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CHAPTER 15

Molecular Rearrangements

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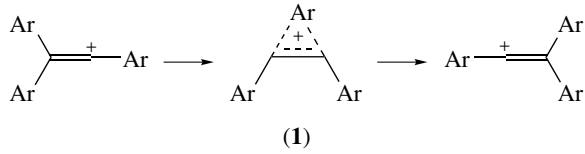
Aromatic Rearrangements

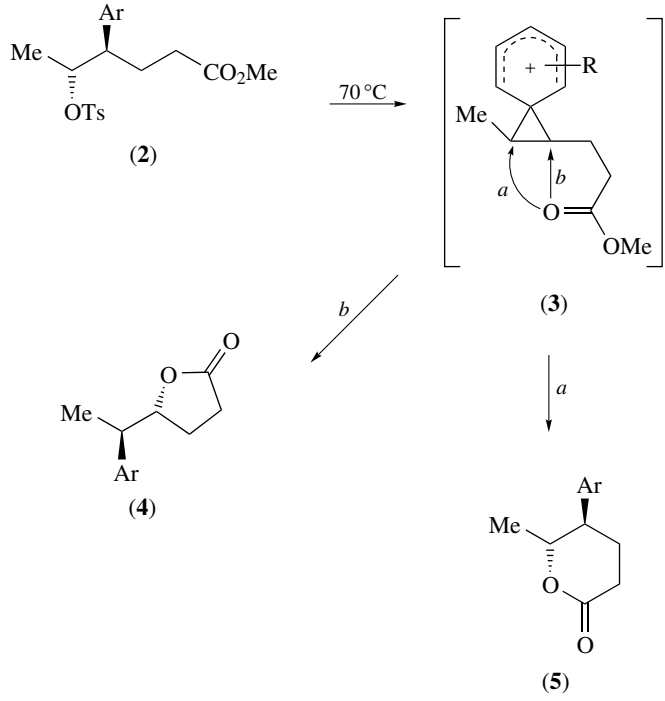
Benzene Derivatives

The thermodynamic stabilities of phenonium ions have been determined[1] based on bromide-transfer equilibria in the gas phase and, depending on the substituents, the bridged species (**1**) has been proposed[2] as an intermediate or transition state on the potential-energy surface for the 1,2-aryl rearrangement of triarylvinyl cations (see Scheme 1). Phenonium ion (**3**) has been presented[3] as an intermediate to account for the fact that lactonization of methyl 4-aryl-5-tosyloxy hexanoate (**2**) produces γ-lactone (**4**) selectively under thermodynamic conditions, but affords δ-lactone (**5**) preferentially under kinetic conditions. It has been shown that anodic oxidation of *trans*-stilbene in alcohols in the presence of KF or Bu_4NBF_4 is accompanied by its electro-oxidative rearrangement into diphenylacetaldehyde acetals. The mechanism outlined in Scheme 2 has been proposed[4] for the transformation.

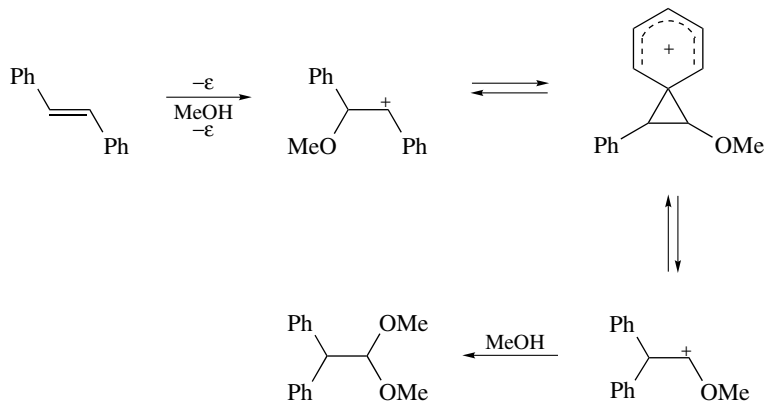


(**1**)

SCHEME 1

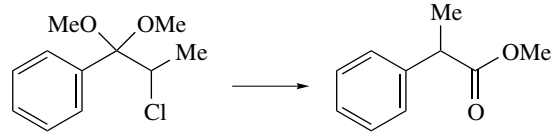


(**2**) (**3**) (**4**) (**5**)

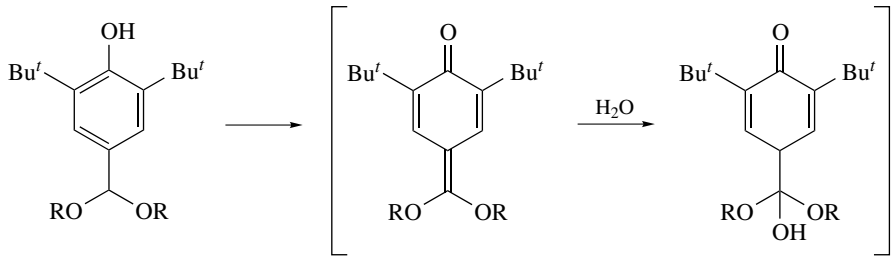


SCHEME 2

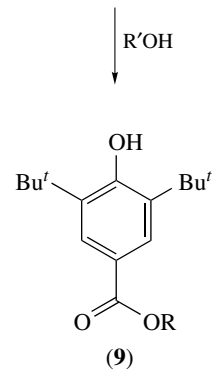
The $AgBF_4$-catalysed phenyl rearrangement of the dimethyl acetal of 2-chloropropiophenone (**6**) has been found[5] to proceed with inversion of stereochemistry at the reaction centre to give 2-phenylpropionic acid (**7**) with high stereoselectivity. This result suggests an Ag^+-aided, phenyl-assisted, intramolecular S_N2 mechanism for the rearrangement. 3,5-Di-*t*-butyl-4-hydroxybenzaldehyde acetals have been observed to rearrange to various esters when oxidized with potassium ferricyanide in alkaline medium. The authors[6] suggested that the initial step in the transformation involves formation of quinone methide (**8**). Addition of water and subsequent elimination of alcohol would lead to the formation of ester (**9**). A free-radical mechanism involving initial homolysis of different bonds in the acetal molecules has been postulated[7] to explain the plethora of products obtained on the thermal rearrangement of aromatic acetal and thioacetal derivatives. On the other hand, a carbocation mechanism (see Scheme 3) has been proposed[8] to account for the fact that aromatic acetals react with iodobenzene dichloride to give esters and aldehydes depending on the solvent.



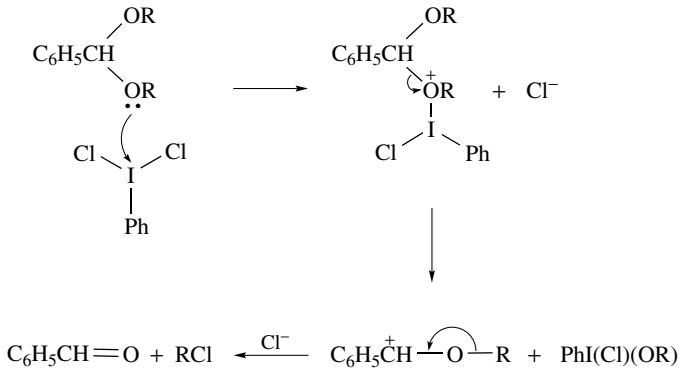
(**6**) (**7**)



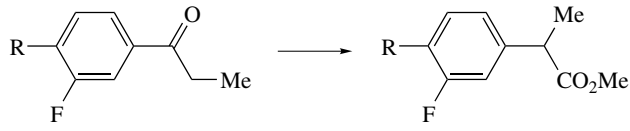
(**8**)



(**9**)



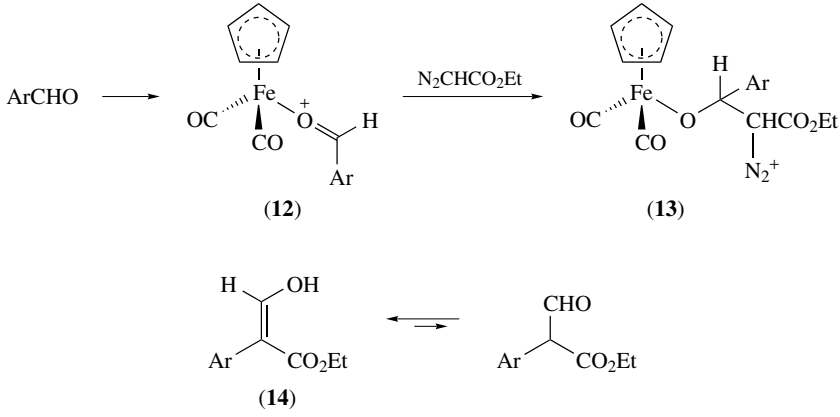
SCHEME 3



(**10**) (**11**)

R = cyclohexyl

It has been shown[9] that the lead tetraacetate-mediated 1,2-aryl shift of various *meta*-substituted *p*-cyclohexyl aryl ketones, e.g. (**10**), results in excellent yields of the corresponding rearranged esters (**11**). A unique reaction, providing 3-hydroxy-2-arylacrylic acid ethyl esters (**14**), has been observed[10] between aryl aldehydes and ethyl diazoacetate in the presence of the iron Lewis acid [$\eta^5 - (C_5H_5)Fe(CO)_2(THF)BF_4$]. It appears that the enol esters are formed by an unusual 1,2-aryl shift from a possible intermediate (**13**), which in turn is formed from the reaction of the iron aldehyde complex (**12**) with ethyl diazoacetate (see Scheme 4).



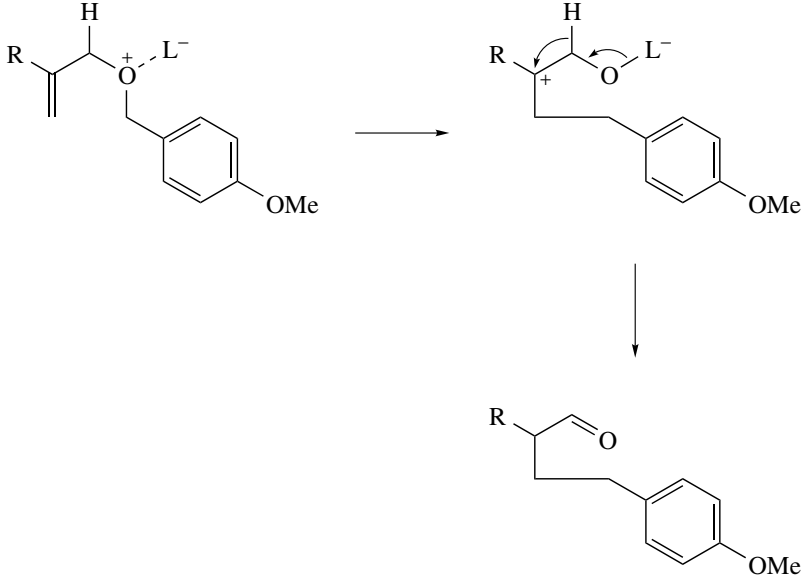
(**12**) (**13**)

(**14**)

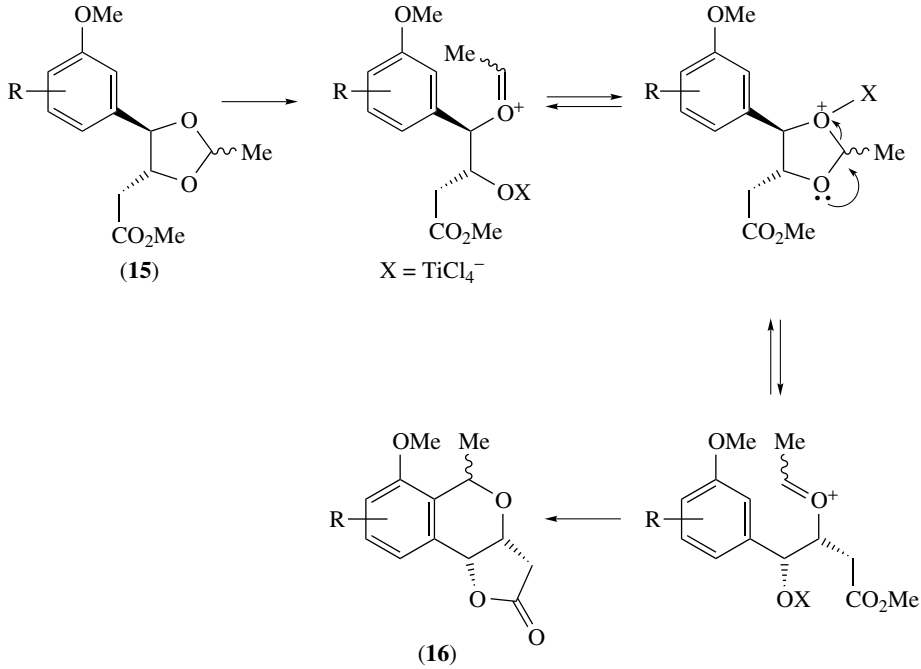
SCHEME 4

The rearrangement reaction of a variety of alkyl phenyl ethers over a dealuminated HY zeolite has been shown to involve both intramolecular and intermolecular processes to afford phenol, (alkoxyalkyl)benzenes and alkylphenols as the main products.[11] *o*-Benzylphenol has been obtained[12] as the exclusive product in the rearrangement of benzyl phenyl ether in the presence of montmorillonite. The mechanism for a novel zeolite β-catalysed rearrangement of alkoxybenzyl allyl ethers to aldehydes and ketones has been investigated by the use of cross-over reactions and deuterium labelling. The reaction was found to be mainly intramolecular and has been described[13] as a nucleophilic attack of the double bond on the electrophilic benzylic carbon of the ether–Lewis acid complex, followed by a 1,2-hydride (or alkyl) migration (see Scheme 5). The best conditions for this rearrangement have been examined,[14] and preliminary results have indicated that there is a dependence between the size of the substrate and the pore size of the zeolite. Several allylic *p*-methoxybenzyl ethers have been rearranged under these conditions to afford a variety of 4-arylbutanals or 5-arylpentan-2-ones, depending on the substituent pattern of the allylic moiety.[15] The Lewis acid-catalysed diastereoselective rearrangement of methyl 4,5-*trans*-4-aryldioxolan-5-yl acetates (**15**) has been used[16] to provide a convenient route to substituted isochromane-γ-lactones (**16**) (see Scheme 6).

