

CHAPTER 14

Addition Reactions: Cycloaddition

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Density functional theory and MC-SCF calculations have been applied to competing concerted and stepwise mechanisms of cycloaddition reactions.¹

Diphenylketene undergoes 2 + 2- or 2 + 4-cycloaddition reactions with various 1,3-diazabuta-1,3-dienes.² The 2 + 4-, 4 + 2-, 6 + 4- and 8 + 2-cycloaddition reactions of heptafulvenes have been reviewed.³

The acceleration effect on 4 + 2-, 3 + 2- and 2 + 2-cycloadditions in the presence of aluminium, gallium and boron halides is due to the increase of π -acceptor properties of the dienophiles.⁴

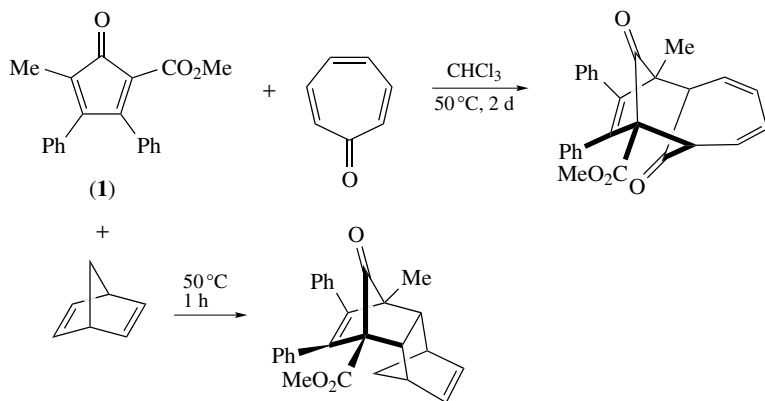
2-Methoxycarbonyl-5-methyl-3,4-diphenylcyclopentadienone (**1**) undergoes 4 + 2- and 4 + 6-cycloadditions with a variety of dienophiles (Scheme 1).⁵

The reaction of 1,4-diphenylbuta-1,3-diene (**2**) with trithiazyl trichloride (**3**) yields a bi(thiadiazole) (**4**), an isothiazoloisothiazole (**5**), a dithiazolothiazine (**6**), and two thiazinodithiazepines (**7**) and (**8**) by 1,2-, 1,3-, and 1,4-cycloaddition reactions (Scheme 2).⁶

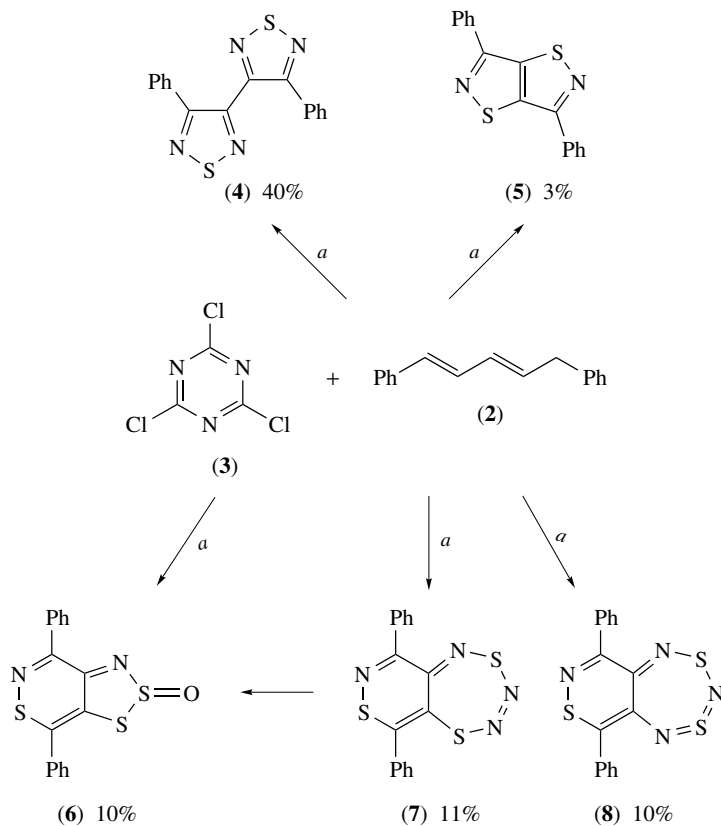
The bridged-mode (β -tether) tandem inter-[4 + 2]/intra-[3 + 2] cycloaddition of (*E*)-2-methyl-2-nitrostyrene (**9**) with 1-butoxypenta-1,4-diene (**10**) produces stable tricyclic nitroso acetals (**11**) which afford, after reduction and protection, highly functionalized aminocyclopentanedimethanol triacetates (**12**) (Scheme 3).^{7,8}

2 + 2-Cycloaddition

The mechanisms of regioselective and stereoselective 2 + 2-photocycloadditions have been extensively reviewed.⁹ The intramolecular 2 + 2-photocycloaddition of 2-allyl-2-(1*H*)-naphthalenone (**13**) on the surface of silica produces all four cycloadducts (**14**)–(**17**) (Scheme 4).¹⁰ Molecular mechanics have been used to study the regio- and stereo-selectivity of the 2 + 2-photocycloadditions in complexes containing crown ether styryl dyes and alkaline earth metal cations.¹¹

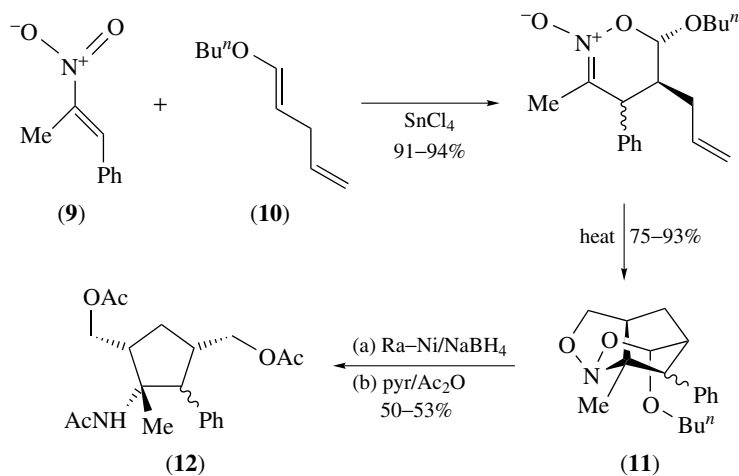


SCHEME 1

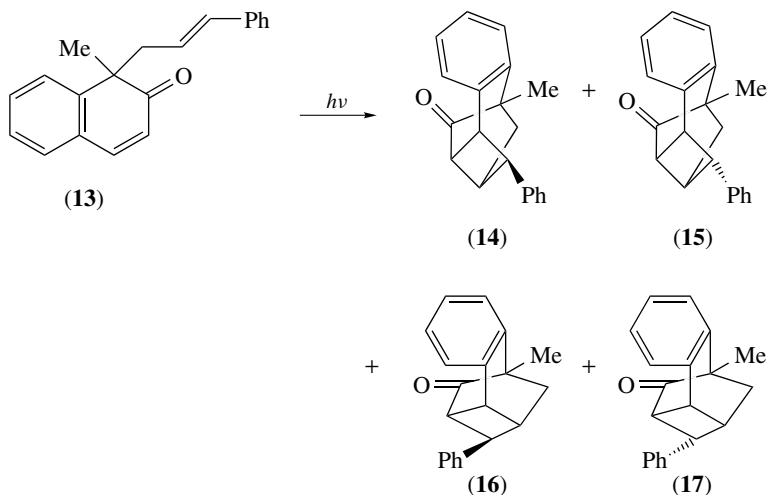


a: toluene, reflux, 1 h

SCHEME 2



SCHEME 3

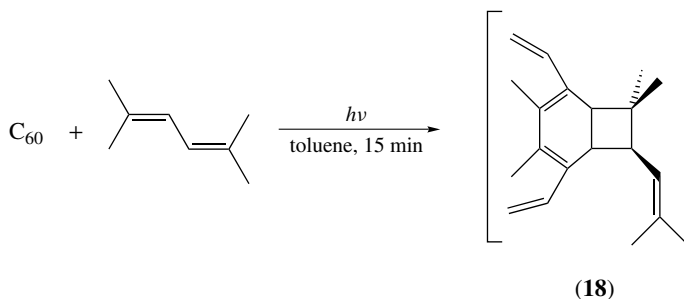


SCHEME 4

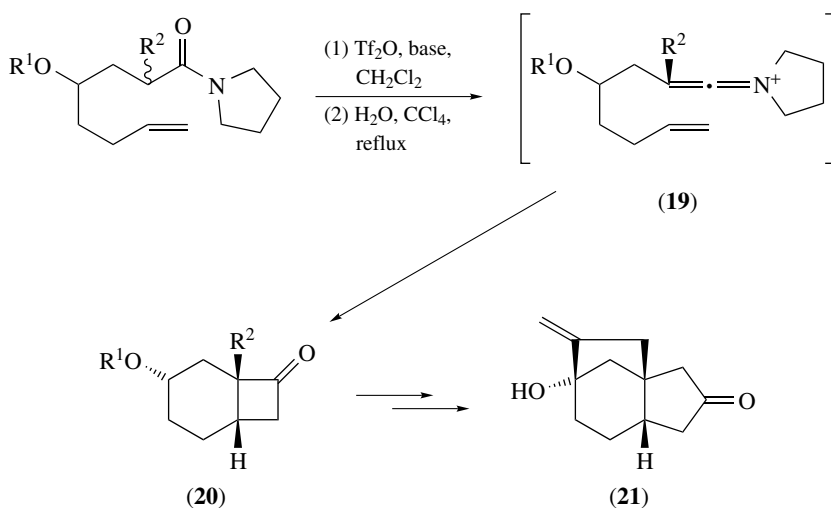
A study of the stereochemistry and secondary isotope effects for the 2 + 2-cycloaddition of alkyl-substituted buta-1,3-dienes with C_{60} indicates the formation of an open biradical intermediate in the rate-determining step leading to the cycloadduct (**18**) (Scheme 5).¹² The addition of benzyne to C_{70} produces four isomeric monoadducts. One of these adducts is the first example of an adduct of a 5–6 ring fusion where the ring-fusion bond remains intact.¹³

A review of the mechanism of thermal 2 + 2-cycloadditions of activated alkenes to allenes and ketenes has been published.¹⁴ Stereoselective intramolecular 2 + 2-cycloadditions of alkene–keteniminium salts (**19**) derived from L-glutamic salts yield

