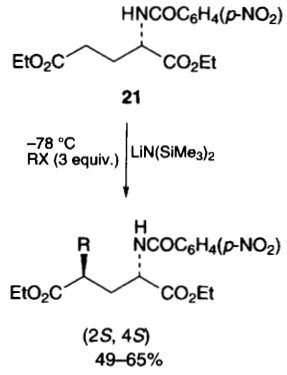
Scheme 48

The use of borane to generate a temporary chiral, quaternary nitrogen has been demonstrated in the α-alkylation of an enolate containing a chiral borane–amine moiety. The alanine derivative **20** is treated with borane–dimethyl sulfide complex in hexane to give a single diastereomer, which crystallises out in good yield (**Scheme 49**).[71] This borane derivative can be alkylated with a variety of electrophiles to give, after decomplexation, disubstituted α-amino esters of up to 68–82% ee.



Scheme 49

A highly diastereospecific route to the preparation of *threo*-4-alkylglutamic acid derivatives involves the γ-alkylation of the *N*-*p*-nitrobenzylglutamic diester **21** (**Scheme 50**).[72] The increased acidity of the NH due to the electron withdrawing protecting group prevents racemisation of the adjacent stereocentre.



Scheme 50

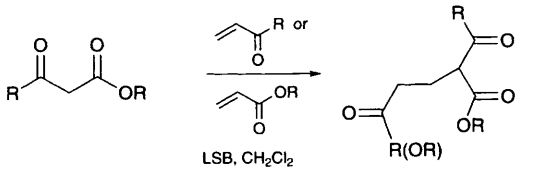
Chymotrypsin catalyses the selective hydrolysis of Schiff bases derived from racemic α-amino esters and aromatic aldehydes.[73] The L-amino acid precipitates in >85% to 99% ee. The addition of an organic base such as DABCO results in a dynamic kinetic resolution resulting in the conversion of 88% of the initial racemate into the L-enantiomer. Enantiopure β-enamino esters can be reduced diastereoselectively with sodium triacetoxyborohydride in acetic acid (**Scheme 51**).[74] The reduction proceeds through an enol ester–diacetoxyborohydride intermediate, which results in the hydride delivery taking place in a six-membered transition state with the protonation occurring from the less hindered side.

Scheme 51

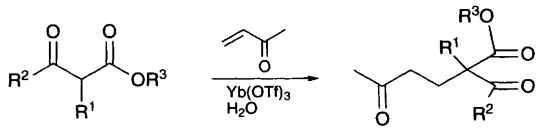
3.3 Keto esters

A highly *syn*-selective Mukaiyama–Michael reaction occurs when ketene silyl acetals containing bulky siloxy and/or alkoxy groups react, in the presence of titanium chloride, with α,β-unsaturated ketones with bulky acyl groups (**Scheme 52**).[75] The stereoselectivity is thought to be due to the suppression of an electron transfer process by the bulky groups, while encouraging a nucleophilic one. La–Na–BINOL complex (LSB) efficiently promotes the catalytic asymmetric Michael reaction of β-keto esters giving products of high ee (**Scheme 53**).[76] The Michael addition of β-keto esters to α,β-unsaturated enones and enals proceeds under mild conditions in water, in the presence of ytterbium triflate (**Scheme 54**).[77]

Scheme 52

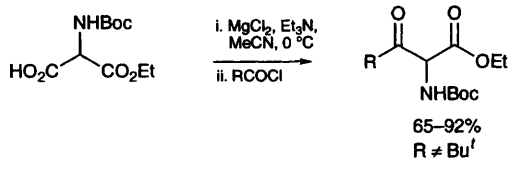


Scheme 53

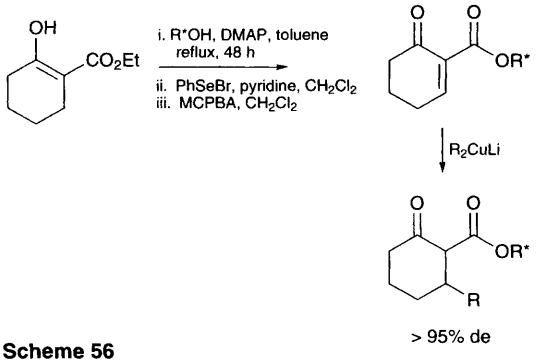


Scheme 54

The methodology developed by Wemple *et al.* for the synthesis of β-keto esters has been extended by Krysan to the synthesis of α-acylamino-β-keto esters, enabling their large scale synthesis in high purity (**Scheme 55**).[78] The transesterification of 2-oxocyclohexanecarboxylate with camphor derived alcohols and subsequent introduction of a double bond *via* a phenyl selenide gives a 2-oxocyclohexene carboxylate (**Scheme 56**).[79] This undergoes cuprate addition from the less hindered face of the s-*trans* enoate with excellent de (>95%) to give, after methanolysis, enantiomerically pure methyl esters.

