Nitro and related compounds

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Reviewing the literature published between May 1995 and October 1996
Continuing the coverage in *Contemporary Organic Synthesis*, 1995, **2**, 357

1 Introduction

This review covers the recent advances in the synthesis and reactions of nitro compounds and related derivatives and is complementary to the review published in this journal in 1995.[1] It also includes extra areas, such as the reduction and cycloadditions of nitro groups and concentrates on new methodology and chemistry leading to useful chemical or biological targets.

2 Nitro compounds

2.1 Aryl nitro compounds

Aromatic amines can be converted into aromatic nitro compounds by treatment with two to three equivalents of potassium ferrate with sodium hydroxide in water. If 0.1 equivalents of the ferrate are used in a pH 9 buffered solution then diaryl azo compounds are formed instead.[2]

Anilines can be oxidised to the corresponding nitro derivatives by the combination of hydrogen peroxide and trifluoroacetic anhydride in dichloromethane.[3] This conversion can also be achieved on a variety of primary amines by 70% *tert*-butyl hydroperoxide catalysed by chromium silicate-2 (CRS-2, a form of chromium containing medium-pore molecular sieves) (52–91% yield).[4]

Solid supported nitrating agents have been used in a variety of systems to nitrate aromatic substrates directly.

A new class of solid acid catalyst system, a high-surface-area Nafion resin entrapped within a porous silica network, has been developed to mono-nitrate benzene in 82% conversion with >99% selectivity for the product.[5] Silica gel impregnated with nitric acid has also been used to efficiently mono-nitrate *N*-substituted methoxyindoles under mild conditions (78% of the 3-nitro derivative).[6] Sulfuric acid supported on silica gel can act as an inexpensive catalyst to nitrate a range of aromatics under mild conditions, in processes that have a wide range of industrial applications.[7]

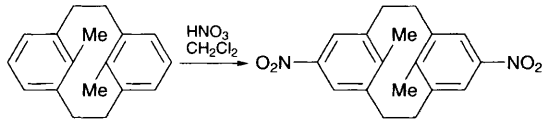
Systems using zeolites have also been used in nitration reactions. Toluene has been nitrated directly by nitrogen dioxide in the presence of zeolite catalysts, in environmentally friendly processes.[8] The nitration of simple aromatic systems under conditions using stoichiometric nitric acid–acetic anhydride mixtures in the presence of zeolite β results in near quantitative yields with high *para*-selectivity (82–100% yields).[9]

'Claycop', an acidic montmorillonite clay impregnated with anhydrous cupric nitrate, has been used in a one-pot nitration of aromatics. Selectivity for either mono- or poly-nitrations can be achieved by varying conditions.[10]

The two aromatic rings in metacyclophanes **1** (MCPs) can be nitrated under mild conditions using nitric acid in dichloromethane, in 88% yield (**Scheme 1**).[11]

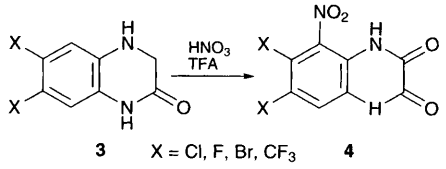
An improved method for the regioselective oxidative nitration of 6,7-disubstituted quinoxaline-2(1*H*)-ones **3** has been designed using nitric acid–trifluoroacetic acid. The resulting 5-nitro-quinoxaline-2,3-diones **4** are potent NMDA (*N*-methyl-D-aspartic acid)/glycine antagonists. This method is superior to the direct nitration of the corresponding diones giving the products in higher yields (80–90%, **Scheme 2**).[12]

Calixarenes can undergo *ipso*-nitration of *p-tert*-butyl derivatives with good yields (85%) in multigram quantities, using a mixture of nitric and acetic acids.[13]



1 **2**

Scheme 1



3 4

Scheme 2

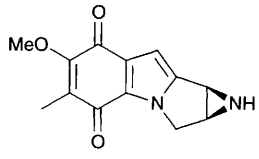
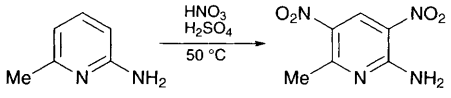


Fig. 1

Sulfolane–$NO_2^+BF_4^-$ has been used to dinitrate a dimethylanisole in the synthesis of an aziridinomitosene analogue (**Fig. 1**) in 75% yield.[14] A $NO_2^+BF_4^-$ and acetic acid mixture has been used under mild conditions to nitrate hydroxyphthalonitriles which can be used as precursors in phthalocyanine syntheses (13–15% yields).[15]

Dinitrated aminopyridines **6** and diaminopyridines were the unexpected result of the nitration of the corresponding pyridines **5**, using a sulfuric acid and nitric acid mixture (75% yield) (**Scheme 3**).[16]



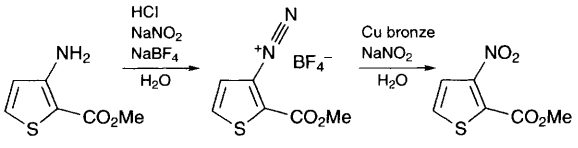
5 6

Scheme 3

Sodium nitrate in trifluoroacetic acid can result in the nitration of indolines (87–94%).[17]

Isoquinolines can be nitrated in the 1-position in one step by treatment with potassium nitrite and acetic anhydride in the presence of HMPA (50–88%).[18]

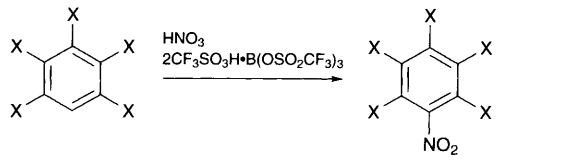
3-Nitrothiophenes **9** can be synthesised in two steps from the 3-amino derivatives **7** in high yields. The amino starting materials **7** are converted to the 3-diazo derivatives **8** and then reacted with sodium nitrite in the presence of copper bronze to give the desired 3-nitrothiophenes **9** in 72% yield (**Scheme 4**).[19]



7 8 9

Scheme 4

Strongly deactivated aromatics, including polyhalobenzenes **10**, can be nitrated with mixed nitric–triflatoboric superacid under conditions which are compatible with many functional groups in yields ranging from 14 to 99% (**Scheme 5**).[20]



10 11

X = H, F, Cl, CF_3, NO_2, CHO in 3-postions
X = H, F, Cl, CF_3 in 2-positions
X = H, F, Cl in 4-position

Scheme 5

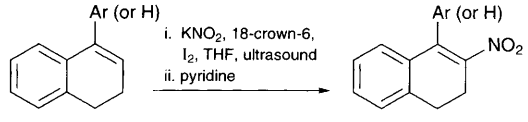
A mixture of nitric and acetic acids can be used to convert 4,5-diphenylimidazole to benzil *via* the 2-nitro derivative (87% over 2 steps).[21]

2.2 Alkyl nitro compounds

Oxidations of the bridgehead amines of aminonorbornanones with MCPBA result in the formation of nitronorbornanones which can be used as 3-substituted homochiral cyclopentanone precursors.[22]

Adamantane can be selectively and rapidly nitrated at the bridgehead position by nitrogen dioxide in the presence of ozone.[23] The methylene group of non-enolisable barbituric acids can be quantitatively nitrated in the direct gas–solid reaction with nitrogen dioxide.[24]

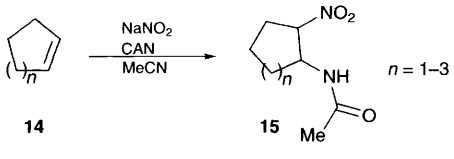
Alkenes can be nitrated in a number of ways. A one-pot procedure involving the *in situ* generation of nitryl iodide, from iodine and potassium nitrite, using 18-crown-6 in THF under sonication results in the nitrations of cyclic conjugated olefins **12** in 52–90% yields (**Scheme 6**).[25]



12 13

Scheme 6

A new, one-pot process has been devised for the nitroacetamidation of cyclic or acyclic olefins using a mixture of ceric ammonium nitrate (CAN) and sodium nitrite in acetonitrile to give the nitroacetamides **15** in 21–71% yields (**Scheme 7**). However, styrene and cinnamyl acetate are unreactive to these conditions.[26]

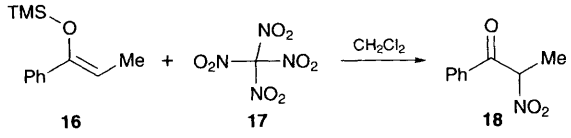


14 15

Scheme 7

Cyclic or acyclic silyl enol ethers **16** can be nitrated with tetranitromethane **17** (TNM) to give

α-nitro ketones **18** in 64–96% yields. The mechanism involves the electron transfer from the silyl enol ether to TNM. A fast homolytic coupling of the resultant silyl enol ether cation radical with $NO_2^{\bullet}$ leads to α-nitro ketones. Photoinduction of these reactions causes the reactions to proceed more rapidly than the corresponding thermal reactions (**Scheme 8**).[27]



16 **17** **18**

Scheme 8

(*E*)-But-2-enylsilanes can be nitrated enantioselectively, with $NO_2^+BF_4^-$ in dichloromethane, to give precursors to (*E*)-olefin dipeptide isosteres.[28]

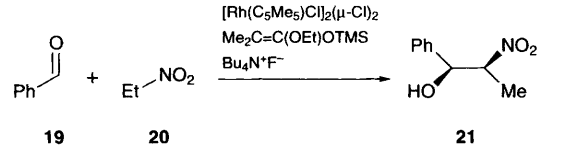
3′-Deoxy-3′-nitrothymidine can be synthesised using a novel method, *viz* nucleophilic substitution of the iodo precursor by nitrite anion (lithium nitrite–phloroglucinol–DMSO). This occurs with complete inversion, but in moderate yield (36% yield).[29]