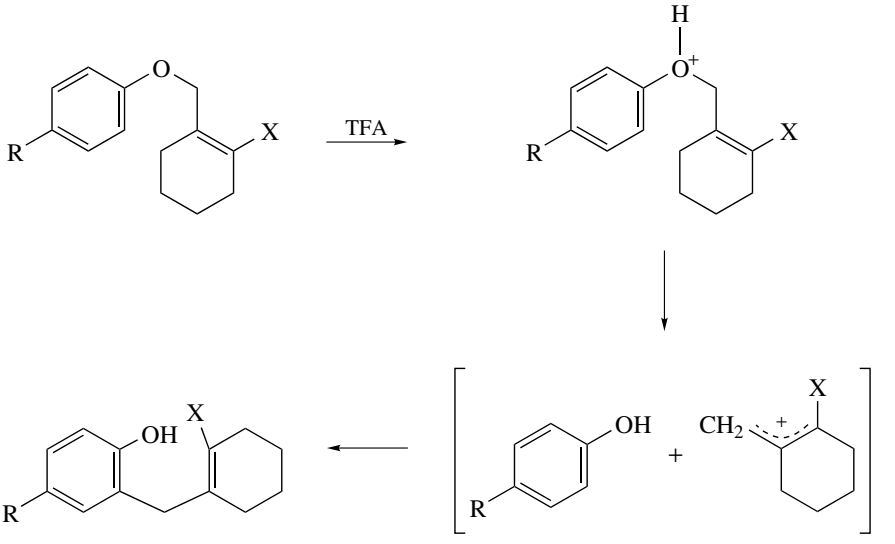
An unusual [1,3]-rearrangement of aryl 2-halocyclohexenylmethyl ethers promoted by trifluoroacetic acid has been observed.[17] Products due to a Claisen rearrangement were not formed and the proposed pathway for the process is outlined in Scheme 7. It has been shown[18] that $AlCl_3$-mediated decomposition of *N*-phenoxybenzamide



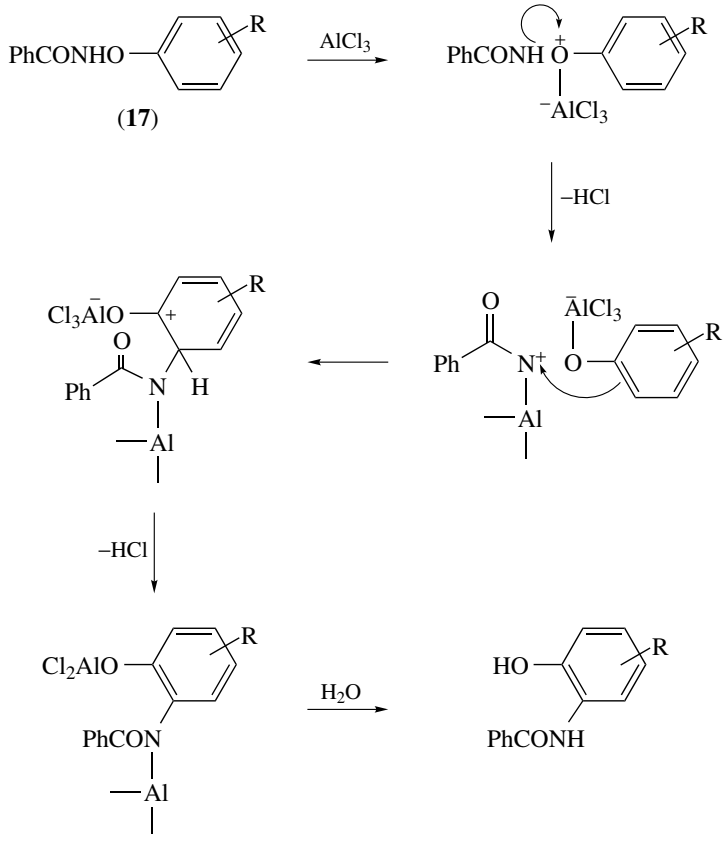
SCHEME 5



SCHEME 6

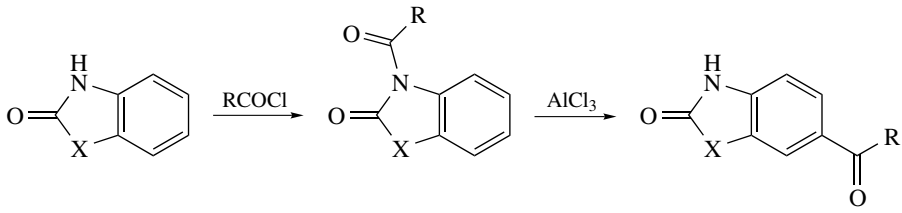


SCHEME 7



SCHEME 8

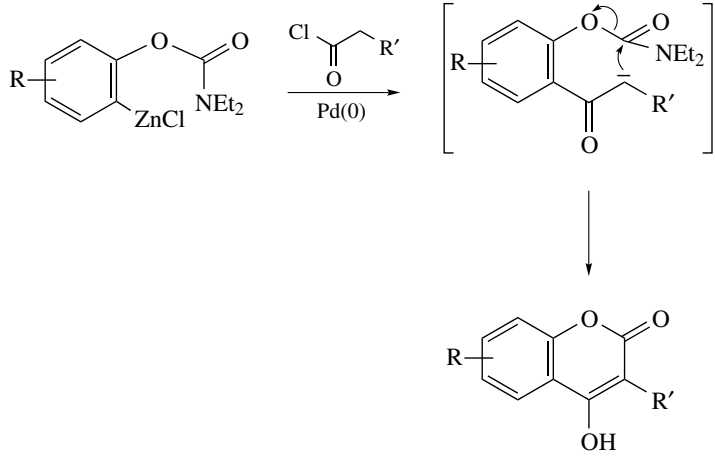
derivatives (**17**) leads mainly to regioselective intramolecular migration of the benzamido group from oxygen to the *ortho* position of the phenyl group as shown in Scheme 8. Zeolite catalysts have been evaluated[19] for the Fries rearrangement of acetanilide to the corresponding aminoacetophenones, and the selectivity of the Fries rearrangement over various silica composite catalysts has been compared.[20] Alumina in methanesulfonic acid has been used as an efficient reagent for the Fries rearrangement of phenolic esters.[21] A novel method of acylating 2(3*H*)-benzoxazolone and 2(3*H*)-benzothiazolone at the 6-position has been described.[22] It consists of a Fries-like transposition of the acyl group from the nitrogen atom to the 6-position (see Scheme 9). The photo-Fries rearrangement of *N*-acetyl- and *N*-benzoyl-carbazoles has been studied.[23] The anions resulting from the treatment of mono- or dicarbamates of 1,1′-bi-2-naphthols with Bu^{t}Li/TMEDA have been found[24] to undergo anionic Fries rearrangements to yield mono- and di-(3-alkyl)- or -(3-amido)-substituted 2, 2′-binaphthols. The Fries migration of various calix(*n*)arene esters ($n = 4, 6, 8$) under the influence of different solvents and Lewis acid catalysts has been examined,[25]



SCHEME 9

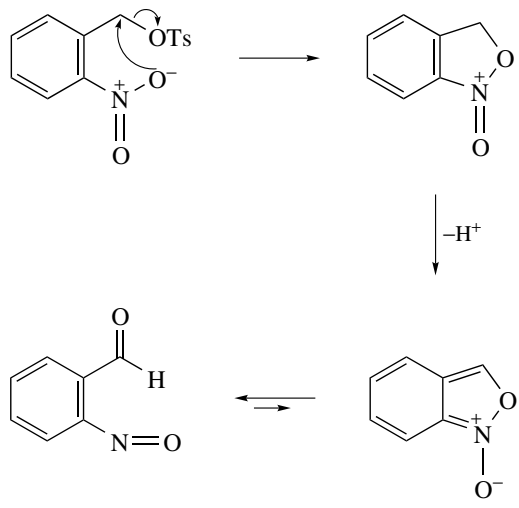
and an unusual benzoyl rearrangement has been observed[26] during the synthesis of asymmetrically substituted calix(4)arenes.

A new synthetic protocol consisting of sequential directed *ortho* metallation, cross-coupling and a carbamoyl Baker–Venkataraman rearrangement has been applied[27,28] to an efficient construction of coumarins (see Scheme 10). The formation of *o*-nitrosobenzaldehyde during the hydrolysis of *o*-nitrobenzyl tosylate in aqueous acetonitrile has been presented[29] as a strong indication that the nitro group participates in the departure of the tosylate group as shown in Scheme 11.

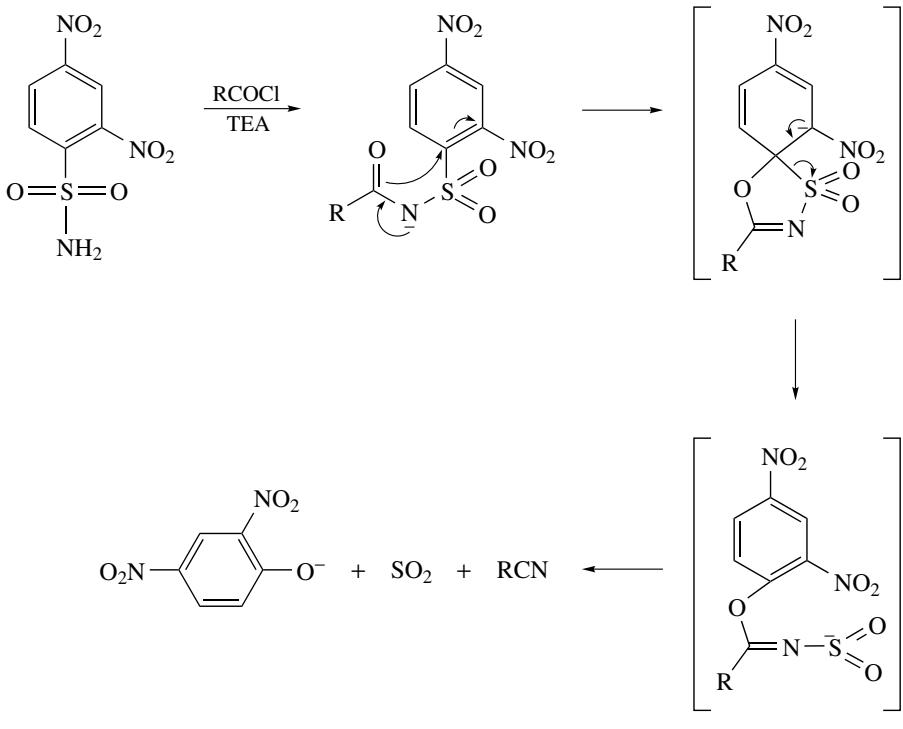


SCHEME 10

The α- and β-cyclodextrins have been found to accelerate the Smiles rearrangement of 4-nitrophenyl salicylate.[30] The reaction of 2,4-dinitrobenzenesulfonamide with acyl chlorides in the presence of excess triethylamine has been found to produce the corresponding nitrile in good yield. Mechanistic studies have indicated[31] that the reaction proceeds via a Smiles rearrangement of the initially formed *N*-(2,4-dinitrobenzenesulfonyl)amide to form the nitrile, 2,4-dinitrophenol, and sulfur dioxide (see Scheme 12). 1-Chloro-3-fluorophenothiazines have been prepared[32] by Smiles rearrangement of 3-chloro-5-fluoro-2-formamido-2′-nitrophenyl sulfides in alcoholic