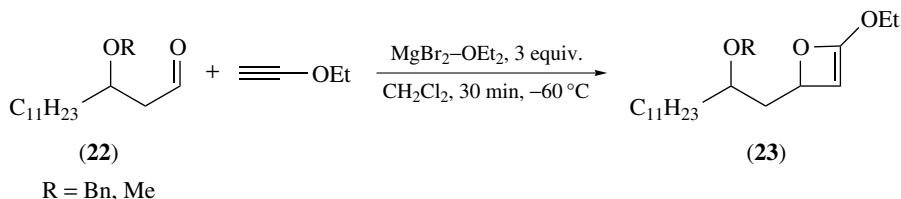
optically active bicyclo[4.2.0]octan-7-ones (**20**) which can be converted into (+)-gibberellic acid intermediates (**21**) (Scheme 6).¹⁵ *Ab initio* calculations predict that the thermal 2 + 2-cycloaddition reactions between C_{2v} -symmetric ketenes and enantiopure aldehydes proceed with high stereocontrol.¹⁶ The influence of photoinduced electron-transfer steps in the regio- and diastereo-specificity of Paterno–Büchi reaction with 2,3-dihydrofuran in polar solvents has been demonstrated.¹⁷ The reaction of ethoxyacetylene with alkoxyaldehydes (**22**) in the presence of $MgBr_2 \cdot Et_2O$ yields 4-ethoxy-2*H*-oxetes (**23**), thus providing experimental evidence for a 2 + 2-cycloaddition mechanism (Scheme 7).¹⁸ The asymmetric 2 + 2-cycloaddition of silylketenes and aldehydes, in the presence of Ti–TADDOL catalysts, proceeds with good reactivity and moderate enantioselectivity.¹⁹ *Ab initio* and MNDO-PM3 treatment of the Wittig reaction of ylides with acetaldehyde indicate that the oxaphosphetane formation is a very asynchronous cycloaddition.²⁰



SCHEME 5



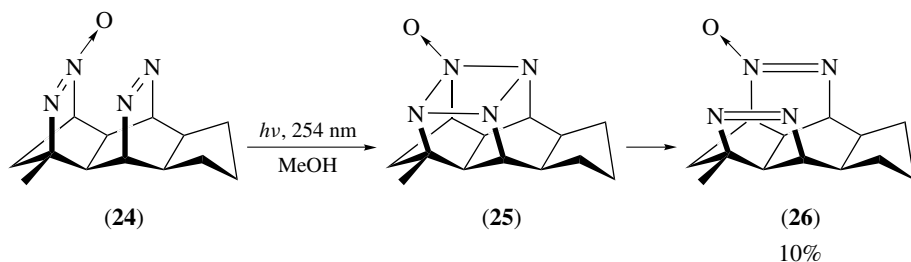
SCHEME 6



SCHEME 7

A very remote secondary H/D isotope effect has been measured for the 2 + 2-cycloaddition of TCNE to 2,7-dimethylocta-2,*trans*-4,6-triene.²¹ The reaction of nitric oxide with *N*-benzylidene-4-methoxyaniline to produce 4-methoxybenzenediazonium nitrate and benzaldehyde is thought to proceed via a 2 + 2-cycloaddition between nitric oxide and the imine double bond.²² A novel mechanism for the stepwise dimerization of the parent silaethylene to 1,3-disilacyclobutane involves a low-barrier [1,2]-sigmatropic shift.²³ Density functional, correlated *ab initio* calculations, and frontier MO analysis support a concerted 2 + 2-pathway for the addition of SO₃ to alkenes.²⁴ The enone cycloaddition reactions of dienones and quinones have been reviewed.²⁵ The 2 + 2-photocycloadditions of homochiral 2(*5H*)-furanones to vinylene carbonate are highly diastereoisomeric.²⁶

Monochromatic π , π^* excitation of the proximate (24) yielded the metathesis isomer (26) with retention of optical purity thus providing support for the $\pi 2 + \pi 2$ -photocycloaddition pathway involving a tetrazetidine oxide intermediate (25) (Scheme 8).²⁷

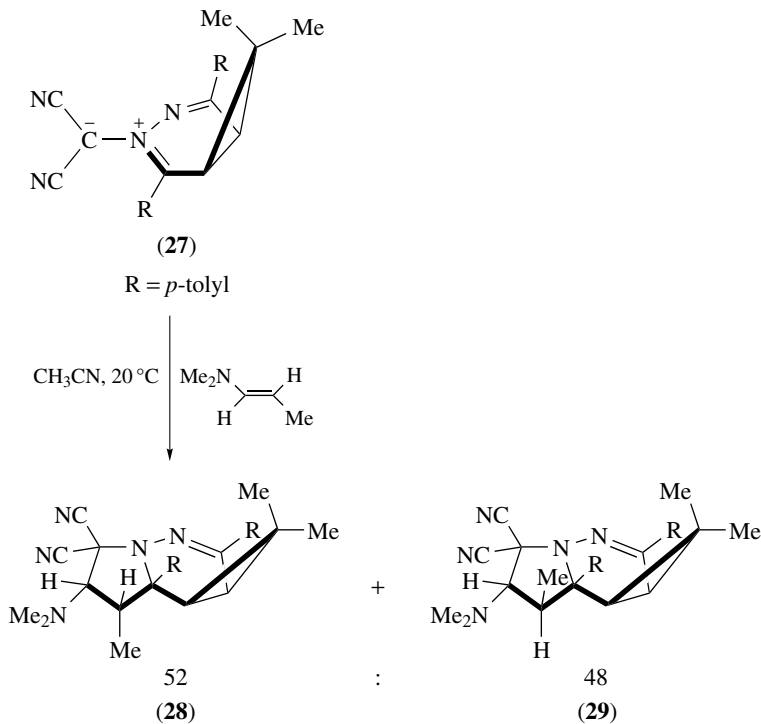


SCHEME 8

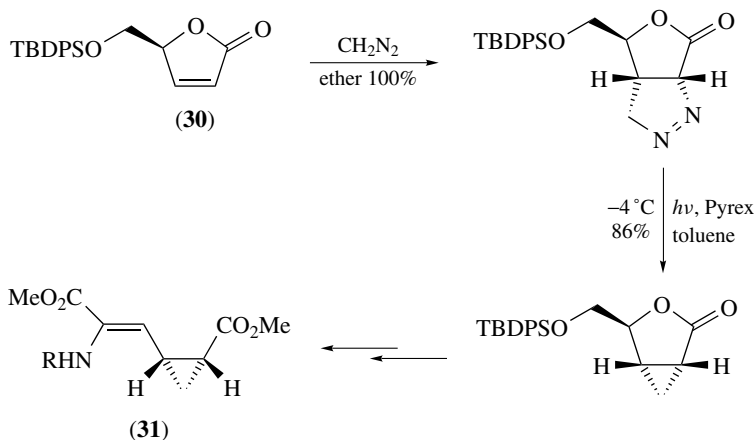
2 + 3-Cycloaddition

The 3 + 2-cycloaddition of 1,2-dithiophthalides with nitrilimines yields benzo[*c*]thiophenespirothiadiazoles regioselectively.²⁸ The azomethineimines isoquinolinium-*N*-aryllimide and *N*-(2-pyridyl)imide readily undergo 1,3-dipolar cycloaddition with electron-deficient dipolarophiles, dimethyl fumarate and dimethyl maleate, to yield tetrahydropyrazolo[5,1-*a*]isoquinolines in high yield.^{29,30} The 1,3-dipolar cycloadditions of electron-poor 1,3-dipoles, bicyclic azomethine ylides (27), with (*E*)-1-*N,N*-dimethylaminopropene to yield cycloadducts (28) and (29) are examples of non-stereospecific cycloadditions (Scheme 9).³¹ The synthesis of protected

2,3-didehydro-4,5-methano amino acids (**31**) involves the π -diastereoselective 1,3-dipolar cycloaddition of diazomethane with chiral furanones (**30**) derived from D-glyceraldehyde acetonide as the only chiral precursor (Scheme 10).³²

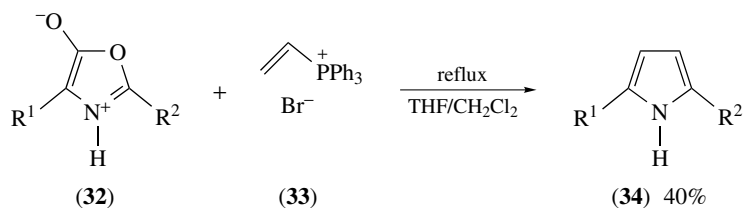


SCHEME 9



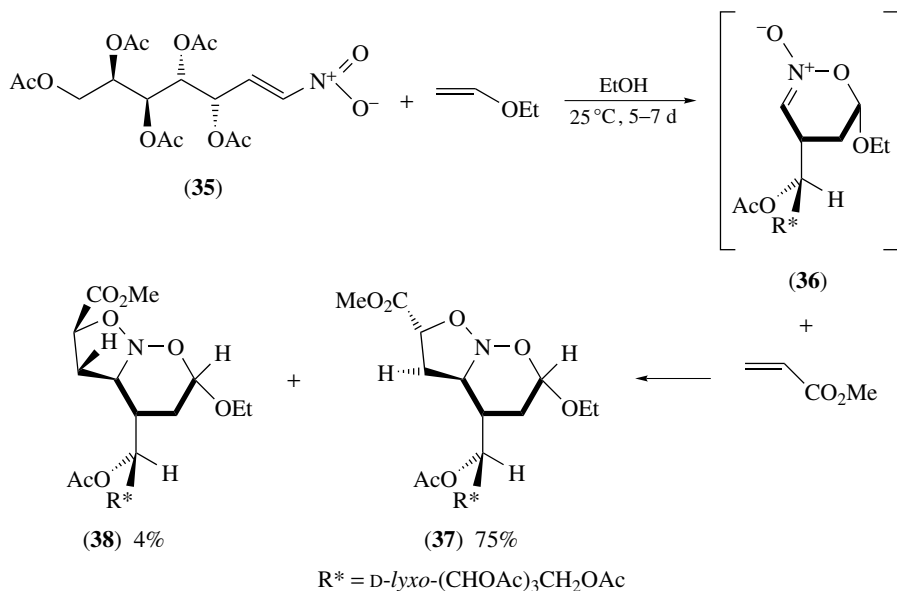
SCHEME 10

The reaction of 5(4*H*)-oxazolones (**32**) and münchnones with triphenylvinylphosphonium bromide (**33**) provides a mild synthesis of substituted pyrroles (**34**) (Scheme 11).³³ The cycloaddition–elimination reactions of 5-imino-1,2,4-thiadiazolidin-3-ones with enamines and ester enolates produce 2-iminothiazolidines.³⁴ Chiral isomünchnone dipoles show π -facial diastereoselectivity with *N*-phenyl- or *N*-methyl-maleimide in refluxing benzene.³⁵



R ¹	R ²
Ph	Ph
4-ClPh	Ph
Ph	4-ClPh
4-MePh	Ph
Ph	4-MePh
Ph	<i>i</i> -Pr
<i>i</i> -Pr	Ph