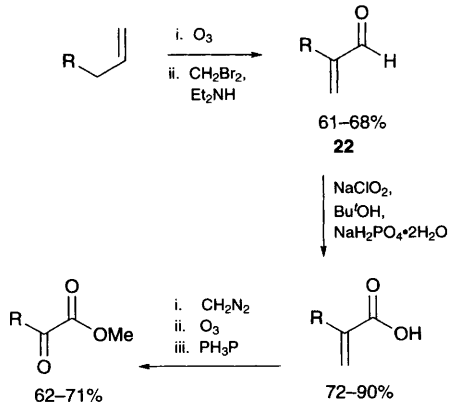


Scheme 55

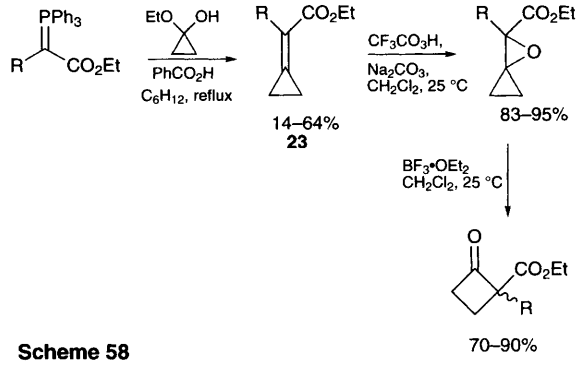


Scheme 56

The one-pot ozonolysis of terminal alkenes, followed by addition of a preheated mixture of CH_2Br_2–Et_2NH affords the acrylaldehyde **22** in good yield (**Scheme 57**).[80] Sodium chlorite in the presence of a chlorine scavenger oxidises **22** to the corresponding acrylic acid which, after diazotisation, can be converted to a variety of α-keto ester derivatives by ozonolysis. Ketones, halides, alcohols and esters are tolerated under the reaction conditions. Previously unknown α-substituted cyclobutane β-keto esters can be prepared from the cyclopropylideneacetate **23** by epoxidation and Wagner–Meerwein rearrangement (**Scheme 58**).[81]

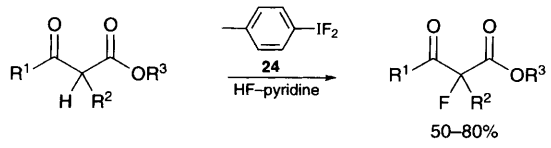


Scheme 57



Scheme 58

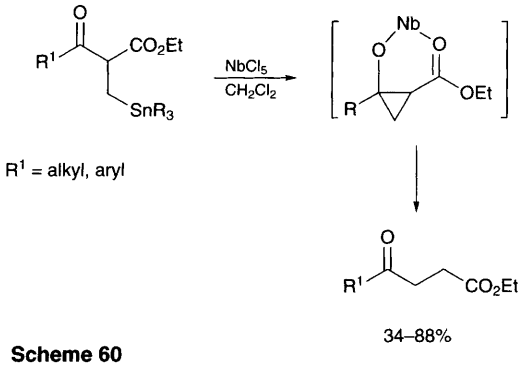
β-Keto esters are selectively fluorinated at the α-position with the iodoarene difluoride **24** in the presence of HF–pyridine complex (**Scheme 59**).[82] Niobium pentachloride homologates α-trialkylstannylmethyl-β-keto esters to the corresponding γ-keto esters in good yields (**Scheme 60**).[83] *N*-Acyl-2-methylaziridines, which can be prepared in a one-pot procedure, are stable intermediates for the exclusive *C*-acylation of dianions derived from β-keto esters (**Scheme 61**).[84] A facile synthesis of β-keto esters involves the reaction of an aldehyde with ethyl diazoacetate, in the presence of the zeolite H-beta catalyst. Ketones do not react under these conditions (**Scheme 62**).[85]