A tetramethylguanidine promoted intramolecular Henry reaction of a nitroaldehyde moiety has been utilised to assemble the A-ring of Taxol.[30]

Asymmetric La–Li BINOL catalysts have been used to mediate the diastereo- and enantio-selective condensations of nitroalkanes and prochiral aldehydes (70–97% yields in 85–97% ee).[31]

A rapid and stereoselective approach to 1,3-diamino-2-alcohols has been achieved in high yields with *anti,anti* selectivities *via* the tetrabutylammonium fluoride mediated condensation of α-amino aldehydes and nitroalkanes.[32]

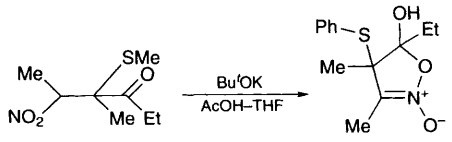
A diastereoselective nitro-aldol reaction catalysed by a rhodium complex, in the presence of a silyl ketene acetal, proceeds under mild and neutral conditions to produce a good *anti,syn* ratio (61:39) of the α-hydroxy nitro products **21** (**Scheme 9**).[33]



19 **20** **21**

Scheme 9

2-Isoxazoline 2-oxides **23** can be synthesised in a new approach from α,β-unsaturated nitro compounds *via* the intermediacy of β-nitro sulfides **22** (**Scheme 10**).[34]



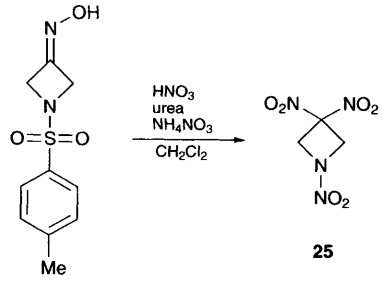
22 **23**

Scheme 10

A new approach to 1-thio-4-nitrodienes ('push–pull' dienes) has been devised involving the DBU catalysed nitro-aldol reactions of nitroalkanes and various 3-thiopropanals. This three-step procedure gives good overall yields.[35]

A nitro-aldol reaction of ethyl nitroacetate with difluorinated aldehyde ethyl hemiacetals is the key step in a new approach to racemic 4,4-difluoroglutamic acid (*ca.* 38% yield overall). This methodology offers an alternative approach to the synthesis of difluoromethylene containing molecules which are not amenable to synthesis *via* diethylaminosulfur trifluoride (DAST).[36]

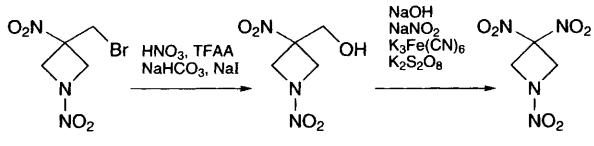
1,3,3-Trinitroazetidine **25** has been synthesised in two contrasting approaches. Oxidative nitrolysis of *N*-(*p*-tosyl)azetidin-3-one oxime **24**, with a mixture of nitric acid, urea and ammonium nitrate gives the required product **25** in 40% yield (**Scheme 11**).[37]



24 **25**

Scheme 11

The azetidine **25** can also be formed in three steps from a simple amine substrate *via* 1,3-dinitro-3-(bromomethyl)azetidine **26**. The alcohol **27**, obtained by hydrolysis of this derivative, can undergo a retro-Henry reaction and *in situ* trapping of the α-nitro anion to furnish the trinitrated product **25** (**Scheme 12**).[38]



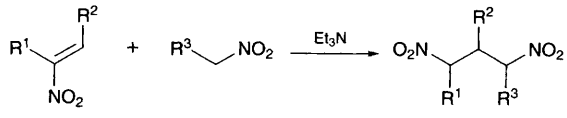
26 **27** **25**

Scheme 12

2.3 α-Substituted nitro compounds

Michael reactions of a great variety of nitroalkanes with β-substituted alkenes can be heterogeneously

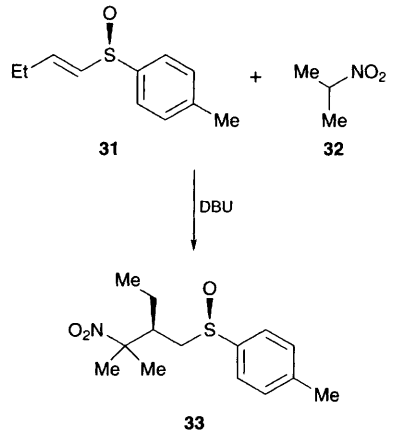
catalysed by Amberlyst A-27 ion-exchange resin in high yields under mild conditions.[39] Nitroalkanes **29** are also used in the syntheses of aliphatic 1,3-dinitro compounds **30** using a base catalysed reaction with α,β-unsaturated nitro compounds **28** (**Scheme 13**).[40]



28 **29** **30**

Scheme 13

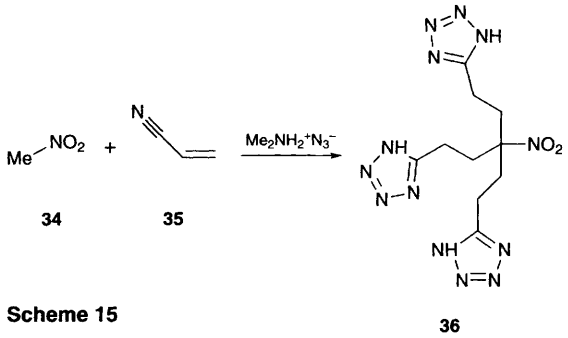
The reaction of 2-nitropropane **32** and an α,β-unsaturated chiral sulfoxide **31**, (**Scheme 14**), provides the key step in a synthetic approach towards the plant sterols sitosterol and stigmasterol (73% yield of the desired diastereomer).[41]



31 **32** **33**

Scheme 14

Tris(2-tetrazol-5-ylethyl)nitromethane **36**, the first example of a branched polynuclear tetrazole system, has been formed for the first time in 60% yield from multiple Michael reactions of nitromethane **34** on acrylonitrile **35** using excess dimethylammonium azide (**Scheme 15**).[42]



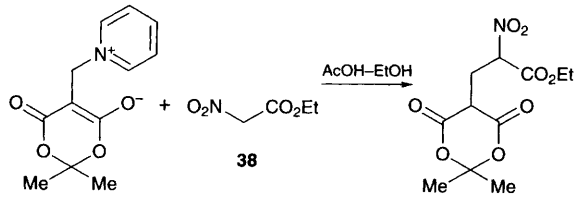
34 **35** **36**

Scheme 15

Sinigrin has been formed in 3 steps in 42% overall yield, the crucial stage being the reaction of 4-nitrobutene with a thiol sugar derivative.[43]

Palladium(0) catalysed alkylations of chiral cyclopentenes with nitromethane give 1,4-*cis*-disubstituted carbocyclic precursors which can lead to carbocyclic nucleoside precursors.[44]

Ethyl nitroacetate **38** can react with Meldrum's acid derivatives **37** to provide the conjoined nitro ester product **39** in 79% yield (**Scheme 16**).[45]



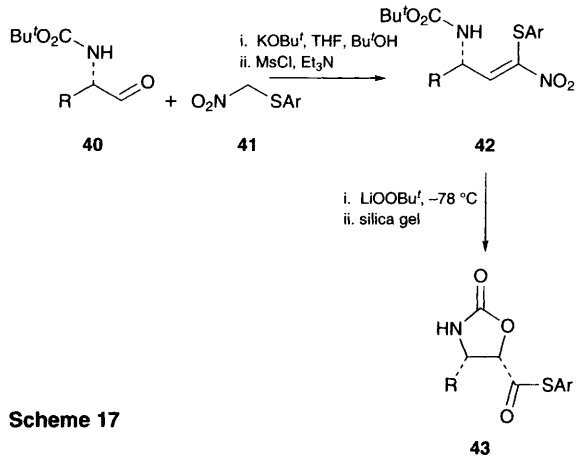
37 **38** **39**

Scheme 16

2.4 α,β-Unsaturated nitro compounds

A variety of olefins can be directly nitrated with NO at atmospheric pressure and room temperature with acidic alumina in excellent yields.[46]

α,β-Unsaturated nitro compounds **42**, formed from the condensation of α-amino aldehydes **40** and thionitromethanes **41**, are used in the syntheses of *cis*-oxazolidinones **43**. The initial mixture of diastereomers which is obtained is completely converted to diastereomerically pure material on exposure to silica gel (**Scheme 17**).[47]

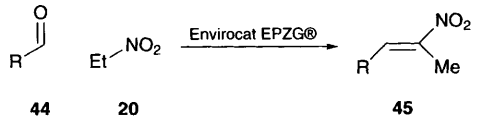


40 **41** **42** **43**

Scheme 17

Conjugated (*E*)-nitroolefins **45** can be formed exclusively in excellent yields (90–97%) from the condensation of nitroalkanes, for example nitroethane **20,** and aldehydes **44** by utilising the heterogenous catalyst Envirocat EPZG®. This new catalyst can be recycled from the solvent-free reaction leading to the easy isolation of products after filtration (**Scheme 18**).[48]

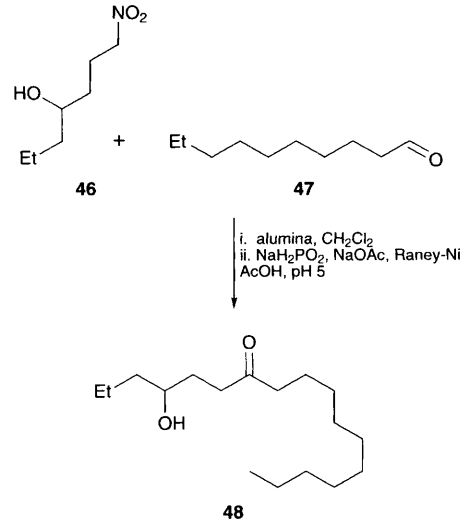
Two new hydroxy ketones, 4-hydroxyheptadecan-7-one **48** and 14-hydroxyoctadecan-8-one, recently