SCHEME 11

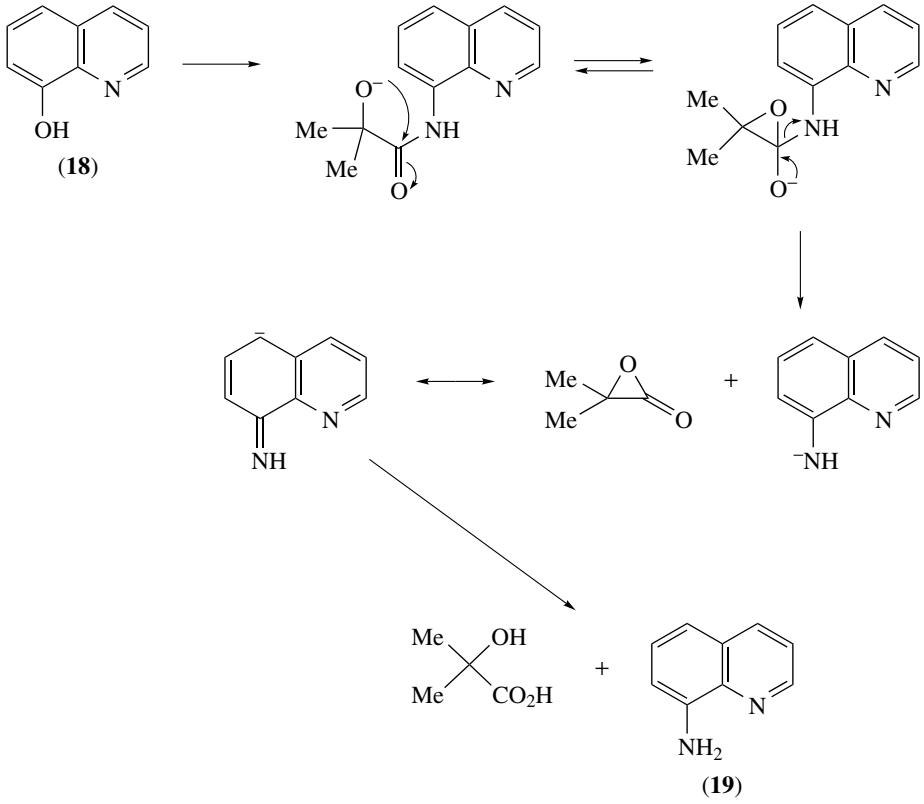


SCHEME 12

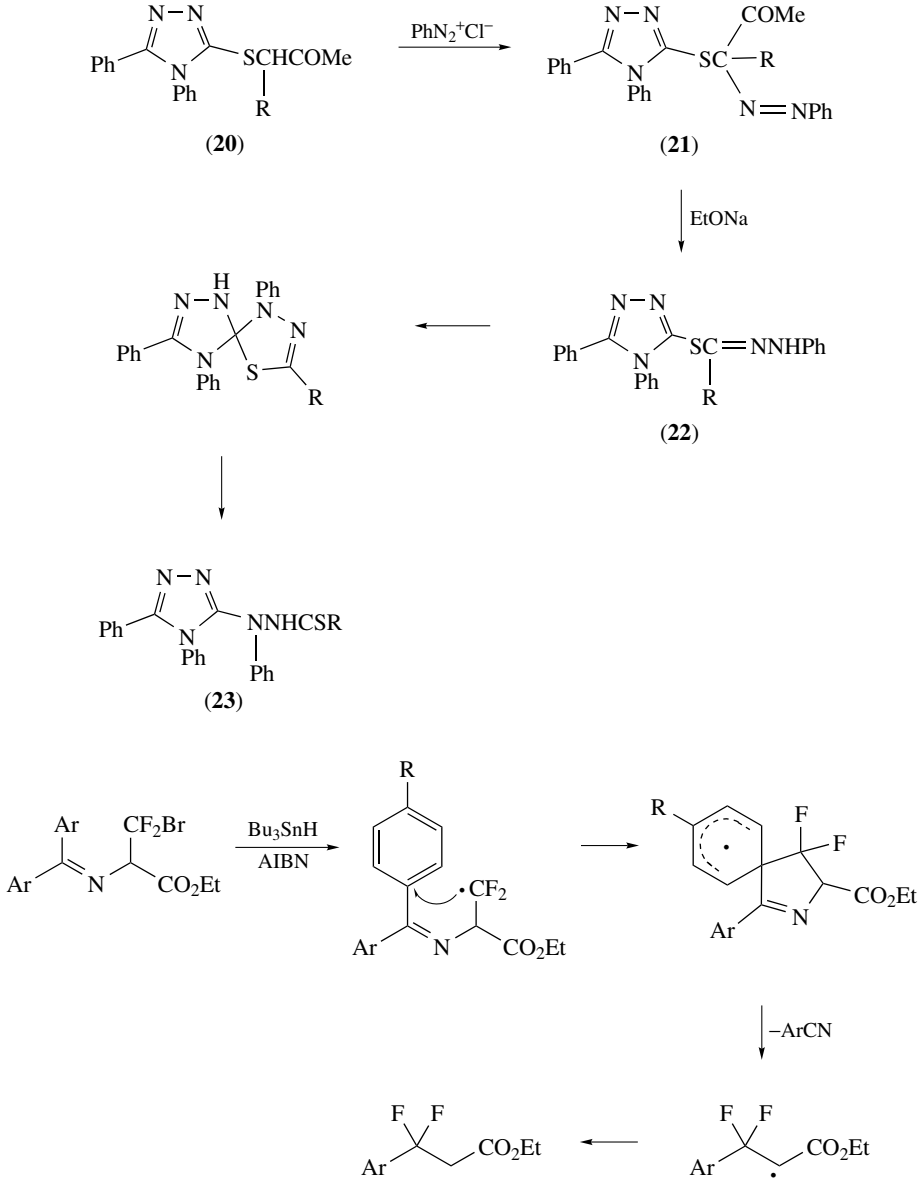
potassium hydroxide solution, and 8-hydroxyquinoline (**18**) has been converted[33] into 8-aminoquinoline (**19**) in a one-pot procedure involving alkylation with 2-bromo-2-methylpropionamide followed by Smiles rearrangement and hydrolysis (see Scheme 13). The reaction of benzenediazonium chloride with 3,4-diphenyl-1,2,4-triazol-5-yl-thiomethylene compounds (**20**) resulted in the formation of azo coupling products (**21**), which upon treatment with sodium ethoxide in ethanol have been found[34] to yield thiohydrazonate esters (**22**) that rearrange *in situ* by a Smiles-type rearrangement to afford thiohydrazides (**23**).

The formation of 3,3-difluoro-3-arylpropanoates in good yields from the radical-induced rearrangement of 3-bromo-3,3-difluoroalanine Schiff bases has been explained[35] by postulating a radical *ipso*-substitution at the aromatic ring as shown in Scheme 14.

Montmorillonite K10 clay and its various cation-exchanged forms have been found to promote the formation of an unexpected product, *p*-nitrosodiphenylamine, from *N*-phenylhydroxylamine, rather than the typical Bamberger products.[36] A Bamberger rearrangement has been shown to occur during the metabolism of 2,4,6-trinitrotoluene



SCHEME 13



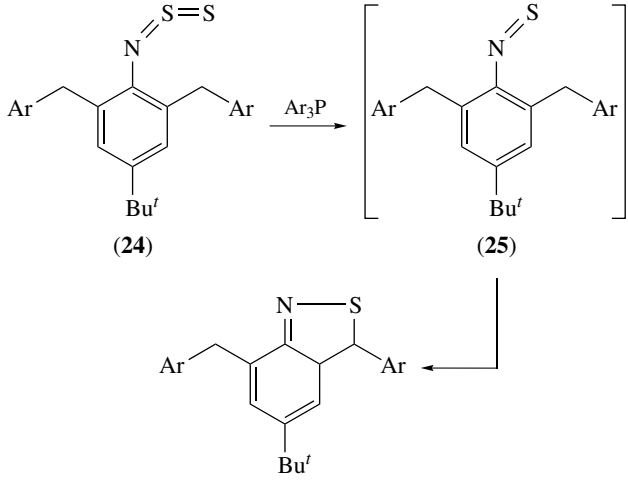
(**20**) (**21**) (**22**) (**23**)

SCHEME 14

by *Clostridium acetobutylicum*.[37] Daszkiewicz *et al*.[38] have discussed the mechanism of the nitramine rearrangement in the light of the fact that the acid-catalysed rearrangement of *N*-methyl-*N*-phenylnitramine was found to be accompanied by side-reactions involving nitrosation and methylation. MO theory employing the semiempirical AM1 method has been used to locate and discuss the energetics of the intermediates and

transition states for the Wallach rearrangement.[39] A study of the acid-catalysed benzidine rearrangement of unsymmetrical hydrazoaromatics has been undertaken, and the results have indicated[40] the importance of disproportionations to understanding benzidine rearrangements.

Products isolated from the thermal fragmentation of *N*-arylbenzamide oximes and *N*-arylbenzamide *O*-phenylsulfonyl oximes have been accounted for by invoking a free-radical mechanism which is initiated by the preferential homolysis of the N—O bond.[41] Time-resolved IR spectroscopy has revealed that photolysis of *N*, *N′*-dipheny1-1,5-dihydroxy-9,10-anthraquinone diimine affords acridine-condensed aromatic products via excited-state intramolecular proton transfer.[42] The absolute and relative rates of thermal rearrangements of substituted benzyl isocyanides have been measured,[43] and it has been found that the relative rates are independent of temperature and exhibit excellent Hammett correlations. Thionitrosoarene (**25**), thought to be generated by desulfurization of the stable *N*-thiosulfinylaniline (**24**), has been established[44] as an intermediate in the formation of 3,3a-dihydro-2,1-benzisothiazole (**26**) from *o*-alkylthionitrosoarene (**24**).



(**24**) (**25**)

(**26**)

The pyrolysates obtained from the flash vacuum pyrolysis of the allyl esters of a number of biphenyl carboxylic acids, biphenyldicarboxylic acids and biphenyldicarboxylic anhydrides have been examined by ^{1}H NMR spectroscopy. In all cases the spectra showed the presence of cyclopent[*a*]indene and acenaphthylene with other products. On the basis of the findings the authors[45] have postulated that high-temperature reactions of polycyclic aromatic hydrocarbons that result in the loss of two hydrogen atoms and formation of polycyclic hydrocarbons containing five-membered rings take place by loss of a sterically constricted hydrogen atom; this is followed by ring contraction of the resulting six-membered aryl radical, radical-induced

ring formation, loss of a second hydrogen atom and further rearrangement by interconversion of five- and six-membered rings. On the other hand, pyrolytic reactions which result in the loss of the elements of acetylene from polycyclic aromatic hydrocarbons are considered to take place by loss of a hydrogen atom followed by ring contraction and radical-induced ring formation, loss of a second hydrogen atom followed by rearrangement of the rings, loss of a C_2 fragment and hydrogen-atom shifts. Electronic structure studies have provided a wealth of information on the 1,2-didehydrogenation of polycyclic aromatic hydrocarbons and the ring contraction of the resulting arynes. The calculations have confirmed[46] the experimentally postulated existence of a cyclopentadienylidene carbene in these processes. More recently, three distinct pyrolytic pathways connecting the thermally induced cyclodehydrogenation of 1-phenylnaphthalene to fluoranthene have been identified.[47] The thermal conversion of 1-phenylbut-1-en-3-yne into its cyclo-isomerization products, viz. naphthalene, azulene, and 1-methylene-1*H*-indene, has been studied[48] at high temperatures, while an investigation of the reactions on the C_6H_6 potential-energy surface has revealed that, although several mechanisms operate simultaneously, benzvalene is one of the key intermediates in the thermal intramolecular topomerization of benzene.[49]

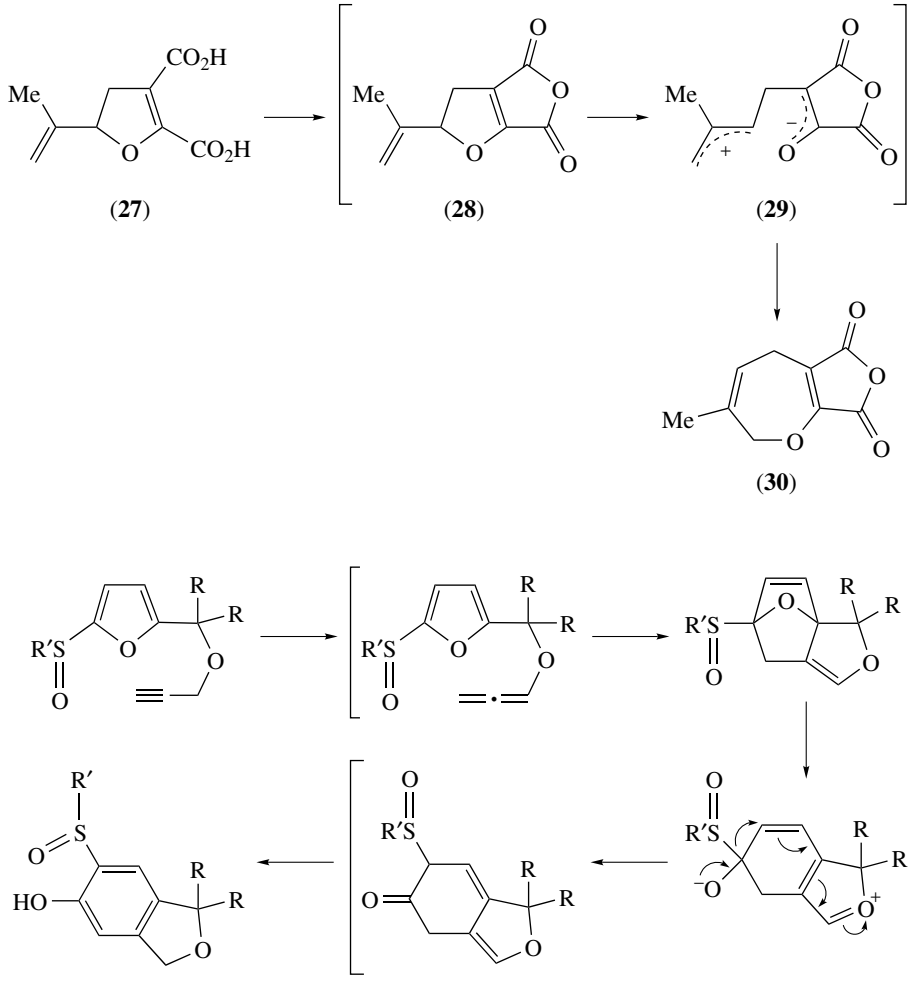
Heterocyclic Derivatives

A novel transformation of *N*-alkoxycarbonylprolines to trifluoroacetyl-2,3-dihydropyrroles has been achieved[50] by utilizing trifluoroacetic anhydride. A mesoinic 1,3-oxazolium-5-olate is thought to be the probable intermediate in this transformation.