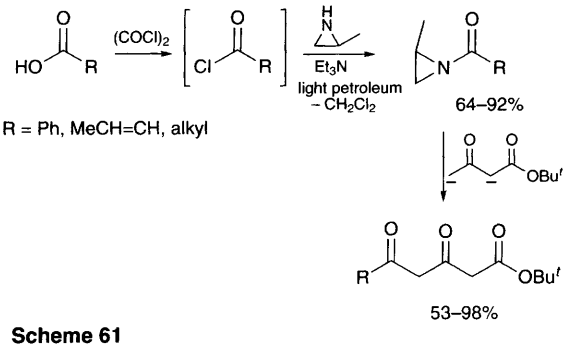
Scheme 59

The Brønsted and Lewis acidity of metal oxides can be modified by the treatment with acids. Thus sulfated SnO_2, which can be generated from tin tetrachloride and sulfuric acid, can be used for the transesterification of β-keto esters using even hindered alcohols such as *tert*-butyl alcohol.[86] Advantages over existing methods include the need to use only one equivalent of the alcohol and the fact that ordinary esters remain unchanged. The products are isolated simply by filtration.

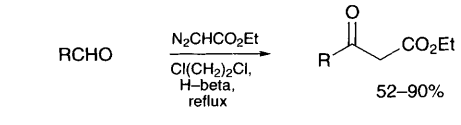
A facile synthesis of α-fluoro-β-keto esters involves the diacylation of diethyl (ethoxycarbonyl)-fluoromethylphosphonate with aromatic carboxylic acid chlorides in the presence of $MgCl_2$–Et_3N, followed by deacylation under mild conditions (**Scheme 63**).[87] Aliphatic acyl chlorides give complex mixtures. The Reformatsky reagent adds in a Michael fashion to unsaturated nitro compounds to



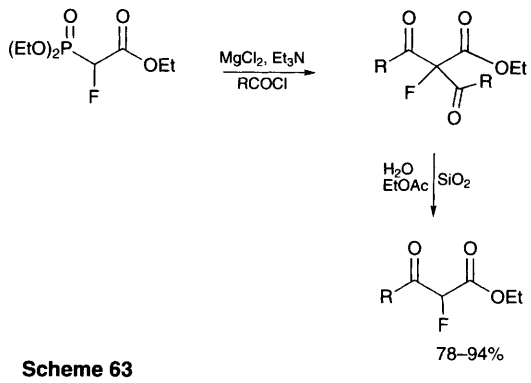
Scheme 60



Scheme 61



Scheme 62



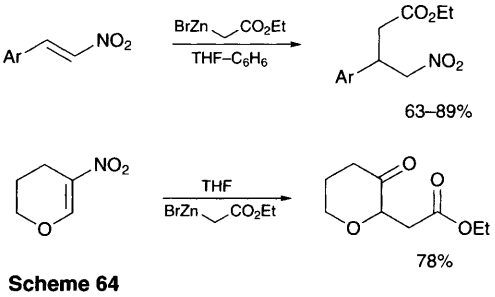
Scheme 63

give 4-nitroalkanoates or γ-keto esters (**Scheme 64**).[88]

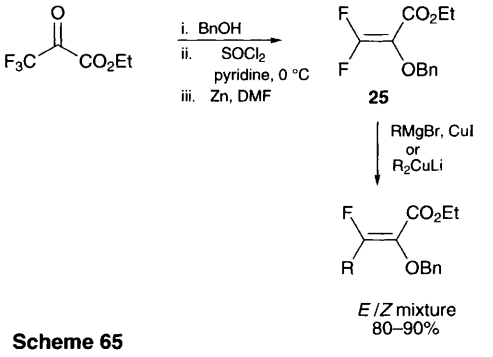
3.4 Halo esters

Ethyl trifluoropyruvate can be converted into the difluoropropenoate derivative **25** which undergoes substitution with a variety of nucleophiles, including lithio anions, to give β-fluoro-α-keto esters in good yields (**Scheme 65**).[69] Methyl 3,3,3-trifluoro-2-diazo-propionate reacts with *N*,*N*-dialkylamines under rhodium catalysis *via* a [1,2]-Stevens rearrangement to give α-trifluoromethylated amino acid derivatives (**Scheme 66**).[90] The diazo ester **26** also reacts under rhodium or copper catalysis with carbamates, amides and secondary amines, to give N–H insertion products.