44 20 45

Scheme 18

isolated from *Chiococca alba*, have been assembled. The two step syntheses occur *via* the nitro-aldol reactions of hydroxynitroalkanes with aldehydes (*e.g.* nitroalkanol **46** with decanol **47**) in 41–48% yield, followed by the Nef conversion of the vinyl nitro groups, using sodium hypophosphite, to the corresponding carbonyls in 60–66% yields (**Scheme 19**).[49]

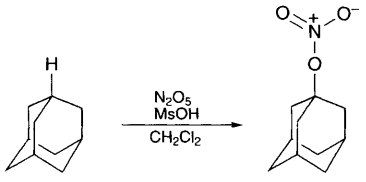


46 47 48

Scheme 19

3 Nitrate esters

The adamantyl nitrates **50** can be selectively formed by the treatment of adamantane **49** with dinitrogen pentoxide and methanesulfonic acid (**Scheme 20**).[23]



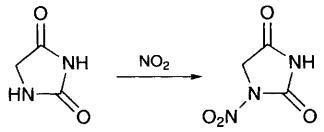
49 50

Scheme 20

2-(4-Nitrophenyl)ethyl nitrate is synthesised as an intermediate in a simplified, two-step preparation of 2-(4-nitrophenyl)ethanol from phenylethanol using nitric acid in the presence of urea (40–41% yield).[50]

4 Nitramines

The direct reaction of nitrogen dioxide with hydantoin **51** at reduced pressure can give the nitramine **52** in quantitative yield (**Scheme 21**).[24]



51 52

Scheme 21

Marchand's approach to 1,3,3-trinitroazetidine (mentioned in Section 2.2, **Scheme 12**) also involves the formation of a nitramine. An *N*-nitroso derivative is oxidised to the nitramine intermediate, by a mixture of nitric acid and trifluoroacetic anhydride in 63% yield.[38]

5 Nitroso compounds

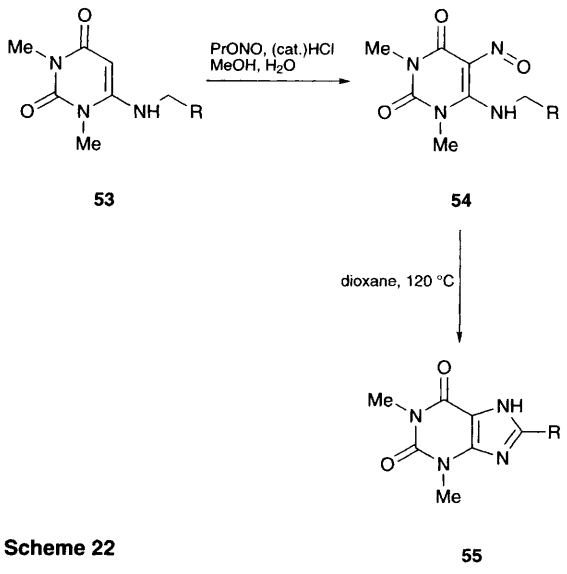
The oxidation of aniline by treatment with aqueous hydrogen peroxide over titanium silicate molecular sieves, TS-1, gives nitrosobenzene in more than 73% selectivity but only 7% conversion.[51] Diphenylamine can be efficiently *N*-nitrosated with nitrogen monoxide and oxygen in benzene in 90% yield.[52]

The improved nitrosation of deoxybenzoins (with *tert*-butyl nitrite and HCl) results in the formation of the corresponding oximino ketones which can then be converted, in two steps, to tetrahydroisoquinolines in high overall yields.[53] The two possible regioisomers of oximino ketones were obtained from the nitrosation of the α-α′-dianion of unsymmetrical ketones with *tert*-butyl nitrite in ether. The ratio of the two isomers can be reversed by the inclusion of HMPA, although low yields for both conversions are observed.[54] 8-Substituted-7*H*-purinediones **55** can be synthesised in a three-step strategy. The methodology is based around the cyclisation of nitroso *N*,*N*-dimethylpyrimidines **54**. These derivatives are prepared from the corresponding pyrimidines **53** by treatment with propyl nitrite and hydrochloric acid in aqueous methanol (**Scheme 22**).[55]

2-Methylbut-2-ene can be nitrosated, with concomitant chlorination, by treating 2-methylbut-2-ene with 2-methylbutyl nitrite and hydrochloric acid. This chloronitroso derivative is a useful precursor for propylene amine oximes.[56]

The electrophilic aminating reagent 1-chloro-[1-^{15}N]nitrosocyclohexane can be prepared in two steps from cyclohexanone *via* the ^{15}N-labelled oxime which is converted in 90% to the nitroso derivative by treatment with chlorine gas. This reagent is useful for the stereoselective synthesis of [α-^{15}N]amino acids.[57]

A variety of anilines possessing electron withdrawing groups in the 3- or 4-positions can be oxidised to the corresponding nitro derivatives by

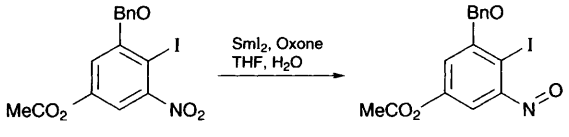


53 54 55

Scheme 22

treatment with hydrogen peroxide, tetrabutylammonium bromide and phosphoric acid mixtures with sodium tungstate (76–92% yields). Simple anilines, not containing electron-withdrawing groups, require just the ammonium salt, hydrogen peroxide and the tungsten catalyst (82–96% yields). This system is not suitable for 2-substituted anilines where the oxidation is achieved in the absence of the ammonium salt.[58]

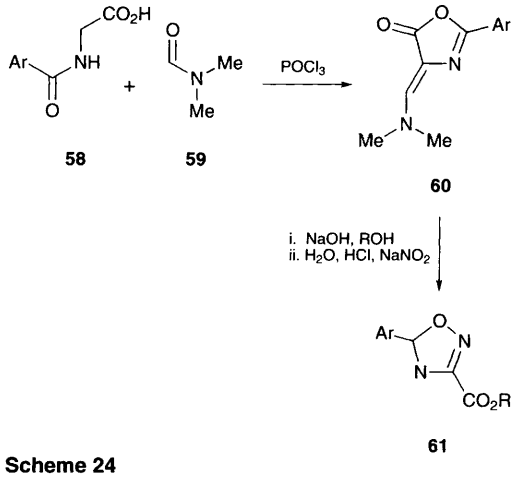
The formation of nitroso intermediates is important in the syntheses of several natural products. The reduction of a polysubstituted nitrobenzene **56** to the corresponding nitroso derivative **57** is used in the total sythesis of (±)-FR-900482. The reaction is performed with samarium diiodide and Oxone in 85% yield at low temperatures (**Scheme 23**).[59]



56 57

Scheme 23

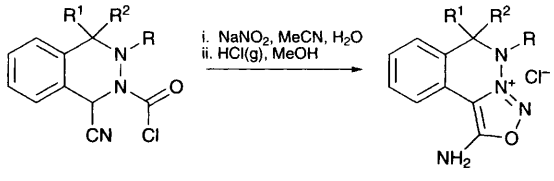
5-Substituted-1,2,4-oxadiazole-3-carboxylates **61** can be prepared in a simple two-step procedure from *N*-acylglycines **58**. The glycines are converted to the 2-substituted-4-dimethylaminomethylidene-oxazol-5(4*H*)-ones **60** *via* treatment with phosphorus oxychloride in DMF. Ring opening of these adducts leads to the corresponding 2-aroylamino-3-dimethylaminopropenoates, which are subsequently nitrosated in the same step to oximes. The oximes spontaneously cyclise to give the desired products in one pot (**Scheme 24**).[60]



58 59 60 61

Scheme 24

A novel two-step approach to annulated sydnone imines **63**, some of which exhibit vasodilator activity, has been designed. The key step involves the nitrosation and subsequent cyclisation of the carbonyl chloride Reissert adducts of phthalazines **62** (**Scheme 25**).[61]



62 63

R = Me, Bu
R¹, R² = H, Me

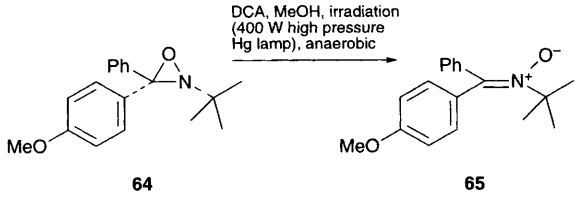
Scheme 25

6 Nitrones

There are several methods for the conversion of amines into nitrones. One such procedure involves the oxidation of secondary amines catalysed by methyltrioxorhenium with hydrogen peroxide or urea–hydrogen peroxide complex to give the corresponding nitrones in good yields (60–95%).[62] A second example of this oxidation used the same hydrogen peroxide–urea complex as oxidant in the presence of metal catalysts in methanol. Sodium tungstate was observed to be the most effective catalyst (yields 60–92%).[63] Titanium silicate-1 in the presence of 30% hydrogen peroxide can also efficiently convert secondary amines to nitrones (50–100% yield).[64]

Keto nitrones can be readily synthesised from the corresponding ketones by the action of an *N*-substituted hydroxylamine in the presence of zinc chloride and magnesium sulfate in dichloromethane (28–98% yield).[65]