The molecular mechanism for the pyrrole ring expansion to yield 3-chloropyridine as a model for the abnormal Reimer–Tiemann rearrangement has been characterized theoretically,[51] while extensive rearrangement reactions, in particular ring expansions, have been observed for differently *N*-substituted 2,5-dimethylpyrroles under electron ionization.[52] The rearrangements of model pyrrolenines carrying one or two pyrrolylmethyl groups at the disubstituted 2-position of the 3,4-disubstituted pyrrolenine ring have been investigated.[53] The results have shown that the rearrangement of pyrrolylmethylpyrrolenines matches exactly that proposed for the porphyrin biosynthesis and occurs readily under both acid-catalysed and thermal conditions. By far the major route for the rearrangement is by a mechanism involving fragmentation–recombination; indeed, it appears highly probable that this is the sole route; no evidence was found to implicate possible [1,5]-sigmatropic shifts in the process. A detailed investigation of the reaction path for the thermal rearrangement of 3,4-dihydro-1 αH-azirine[2,3-*c*]pyrrol-2-one to a cyanoketene–formaldimine complex has been carried out.[54]

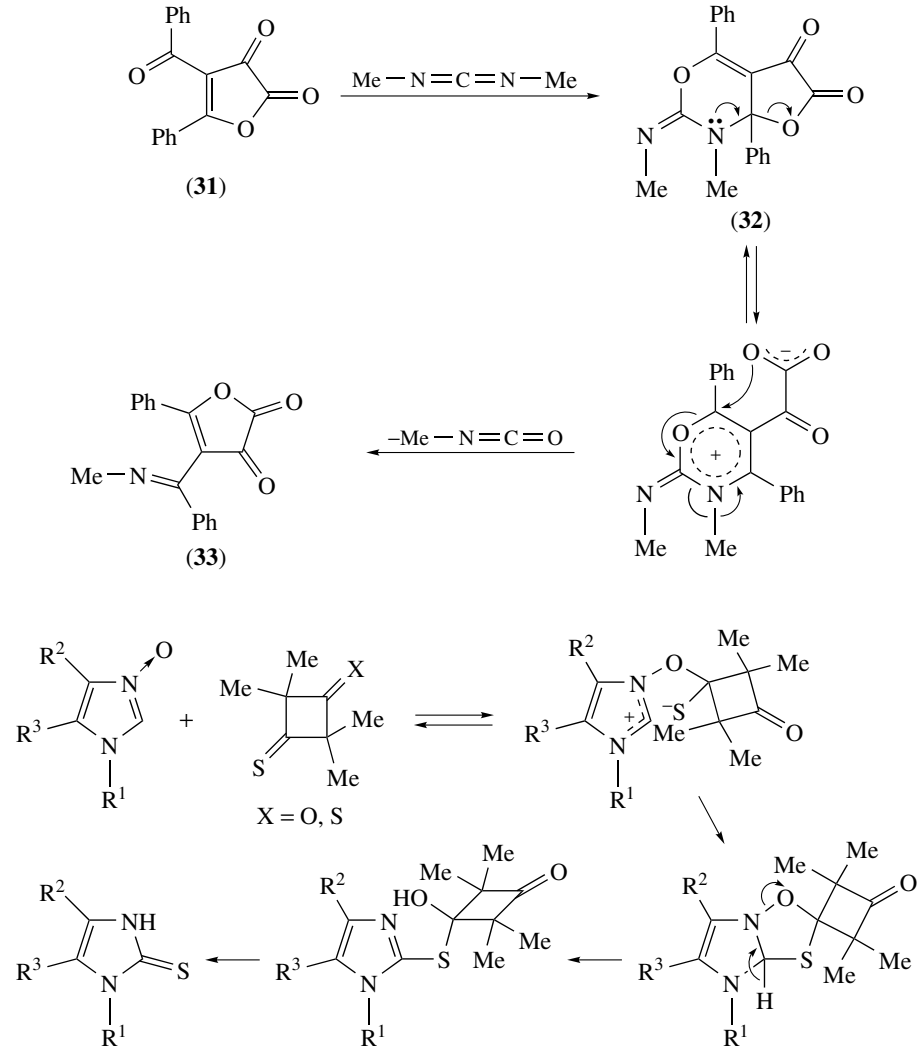
A review of the indoledione–indole rearrangement has appeared.[55] The photoirradiation of 1-ethoxy-2-phenylindole in methanol has been shown to afford 3- and 6-ethoxy-2-phenylindoles.[56]

An unexpected ring expansion of 5-isopropenyl-4,5-dihydrofuran-2,3-dicarboxylic acid (**27**) to 4,7-dihydro-6-methyloxepin-2,3-dicarboxylic anhydride (**30**) has been reported.[57] The transformation is thought to proceed via anhydride (**28**) which is converted into the seven-membered oxepindicarboxylic anhydride (**30**) via (**29**) to



SCHEME 15

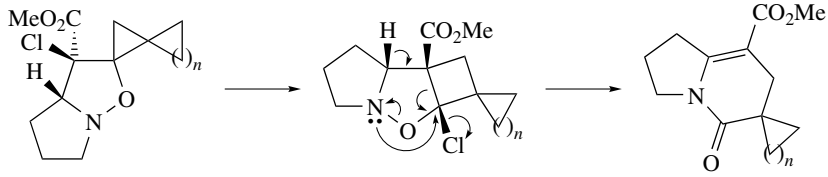
release the ring strain. A series of reactions involving the intramolecular Diels–Alder reaction of a furan diene with an allenyl ether dienophile, followed by alkylsulfinyl group, alkylsulfonyl group, and trimethylsilyl group rearrangements, has been accomplished.[58] A typical example of the methodology is outlined in Scheme 15. The reaction of 4-benzoyl-5-phenylfuran-2,3-diene (**31**) with carbodiimides has been shown to afford novel mono- and/or bi-cyclic heterocyclic systems. The reaction is considered[59] to start with a cycloaddition of the carbodiimide to the oxadiene moiety of (**31**) leading to adduct (**32**). These primary adducts undergo the furandione rearrangement, probably initiated by a 4 + 2-cycloreversion with loss of the corresponding isocyanate, leading to an iminobenzylfurandione system (**33**).



SCHEME 16

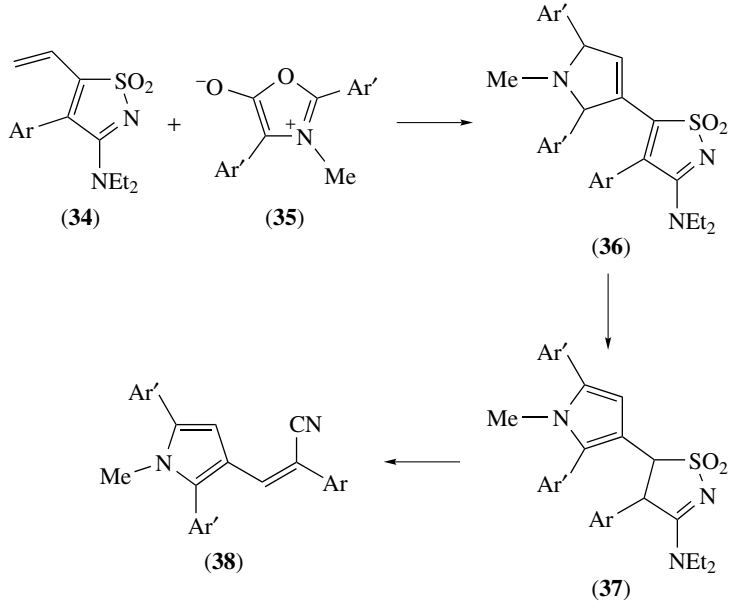
α-Carboline has been obtained[60] on pyrolysis of 1-benzylpyrazole in chloroform at 550 °C. 4-Benzoyl-5-hydroxy-3-trifluoromethylpyrazole derivatives have been synthesized by a new procedure[61] which involves the rearrangement of the benzoyl group in 5-benzoyloxy-4-bromo-3-trifluoromethylpyrazole derivatives via lithium–bromide exchange using *t*-butyllithium.

It has been demonstrated that the reaction of azole *N*-oxides with cycloalkane thiones offers a simple and efficient route to azole-thiones.[62] The described reaction sequence has subsequently been found to constitute a useful synthesis of imidazole-2(3*H*)-thiones (see Scheme 16).



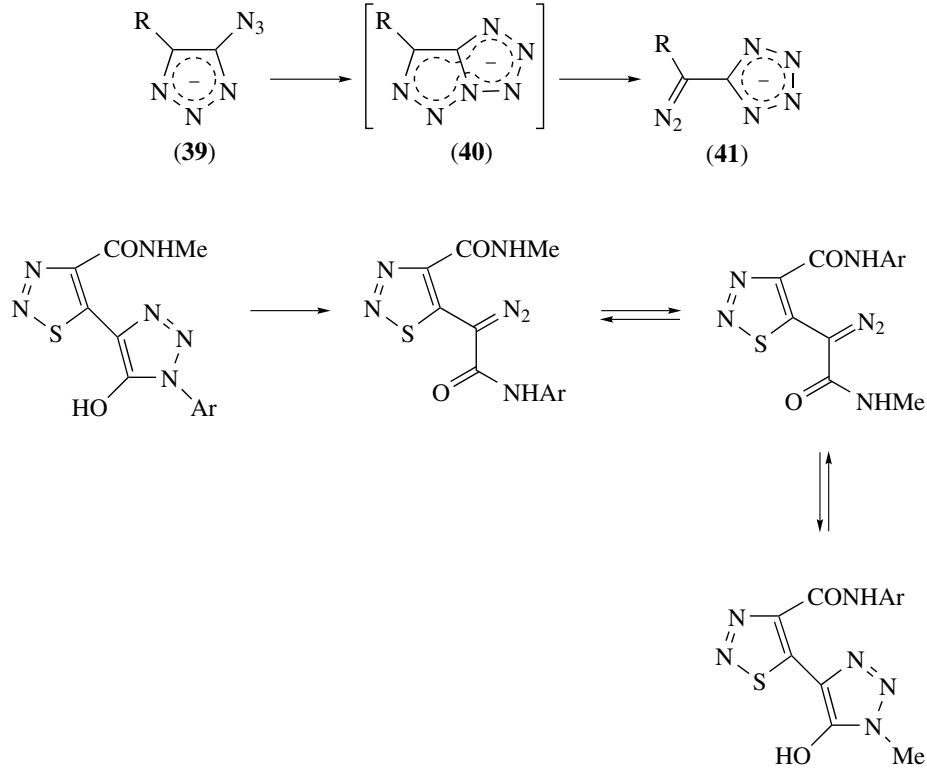
SCHEME 17

A new selective thermal cascade ring-enlargement process of 4-chloro-substituted spiro[cyclopropane-1,5′-isoxazolidines], leading to a new method for the synthesis of the indolizine skeleton, has been reported[63] (see Scheme 17). Apparently, the process is made possible by the presence of a chlorine substituent on the carbon α to the spirocyclopropane ring which facilitates a cyclopropyl-to-cyclobutyl ring enlargement mediated by a polar solvent.



In the presence of various metal ions, 2-(fluoroenone)benzothiazoline has been found to rearrange to *N*-2-mercaptophenylenimine,[64] while a free radical mechanism involving the homolysis of C−S and C−N bonds has been invoked[65] to explain the formation of 3-phenyl-1,2,4-triazole derivatives from the thermal fragmentation and rearrangement of 2-(arylidenehydrazino)-4-(5*H*)-thiazolone derivatives. The cycloadducts (**36**) formed from the reaction of 3-diethylamino-4-(4-methoxyphenyl)-5-vinyl-isothiazole 1,1-dioxide (**34**) with nitric oxides or münchnones (**35**) have been found[66] to undergo pyrolytic transformation into α, β-unsaturated nitriles (**38**) by way of pyrrole–isothiazoline 1,1-dioxide intermediates (**37**).