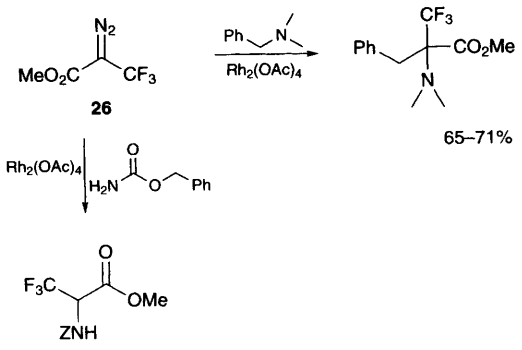
The magnesium bromide–diethyl ether mediated ring opening of α,β-epoxy esters proceeds regioselectively, and offers advantages over the reported methodology involving magnesium iodide, in that the former is commercially available and that the subsequent displacement reactions involving **27**



Scheme 64



Scheme 65



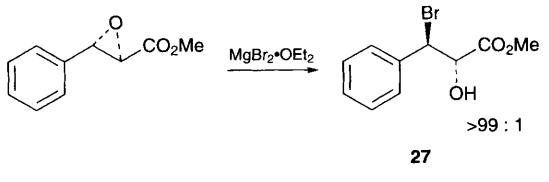
Scheme 66

proceed with complete inversion (**Scheme 67**).[91] Bromination of the homochiral α-chloro acid **28**, readily available from the corresponding α-amino acid, gives a 19:1 diastereomeric mixture of β-bromides **29** and **30** in 87% yield. The major (2*R*,3*S*) isomer may be isolated by fractional crystallisation (**Scheme 68**).[92] In contrast the α-bromo ester gives racemic material on bromination.

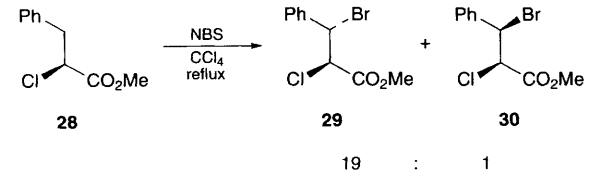
3.5 Unsaturated esters

2,2-Diethoxyvinyllithium can be generated from 2-bromo-1,1-diethoxyethylene with butyllithium and reacts with aldehydes yielding α,β-unsaturated esters after acid catalysed hydrolysis (**Scheme 69**).[93] Tungsten–bipyridine complexes can be generated *in situ* to catalyse the allylic alkylation of isocinnamyl methyl carbonate **31** using dimethyl sodiomalonate with complete *syn* selectivity (**Scheme 70**).[94] The palladium catalysed addition of lithium halides to alkynyl esters and α,β-unsaturated aldehydes and ketones gives β-halo-α,β-unsaturated esters in high yields with excellent stereoselectivity (**Scheme 71**).[95]

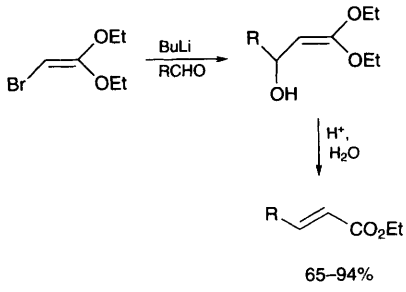
Moderate enantioselectivity has been obtained in the bis-(*S*)-proline–copper(II) catalysed allylic oxidations with *tert*-butyl hydroperoxide (**Scheme 72**).[96] Up to 63% ee has been obtained by the addition of anthraquinone to the reaction mixture. 2,6-Di-*tert*-butyl-4-methylphenyl esters of disubstituted carboxylic acids can be converted in a one-pot procedure into methyl allenecarboxylates using the