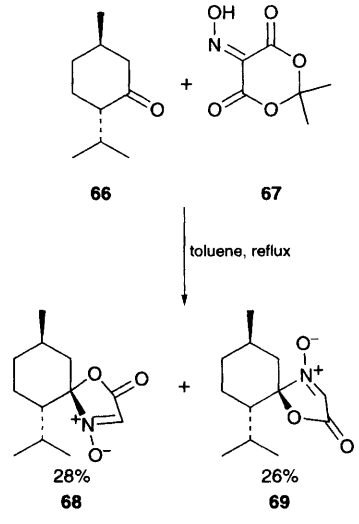
The stereoselective isomerisations of geometrically constrained oxaziridines **64** to the corresponding nitrones **65** can be induced by a photosensitised electron transfer using 9,10-dicyanoanthracene (DCA) as sensitiser in yields of 58–99% (**Scheme 26**).[66]



64 **65**

Scheme 26

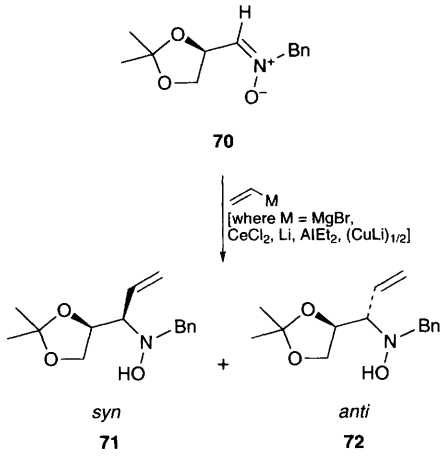
The reaction of the oxime derivative **67** of Meldrum's acid with (−)-menthone **66** resulted in the formation of two diastereomers (**68** and **69**) of a novel cyclic chiral nitrone (**Scheme 27**) *via* a nitrosoketene. The resulting nitrones can undergo 1,3-dipolar cycloaddition reactions with allyltrimethylsilane to give the corresponding isoxazolidine derivatives diastereoselectively.[67]



66 **67** **68** **69**

Scheme 27

The addition of vinyl (or ethynyl) organometallic reagents to the D-glyceraldehyde derived nitrone **70** affords the corresponding *syn*-allylhydroxylamine **71** or *anti*-allylhydroxylamine **72** (**Scheme 28**). The diastereoselectivity of these additions can be controlled by the presence (or absence) of diethylaluminium chloride.[68]

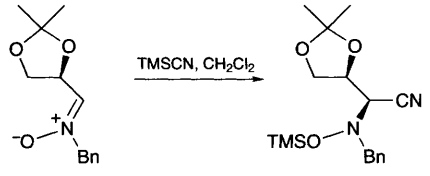


71 **72**

Scheme 28

The addition of Grignard reagents to *N*-benzylthiazol-2-ylnitrone in the presence of Lewis acids and chiral additives leads to hydroxylamines in enantiomeric excesses of 41–74% (yields 69–77%).[69]

The addition of cyanide reagents to the nitrone derived from D-glyceraldehyde acetonide **70** affords mixtures of *syn*- and *anti*-products. Trimethylsilyl cyanide was found to give predominantly the *syn*-stereoselectivity product **73** in high yield (84%, *syn*:*anti* 95:5) (**Scheme 29**).[70]

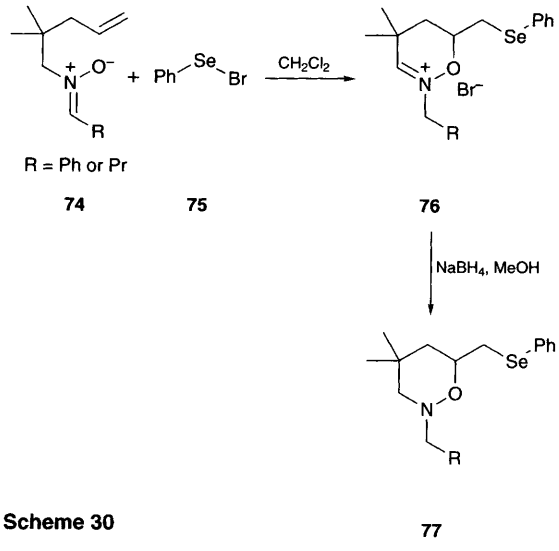


70 **73**

Scheme 29

An enantioselective asymmetric Pictet–Spengler reaction has been employed to give 2-hydroxytetrahydro-β-carbolines in 65–97% yields. The chiral Lewis acid diisopinocampheylchloroborane resulted in enantioselectivities in the range from 35–90% ee.[71]

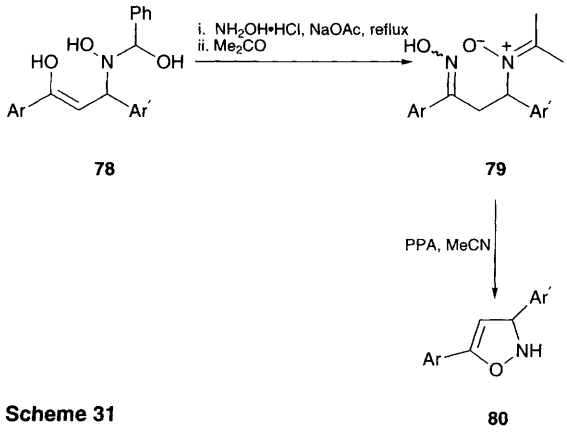
δ-Alkenyl nitrones **74** react with benzeneselenyl bromide **75** to afford ring closure products **76** resulting from the intramolecular capture of the seleniranium intermediates by the oxygen atom. The six membered cyclic iminium salts thus formed can be directly treated with nucleophilic reagents to afford 1,2-oxazinane derivatives **77** in good yields (**Scheme 30**).[72]



Scheme 30

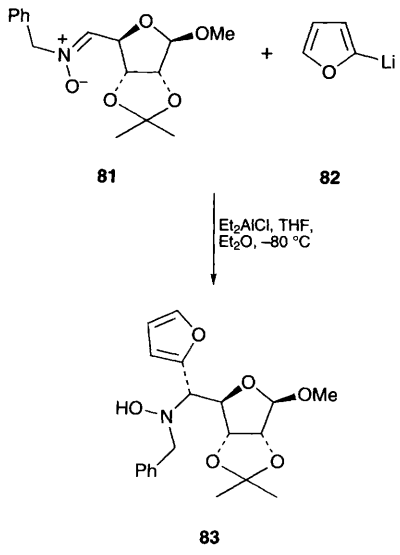
The deoxygenation of nitrones to give aldimines can be achieved readily by the use of triphenylphosphine at 200 °C in yields of 79–87%.[73] The deoxygenation can also be achieved using benzyltriethylammonium tetrathiomolybdate in acetonitrile at 25 °C (60–88% yields).[74]

A novel approach to the synthesis of 3,5-diarylisoxazolines **80** from nitrones relies on the synthesis of the nitrones **79** from the corresponding hydroxylamines **78** (50–62% yield) and subsequent intramolecular cyclisation using polyphosphoric acid (PPA) (**Scheme 31**).[75]



Scheme 31

In the total synthesis of (+)-polyoxin J the diastereoselective addition (ds 82% of the desired isomer, *i.e.* 64% de) of 2-lithiofuran **82** on nitrone **81** gave the hydroxylamine **83** in 72% yield (**Scheme 32**).[76] (**Scheme 32**)



Scheme 32

7 Reduction of nitro groups

A number of new reagent systems have been developed to reduce nitro groups to the corresponding amines and other reduced products. These are mixtures of reducing agents, metal catalysts in new combinations or with new ligands, and bio- or electro-chemical reductions and are listed in **Table 1** (refs. 77–107)

Nitro groups incorporated into precursors of natural products and biologically active compounds have been reduced to furnish key intermediates. These transformations are listed in **Table 2** (refs. 108–115).

8 Cyclisations

8.1 Cyclisations involving nitro groups

The nitro group has shown itself to be an extremely adept functionality for cyclisation reactions. Perhaps the single most widely used method for cyclisations involving nitro functions, through their conversion to nitrile oxides, are 1,3-dipolar cycloadditions. Several examples are listed in **Table 3** (refs. 116–139). An example of this methodology has been used in the 1,3-dipolar cycloadditions of nitro derivatives, for example nitroethane **20,** with enamines **84**. This reaction sequence provided a convenient route to 3-acyl-4-hydroxydihydropyridin-2-ones and 3-acyl-4-hydroxydihydropyran-2-ones **86** (**Scheme 33**).[125]

The 1,3-dipolar cycloadditions become extremely efficient for multi-ring syntheses when they are used in conjunction with Diels–Alder reactions. The nitroalkene inter [4+2]–intra [3+2] cycloaddition reactions give high levels of asymmetric induction with chiral enol ethers **87** derived from (*R*)-(−)-2,2-diphenylcyclopentanol (**Scheme 34**).[121]

The nitro function is also a powerful adjunct for cyclisations by virtue of its strong electron withdrawing effect. Hence 2,3-diphenyl-4-nitropyrrole **92** has been readily prepared by the reaction of tosylbenzyl isocyanide **90** with the Michael acceptor 1-nitro-2-phenylethene **91** in the presence of *n*-butyllithium (100% yield, **Scheme 35**).[126]

8.2 Cyclisations involving nitrone groups

1,3-dipolar cycloaddition reactions of nitrones across olefins provide highly efficient syntheses of isoxazo-