SCHEME 11

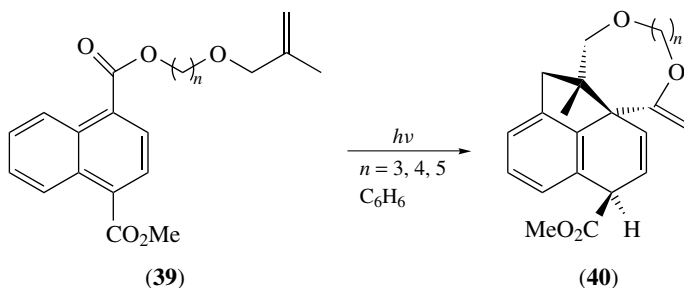


SCHEME 12

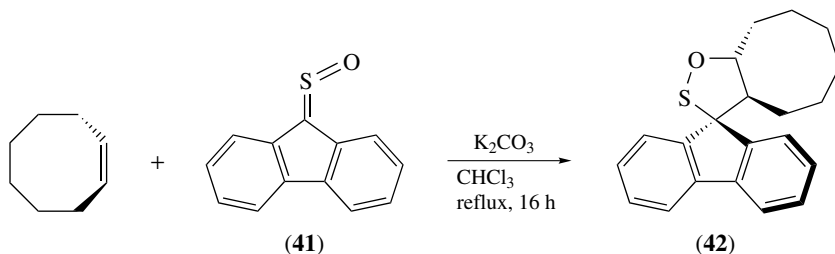
The asymmetric tandem cycloaddition of the chiral carbohydrate nitroalkene (**35**) with ethyl vinyl ether involves the initial formation of the nitronate (**36**) which reacts exclusively with electron-withdrawing alkenes by 3 + 2-cycloaddition to yield chiral bicycles (**37**) and (**38**) (Scheme 12).³⁶

Intramolecular 3 + 2-photocycloadditions of alkenyl methyl 1,4-naphthalenedicarboxylates (**39**) yield 3 + 2-cycloadducts (**40**) having 9–11-membered ring systems in addition to the characteristic five-membered ring structure (Scheme 13).³⁷

The 1,3-dipolar cycloaddition of fluorenethione *S*-oxide (**41**) and *trans*-octene yields the corresponding sultine (**42**) which readily converts olefins to episulfides (Scheme 14).³⁸

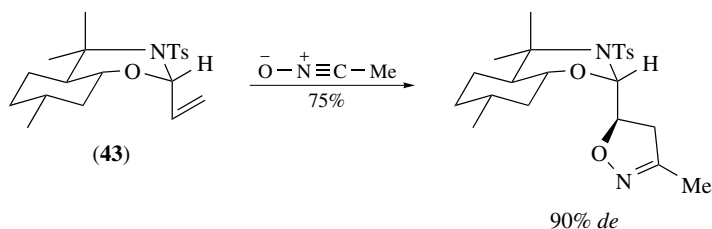


SCHEME 13



SCHEME 14

A study of the regioselectivity of the 1,3-dipolar cycloaddition of aliphatic nitrile oxides with cinnamic acid esters has been published.³⁹ AM1 MO studies on the gas-phase 1,3-dipolar cycloaddition of 1,2,4-triazepine and formonitrile oxide show that the mechanism leading to the most stable adduct is concerted.⁴⁰ An *ab initio* study of the regiochemistry of 1,3-dipolar cycloadditions of diazomethane and formonitrile oxide with ethene, propene, and methyl vinyl ether has been presented.⁴¹ The 1,3-dipolar cycloaddition of mesitronitrile oxide with 4,7-phenanthroline yields both mono- and bis-adducts.⁴² Alkynyl(phenyl)iodonium triflates undergo 2 + 3-cycloaddition with ethyl diazoacetate, *N*-*t*-butyl- α -phenyl nitron and *t*-butyl nitrile oxide to produce substituted pyrroles, dihydroisoxazoles, and isoxazoles respectively.⁴³ 2 β -Vinyl-*trans*-octahydro-1,3-benzoxazine (**43**) undergoes 1,3-dipolar cycloaddition with nitrile oxides with high diastereoselectivity (90% *de*) (Scheme 15).⁴⁴

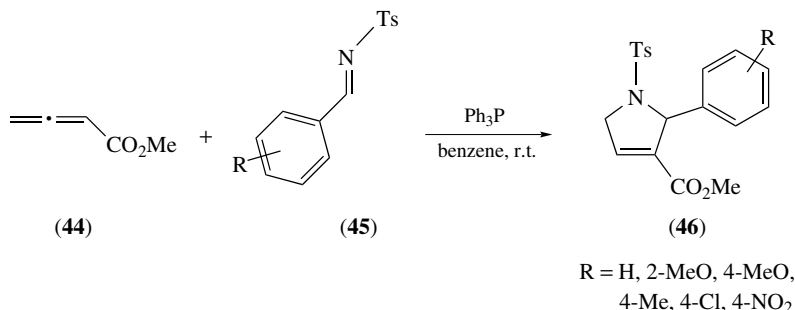


SCHEME 15

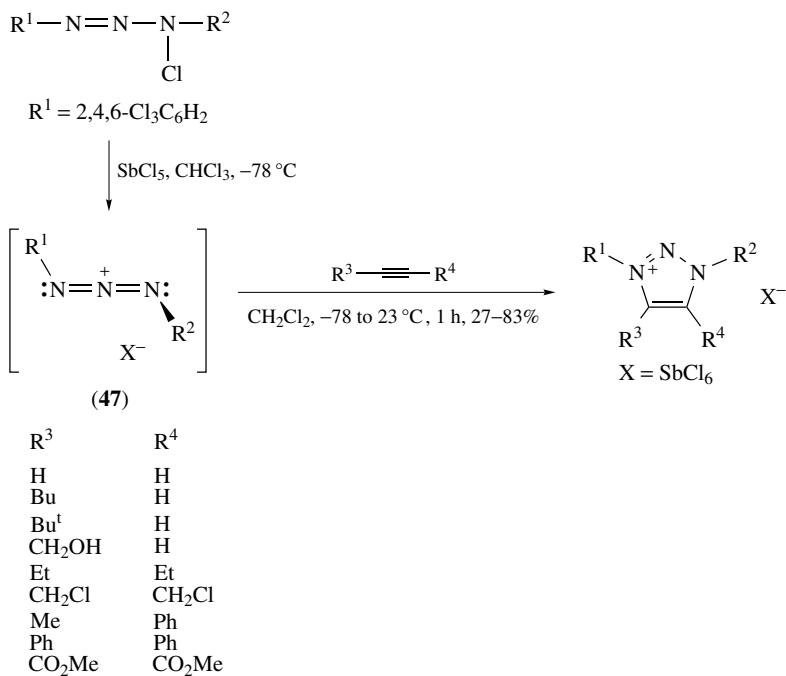
The 1,3-dipolar cycloadditions of benzonitrile oxides with tertiary cinnamides yield the 5-phenyl and 4-phenyl regioisomers in a reversal of the expected regioselectivities shown with methyl cinnamate. Calculations have shown that steric factors are responsible for this reversal of regioselectivity.⁴⁵ The 1,3-dipolar cycloadditions of benzonitrile oxide with electron-rich and electron-poor dipolarophiles are accelerated by sodium dodecyl sulfate micelles.⁴⁶ Phenyl nitrile ylides react with electron-deficient alkenes to produce five-membered *N*-heterocycles where measured rate constants are between 4×10^5 and $7 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$.⁴⁷

The reaction of buta-2,3-dienoates (**44**) with electron-deficient imines (**45**) in the presence of triphenylphosphene yields 3 + 2-cycloadducts (**46**) in excellent yields and high chemoselectivity (Scheme 16).⁴⁸ The 1,3-diaza-2-azoniaallene salts (**47**) react with alkynes, *N,N'*-dialkylcarbodiimides, and *N,N'*-dialkylcyanamides to produce 1,2,3-triazolium salts, 1,3,4,5-tetrasubstituted 4,5-dihydrotriazolium salts, and 1,3,5-trisubstituted tetrazolium salts, respectively (Scheme 17).⁴⁹

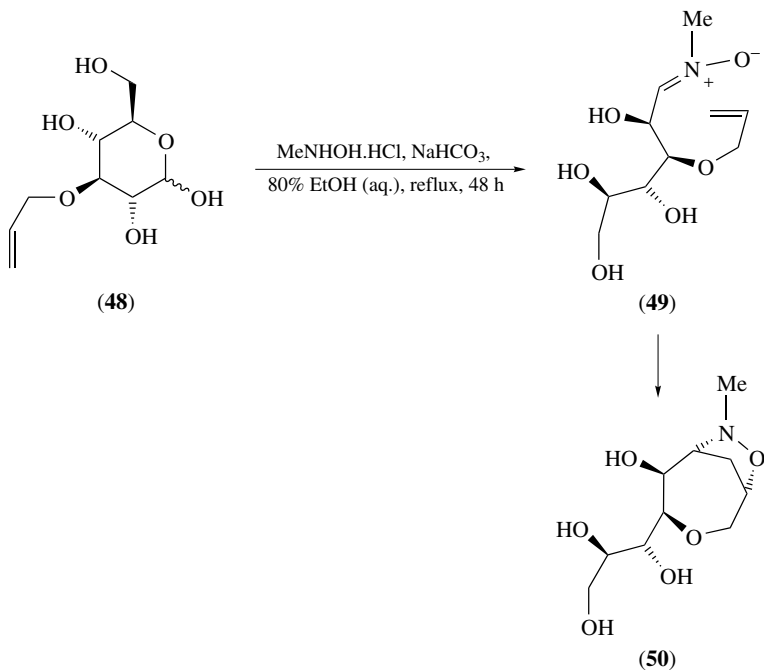
For the first time, DFT theory has been applied to a study of diastereofacial selectivity in 1,3-dipolar cycloadditions of nitrones to *cis*-3,4-dimethylcyclobutene.⁵⁰ The stereochemical outcome of the INAC reactions of nitrones (**49**) and (**52**) derived from 3-*O*-allyl-D-hexoses is dependent only on the relative configuration at C(2,3), and thus 3-*O*-allyl-D-glucose (**48**) and -D-altrose (*threo* configuration) afford oxepanes (**50**) selectively whereas 3-*O*-allyl-D-allose (**51**) and -D-mannose (*erythro* configuration) give tetrahydrofurans (**53**) and (**54**) selectively (Scheme 18).⁵¹ *trans*-2-Methylene-1,3-dithiolane-1,3-dioxide (**55**) reacts regioselectively with acyclic and cyclic nitrones (**56**) to produce 4,4- (**57**) rather than 5,5-disubstituted isoxazolidines (Scheme 19).⁵²