Scheme 67



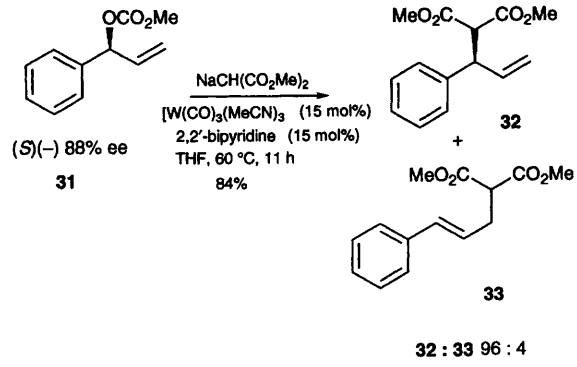
Scheme 68



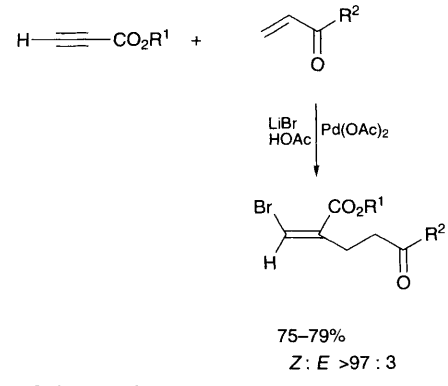
Scheme 69

anion of trimethylphosphonoacetate in the presence of zinc chloride or tin(II) chloride (**Scheme 73**).[97]

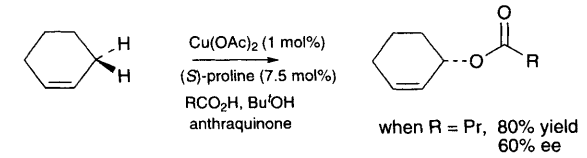
The readily available zeolite H-ZSM5 (Si:Al 35:1) regioselectivity isomerises a variety of glycidic



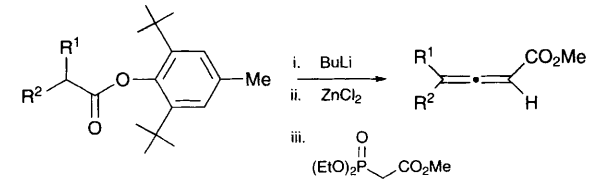
Scheme 70



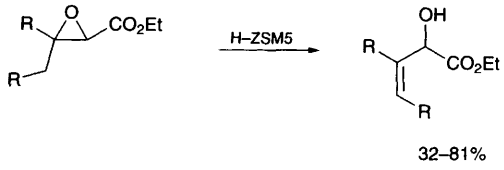
Scheme 71



Scheme 72



Scheme 73

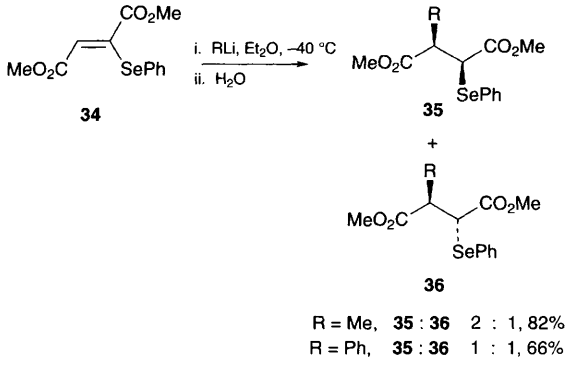


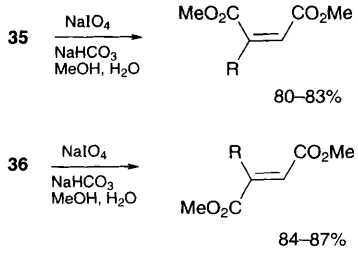
Scheme 74

esters into the corresponding α-hydroxy-β,γ-unsaturated esters in good yields (**Scheme 74**).[98] The exclusive 1,4-addition of organolithiums to the α-seleno ester **34** occurs regioselectively and with moderate stereoselectivity to give seleno esters which individually undergo oxidative elimination to give maleates or fumarates (**Scheme 75**).[99] This methodology could be extended further by alkylating the initial incipient anion with electrophiles. Dimethyl 2-(tosylmethyl)fumarate can be prepared on a multigram scale and reacted with carbon nucleophiles and sodium methoxide predominantly in an S_N2' fashion (**Scheme 76**).[100]