Table 1 Reduction of nitro groups

Substrate	Product	Yield (%)	Conditions	Comments	Ref.
Nitroarenes	Amino derivatives	30–65	$Na_2S_2O_4$, $NaHCO_3$	Inexpensive reagent	77
Nitroarenes	Amino derivatives	83–95	$BiCl_3$, $NaBH_4$	Mild conditions ($SbCl_3$ can also be used)	78
Nitroarenes	Amino derivatives	70–90	$(NH_4)_2SO_4$, $NaBH_4$	Selective, rapid reaction	79
Nitrophenol	Aminophenol	100	CO, H_2O $[H_2S/(NH_4)VO_3/base]_{cat}$	Selectivity of carbonylative reduction determined by ratio of substrate to H_2O	80
Nitroarenes	Amino derivatives	76–91	$NaBH_4$, $CuBr \cdot SMe_2$		81
Nitroarenes	Amino derivatives	100	$FeCl_3$, Me_2NNH_2	Mild conditions, compatible with many funct. grps.	82
β-(*N*,*N*)Dimethylamino)-2,4-dinitrostyrene	6-Aminoindole	64	Al–Hg, ultrasound	Improved two-step synthesis of indole	83
1-Nitrophosphonate	1-Amino phosphonate	93–98	$LiBH_4$, TMSCl	High spectroscopic purity	84
4-Nitro-5-aminobenzothiadiazine	Aryltetramine	89	Sn(m), HCl	Improved yield of tetramine	85
p-Chloronitrobenzene	*p*-Chloroaniline	97	Polymer supported Pd/Ru catalysts	Bimetallic catalysts give 95% selectivity for product	86
Nitrobenzaldehyde or phenyl ketones	Quinazolines	5–47	$PdCl_2(Ph_3P)_2$, $MoCl_5$, formamide, CO	Novel approach to quinazolines	87
Dinitro aromatics	Aryl dicarbamates	86 selectivity	$Pd(phenanthroline)_2(OTf)_2$, $4\text{-}ClPhCO_2H_{(cocat)}$, CO		88
Nitroarenes	Amino derivative	5–65	$PdCl_2$, TPPTS, CO in H_2O	First selective reductions using water-soluble Pd catalysts	89
Nitro derivatives of hydroquinolines	Amino derivatives	85	Pd-4-(2-pyridylazo)-resorcinol-Al_2O_3, H_2, $NaBH_4$		90
Nitroarenes	Amino derivatives	93–97	9,10-Dihydroanthracene, *N*-methylacetamide	Reduction by homolytic retrodisproportionation	91
Nitrobenzene	Aniline		Pd–Ni cluster, H_2	Bimetallic catalyst shows greater catalytic activity than the monometallic clusters	92
Nitrobenzene	Phenylurethane (homogen. cat.)	61	Pd^{II} (subst. pyridine ligands), $FeCl_3$, CO	New catalysts synthesised and used in reductive carbonylations	93
Nitrobenzene	Aniline	95	$Ru_3(CO)_{12}$, ligand, CO	New bis(azaheteroaryl) methane type ligands give improved selectivities and yields	94
Nitrobenzene	Aniline	80	Cationic Rh^I cat., CO	Higher catalytic activity than previous methods	95
Nitroarenes	Amino derivatives	49–90	$RhCl(Ph_3P)_3$, Et_3SiH	Reductions of 4-bromonitrobenzene and *p*-nitrobenzaldehyde not selective	96
Aryl nitro	*Strychnos* indole alkaloid	40	$Ni(COD)_2$, LiCN, Et_3N		97
(*Z*)-3-Substituted-2-phenyl-3-nitropropenenitriles	Isoxazoles	50–82	Bakers' yeast, glucose, buffer	Biohydrogenation in good yields	98

Table 1 *continued*

Substrate	Product	Yield (%)	Conditions	Comments	Ref.
Polysubstituted nitroarenes	Denitrated derivative	68	Electrolysis aq. HNO_3, THF	Pd anode/Pt cathode	99
Dinitro aromatics	Diamino derivatives	90	Electrolysis $TiOSO_4$–H_2SO4	Variety of electrochemical systems investigated	100
Nitroarenes	Aryl isonitrile	87	Zn(m), HCO_2COMe, pyridine, triphosgene	Isonitrile cyclised to disubstituted indole	101
Nitroarenes	Diarylazoamines	10–99	Mg(m), I_2	Reductive coupling proceeds *via* single electron transfer from metal to substrate	102
Nitroalkane	Hydroximoyl chloride	63–78	NaOMe, $TiCl_4$	New one-pot process	103
Nitroarenes	Azoxy compounds	50–96	Bi(m), $NaBH_4$	Catalytic, selective reductions	104
α,β-Unsaturated nitroalkene sugar derivatives	Oximes	90	Zn(m), AcOH	Versatile route to 2,3-unsaturated sugar derivatives or free deprotected sugars	105
Nitroalkanes	Aldehydes/ ketones	30–90	Cu(m), TMEDA, pyridine, O_2	Reaction mixture pretreated under Ar prior to introduction of O_2	106
Nitroalkene	Nitro	65–79	Zeolite H-ZSM 5, $NaBH_3CN$	Selective reduction of alkene (nitro group not affected)	107

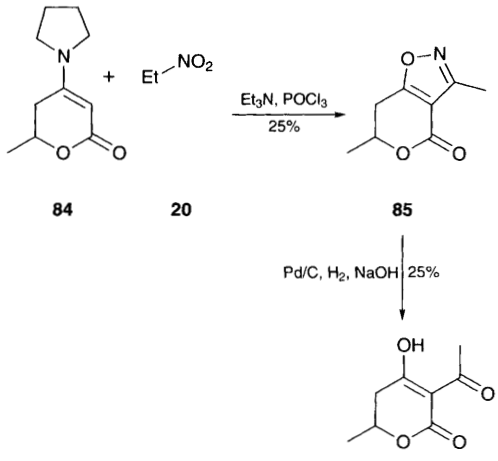
Table 2 Reductions leading to intermediates in the synthesis of natural products and biologically active compounds

Substrate	Product	Yield (%)	Conditions	Comments	Ref.
α-Nitro enone (steroid)	α-Amino enone (MDL 19687)	64	Pd(m)/$CaCO_3$, quinoline, H_2	First example of reduction of α-nitro enone to α-amino enone	108
Nitroarenes	2° amine (*via* reductive alkylations)	60–93	Pd(m)C, H_2, Na_2SO_4	Access to amino acid derivatives. Some diastereoselectivity is exhibited in some examples	109
Nitroarenes	*Strychnos* alkaloids (*via* reductive alkylations)	12–60	Pd(m)/CH_2	Alkaloids: turibfolidine, akuammicine and dihydroakuammicine synthesised	110
Nitroarenes	1,4-Benzo-diazepine and 5-thio-analogue	65–75	Fe(m), AcOH	Approach to the antibiotic DC-81 and analogues based on new reductive cyclisation procedure	111
	Azaguanine	92	Raney nickel, H_2, $NaNO_2$, AcOH	One-pot	112
Nitrocyanomethyl-pyrimidine	Pyrrolo-pyrimidine	60–82	Pd(m)/C, H_2, HCl	9-Deazaguanines synthesised by cyclodeaminations	113
Nitroarene	4*H*-Quinolone (Graveoline)	96	$Pd(TMB)_2$,[a] TMPhen,[b] CO, DDQ,	One-pot reductive *N*-heterocyclisation	114
Dinitro aromatic	Fused bisindole	48	Ph_3P, base	Intermediate in the synthesis of (±)-K252a	115

[a]TMB = 2,4,6-trimethylbenzoate. [b]TMPhen = 3,4,7,8-tetramethyl-1,10-phenanthroline.