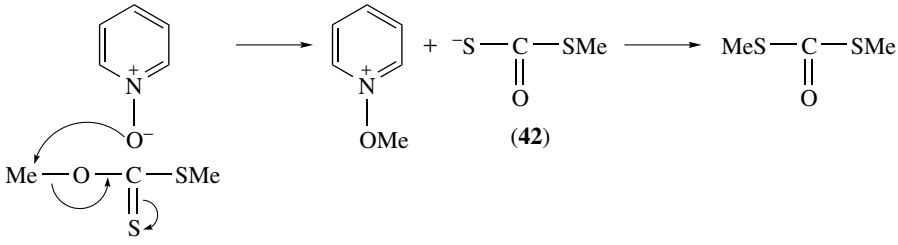
Spiro-fused tricyclic 7,8,9,10-tetrahydro-3*H*,5*H*-benzo[*d*]pyrrolo[1,2-*c*][1,2,3-triazoles] have been found to rearrange on heating to afford high yields of 1-arylamino-2-(4-cyanobutyl)-3,4-bis(alkoxycarbonyl)pyrroles.[67] An interesting base-catalysed rearrangement of α-benzotriazolyl alkoxide anions in the presence of aldehydes has been found to result in the formation of one-carbon homologated α-substituted alkyl ketones.[68] A detailed study of the rearrangement of substituted azido-1,2,3-triazolides (**39**) to (α-diazoalkyl)tetrazolides (**41**) via (**40**) has been undertaken.[69] Anions (**39**), having R = H, substituted Ph, and CO_2Me, were all found to react cleanly. A method for the synthesis of heterocyclic ring conjugates containing 1,2,3-triazole and 1,2,3-thiadiazole nuclei has been elaborated, and their rearrangements studied. A mechanism involving ring opening of the triazole ring to form the diazo compound which rearranges to the isomeric diazo compound followed by cyclization to the final product has been proposed[70] for these transformations (see Scheme 18). The isomerization of 5-(1-aryl-1,2,3-triazol-4-yl)-1,2,3-thiadiazole-4-(*N*-methyl)carboxamide to the corresponding *N*-arylcarboxamides has been studied. The isomerization is considered to proceed by a three-step process, involving ring opening, isomerization of the diazothiadiazole, and ring closure.[71]



SCHEME 18

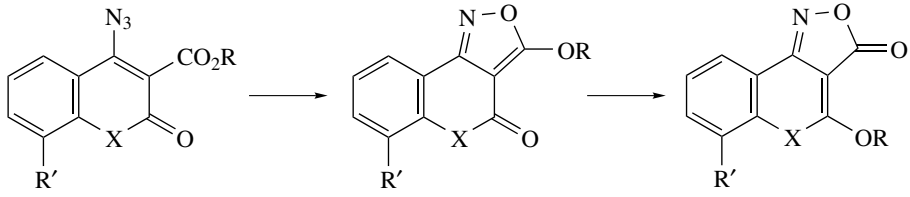
A theoretical study of degenerate Boulton–Katritzky rearrangements concerning the anions of 3-formylamino-1,2,4-oxadiazole and 3-hydroxy-iminomethyl-1,2,5-oxadiazole has been carried out.[72] The treatment has shown the participation of asymmetric transition states and non-concerted processes via symmetrical intermediates. A detailed *ab initio* and density functional study of the Boulton–Katritzky rearrangement of 4-nitrobenzofuroxan has indicated a one-step mechanism for the process.[73]

A study of the mechanism of the rearrangement of the oxide of a tertiary amine to the *O*-substituted hydroxylamine has been carried out by the semiempirical method AM1, using the *N*-oxide of *N*-(2,4-dinitrophenyl)piperidine as a model.[74] It has been proposed[75] that a benzidine rearrangement-type mechanism is the most likely mechanism for the acid-catalysed disproportionation of 4-[*N*′-(4-hydroxyphenylhydrazino)]pyridine and 4-(*N*′-phenylhydrazino)pyridine. A bimolecular mechanism involving an intermolecular transfer of the alkyl group, with inversion of configuration, to the *N*-oxide, followed by a second transfer of one of the alkyl groups of the cationic intermediate to one of the oxygens of the anionic intermediate, also with inversion of configuration, has been confirmed[76] to account for the thermal rearrangement of 2-alkoxypyridine-1-oxides to 1-alkoxy-2-pyridones. The pyridine *N*-oxide-catalysed thione-to-thiol rearrangement of *O,S*-dialkyl xanthates has been analysed[77] by semiempirical and *ab initio* molecular-orbital methods. The transition-structure analyses have indicated that the attack of pyridine *N*-oxide toward xanthates proceeds through an S_N2 mechanism to give the dithiolcarbonate anion (**42**), which acts as actual catalyst (see Scheme 19).



SCHEME 19

1-Alkyl-1,4-dihydro-4-imino-3-quinolinecarboxylates have been found to undergo basic hydrolysis to afford the corresponding 1-alkyl-4-oxo-3-quinolinecarboxylic acids together with a variety of other rearranged products.[78] Acridine has been obtained from the acid-catalysed rearrangement of *N*-aryl-2-vinyltetrahydro-4-oxoquinoline. A mechanism involving a retro-Michael process followed by the attack of the electron-rich aromatic ring on to the keto group has been proposed[79] for the transformation. Upon thermolysis, 4-azido-2-oxoquinoline 3-carboxylates (**43**; X = NH) and 4-azidocoumarin-3-carboxylates (**43**; X = O) have been found



(**43**) (**44**) (**45**)

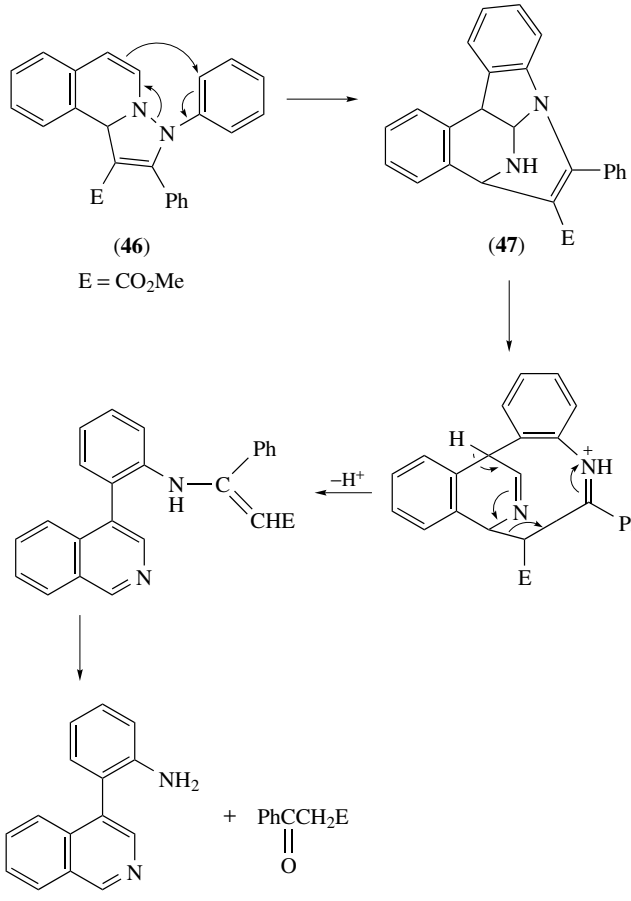
to cyclize to 3-alkoxyisoxazolo[4,3-*c*]quinolin-4(5*H*)-ones (**44**; X = NH) or the corresponding coumarins (**44**; X = O), whereas at slightly higher temperatures a 3-*O*, 4-*O* rearrangement was found to occur, yielding the 4-alkoxyisoxazolo[4,3-*c*]quinolin-3-ones (**45**; X = NH) and the corresponding coumarins (**45**; X = O). The mechanism for the formation of (**45**) from (**44**) is assumed to involve a thermally allowed suprafacial [1,5]-sigmatropic rearrangement.[80] 1,2,3,5,6,10b-Hexahydro-8,9-dimethoxypyrrolo[2,1-*a*]isoquinolin-2-ones have been obtained from the reaction of 5,6-dimethoxy-3,4-dihydroisoquinoline *N*-oxide with diketene. The formation of these novel hexahydropyrrolo[2,1-*a*]isoquinolines has been proposed[81] to arise via an initial cycloaddition reaction of the nitrone to the exocyclic double bond of diketene followed by a novel consecutive rearrangement involving NO bond cleavage rather than elimination of carbon dioxide. The cycloadducts (**46**) formed from isoquinolinium *N*-arylamides and acetylenic dipolarophiles have been found[82] to undergo a [3,3]-sigmatropic rearrangement to yield a pentacyclic product (**47**), which on treatment with strong base furnishes 4-(*o*-aminophenyl)isoquinoline and methyl benzoylacetate (see Scheme 20).

1,7b-Disubstituted cyclopropa[*c*]isoquinolines (**48**) have been found to undergo the usual thermal rearrangement to yield 5-substituted 2-benzazepines (**49**). However, when R^2 and $R^3 \neq H$ and either was an alkyl group, the reaction was found to divert into a new reaction pathway leading to the formation of 1,4-dihydro-4-alkenylisoquinolines (**50**) in high yield. It seems likely that these latter products are formed via a homo-[1,5]-sigmatropic hydrogen shift, a new mode of rearrangement for this system.[83]

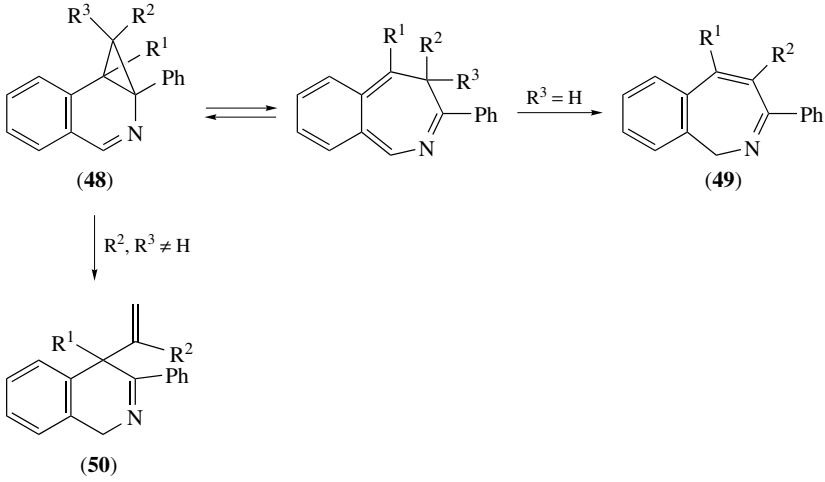
New rearrangements of 2-imino-2*H*-1-benzopyran-3-carboxamides under the action of anthranilic acid as an *N*-nucleophile have been revealed.[84] Depending on the conditions 2-(2-oxo-2*H*-1-benzopyran-2-yl)-3*H*-quinazolin-4-ones or 2-oxo-2*H*-1-benzopyran-3-(*N*-2-carboxyphenyl)carboxamides were found to be the products.

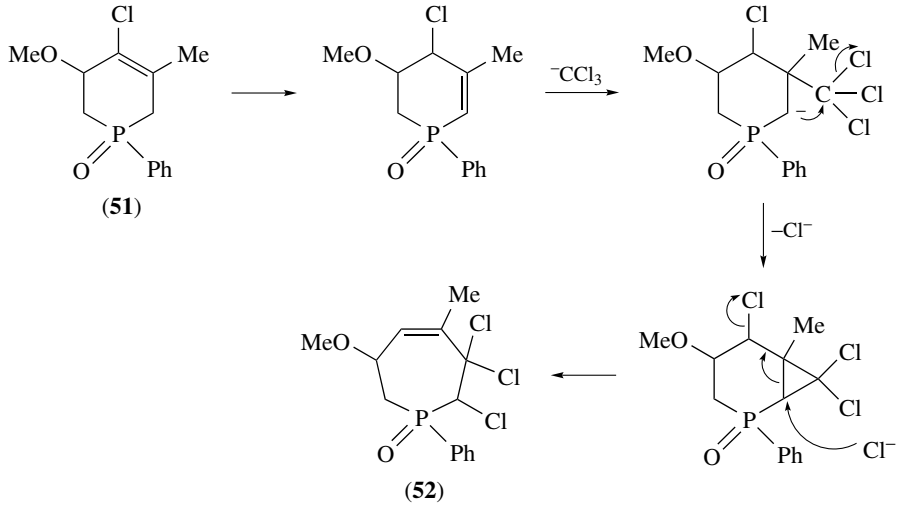
Reaction of the regioisomers of tetrahydrophosphinine oxide (**51**) with $NaOH–H_2O–CHCl_3$ under phase-transfer conditions was found to afford tetrahydrophosphepine oxides (**52**) through an unexpected path[85] involving isomerization of (**51**) and cyclopropanation via Michael addition of $^{-}CCl_3$. (Scheme 21).