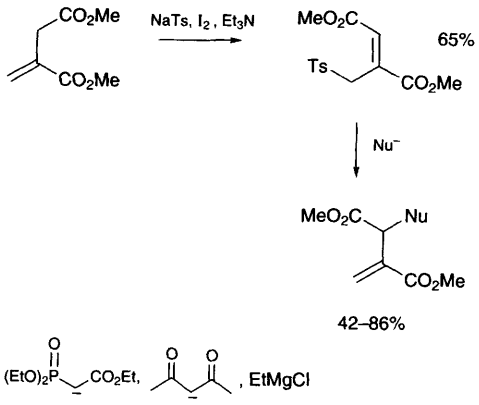
Stereoisomerically pure methyl (*E*)-2-aryl-3-alkoxy- and thioalkoxy-propenoates can be obtained by the palladium catalysed cross coupling of arylzinc chlorides and arylboronic acids with 3-alkoxy, 3-phenylthio or 3-methylthio substituted *Z*-bromopropenoates (**Scheme 77**).[101] Arylstannanes, however, do not react with derivatives such as **37**. The *Z*-bromopropenoate is available by the addition of bromine to methyl propionate, followed by the regiospecific addition of SnOR, SnSPh or SnSMe. The *E* isomer on the other hand is obtained by the addition of the tin reagent to the *E*-2,3-dibromopropenoate which can be prepared by previously described literature method.

Whereas methoxycarbonylmethylene(triphenyl)phosphorane fails to react with the lactone





Scheme 75

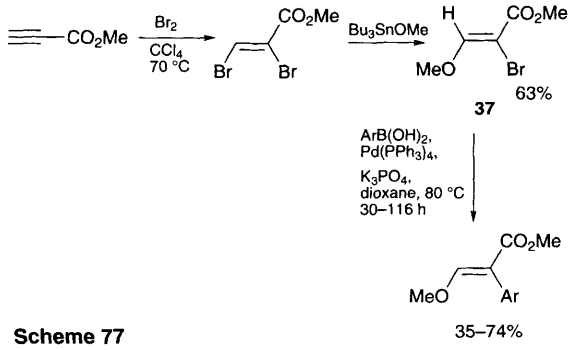


Scheme 76

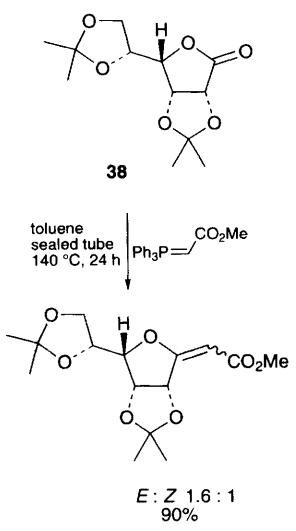
38 in refluxing toluene, it does react to give an *E*/*Z* mixture of α,β-unsaturated esters at 140 °C in a sealed reaction vessel (**Scheme 78**).[102] 1,5-Lactones and benzolactones also react under these conditions, although the reaction is limited to bicyclic lactones where the C-6 hydroxy is tethered in a ring. There are two possible stereochemical outcomes in the Johnson–Claisen rearrangement of methylenealkanoates depending on whether they are alkyl or aryl substituted (**Scheme 79**).[103] Methyl chloroformate can be introduced selectively at the 2-position of acyclic and cyclic 1,3-dienes to give β,γ-unsaturated esters in good yields from readily generated allyltitanium complexes (**Scheme 80**).[104]

3.6 Diesters

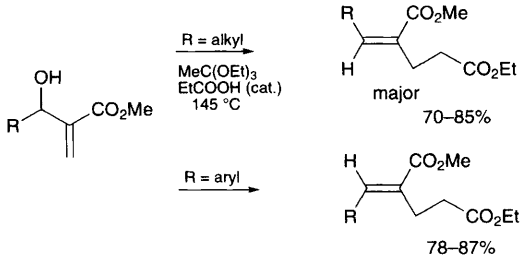
The readily synthesised non-symmetrical allylic acetate **39** undergoes a highly enantioselective palladium catalysed allylic substitution in the presence of an oxazoline ligand (**Scheme 81**).[105] The products can be converted to succinic acids in good enantiomeric excess by oxidative cleavage of the double bond followed by hydrolysis. The γ-hydroxy diester **40** is formed in good yield when a solution of diethyl maleate and acetophenone is added to a solution of LDA (**Scheme 82**).[106] However, pretreat-