Table 3 Nitro cyclisations

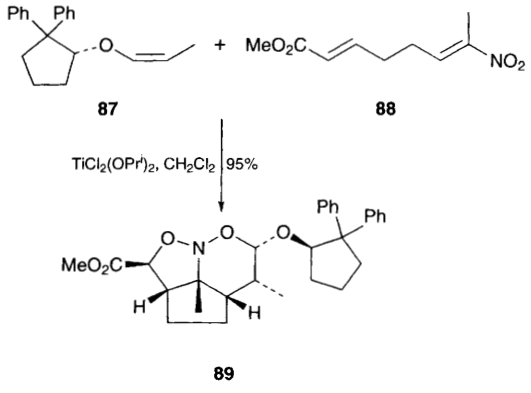
Substrate	Product	Yield (%)	Comments	Ref.
2-Nitro-3-substituted buta-1,3-dienes	1,2-Oxazole-3-propionaldehydes	29–94	Diels–Alder reaction with ethyl vinyl ether then thermal rearrangement of oxazine *N*-oxides	116
Oxygen functionalised nitrile oxides	3-Formylisoxazole	31	1,3-Dipolar cycloaddition onto an enamine	117
Nitroketene *N,S*-acetals	1-Substituted 3-nitro-5-methyl-2-(methylsulfanyl)pyrroles	49–81	Cyclisation utilising prop-2-ynyl bromide and cuprous bromide	118
Acyclic carbohydrate substituted nitroalkene	Nitronate (cyclic nitronic ester)	89	Diastereoselective tandem[4+2]–[3+2]cycloaddition utilising a D-galactose substituted nitroalkene, conducted at 25 °C	119
Ethyl nitroacetate	5-Acyl-3-(ethoxycarbonyl)-2-isoxazoline 2-oxides	63–99	Tandem conjugate addition and ring closure using α-bromoenones	120
Nitroalkenes	Nitronates	84–95	Tandem intermolecular [4+2] and intramolecular [3+2] cycloadditions, using chiral enol ethers and Lewis acid; 83–92% ee observed	121
Nitroalkenes	Nitroso acetals and nitronates	76 (over 2 steps)	Bridged mode [4+2]–[3+2] cycloadditions with 1,4-dienes	122
Nitroalkanes	Spiro[4.5]decanes	65–75	1,3-Dipolar cycloadditions onto tricarbonyl[(1,2,3,4-η)-2-methoxy-5-methylenecyclohexa-1,3-diene]iron	123
Trimethylsilylnitronates	3-Alkyl-5-hydroxy-5-per(poly)fluoroalkyl-4,5-dihydroisoxazoles	50–77	1,3-Dipolar cycloaddition onto 1-bromo-1-per(poly)fluoroalkylethene	124
Nitroethane	4-Carboxyisoxazoles	25–59	1,3-Dipolar cycloaddition onto enamines	125
1-Nitro-2-phenylethene	2,3-Diphenyl-4-nitropyrrole	100	Reaction of tosylbenzyl isocyanide with a Michael acceptor	126
6-Methyl-2-nitroaniline	Benzimidazoles	73–98	One-pot *N*-alkylation–heterocyclisation–*O*-alkylation sequence	127 128
Iodoaryl nitroalkene	2,2-Disubstituted 1-nitroalkene and saturated nitroalkane	43	Intramolecular Heck cyclisation	129
6-Nitro-1-dimethylamino-[6-^{11}C]hexatriene	Nitro[1-^{11}C]benzene	5–⩾80	Synchronous six-electron cyclisation of hexatriene systems into aromatics	130
β-Nitrostyrenes	3-Aryl-4-nitropyrrolidines	46–83	1,3-Dipolar cycloadditions with the azomethine ylide derived from sarcosine and paraformaldehyde	131
Nitro olefins or 2-nitroalkyl acetates	Pyrroles	12–84	Reaction with thioimidate in the presence of organic bases	132
α-Acetoxy-β-nitroalkanes	2-Cyano-3,4-substituted pyrroles	70–90	Base promoted condensation with isocyanoacetonitrile	133
Nitroalkenes	4,5-Dihydrothiophenes: 4,5-*syn* 4,5-*anti*	 18–20 72–78	1,3-Dipolar cycloadditions with thioisomunchones followed by fragmentation	134
Nitro olefins	Isoxazoline *N*-oxides	10–91	Reaction with sulfur ylides	135
Nitroalkenes	Pyrrolidines	52–66	Intermediate *O*-silyl α-allylaminoalkyl nitronates undergo steroselective intramolecular silyl nitronate–olefin 1,3-dipolar cycloaddition	136
Nitro olefin	Isoxazoline	100	Intramolecular nitrile oxide cycloaddition	137
Nitroethane	2-Isoxazolines	72–76	1,3-Dipolar cycloaddition of *N*-acryloyl sultams with silyl nitronate generated *in situ* from nitroethane	138
Nitromethane	Isoxazolidine	93	Selective addition across a bridging olefin	139



84 20 85 86

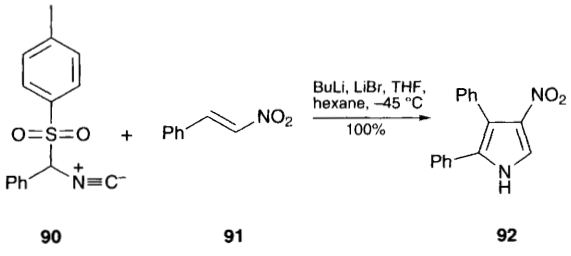
Scheme 33

lidines (see **Table 4**, refs. 140–171). A representative example of this work can be observed in the reaction of *C*-alkoxycarbonyl nitrones **93** with vinyl acetate (**Scheme 36**). In this reaction the isoxazolidine **94** was formed in 90% yield but little stereocontrol was observed and a 1:1 ratio of *cis*:*trans* products was obtained. A high degree of *endo*-selectivity (*endo*:*exo* > 20:1) has been induced in the 1,3-dipolar cycloaddition when a catalytic magnesium phenanthroline complex was used. If the reaction was performed on an alkene bearing a chiral auxiliary then one of four possible diastereomers of the isoxazolidines is exclusively formed.[143]



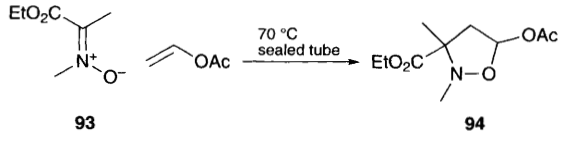
87 88 89

Scheme 34



90 91 92

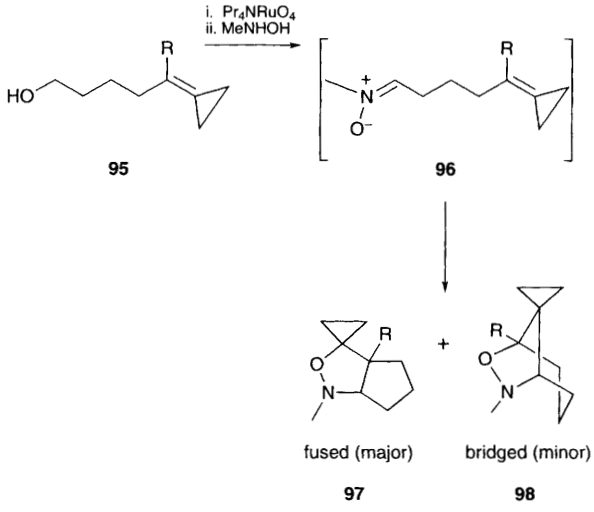
Scheme 35



93 94

Scheme 36

The use of microwave radiation as a method to enhance the rate of nitrone 1,3-dipolar cycloadditions is becoming more prominent. The reactions are typically carried out under solvent free conditions with the reaction times of only a few minutes (< 5 minutes) and yields are enhanced above those obtained using simple thermal activation (**Scheme 37**).[144,150,151]

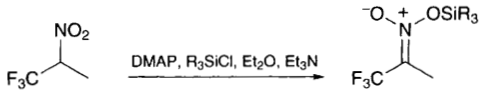


95 96 97 98

Scheme 37

9 Miscellaneous

Silyl nitronates **100** of 1,1,1-trifluoro-2-nitropropane **99** can be prepared by the action of a silyl chloride in the presence of DMAP and triethylamine using diethyl ether as solvent; yields of 25–66% have been obtained (**Scheme 38**).[172]



99 100

Scheme 38

Nitrocyclitols have been sythesised based on enzymatic aldol reactions using fructose 1,6-diphosphate (FDP) aldolase followed by intramolecular nitroaldol reactions.[173]

In the synthesis of (−)-rosmarinecine **101**, used to exemplify a general strategy for the synthesis of *cis*-substituted pyrrolizidine bases, a retrosynthetic

Table 4 Nitrone cyclisations

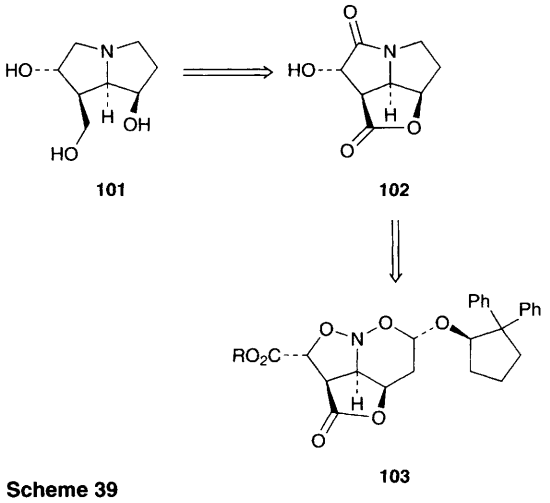
Substrate	Product	Yield (%)	Comments	Ref.
C-Alkoxycarbonyl nitrone	Isoxazolidine	90	Addition across vinyl acetate	140
Various	2,3-Dihydro-1,2,4-oxadiazoles	32–90	Addition across nitrile under elevated pressures (9870 atm)	141
Dialkyl nitrone	Isoxazolidine	86	Addition across dimethyl maleate, used in the synthesis of (±)-Plakoridine-A, a marine alkaloid	142
C,*N*-Diphenyl nitrone	Isoxazolidine	>95	Addition across an olefin attached to a chiral auxiliary (79–82% ee), *endo* selectivity	143
N-(Benzylidene)methylamine *N*-oxide	Fluorinated isoxazolidines	76–94	Addition across fluorinated dipolarophiles under solvent free microwave activation	144
N-Benzyl *C*-phenyl nitrone	Isoxazolidines	79–84	Addition across *trans*-4-cyclohexylcyclohexyl and *p*-phenylphenyl cinnamates in the smectic *meso* phases of BPCD[a] give high *endo* selectivity	145
N-Methyl or *N*-benzyl nitrones	Isoxazolidines	54–75	Addition to α,β-unsaturated γ-lactams	146 147
Cyclopropylidene nitrones **96**	5-Spirocyclopropane isoxazolidines	87 (over 2 steps)	Intramolecular 1,3-cycloaddition to give fused **97** rather than bridged adducts **98** either predominantly or exclusively (see **Scheme 37**)	148
Carbonyl conjugated nitrones	Isoxazolidine-5-methanols	50–97	Lewis acid (magnesium bromide etherate) promoted *E*–*Z* isomerisation and highly stereo- and regio-selective cycloadditions to allylic alcohol dipolarophiles	149
Various nitrones	2,3-Dihydro-1,2,4-oxadiazoles or 1,2,4-oxadiazoles	29–91	Addition to nitriles under solvent free conditions using microwave activation	150
C,*N*-Diphenyl nitrone	Spiro isoxazolidines	98	Cycloaddition using a chiral ketene acetal under microwave irradiation under solvent free conditions. Some facial selectivity was observed	151
C,*N*-Diphenyl nitrone	5,5-Dialkoxy isoxazolidines	80–99	Dramatic solvent effects were observed in the enantioselectivity in the chiral oxazaborolidine catalysed addition of ketene acetals to the nitrone	152
Z-Nitrones	3-Stereoisomers of an isoxazolidine	83	1,3-Dipolar cycloaddition onto a chiral dipolarophile (chiral allylic alcohol)	153
N-Methyl *C*-phenyl nitrone	CF_3 Substituted isoxazolidines	65	1,3-Dipolar cycloaddition with CF_3-substituted alkenes	154
Nitrone enolates	Isoxazolidines	23–65	Enolate group acts as a dipolarophile in intramolecular cycloadditions of nitrones with high diastereoselectivity	155
C-Aryl *N*-phenyl nitrone	5-Acetylisoxazoles and 5-acetylpyrazoles	70–80	1,3-dipolar cycloaddition of captodative olefins 1-acetylvinyl carboxylates with nitrones	156
4-Hydroxy-2-isoxazoline 2-oxides		95–99	Silicon tethered 1,3-dipolar cycloadditions using vinylchlorodimethylsilane	157
C-Carboxy *N*-benzylnitrone	Isoxazolidines	16–80	1,3-Dipolar cycloaddition of the 1-carboxy nitrone with mono-substituted olefins gives predominantly *cis* products. In the presence of triethylamine predominantly *trans* products are obtained	158

[a]BPCD = bis(4-pentyloxyphenyl) *trans*-1,4-cyclohexanedicarboxylate.