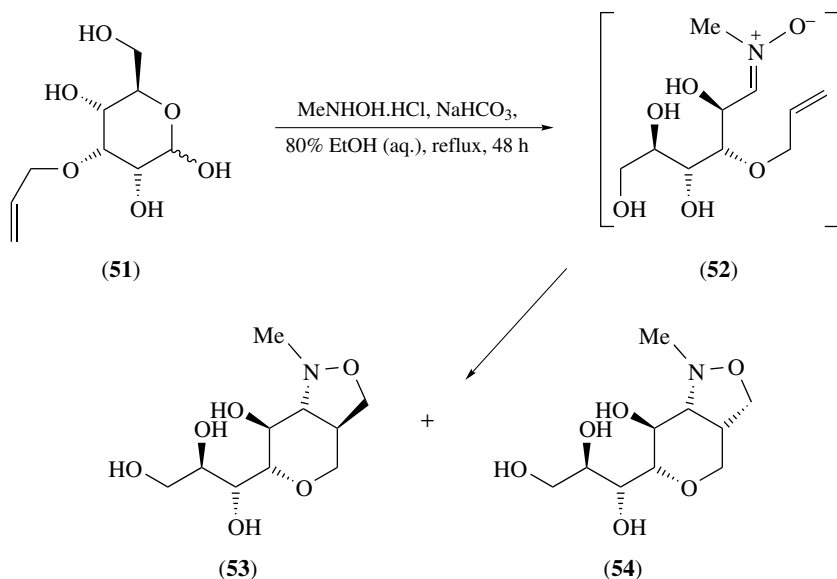


SCHEME 16

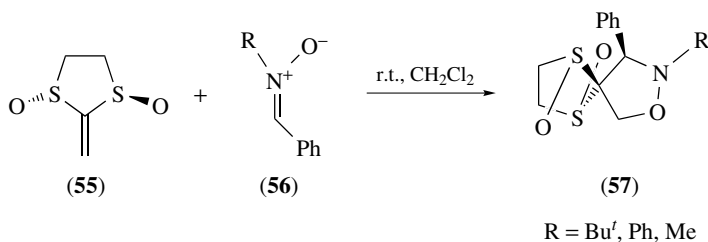


SCHEME 17





SCHEME 18



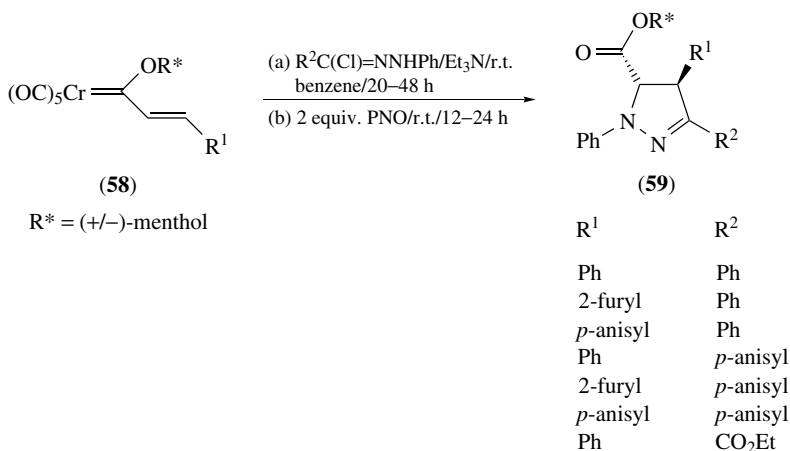
SCHEME 19

α -Phenyl-*N*-butyl nitronium ion undergoes 1,3-dipolar cycloadditions with dibromo- and dichloro-malononitrile, chlorotricyanomethane, tetracyanomethane, trichloroacetone, and carbamoylchlorodicyanomethane to yield 2-butyl-3-phenyl-5-*R*-2,3-dihydro-1,2,4-oxadiazoles.⁵³ The stereochemical outcome of the 1,3-dipolar cycloaddition of formaldehyde *N*-benzyl nitronium ion with β' -alkoxy- and γ -alkoxy- α,β -unsaturated esters was explained by application of the 'inside alkoxy' theory emphasizing the electrostatic interactions in the transition state.⁵⁴ Cyclic nitronium ions react with γ -bromo α,β -unsaturated esters and lactones to yield isoxazolines with major isomer showing *endo* regiochemistry.⁵⁵ Cyanomethylenecyclopropane is more reactive than ethoxycarbonylmethylenecyclopropane in 2 + 3-cycloaddition reactions with 5,5-dimethylpyrrolidine *N*-oxide.⁵⁶

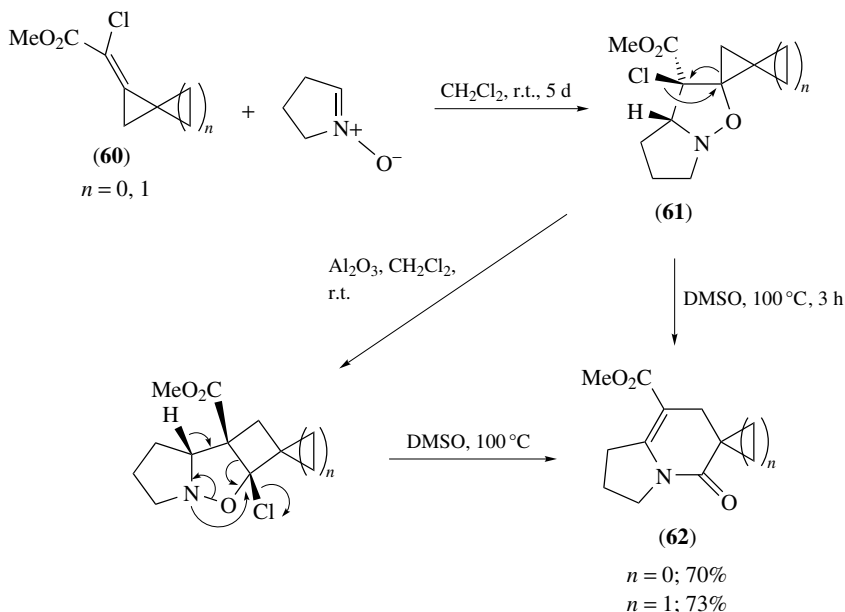
A kinetic study of the 1,3-dipolar cycloadditions of alkynyl Fischer carbene complexes with nitronium ions showed first-order kinetics for both nitronium ions and the alkynyl carbene complexes.⁵⁷ The 1,3-dipolar cycloaddition of chiral non-racemic Fischer

carbene complexes (**58**) with nitrilimines yield Δ^2 -pyrazolines (**59**) with high regio- and diastereo-selectivity (Scheme 20).⁵⁸

The 3 + 2-cycloaddition of pyrroline *N*-oxide to 2-chloro-2-cyclopropylidene acetate and its spirocyclopentane analogues (**60**) yields spiro[cyclopropane-1,5'-isoxazolidine]s (**61**) which undergo a novel cascade ring enlargement to yield indolizinones (**62**) in high yield (Scheme 21).⁵⁹



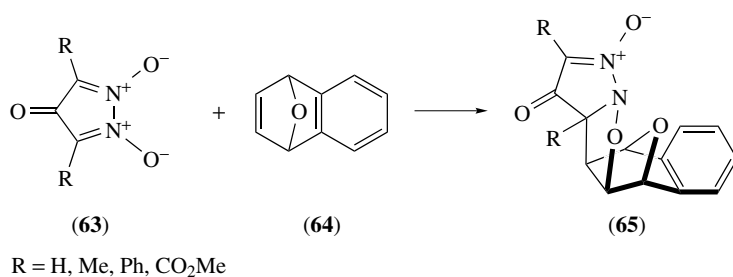
SCHEME 20



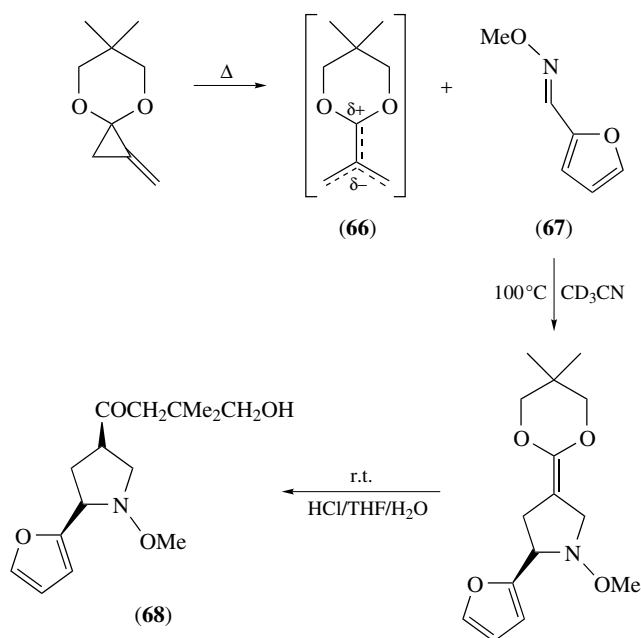
SCHEME 21

Camphor-derived oxazoline *N*-oxides react with α,β -unsaturated esters or nitroalkenes to produce cycloadducts which exhibit high regio- and stereo-selectivities.⁶⁰ The 3 + 2-cycloaddition of pyrazolone *N,N*-dioxide (**63**) with epoxynaphthalene (**64**) yields only the *endo*-cycloadduct (**65**) as a result of interaction between the epoxide oxygen and the N–O group in the dioxide (Scheme 22).⁶¹ The thermal isomerization of 1,3-dipolar cycloadducts of 3,4-dihydro- β -carboline 2-oxide has been investigated using ¹H NMR spectroscopy.⁶² The 1,3-dipolar cycloaddition of iminodifluoromethanes with carbonyl compounds produces oxazolidine derivatives.⁶³

An *ab initio* computational study of the 3 + 2-cycloaddition of allyl-, 2-borylallyl-, and 2-azaallyl-lithium to ethylene favours the two-step pathway over the $4\pi_s + 2\pi_s$



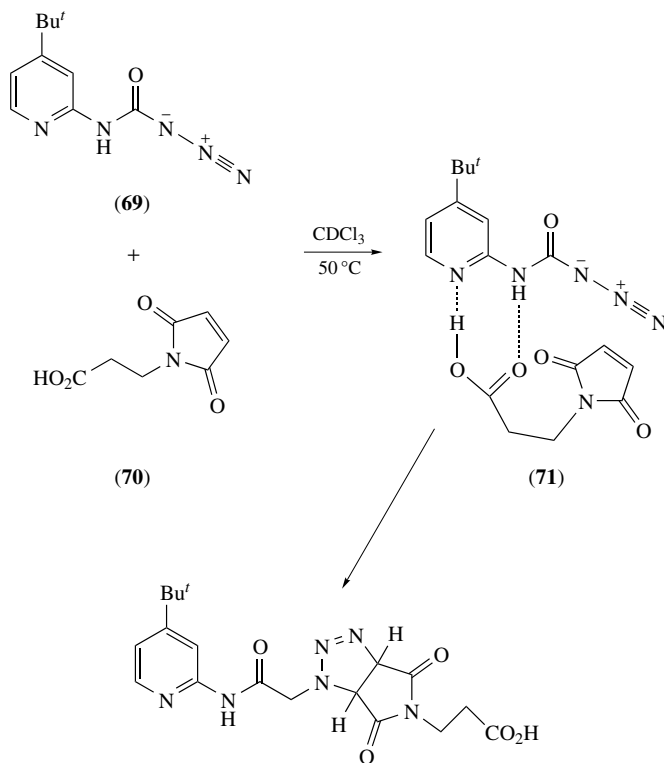
SCHEME 22



SCHEME 23

mechanism.⁶⁴ 3-(Alkylthio)-2-siloxyallyl cationic species undergoes regio- and stereoselective 3 + 2-cycloaddition with various alkenes to produce cyclopentanones in good yields.⁶⁵ The thermal 3 + 2-cycloaddition of dipolar trimethylenemethane (**66**) to *anti*-*O*-alkyl oximes (**67**) provides a synthetic route to substituted pyrrolidines (**68**) and prolines (Scheme 23).⁶⁶

PM3 calculations of the 2 + 3-cycloaddition of *t*-butylphosphaacetylene with 2,4,6-triazidopyridine are consistent with the dipole-LUMO-controlled reaction type.⁶⁷ An FTIR spectroscopic study of the 1,3-dipolar cycloaddition of aryl azides with acetylenes shows that the rate of reaction increases logarithmically with pressure (below 1 GPa).⁶⁸ The 3 + 2-cycloaddition between an azide (**69**) and a maleimide (**70**) has been greatly accelerated by utilizing molecular recognition between an amidopyridine and a carboxylic acid [see (**71**)] (Scheme 24).^{69,70}