Advances in the Dimroth rearrangement in the adenine series have been reviewed.[86] *N*-1-Methoxy derivatives of adenosine and 2′-deoxyadenosine have been found to

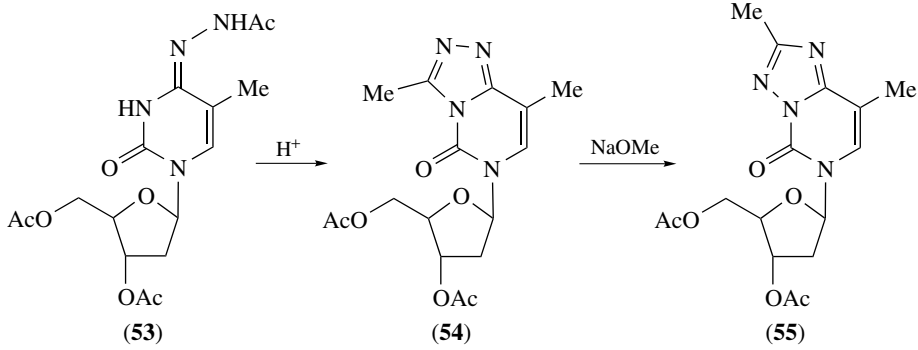

N
N
E
Ph
(46)
E = CO2Me
N
NH
Ph
E
(47)
H
+
NH
N
Ph
E
–H+
Ph
N
H
C
CHE
N
NH2
N
+ PhCCH2E
O

SCHEME 20


R3
R2
R1
Ph
N
(48)
R1
R2
R3
Ph
N
R3 = H
R1
R2
Ph
N
(49)
R2, R3 ≠ H
R1
R2
Ph
N
(50)

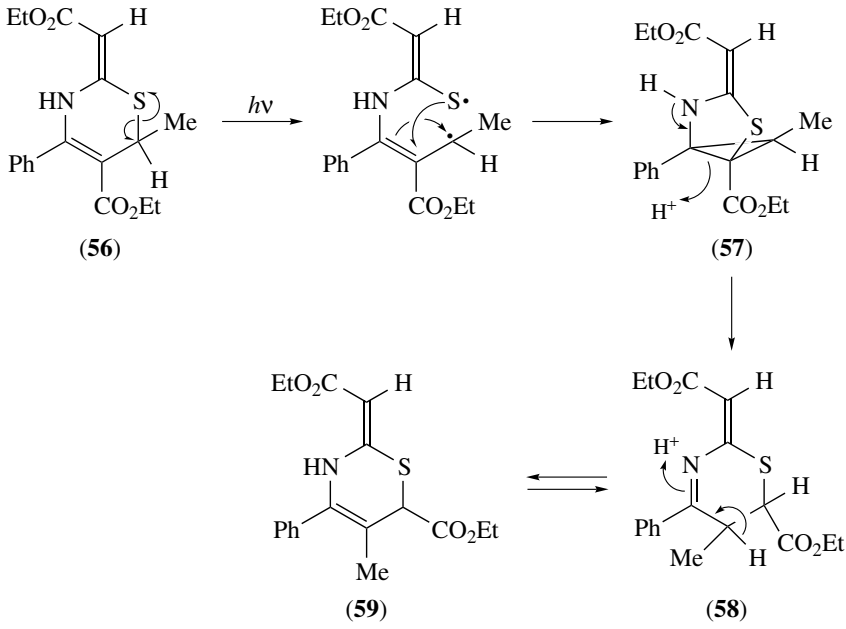


SCHEME 21



undergo a Dimroth rearrangement in which the intermediate *N,N*-dimethylamino adducts turn out to be stable compounds.[87] It has been shown[88] that, in reactions between styrene oxide and the ring nitrogen at the 1-position of deoxyadenosine, the epoxide is opened at both the α-(benzylic) and β-carbons. The 1-substituted nucleosides formed in the reaction are unstable and have been found to undergo either Dimroth rearrangement to give *N*-6-substituted deoxyadenosines or deamination to give 1-substituted deoxyinosines. The 1,2,4-triazolo[4,3-*c*]pyrimidinone (**54**) formed by acid-promoted cyclization of *N*-4-acetylamino-2′-deoxycytidine (**53**) has been observed[89] to isomerize under basic conditions via a Dimroth-type rearrangement to yield the 1,2,4-triazolo[1,5-*c*]pyrimidinone (**55**). The Dimroth rearrangement of a new class of tetracyclic condensed quinolines, viz. pyrimido[4′, 5′:4,5]selenolo[2,3-*b*]quinolines, has been studied.[90]

A possible mechanism for the observed[91] photochemical rearrangement of dihydrothiazine (**56**) to dihydrothiazine (**59**) is shown in Scheme 22. It involves a

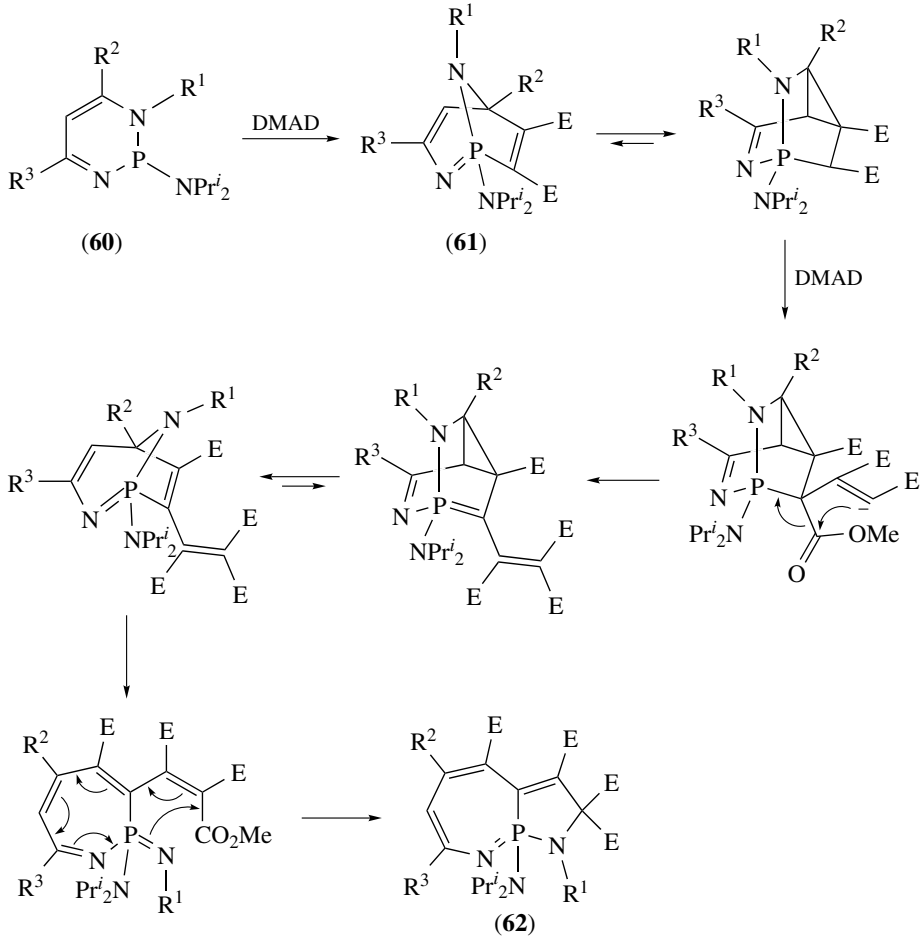


SCHEME 22

sulfur–carbon homolysis followed by ring closure to the cyclopropathiazolidine (**57**) which could ring open to the photo-product (**58**). A subsequent hydrogen shift would give the dihydrothiazine (**59**).

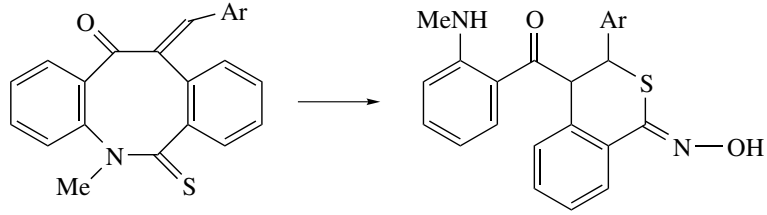
It has been shown[92] that readily available 1,2-dihydro-1,3,2-diazaphosphinines (**60**) are excellent precursors for the efficient synthesis of novel phosphorus heterocycles. Thus reaction with acetylenic diesters yields the monoadduct (**61**) which is readily converted into the λ^5-diazaphosphaazulene skeleton (**62**), probably by the pathway outlined in Scheme 23.

The reaction of the benzylidene derivative of 5-methyl-6-thioxo-5,6,11,12-tetrahydrodibenzo[*b*,*f*]azocin-12-one (**63**) with hydroxylamine has been found[93] to initiate a novel rearrangement to yield the hydroximinoisothiochromene (**64**), while the mechanism shown in Scheme 24 has been invoked[94] to explain the formation of 2,3,4,4a-tetrahydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one-1-carboxylic acids from the treatment of 1,10,11,11a-tetrahydropyrrolo[2,1-*c*][1,4]benzodiazepin-5,11-diones (**65**) with concentrated hydrochloric acid. De Lucca[95] has discovered that hexahydro-5,6-dihydroxy-1,3-diazepin-2-ones can undergo a stereospecific, stereoselective rearrangement, ring contraction reaction to give the corresponding tetrahydro-5-hydroxypyrimidin-2-ones. He proposed that the rearrangement proceeds through the formation of the aziridinium cationic intermediate (**66**) which is subsequently opened by nucleophilic attack at the less hindered carbon to give the rearranged product (see

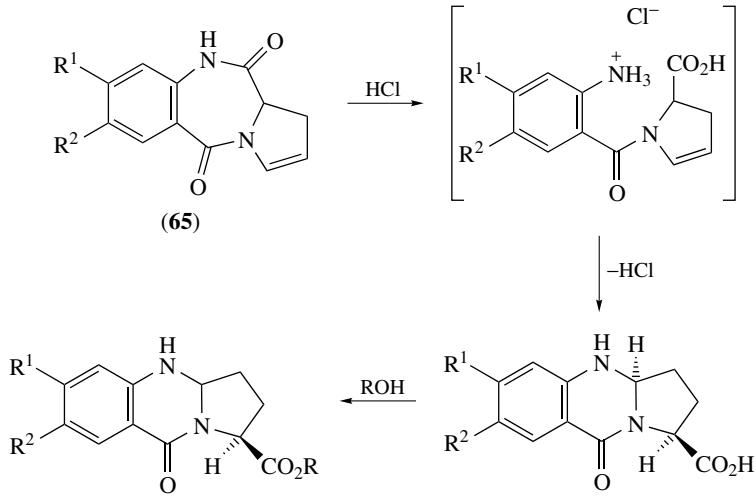


(**60**) (**61**) (**62**)

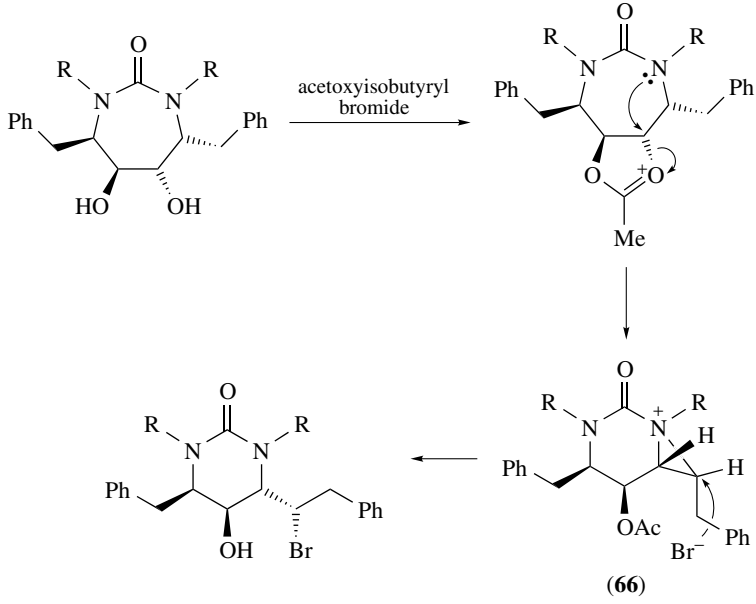
SCHEME 23



(**63**) (**64**)



SCHEME 24

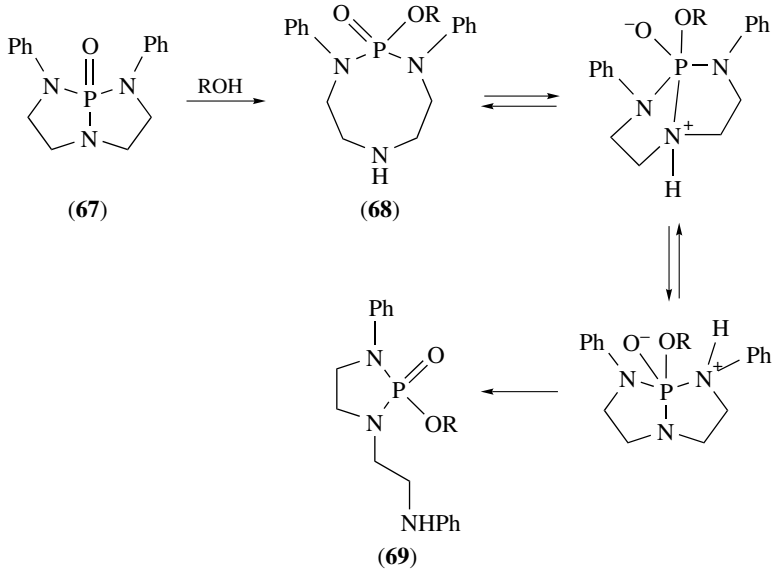


SCHEME 25

Scheme 25). 1-Oxo-2,8-diphenyl-2,5,8 triaza-1 λ^5-phosphabicyclo[3.3.0]octane (**68**) formed by acid catalysis of the bicyclic phosphoric triamide (**67**) has been found to isomerize via a new type of rearrangement to yield the ring contracted 3-[2-(phenylamino)ethyl]-2-oxo-2-ethoxy-1-pheny1-1,3,2 λ^5-diazaphospholidine (**69**). The rearrangement has been explained[96] in terms of intramolecular 1,5-nucleophilic attack

of the amine nitrogen at the phosphoryl centre, followed by proton transfer and P−N bond cleavage (see Scheme 26).