Table 4 *continued*

Substrate	Product	Yield (%)	Comments	Ref.
Chiral cyclic nitrones	Isoxazolidines	60–89	Diastereoselectivities greater than 99% de were achieved	159
Chiral spiro nitrone	Isoxazolidine	69	The first enantiomerically pure synthesis of (2*S*,1′*S*)-cyclopent-2-enylglycine by boron trifluoride mediated asymmetric 1,3-dipolar cycloaddition	160
C,*N*-Diphenyl nitrone	Isoxazolidine	66	Polymer bound titanium TADDOlate results in 52% ee in the 1,3-dipolar cycloaddition with an enone	161
N-Alkenyl nitrone	Tricyclic isoxazolidine	—	*N*-Alkenyl nitrone dipolar cycloaddition routes to piperidines and indolizidines. The nitrones are intermediates in the tandem reactions involving hydroxyalmine–alkyne cyclisations	162
Cyclic chiral nitrone	Isoxazolidine	100	The cycloaddition with butenol is the first step in an improved synthesis of (+)-lentiginosine. The chiral nitrone was derived from L-tartaric acid	163
Homochiral cyclic nitrones	Various bicyclic adducts	10–48	The homochiral cyclic nitrones were derived from 1-deoxynojirimycin and underwent 1,3-dipolar cycloadditions with phenyl isocyanate, trichloroacetonitrile and methyl vinylacetate	164
3-Oxa and 3-aza nitrones	2,6-dioxa-3-azatricyclo-[5.3.1.$0^{4,10}$]-undecanes and 2-oxa-3,6-diazatricyclo-[5.3.1.$0^{4,10}$]undecanes (tricyclic isoxazolidines)	—	The nitrones undergo a spontaneous intramolecular 1,3-dipolar cycloaddition to afford the tricyclic products	165
C-Aryl *N*-phenyl nitrones	Allenyl- and propynyl-phosphonate substituted isoxazolidines	42–72	The reactions of nitrones with allenylphosphonates and propynylphosphonates	166
C,*N*-Diphenyl nitrone	5-Trifluoromethylisoxazolidines	39–99	1,1,1-Trifluoro-3-phenylsulfonyl-propene undergoes the 1,3-dipolar cycloaddition at 110 °C in a sealed tube	167
Hydroxyoximes	*N*-Unsubstituted isoxazolidines	72–92	Dibutyltin oxide acts as catalyst for nitrone formation in the nitrone–olefin cycloaddition and has led to the development of general method for *N*-unsubstituted isoxazolidine derivatives	168
C,*N*-Disubstituted nitrones	Isoxazolidines	38–88	*endo* Selective reactions of α,β-unsaturated hexacarbonyldi iron bridging acyl complexes with nitrones	169
2,3,4,5-tetrahydropyridine 1-oxide	Isoxazolidines	85–97	The cycloaddition with (*Z*)-(*R*)-vinyl sulfoxides proceeds in high yield with complete *exo* selectivity and high asymmetric induction	170
C,*N*-Diphenyl nitrone	4-Sulfonimidoyl isoxazolidines	43–67	The cycloadditions with vinyl sulfoximines proceed with poor to moderate diastereoselectivity (6–50% de)	171

analysis suggested that nitroso acetal **103** would be a viable starting material (**Scheme 39**).[174] Compound **103** is available *via* a double intramolecular cyclisation (exemplified in **Scheme 34**).



101 **102** **103**

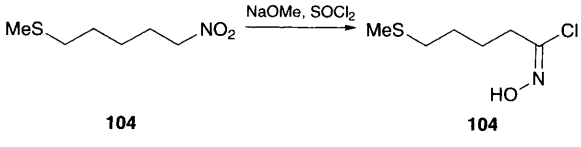
Scheme 39

Activated nitroaromatics can be converted to the corresponding fluoroaromatics using a new fluorodenitration reagent *viz N*-methylhexamethylenetetramine fluoride dihydrate (yields 75–95%).[175]

Di-*tert*-butyl 4-[2-*tert*-butoxycarbonylethyl]-4-aminoheptanedicarboxylate ('Behera's amine'), a useful precursor to several dendritic macromolecules, can be readily prepared from nitromethane in a two step procedure. The nitromethane is treated with *tert*-butyl acrylate, using Triton B as base, to give tri-*tert*-butyl nitromethanetripropanoate in 75–81% yield. The nitro group can be subsequently reduced (89–93%) with Raney nickel, at 4 atm hydrogen pressure, to give Behera's amine.[176]

A new method for the synthesis of 1,2,3-triazole 1-oxides has been developed whereby treatment of 3,4-dinitrofuroxan (3,4-dinitrofurazan 2-oxide) with a primary amine in the presence of methylamine in dichloromethane results in yields of 28–40% of the desired heterocycles.[177]

A hydroximoyl chloride **105** was obtained from the corresponding nitroalkyl methyl sulfide **104** (**Scheme 40**). The hydroximoyl chloride **105** was subsequently used for glucosinolate chemistry.[178]

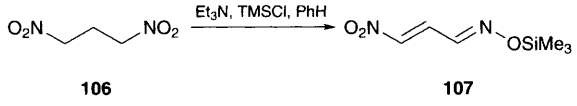


104 **104**

Scheme 40

A novel reaction between 2-aryl-1-nitro-1-alkenes and trialkylgermanium resulted in the substitution of the nitro with an alkyl group (yields 49–81%).[179]

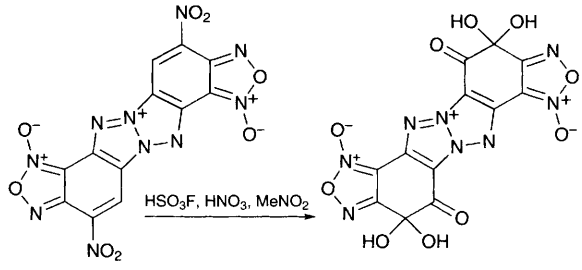
An unusual reaction of 1,3-dinitropropane **106** with trimethylsilyl chloride resulted in the formation of the aza diene **107** (**Scheme 41**).[180]



106 **107**

Scheme 41

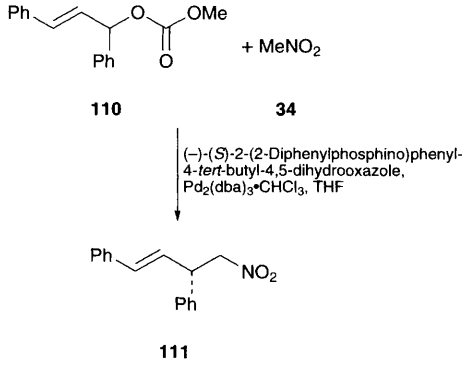
An unusual hydrolysis–oxidation occurred with a dinitro fused heterocycle **108** to give a tetrahydroxy diketone **109** (although in a poor yield, of 20%) (**Scheme 42**).[181]



108 **109**

Scheme 42

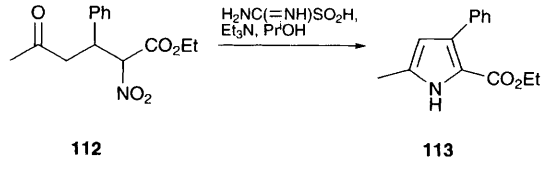
Nitromethane **34** has been used in palladium complex catalysed asymmetric allylic substitututions and has been shown to give enantioselectivities exceeding 99% ee (**Scheme 43**).[182]



110 **34** **111**

Scheme 43

When γ-nitro ketones **112** bearing an electron withdrawing group geminal to the nitro group were heated with formamidinesulfinic acid and triethylamine in propan-2-ol, pyrroles **113** can be produced in yields of 45–89% (**Scheme 44**).[183]



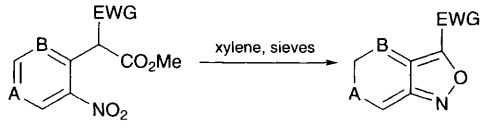
112 **113**

Scheme 44

Cine-substitution of 1-methyl-3,6,8-trinitro-2-quinolone by 1,3-dicarbonyl compounds occurs

efficiently in the presence of triethylamine, affording 4-functionalised 6,8-dinitro-2-quinolone derivatives.[184]

The thermal cyclisation of 2-nitrophenyl and 3-nitroheteroaryl ethanoate derivatives **114** in xylene is facilitated by 5 Å molecular sieves to afford an efficient general method for the construction of 3,4-fused isoxazoles **115** in yields of 31–100% (**Scheme 45**).[185]