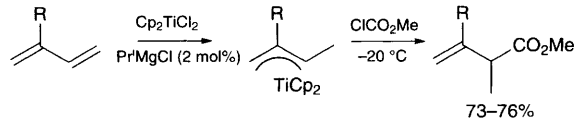
Scheme 77



Scheme 78



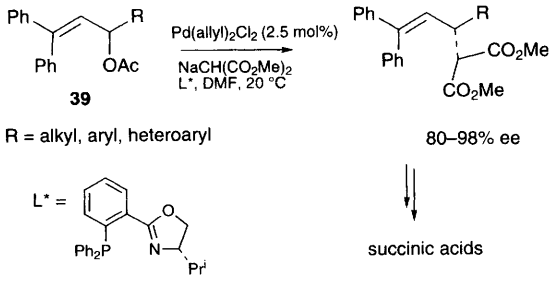
Scheme 79



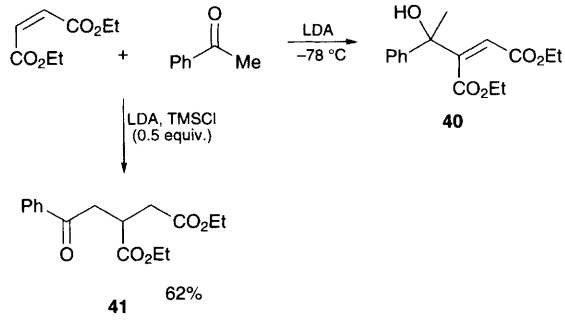
Scheme 80

ment with TMSCl results in the formation of the β-ketodiester **41** in good yield.

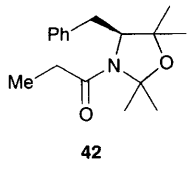
Although 2,2-dialkyloxazolidine auxiliary **42** has not been fully successful in the aldol reaction, it is highly effective in the *anti*-selective Michael addition to α,β-unsaturated esters. The inability to remove the auxiliary without some epimerisation of the product is, however, a limitation.[107] Achiral β-amino ester **43** adds to the chiral acrylate derived from (*S*)-ethyl lactate, (*R*)-pantolactone or (*S*)-*N*-methyl-2-hydroxysuccinimide in the presence of a Lewis acid, to give α,α-disubstituted β-keto esters of high enantiomeric purity in good yield (**Scheme 83**).[108] The addition of alcohols to diethyl methylenemalonate under acidic conditions gives the corresponding 2-alkoxymalonates in good yields (>86%).[109] These compounds can also be synthesised by the inverse addition of the sodio anion of diethyl malonate to chloromethyl methyl ether.

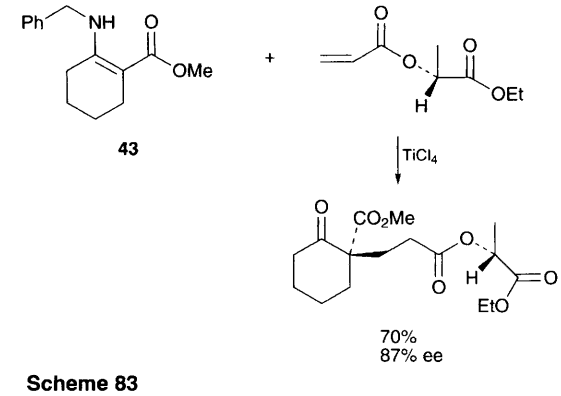


Scheme 81



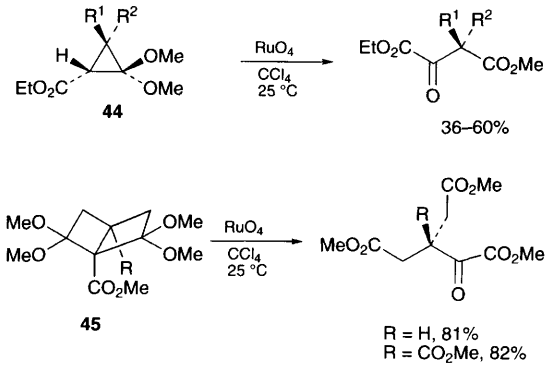
Scheme 82



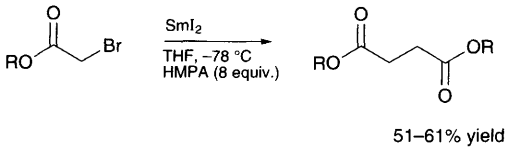


Scheme 83

Ruthenium tetroxide reacts even with electron rich σ-bonds in strained systems such as the cyclopropane **44** and bicyclobutane **45** to give triester and diester derivatives (**Scheme 84**).[110] Primary and secondary α-halo esters can be converted into succinic diesters in good yield by treatment with samarium iodide–HMPA (**Scheme 85**).[111] Previous reports have shown that the absence of HMPA results in the β-keto ester. The fact that tertiary halo



Scheme 84



Scheme 85

esters do not couple under these conditions rules out the possibility of a radical mechanism.

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