The origin of equilibria (see Scheme 27) involving 16-membered diimine, 24-membered triimine, and 32-membered tetraimine oligomers of 3,4-dihydro-2*H*-1,5-benzooxazocines and -benzothiazocines and 1,2,3,4-tetrahydro-1,5-benzodiazocines has been ascribed to facile acid-catalysed rearrangements between the macrocyclic imines. A stepwise mechanism involving 1,3-diazetidine intermediates has been suggested.[97]



SCHEME 26

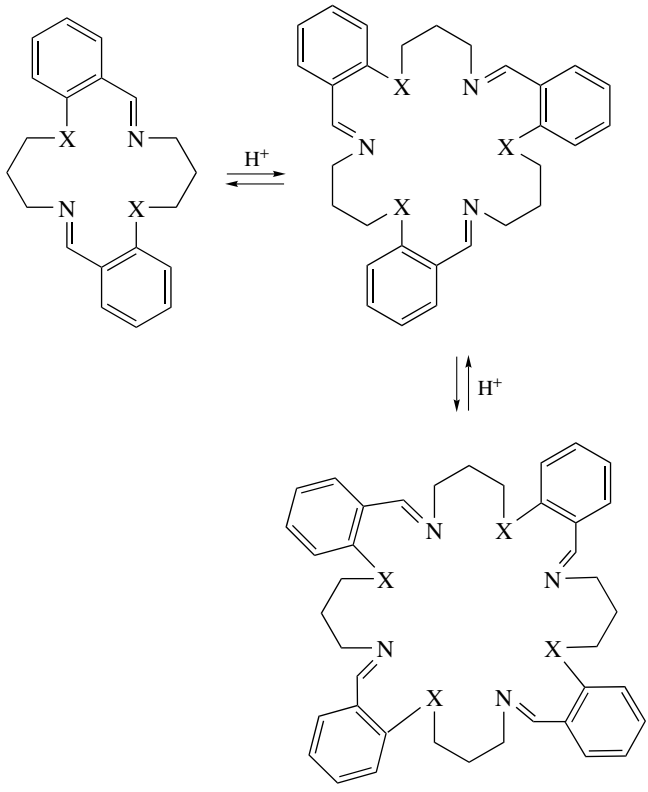
Sigmatropic Rearrangements

[3,3]-Migrations

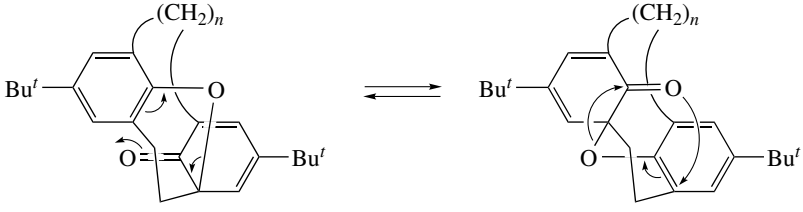
Claisen and related rearrangements

A review of Claisen rearrangements in aqueous solution has appeared.[98] The synthesis of natural products utilizing tandem Diels–Alder additions with sigmatropic rearrangement processes has been reviewed,[99] and a brief review of the regioselective synthesis of coumarins, quinolones and thiocoumarins with 3,4-fused pyran or furan ring systems by the Claisen rearrangement has been presented.[100]

A quantum-chemical study has been undertaken[101] on the isomerization of *cis*-1-vinyl-, -1-formyl-, -1-thioformyl-, and -1-iminomethyl-2-vinylcyclopropane to cyclohepta-1,4-diene, 2,5-dihydrooxepine, 2,5-dihydrothiepine, and 2,5-dihydroazepine, respectively. Reaction pathways for circumambulatory rearrangements of main group migrants (NO, PO, NCS, SCN, NCO, OCN, SR, Cl, Br, and XX where X



SCHEME 27

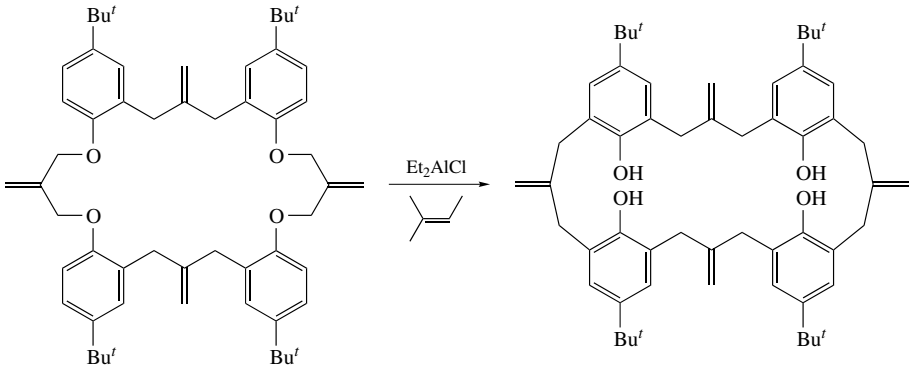


(**70**) (**71**)

is CH_2, NH, O, S) around the periphery of a cyclopropene ring have been studied computationally by the use of semiempirical methods.[102]

Zeolites[103] and silica gels and mesoporous molecular sieves[104] have been used to initiate Claisen rearrangements. A synthetic route has been devised[105] to the neurotrophic illicinones using sequential aromatic Claisen rearrangements, and it has been systematically demonstrated[106] for the first time that the strain of a medium ring lowers not only the rearrangement barriers but also the conformational fixation of a [3,3]-sigmatropic rearrangement by means of the bridge; see (**70**) ⇄ (**71**).

A new method has been developed for the preparation of calixarene analogues[107] from macrocyclic polyethers via intramolecular successive carbon–carbon bond formation in a tandem Claisen rearrangement, and a similar tandem Claisen rearrangement promoted by Et_2AlCl and 2-methylbut-2-ene, has been used[108] to synthesize macrocycles containing phenolic moieties from the corresponding macrocyclic polyether compounds (see Scheme 28). A number of furo[3,2-*c*:5,4-*f*]bis[1]benzopyran-3-ones have been synthesized regioselectively by the sequential [3,3]-sigmatropic rearrangements of 6-(4-aryloxybut-2-yn-1-yloxy) [1]benzopyran-2-ones.[109]

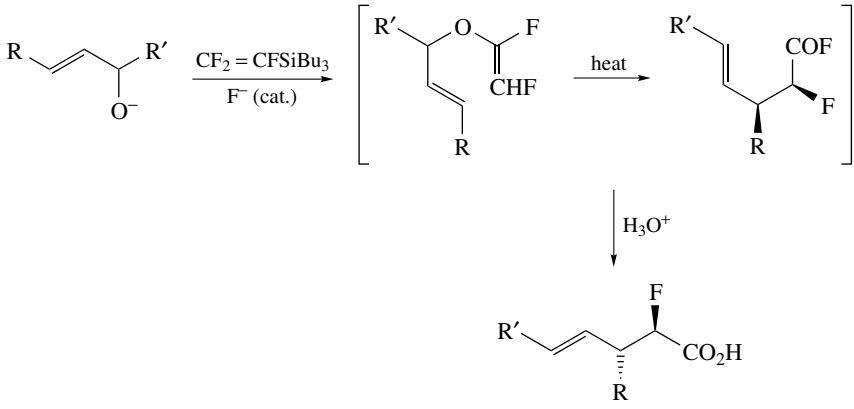


SCHEME 28

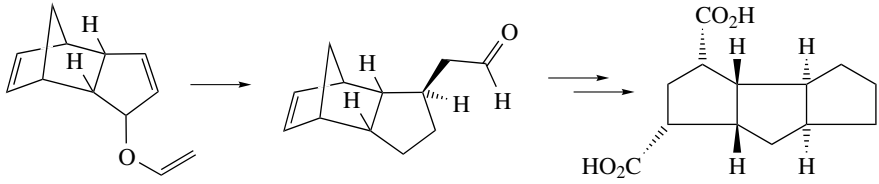
The ratios of nucleophilic substitution versus [3,3]-sigmatropic rearrangement for the collapse of allenyl(aryl)iodine(III), generated from the reaction of aryliodanes with propargylsilanes in the presence of $BF_3.OEt_2$ in alcohols, have been determined. The mechanism proposed by the authors[110] involves the generation of propargyl cations from the allenyliodine (III) via a unimolecular pathway.

The $SnCl_4$-catalysed Claisen and Cope rearrangements of *N*-allylanilines and *N*-allylenamines,[111] and the effect of *meta*-substituents in the aromatic ring on the Claisen aromatic amino rearrangement of a series of fluorinated anilines,[112] have been investigated.

A short and novel synthesis of hitherto unknown 3-allylbenzofurans using a Wittig olefination of protected 2-hydroxybenzaldehydes followed by a Claisen rearrangement, has been described.[113] The enantioselective Claisen rearrangement of difluorovinyl allyl ethers has been achieved[114] for the first time in moderate-to-good enantioselectivity using a chiral boron reagent as the Lewis acid, and a one-pot synthesis of α-fluoro-β-substituted-γ-unsaturated acids via a diastereoselective Claisen rearrangement of allylfluorovinyl ethers has been described[115] (see Scheme 29). The one-pot combination of a Claisen rearrangement of allyl vinyl ethers followed by a rhodium-catalysed intramolecular hydroacylation has been used as a key step in the synthesis of spiro[4.5]decan-2-ones,[116] and in the synthesis of erythrodiene and spirojatamol,[117] and a short, versatile synthesis of pseudo-sugars from sugars utilizing



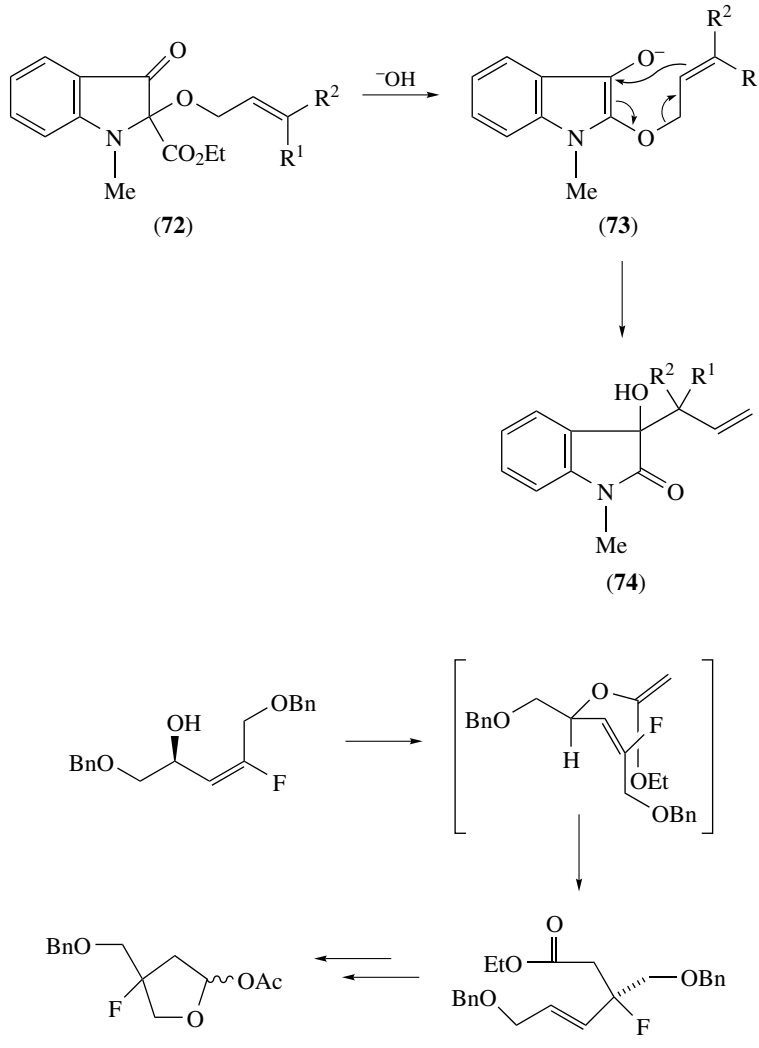
SCHEME 29



SCHEME 30

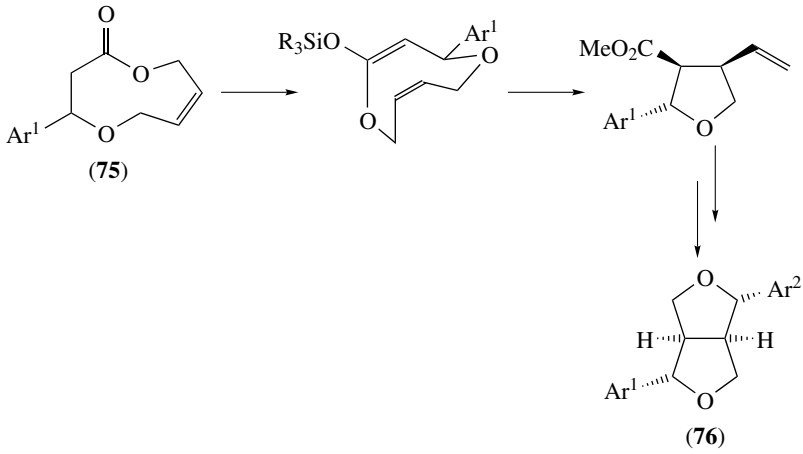
the Claisen rearrangement as the key step has been reported.[118] A Claisen rearrangement methodology using lithium perchlorate–diethyl ether-mediated rearrangement of α- and β-endo-dicyclopentadienyl vinyl ethers has been exploited[119] for the stereospecific generation of new chiral centres in the synthesis of linear triquinanes (see Scheme 30). The conversion of 1,2-di- and 1,2,4-trichloro-6,9-dioxaspiro[4.4]non-1-en-3-ones into 5-allyl(allenyl)-5-chloro-2-(2-hydroxyethyloxy)cyclopent-2-ene-1,4-diones has been reported.[120]