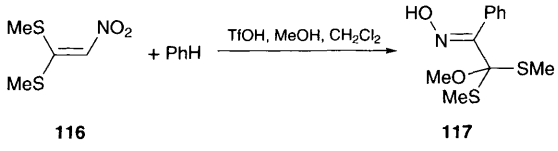
114 **115**

EWG = CO_2R, COR, CN
A = N, B = CH
A = CH, B = N
A = B = CH

Scheme 45

The *meso*-tetrakis(2,6-difluorophenyl)porphinatoiron(III) chloride–MCPBA system, a chemical model of cytochrome P450, can catalyse nitro elimination from *p*-nitrophenol to give *p*-quinone.[186]

When 1,1-bis(methylthio)-2-nitroethene **116** is treated with a trifluoromethanesulfonic acid (or $HF–SbF_5$) at low temperature it forms a stable dication with hydroxynitrilium and bis(methylthio-)carbocationic sites. The hydroxynitrilium site can be trapped *in situ* with suitable nucleophiles (aromatics, fluoride) (**Scheme 46**). Both sites are trapped when quenched with methanol or methanethiol.[187]



116 **117**

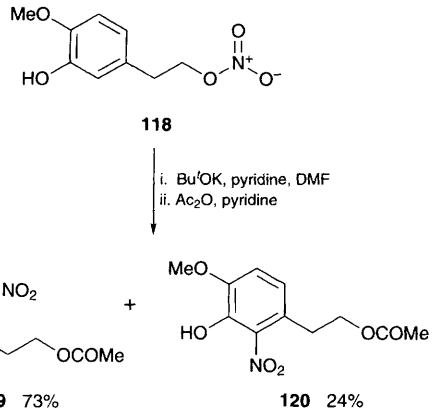
Scheme 46

A very short preparation of 3-benzoylcyclohexanone can be achieved in 70% yield using phenylnitromethane and cyclohex-2-enone in the presence of alumina, hydrogen peroxide and potassium carbonate in methanol.[188]

3-Bromo-2-nitrobenzo[*b*]thiophene can react with amines in DMF to give not only the expected *N*-substituted 3-amino-2-nitrobenzo[*b*]thiophenes but also the 2-amino-3-nitrobenzo[*b*]thiophene analogues. The 2-amino-3-nitrobenzo[*b*]thiophenes are formed in poor yields (13–25%).[189]

The reaction of primary nitroalkanes with aromatic compounds in the presence of aluminium chloride affords carbohydroximoylated aromatic compounds in yields of 25–55%.[190]

A novel phenol nitration can occur for phenols **118** bearing the 2-(nitrooxy)ethyl side chain in high yields and good regioselectivity (**Scheme 47**).[191]

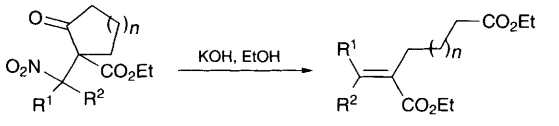


118

119 73% **120** 24%

Scheme 47

Base promoted fragmentations of the products **121** arising from $S_{RN}1$ reactions between *gem*-halonitro alkanes and cyclopentanone β-esters results in the production of di- or tri-functionalised olefins **122**. The olefins are formed in high yields from the fragmentations (69–100%) (**Scheme 48**).[192]

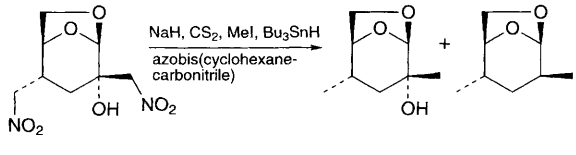


121 **122**

n = 1, 2, 3
R^1, R^2 = -$(CH_2)_{3-}$, H, OMOM, OTHP

Scheme 48

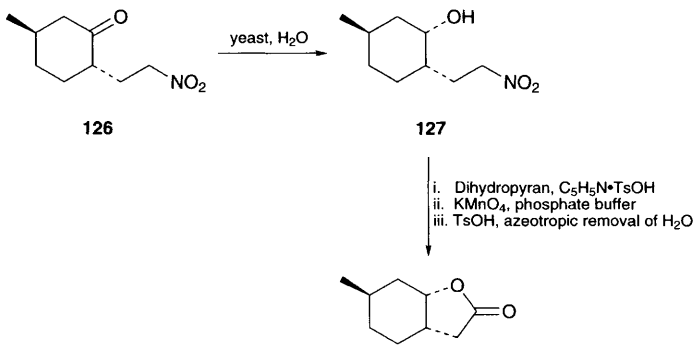
(−)-δ-Multistriatin was synthesised in a six-step procedure where one of the key steps was the radical removal of two nitro groups using tributyltin hydride. The stereochemistry of the α-carbon atoms in the products **124** and **125** was preserved (**Scheme 49**).[193]



123 **124** **125**

Scheme 49

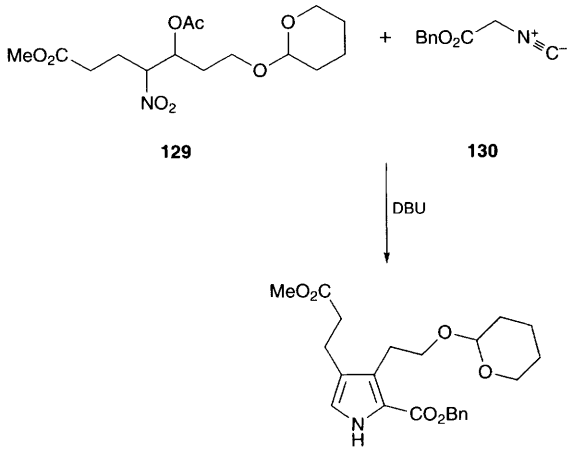
Optically active 2-nitroethylated alcohols **127** can be readily transformed into γ-lactones **128**. The alcohols themselves were obtained in optically active form by a reduction with a yeast of the corresponding 2-nitroethylated cyclohexanones **126** (**Scheme 50**).[194]



126 **127** **128**

Scheme 50

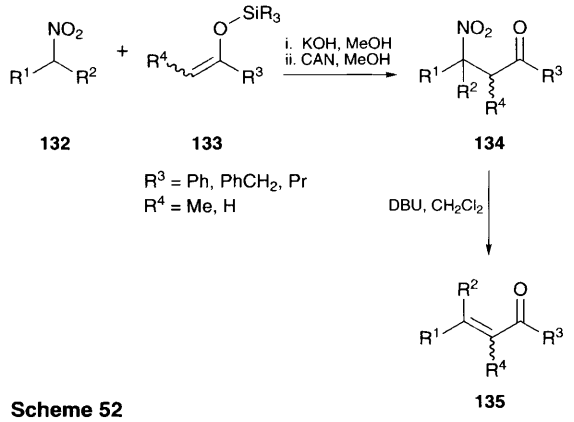
2-Carboxy-3,4-substituted pyrroles **131** can be synthesised by the condensation of α-acetoxy nitro compound **129** with benzyl isocyanate **130** using DBU in 63% yield (**Scheme 51**).[195]



129 **130** **131**

Scheme 51

α-Nitroalkyl radicals can be generated by the oxidation of nitronate anions with cerium(IV) ammonium nitrate. Intermolecular addition of these radicals to silyl enol ethers **133** produces β-nitro ketones **134** which are themselves converted into α,β-unsaturated ketones **135** in good yields (**Scheme 52**).[196]



132 **133** **134** **135**

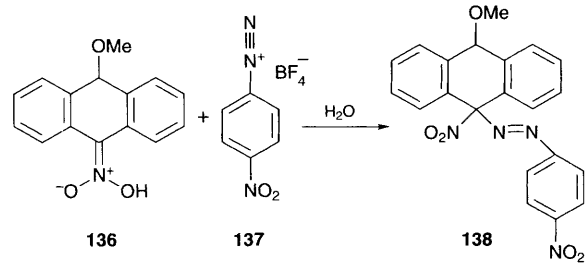
Scheme 52

A one-pot synthesis of 2-alkyltetrahydropyran-3-ones has been developed using the reaction of 4-nitro-2,3-dihydro-1*H*-pyran with primary aliphatic and benzylic Grignard reagents under suitable hydrolysis conditions (yields of 19% to 100%).[197]

A novel synthesis of 1-pyrroline derivatives from γ-nitrocarbonyl compounds using ruthenium complex catalysed reductive *N*-heterocyclisation provides the 1-pyrrolines in good yields (78–91%). High temperatures (140 °C) and elevated pressures (38.7 atm) are required.[198]

A convenient one-pot two-step procedure for the conversion of nitroolefins to the corresponding 1,2-diamines has been established using a Michael addition of *O*-ethylhydroxylamine to the nitroolefin followed by a hydrogenation. The diamines are prepared in 48–90% yield.[199]

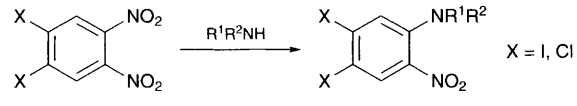
The reaction of 4-nitrophenyldiazonium tetrafluoroborates **137** with the anthracen-9-ylidenazinic acid **136** results in the formation of 9-nitro-9-diazo compounds **138** in good yield (70–75%) (**Scheme 53**).[200]



136 **137** **138**

Scheme 53

Primary and secondary amines can be treated with 1,2-dihalo-4,5-dinitrobenzene **139** under mild conditions (over several days) to give amino derivatives **140** *via* S_NAr in 76–95% yields. Halo functionalities in the substrate are unaffected and can then be used for further elaborations of the ring (**Scheme 54**).[201]



139 **140**

Scheme 54

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