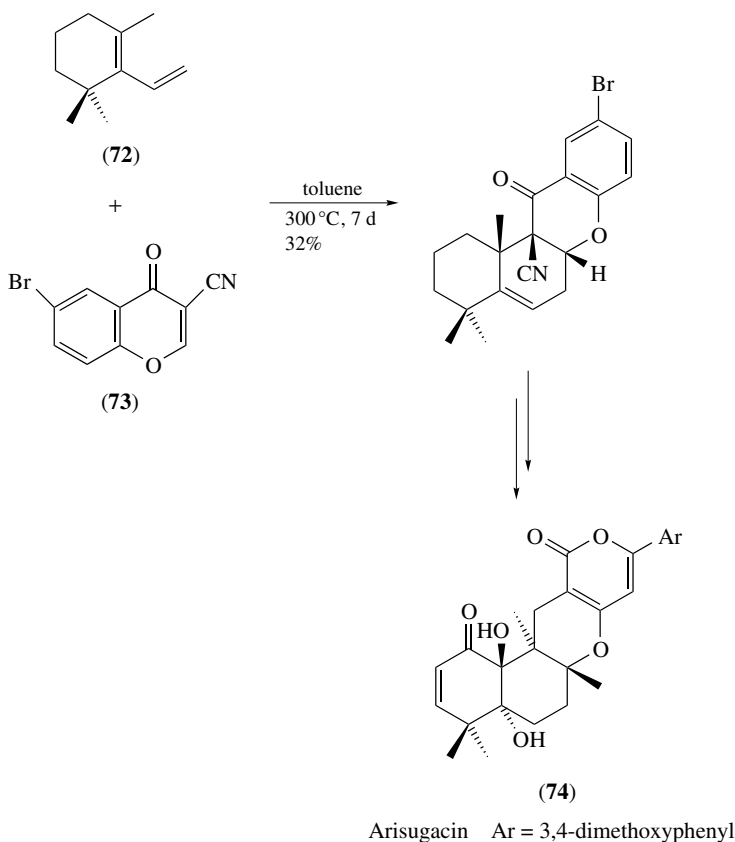
SCHEME 24

2 + 4-Cycloaddition

A modern valence-bond description of the Diels–Alder reaction has been presented.⁷¹ The method of reaction classification by similarity has been expanded to include the effect of steric congestion in the classification of cycloaddition reactions.⁷²

The retro-Diels–Alder reaction has been extensively reviewed (1387 references).⁷³ AM1 MO and density functional theory have been applied to Diels–Alder and retro-Diels–Alder reactions involving heterocyclic compounds as the diene or the dienophile.⁷⁴

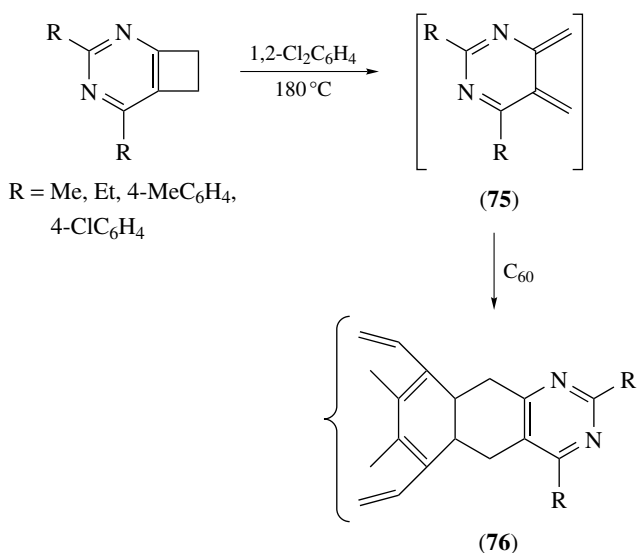
The *ab initio* method at the 3–21G level has been used to investigate the Diels–Alder reaction mechanism of cyclohexa-1,3-diene with propenenitrile.⁷⁵ The *ab initio* UHF/6–31G* method was used to study the 4 + 2-cycloaddition of cyclohexa-1,3-diene with propylene.⁷⁶ Second-order rate constants determined for the Diels–Alder reaction of dienes with *N*-substituted maleimides in different solvents indicate that hydrophobic groups near the reaction centre lose their hydrophobic character completely in the activated complex of the Diels–Alder reaction, whereas more distant groups retain their non-polar character throughout the reaction.⁷⁷ The Diels–Alder addition of push-pull alkenes, dicyanovinyl acrylates with cyclic dienes proceeds with significant stereoselectivity.⁷⁸ The 4 + 2-cycloaddition of 3-cyanochromone derivatives (**73**) with electron-rich dienes (**72**) is highly stereoselective and shows potential for the construction of the ABC tricyclic frame of arisugacin (**74**), a selective inhibitor of acetylcholinesterase (Scheme 25).⁷⁹



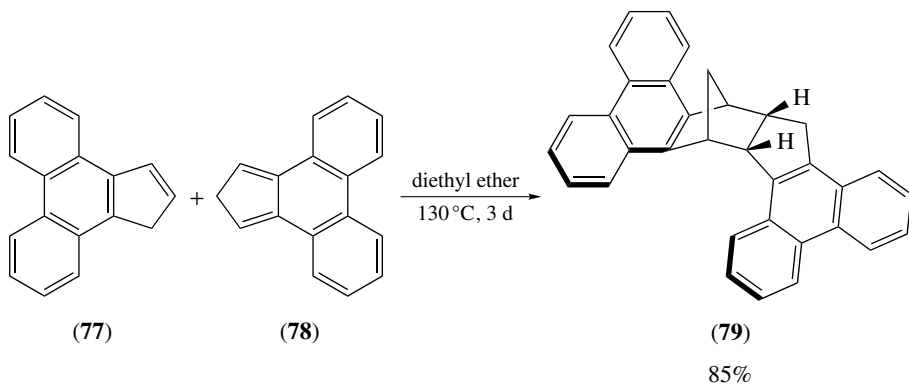
SCHEME 25

A review of Diels–Alder reactions of fullerenes with acyclic and cyclic dienes has been presented.⁸⁰ The addition of substituted pyrimidine *o*-quinodimethanes (**75**) to [60]fullerenes yields novel organofullerenes (**76**) bearing a pyrimidine nucleus covalently attached to the C₆₀ cage (Scheme 26).⁸¹ The Diels–Alder dimerization of cyclopenta[*l*]phenanthrene (**77**) with isobenzindene (**78**) yields the dimer (**79**) in 85% yield (Scheme 27).⁸² Further evidence has been supplied to support an early reorganization of the π -network in the dimerization of 2-methoxycarbonylbuta-1,3-diene.⁸³

The Lewis acid-catalysed Diels–Alder reactions of acrylate derivatives of new carbohydrate-based chiral auxiliaries with cyclohexadiene show excellent *endo:exo*



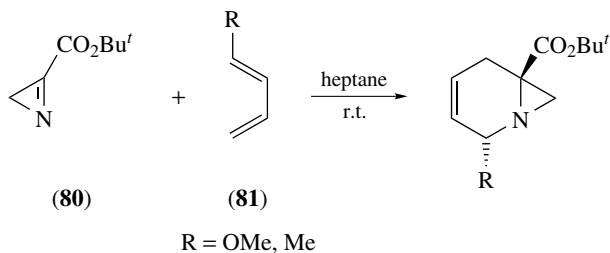
SCHEME 26



SCHEME 27

ratios but only moderate π -facial selectivities.⁸⁴ The 4 + 2-cycloaddition of 2-*N*-(acetylamino)-1-thia-1,3-dienes containing chiral auxiliaries react with dipolarophiles to produce thiopyrans of high optical purity.⁸⁵ Alkyl 1-*N*-benzoyl-2-oxoimidazolidin-4-carboxylates are powerful chiral auxiliaries in the Diels–Alder reactions of their 3-*N*-enoyl derivatives.⁸⁶

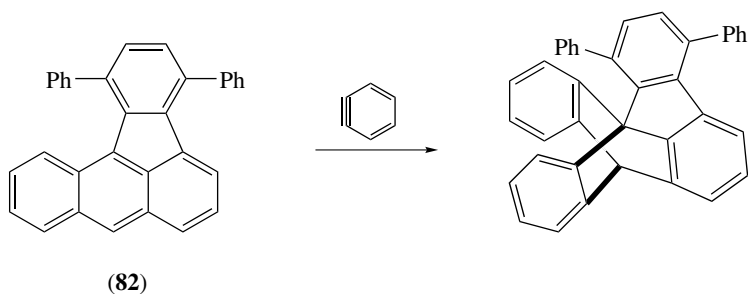
Ab initio calculations on aza-Diels–Alder reactions of electron-deficient imines with buta-1,3-diene show that these reactions are HOMO (diene)–LUMO(dienophile)-controlled and that electron-deficient imines should be more reactive than alkyl- or aryl-imines.⁸⁷ The Diels–Alder reaction of *t*-butyl 2*H*-azirine-3-carboxylate (**80**) proceeds with high diastereoselectivity with electron-rich dienes (**81**) (Scheme 28).⁸⁸ The hetero-Diels–Alder additions of imines with sterically demanding dienes yield perhydroquinolines bearing an angular methyl group.⁸⁹ The asymmetric hetero-Diels–Alder reaction between alkenyloxazolines and isocyanates produces diastereometrically pure oxazolo[3,2-*c*]pyrimidines.⁹⁰



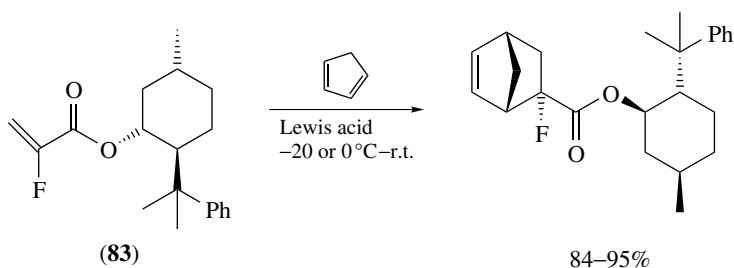
SCHEME 28

An *ab initio* study of the Diels–Alder reaction between 5-substituted cyclopenta-1,3-dienes and various dienophiles indicates that facial selectivity is primarily due to steric hindrance between the dienophile and the plane non-symmetric groups on the diene.⁹¹ A theoretical study of the role of steric and electronic factors in controlling π -facial selectivities in Diels–Alder reactions of π -facially non-equivalent dienes with MTAD, PTAD, and NMM is described.⁹² The Diels–Alder reactions between 1,4-diphenylbenz[*a*]aceanthrylene (**82**) and maleic anhydride, bromomaleic anhydride, *N*-phenylmaleimide, and benzyne show *endo* regiochemical π -facial selectivity (Scheme 29).⁹³ The Diels–Alder cycloadditions of enantiopure hydroxy-2-sulfinylbutadienes with *N*-phenylmaleimide and phenyltriazolinedione show high π -facial selectivity controlled by the chiral sulfur atom.⁹⁴ The Diels–Alder reaction of (*R*)-4-[(*p*-tolylsulfinyl)methyl]quinols with cyclopentadiene and penta-1,3-diene show total π -faced diastereoselectivity from the C–OH side.⁹⁵ The high stereoselectivity observed for the Diels–Alder reactions of 1,5,5-trimethylcyclopentadiene with 4-substituted- and 4,4-disubstituted cyclohexadienones arises from the lower steric demand of oxygen relative to methylene groups.⁹⁶

In the Diels–Alder reaction between 2-pyridones and electron-deficient alkenes, 2,4,6-triisopropylbenzenesulfonyl is a better *N*-substituent than 4-methylbenzenesulfonyl.⁹⁷



SCHEME 29

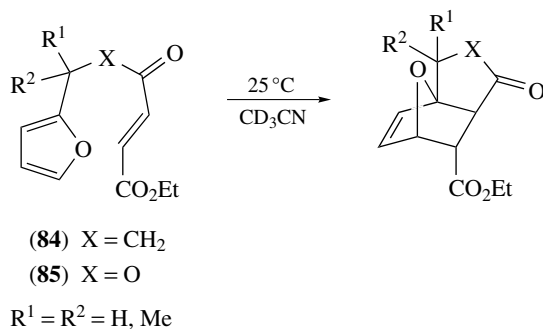


SCHEME 30

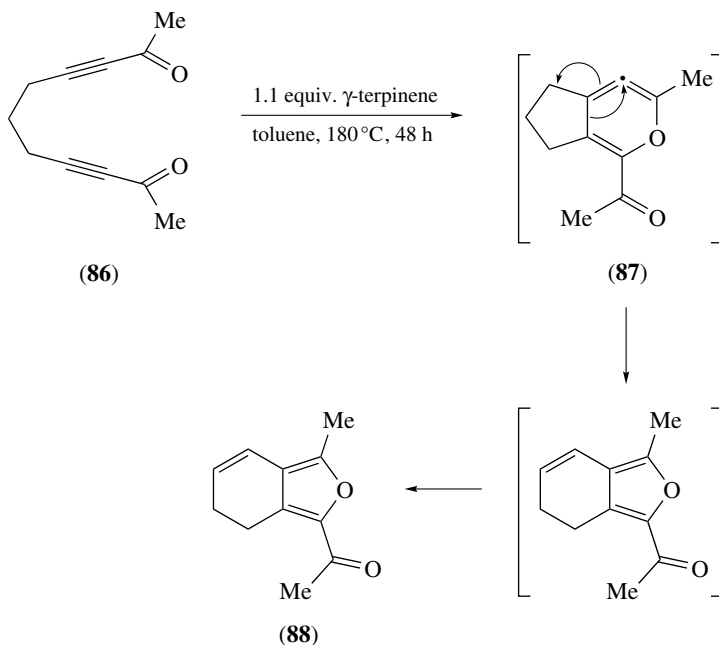
The Diels–Alder reaction between a 2-fluoroacrylic acid derivative of 8-phenylmenthol (**83**) and cyclopentadiene shows high *exo*- and π -diastereofacial selectivity (Scheme 30).⁹⁸ The C(2) of endocyclic ‘cross-conjugated’ 2-(acylamino)-1,3-dienes exerts excellent diastereofacial control on the Diels–Alder addition with electron-deficient dienophiles to produce octahydroquinolines.⁹⁹

The Diels–Alder reactions of the chiral reagents *N*-allyl-*o*-butylanilide and *N*-(*o*-butylphenyl)-2-methylmaleimide proceed with high *endo* and diastereofacial selectivity.¹⁰⁰

A study of the rates of intramolecular Diels–Alder cyclization of furfuryl methyl fumarates (**84**) and the corresponding furyl ethyl keto esters (**85**) provides evidence that the presence of the oxygen atom in the tether is the factor responsible for larger than normal rate enhancement (Scheme 31).¹⁰¹ Bulky protecting groups such as trityl group have been used to stimulate the intramolecular 4 + 2-cycloaddition reactions of *N*-allylfurylamines that normally do not undergo thermal cycloaddition.¹⁰² The activation and reaction volumes of intramolecular Diels–Alder reactions of (*E*)-nona-1,3,8-triene and (*E*)-deca-1,3,9-triene have been shown to be dependant on the ring size.¹⁰³ An intramolecular 4 + 2-cycloaddition of bisalkynones (**86**) yields dihydroisobenzofurans (**88**) via the generation and rearrangement of strained heterocyclic allenes (**87**) in high yields (Scheme 32).¹⁰⁴ 2-*H*-Phospholes undergo intramolecular 4 + 2-cycloaddition to coordinated unsaturated phosphines, phospholes and an arsine.¹⁰⁵



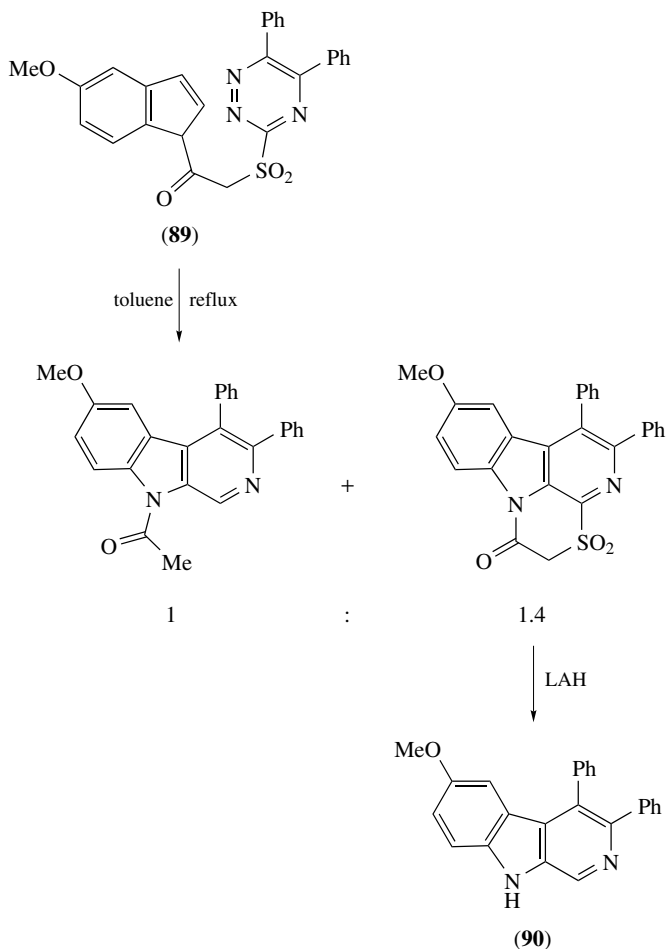
SCHEME 31



SCHEME 32

A semiempirical AM1 study of the inverse-electron-demand Diels–Alder reaction of 4-substituted 6-nitrobenzofurans with enol ethers and enamines favours a stepwise mechanism involving short-lived diradical intermediates.¹⁰⁶ The inverse-electron-demand intermolecular Diels–Alder reactions of 3,6-bis(trifluoromethyl)-1,2,4,5-tetrazine with acyclic and cyclic dienophiles followed by the elimination of N₂ produce 4,5-dihydropyridazines, which cycloadd further to yield cage compounds.¹⁰⁷ The preparation of β -carbolines (**90**) via an intramolecular inverse-electron-demand Diels–Alder

reaction involves the use of a fully removeable β -sulfonyl acetyl tether linking indole with 1,2,4-triazines (**89**) (Scheme 33).¹⁰⁸



SCHEME 33

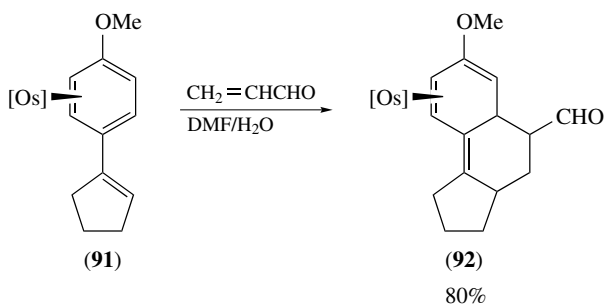
The inverse-electron-demand Diels–Alder reaction of 3,6-dichloro[1,2,4,5]tetrazine with alkenes and alkynes provides the synthesis of highly functionalized pyridazines.¹⁰⁹ Also, the 4 + 2-cycloaddition reactions of the parent [1,2,4,5]tetrazine with donor-substituted alkynes, alkenes, donor-substituted and unsubstituted cycloalkenes, ketene acetals, and amins have been investigated.¹¹⁰

N-Protonated 2-azabuta-1,3-diene undergoes 4⁺ + 2-cycloaddition with alkenes activated by electron-donating and electron-withdrawing substituents.¹¹¹ The 2⁺ + 4-cycloadditions of 1,3-dithian-2-ylum ions with buta-1,3-dienes follow second-order kinetics which do not exclude a mechanism involving a concerted pathway.¹¹² The

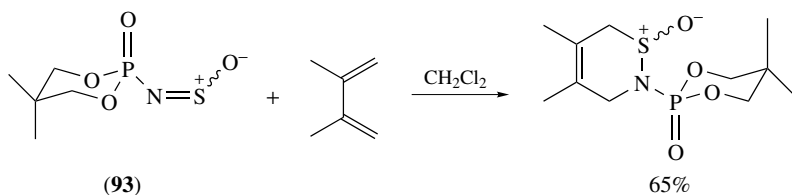
cation radical Diels–Alder addition of aryl vinyl sulfide to cyclopenta-1,3-diene in the presence of tris(4-bromophenyl)aminium hexachloroantimonate does not occur via outer-sphere electron transfer but by strong covalent interaction between aminium salt acting as an electrophile and the aryl vinyl sulfide substrate acting as a nucleophile.¹¹³

C₂-Symmetric Cu(II)–bis(oxazoline) complexes have been used in stereoselective Diels–Alder reaction between α,β -unsaturated acyl phosphonates and enol ethers to produce cycloadducts in 89% yield and 99% *ee*.¹¹⁴ The asymmetric Diels–Alder reactions between α -thioacrylates and cyclopentadiene are catalysed by Cu(II)–bis(oxazoline) complexes to produce cycloadducts in up to 92% yield, 88% *de* and > 95% *ee* for the *endo* adduct.¹¹⁵ Osmium(II) has been used to activate styrene (**91**) towards Diels–Alder reactions with electron-deficient alkenes to yield tetrahydronaphthalene complexes (**92**) (Scheme 34).¹¹⁶ The use of Cu(II) complexes of simple α -amino acids will increase the enantioselectivity of Lewis acid-catalysed Diels–Alder reaction between 3-phenyl-1-(2-pyridyl)prop-2-en-1-one and cyclopentadiene in water.¹¹⁷

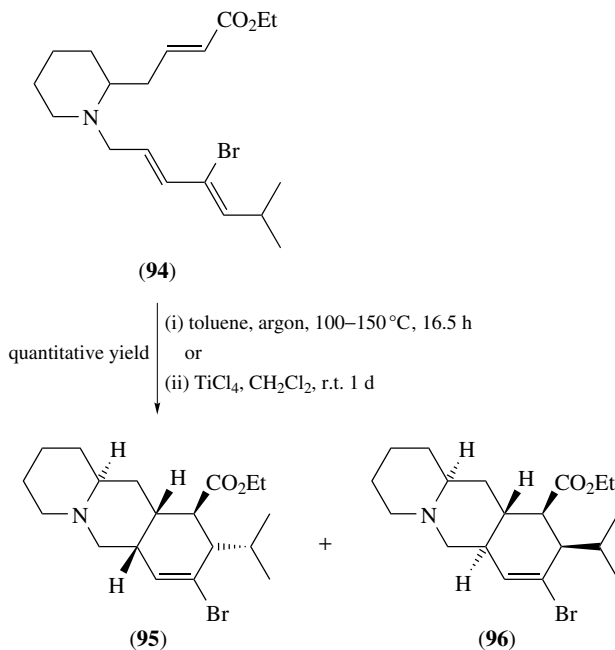
The rhodium complexes $[\eta\text{-C}_5\text{Me}_5]\text{RhCl}[\text{L}]\text{X}$ ($\text{X} = \text{PF}_6, \text{SbF}_6$) prepared from bidentate oxazoline-containing ligands are enantioselective catalysts for asymmetric Diels–Alder reaction of methacrolein with cyclopentadiene.¹¹⁸ The Diels–Alder reaction of *N*-sulfinylphosphoramidates (**93**) with cyclohexa-1,3-diene are highly diastereoselective in both the presence and absence of Lewis acid catalysts (Scheme 35).¹¹⁹ The TiCl_4 -catalysed Diels–Alder addition of trienes [e.g. (**94**)] produce decahydropyrido[2,1-*a*]isoindoles and decahydro-2*H*-pyrido[1,2-*b*]isoquinolines (**95**) and (**96**) stereoselectively in moderate yields (Scheme 36).¹²⁰ Mg(II) complexes of crown ylidene malonates have a strong catalytic effect on the Diels–Alder reaction between crown ylidene malonates and cyclopentadiene.¹²¹



SCHEME 34

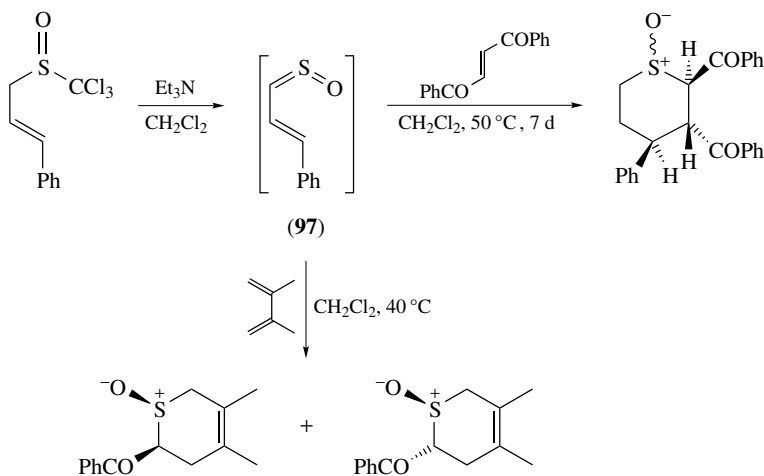


SCHEME 35



SCHEME 36

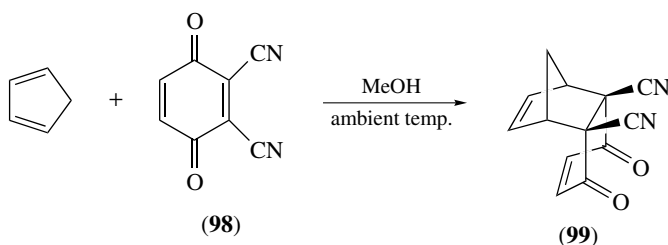
Density functional and semiempirical AM1 molecular orbital calculations have been used to investigate substituent effects on site selectivity in heterocumulene–heterodiene 4 + 2-cycloadditions between ketene imines and acroleins.¹²² The new and novel heterocumulenes α,β -unsaturated thioaldehyde *S*-oxides (**97**) behave as both diene



SCHEME 37

and dienophile in Diels–Alder reactions (Scheme 37).¹²³ AM1 and PM3 calculations show that the Diels–Alder reactions of carbonyl *S*-oxide and thiocarbonyl *S*-oxide with cyclopentadiene form cycloadducts through asynchronous transition states.¹²⁴

The asymmetric Diels–Alder cycloadditions of enantiopure (*S*)-*S*-(*p*-tolylsulfinyl)-1,4-benzoquinones with Dane's diene under thermal and Lewis acid conditions produce tetracyclic quinones after spontaneous elimination of the sulfinyl group.¹²⁵ The Diels–Alder reaction of barrelene with *o*-benzoquinone produces tetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradeca-9,11,13-triene-4,5-dione.¹²⁶ Under kinetic control, the Diels–Alder cycloaddition of 2,3-dicyano-*p*-benzoquinone (**98**) with cyclopentadiene in MeOH produces the single cycloadduct (**99**) (Scheme 38).¹²⁷

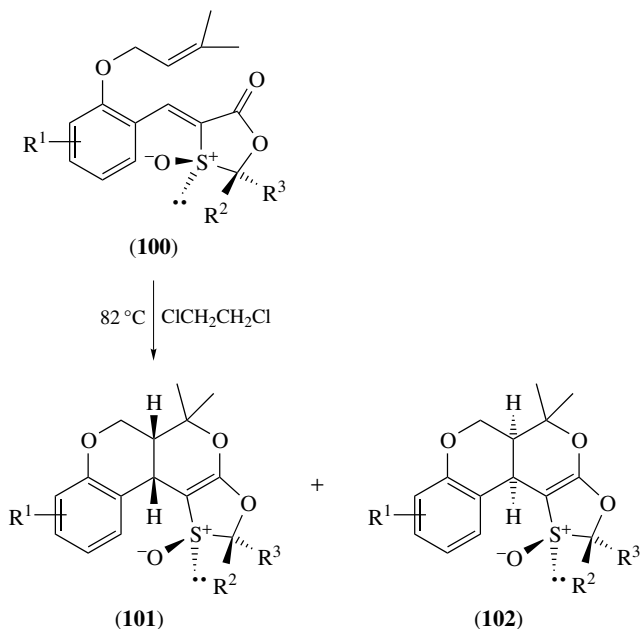


SCHEME 38

An extensive review of the use of chiral Lewis acid catalysts in Diels–Alder cycloadditions has been presented.¹²⁸ Brønsted acid-assisted chiral Lewis acids have been shown to be highly efficient catalysts for the enantioselective Diels–Alder reactions of α - and β -substituted- α,β -enals with numerous dienes.¹²⁹ The chiral Lewis acid-catalysed Diels–Alder reaction between cyclopentadiene and alkenoyloxazolidiones can be catalysed by bis(oxazolone)magnesium catalysts.¹³⁰

An extensive review of the hetero-Diels–Alder reactions of 1-oxabuta-1,3-dienes has been published.¹³¹ *Ab initio* calculations of the Diels–Alder reactions of prop-2-enethial with a number of dienophiles show that the transition states of all the reactions are similar and synchronous.¹³² Thio- and seleno-carbonyl compounds behave as ‘superdienophiles’ in Diels–Alder reactions with cyclic and aryl-, methyl-, or methoxy-substituted open-chain buta-1,3-dienes.¹³³ The intramolecular hetero-Diels–Alder reactions of 4-benzylidene-3-oxo[1,3]oxathiolan-5-ones (**100**) produce cycloadducts (**101**) and (**102**) in high yield and excellent *endo/exo*-selectivity (Scheme 39).¹³⁴ A density functional theoretical study of the hetero-Diels–Alder reaction between butadiene and acrolein indicates that the *endo s-cis* is the most stable transition structure in both catalysed and uncatalysed reactions.¹³⁵ The formation and use of amino acid-derived chiral acylnitroso hetero-Diels–Alder reactions in organic synthesis has been reviewed.¹³⁶ The 4 + 2-cycloadditions of *N*-acylthioformamides as dienophiles have been reviewed.¹³⁷

High-pressure kinetic studies indicate that the concertedness of [$\pi^4 + \pi^2$] cycloadditions is not altered by the presence of a Lewis catalyst.¹³⁸ The intermolecular hetero-Diels–Alder reactions between enantiopure α,β -unsaturated sulfinimines and



R¹ = H, 3-OMe, 4-OMe, 5-OMe, 6-OMe;

R² = Me; R³ = Me, Bu^t; R² - R³ = CH₂

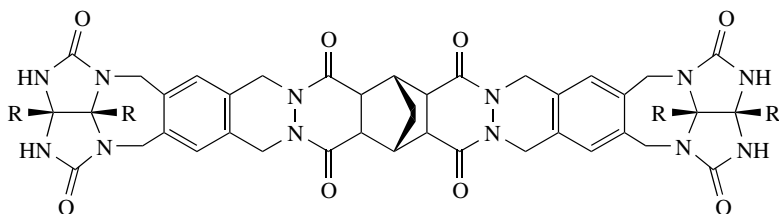
SCHEME 39

enol ethers at 11 kbar produce tetrahydropyridines in high yield and with good *endo/exo* selectivity.¹³⁹ At high pressure (3 kbar), the rates of reaction of intramolecular Diels–Alder addition between furan and bicyclopropylidene or methylenecyclopropane are significantly increased, as shown by FTIR spectroscopy.¹⁴⁰

Density functional theory has been used to investigate the Diels–Alder reactions of triazolinedione with *s-cis*- and *s-trans*-butadiene.¹⁴¹ Combined quantum mechanics–molecular mechanics calculations have been used to investigate the asymmetric Diels–Alder reaction of cyclopentadiene with the complex dienophiles AlCl₃–methyl acrylate and methoxyaluminium dichloride–acrolein.¹⁴² Equilibrium constants have been determined for the molecular complexes formed from 1-alkyl-1-(2-naphthyl)ethenes and 1-vinylnaphthalene with TCNE in Cl(CH₂)₂Cl at 27.1 °C.¹⁴³

Extensive reviews of Diels–Alder reactions and hetero-Diels–Alder reactions in aqueous media have been presented.^{144–146} Micelles in the presence of catalytically active transition-metal ions catalyse the Diels–Alder reaction between 3-(*p*-substituted phenyl)-1-(2-pyridyl)prop-2-en-1-ones with cyclopentadiene by a factor of 1.8 × 10⁶ compared with the uncatalysed reaction in MeCN.¹⁴⁷ Diels–Alder reactions have been shown to be accelerated by encapsulation of both reactants by pseudospherical capsules assembled from self-complementary molecules (103).¹⁴⁸

Experimental and computational studies of the effect of solvents on the rate and selectivity of the concerted Diels–Alder reaction between cyclopentadiene and methyl



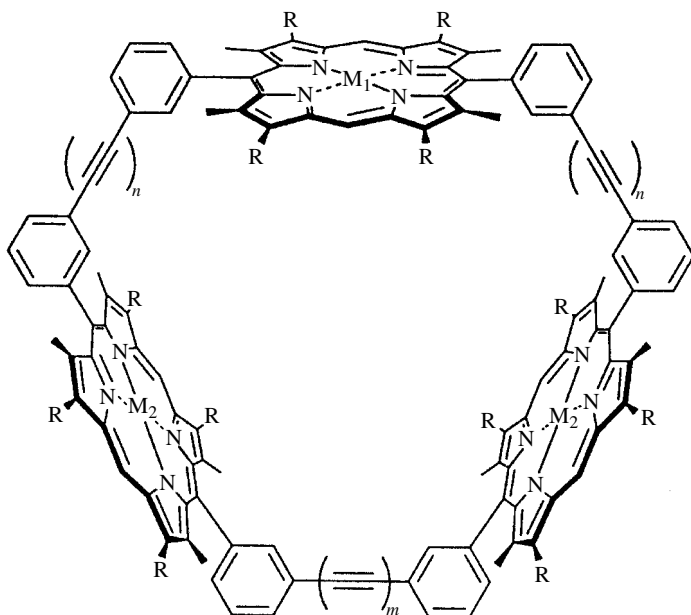
(103)

R = C₆H₅, CO₂-*i*-pentyl

acrylate are presented.¹⁴⁹ The stereoselectivity of Diels–Alder reactions of cyclopentadiene and electron-deficient dipolarophiles in structured solvents such as water and formamide is influenced by the internal pressure.¹⁵⁰ Solvent polarity has been shown to affect the rate coefficients and activation parameters of the hetero-Diels–Alder reaction between enamino ketones and isopropenyl methyl ether under high pressure (5 kbar).¹⁵¹

AM1 computational theory was used to compare the reactivities of benzo[*c*]furan and benzo[*b*]furan in Diels–Alder reactions using several dienophiles.¹⁵²

Zn–metalloporphyrin oligomers (**104**) have been successfully used to reverse the stereochemistry of a Diels–Alder reaction by stabilizing the thermodynamically disfavoured *exo*-transition state.¹⁵³



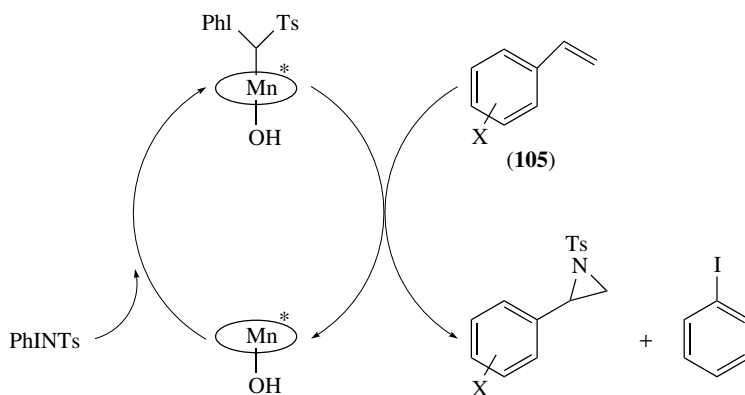
(104)

$n = 1, m = 2, M_1 = M_2 = \text{Zn}; R = \text{CH}_2\text{CH}_2\text{CO}_2\text{Me}$

The domino cycloaddition–*N*-acyliminium ion cyclization cascade has been extensively reviewed.¹⁵⁴ Tandem reactions combining Diels–Alder reactions and sigma-tropic rearrangement reactions in organic synthesis have been extensively reviewed.¹⁵⁵ The tandem Diels–Alder reaction between acetylenedicarboxaldehyde and *N,N'*-dipyrrolylmethane has been extensively studied at the RHT/3–21G and RHF/6–31G* levels.¹⁵⁶ The molecular mechanism of the domino Diels–Alder reaction between hexafluorobut-2-yne and *N,N'*-dipyrrolylmethane has been studied using density functional theory.¹⁵⁷

Miscellaneous Cycloadditions

A chiral D_4 -manganese(III) porphyrin catalyst, $Mn(P^*)(MeOH)(OH)$ [$H_2P^* = 5, 10, 15, 20$ -tetrakis(1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracene-9-yl)porphyrin], has been shown to catalyse the asymmetric aziridination of substituted styrenes (**105**) with enantiomeric excess of 43–68% (Scheme 40).¹⁵⁸

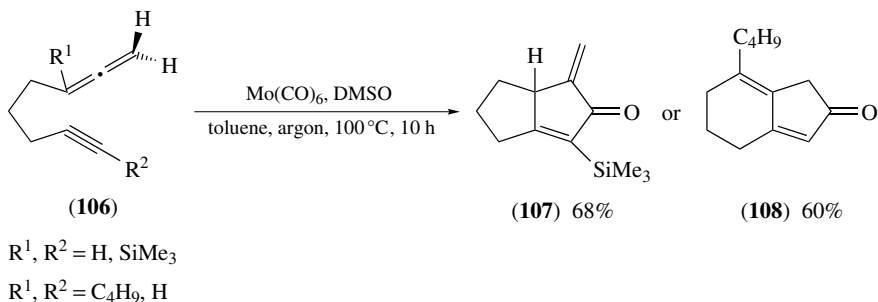


SCHEME 40

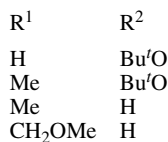
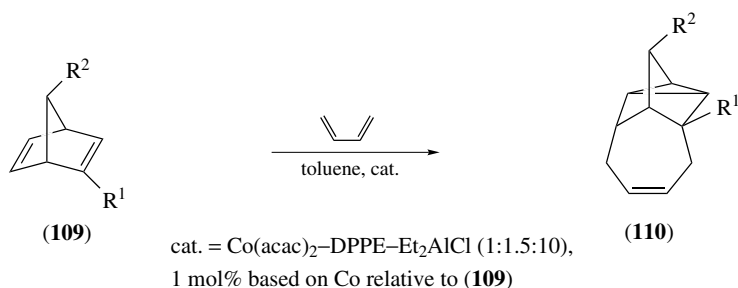
The intramolecular 2 + 2 + 1-cycloadditions of allene, alkyne (**106**), and carbon monoxide yield α -methylene-(**107**) or 4-alkylidene-cyclopentenones (**108**) depending on the allene structure or the reaction conditions (Scheme 41).^{159,160}

The cobalt-catalysed 4 + 2 + 2-cycloaddition of norbornadienes (**109**) with buta-1,3-dienes readily produces cycloadducts (**110**) when a bimetal system is used (Scheme 42).¹⁶¹

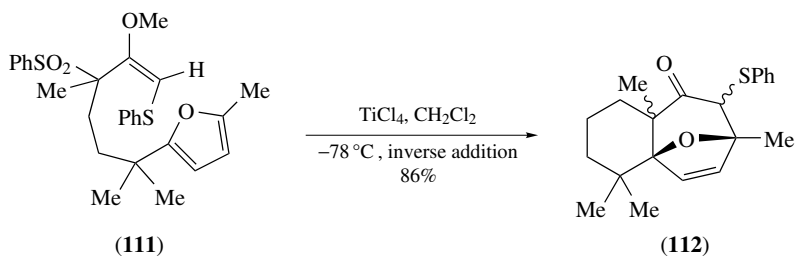
An extensive review of 4 + 3-cycloaddition reactions has been presented.¹⁶² The 1,3-difluoroxyallyl intermediate obtained from 1-bromo-1,3-difluoropropan-2-one undergoes 4 + 3-cycloaddition with cyclopentadiene and furan to give difluorobicyclo[3.2.1]octenones.¹⁶³ The use of 4 + 3-cycloaddition reactions of cyclic oxyallyls in the synthesis of natural products has been extensively studied.¹⁶⁴ The intramolecular 4 + 3-cycloaddition of allylic sulfones (**111**) possessing a diene in the side-chain in the presence of Lewis acids yield cycloadducts (**112**) in good to excellent yields (Scheme 43).¹⁶⁵



SCHEME 41



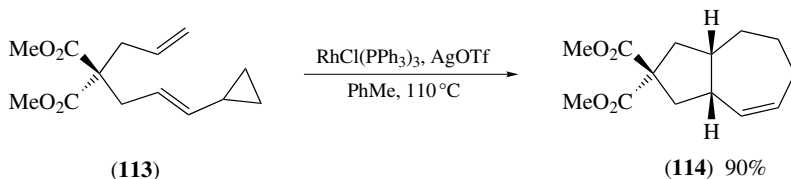
SCHEME 42



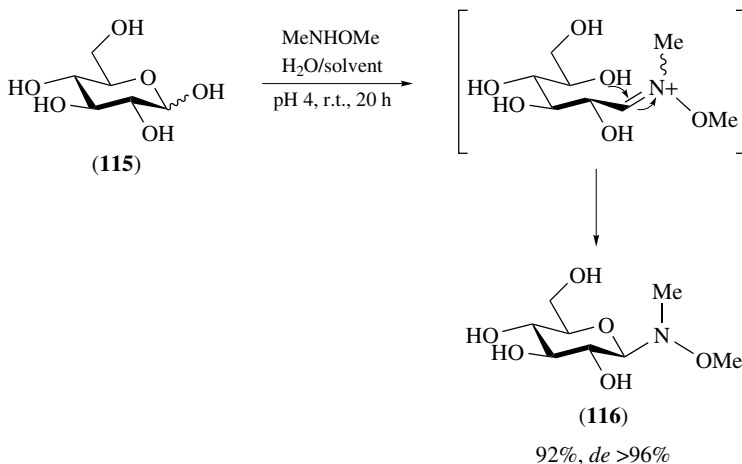
SCHEME 43

Molecular mechanics–valence bond dynamics have been used to study the model 4 + 4-photocycloadditions of butadiene with butadiene.¹⁶⁶ The photoirradiation of *t*-butyl 9-anthroate and furan produces a mixture of 4 + 4-cycloadduct and 4 + 4-cyclodimers.¹⁶⁷

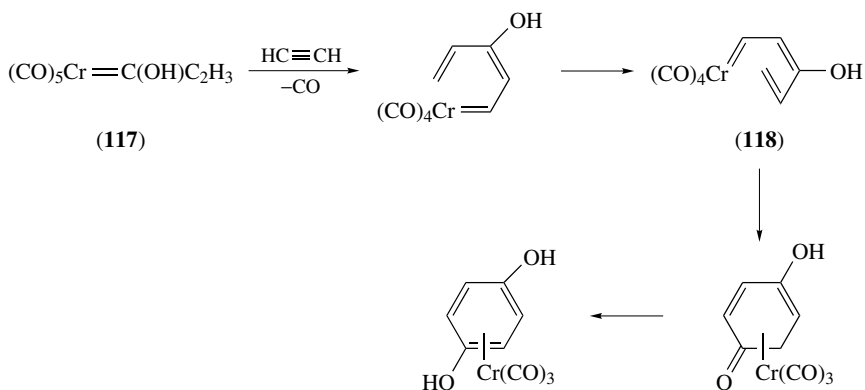
The rhodium(I)-catalysed 5 + 2-cycloadditions between vinylcyclopropanes and alkenes (**113**) yield only *cis*-5,7-fused cycloadducts (**114**) in high yields (Scheme 44).^{168,169}



SCHEME 44



SCHEME 45



SCHEME 46

The glycosylation of *N,O*-disubstituted hydroxylamines with unprotected reducing sugars (**115**) proceeds with high chemo- and stereo-selectivity to yield the cycloadduct (**116**) (Scheme 45).¹⁷⁰

A new chromahexatriene (**118**) route has been proposed for the mechanism of the Dötz benzannulation reaction between vinylcarbene complexes (**117**) and ethynes (Scheme 46).¹⁷¹

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