A two-step synthesis of functionalized dienoic esters has been devised starting from γ-hydroxyvinyl sulfones.[121] Johnson–Claisen and Eschenmoser–Claisen rearrangements of chiral γ-trifluoromethylated allylic alcohols have been shown to be important methods for the preparation of highly functionalized chiral trifluoromethylated compounds.[122] Diastereoselective γ-alkylation of unsaturated carboxylic acids has been attained by esterification of the acid with allylic alcohols and consecutive Ireland–Claisen and Cope rearrangements.[123] The formation of 3-allyl-3-hydroxy-1-methylindol-2(3*H*)-one (**74**) from 2-allyloxyindole keto ester (**72**) has been explained[124] by invoking a Claisen rearrangement of transient 2-allyloxy-3-hydroxymethylindole (**73**) generated by decarboxylation of (**72**). The Ireland–Claisen rearrangement has been employed to provide an efficient route for the stereoselective synthesis of 2,3-disubstituted succinates,[125] and matrix metalloproteinase inhibitors have been synthesized by a route involving an Ireland–Claisen rearrangement which has allowed systematic modification of the substituent α to the hydroxamic function.[126]

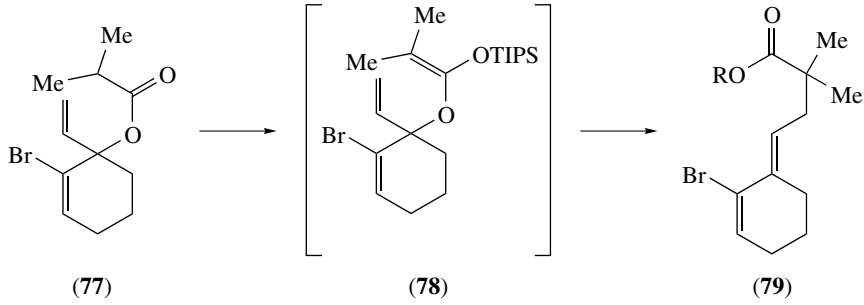


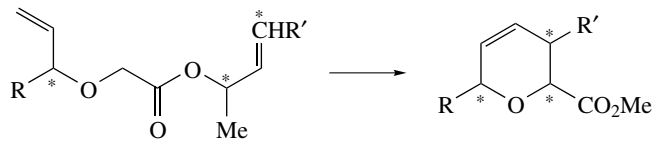
SCHEME 31

A novel synthetic method which can provide enantiomeric apionucleosides with high enantioselectivity has been developed[127] using a [3,3]-sigmatropic Claisen rearrangement (see Scheme 31), and a new diasterospecific approach based on the Ireland–Claisen rearrangement of unsaturated oxamacrolides (**75**) has been used[128] to synthesize furanofuran lignans (**76**) (see Scheme 32). Unsymmetrical bis-allyl silyl-ketene acetals (**78**), derived from cyclohexenones (**77**), have been found to undergo regio- and stereo-selective Ireland–Claisen rearrangements[129] to afford alkylidenecyclohexenes (**79**) in good yield. From a mechanistic point of view an *exo*-Claisen pathway is preferred for the process. A stereochemically general



SCHEME 32

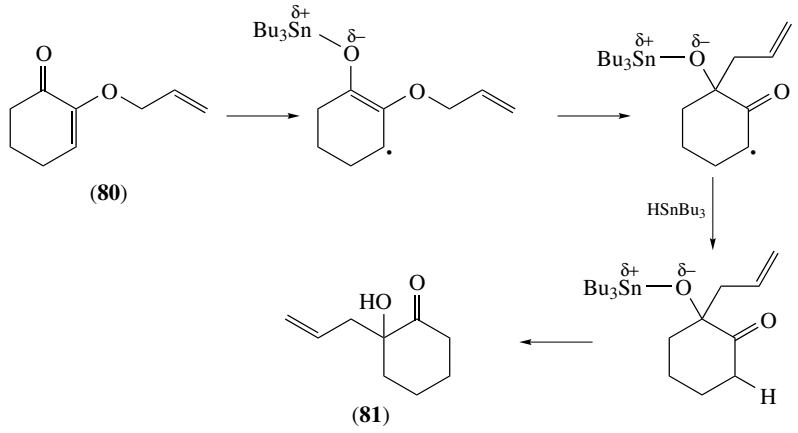




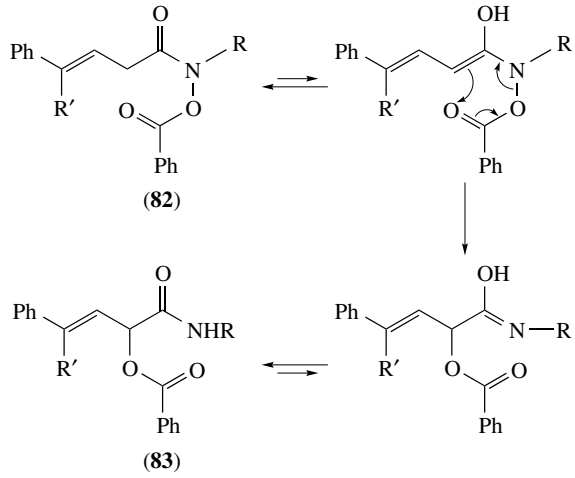
SCHEME 33

synthesis of substituted dihydropyran-2-carboxylates involving a tandem glycolate Claisen rearrangement/ring-closing metathesis has been described[130] (see Scheme 33). It has been demonstrated[131] that Claisen rearrangements can be 'triggered' by a tin-associated ketyl radical anion. Thus treatment of (**80**) with tin hydride and 2,2′-azobisisobutyronitrile afforded the rearranged α-hydroxy ketone (**81**) (see Scheme 34).

It has been shown that the Claisen rearrangement of lithium enolates of amino acid enynol esters allows the synthesis of very sensitive γ, δ-unsaturated amino acids with conjugated enyne side chains.[132] The chelate–enolate Claisen rearrangement has also been applied to the synthesis of unsaturated polyhydroxylated amino acids,[133] polyhydroxylated piperidines,[134,135] and unsaturated peptides.[136]



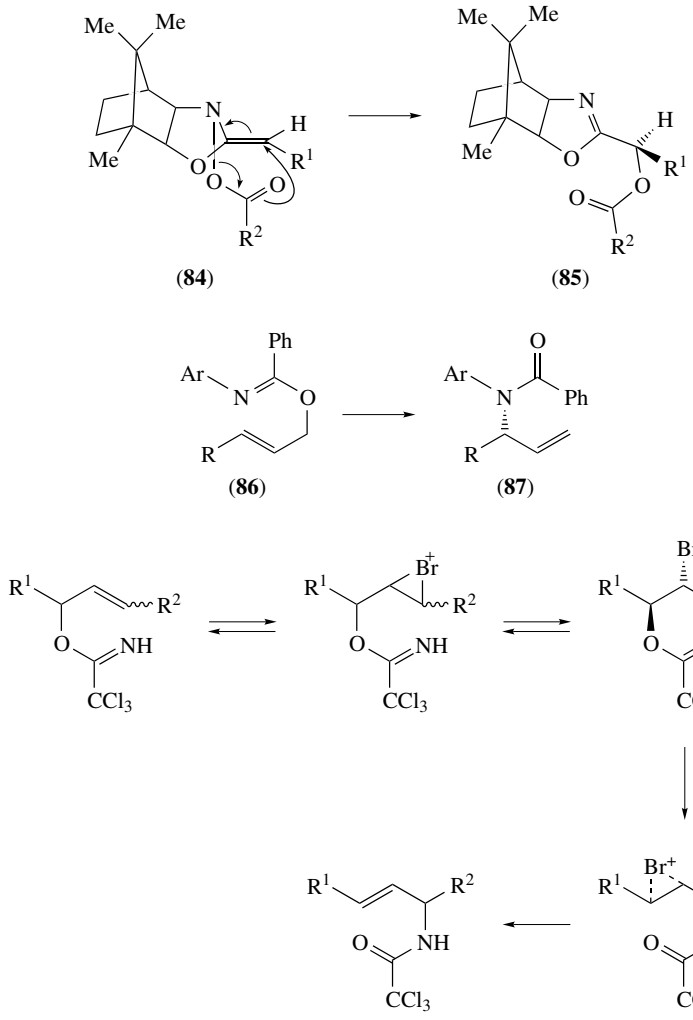
SCHEME 34



SCHEME 35

4-(2-Aminoethyl)indoles have been prepared[137] from 3-hydroxy-2-methoxyindolines by way of a Claisen *o*-amide rearrangement. *O*-Acylhydroxamic acid derivatives (**82**) have been found to undergo a base-catalysed rearrangement to give secondary 2-acyloxyamides (**83**). The authors[138] have suggested that the mechanism proceeds via an anionic hetero[3,3]-sigmatropic rearrangement of the corresponding enol or enolate (see Scheme 35). In the presence of various acylating agents, camphor-derived oxazoline *N*-oxides (**84**) have been found to afford α-acyloxyoxazolines (**85**) resulting from a diastereoselective [3,3]-rearrangement.[139]

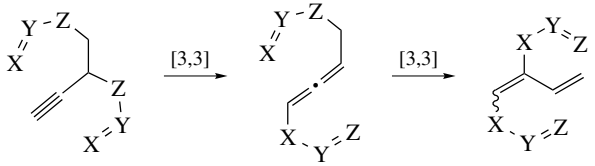
The asymmetric aza-Claisen rearrangement of allyl imidates, (**86**) $\rightarrow$ (**87**), has been shown to be catalysed by homochiral cationic palladium(II) complexes,[140] and a series of enantiopure cyclopalladated ferrocenyl amines and imines have been



SCHEME 36

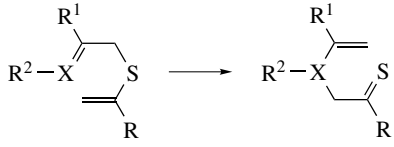
established[141] as efficient catalysts for the [3,3]-sigmatropic rearrangement of allylic imidates to allylic amides. Improved conditions have been developed[142] for the [3,3]-sigmatropic rearrangement of trichloroacetamides, and a novel, efficient and stereospecific method for the [3,3]-sigmatropic rearrangement of (*E*)-allylic trichloroacetimidates bearing electron-withdrawing groups has been reported[143] (see Scheme 36). A sequence of [3,3]-sigmatropic isomerizations of the type (**88**) → (**89**) → (**90**) has been utilized to provide a convenient approach to 1,2-difunctionalized buta-1,3-dienes.[144]

A theoretical study of substituent effects in the thio-Claisen rearrangement (**91**) → (**92**) has been carried out. The study[145] has shown that 2,5-disubstitution leads to tighter transition states and to a substantial lowering of the enthalpy of



(**88**) (**89**) (**90**)

e.g. XYZ = C−CO_2R, C−C=C



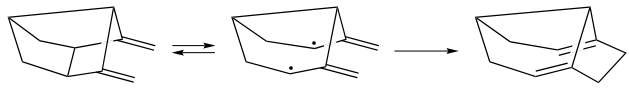
(**91**) (**92**)

X = CH, N

activation. Quantum-chemical calculations of the [3,3]-sigmatropic rearrangement of *S*-allyl *O*-methyl *N*-(2- and 4-substituted acridin-9-yl)thiocarbonimidates have pointed to a chair configuration in the transition state of the reaction,[146] and a new synthetic route to *N*-allyl-*N*-(9-acridinyl)thiocarbamic acid *O*-methyl and *S*-methyl esters via the [3,3]-sigmatropic rearrangement of *O*(*S*)-methyl-*S*(*O*)-allyl-*N*-(9-acridinyl)iminothiocarbonates has been elaborated.[147] The thio-Claisen rearrangement has proved to be a powerful synthetic tool in the preparation of a (−)-trichodiene intermediate bearing vicinal stereogenic quaternary centres.[148] A recent analysis has shown that the concerted [3,3]-sigmatropic rearrangement of allylic xanthates in protic solvents, and the ionic rearrangement in hydroxylic solvents, are extremes in a continuous spectrum of mechanism for the thione-to-thiol rearrangement. The solvation mode for the rearrangement via an ionic intermediate was found to be different from that of the concerted mechanism.[149]

Cope and related rearrangements

Characteristics and energetics of the photo-induced electron-transfer degenerate Cope rearrangement of 2,5-diarylhexa-1,5-dienes have been reported in detail.[150] Oxygen-trapping experiments have established[151] the two-step nature of the rearrangement of (**93**) to (**94**) (see Scheme 37), while it has been shown that both [2.2.2]propellane and the Cope rearrangement of hexa-1,5-diene follow reaction paths that pass through singlet diradicaloid portions of the potential-energy surface.[152] A theoretical analysis of the Cope rearrangements of hexa-1,5-diyne, hexa-1,2-dien-5-yne, hexa-1,2,5-triene,

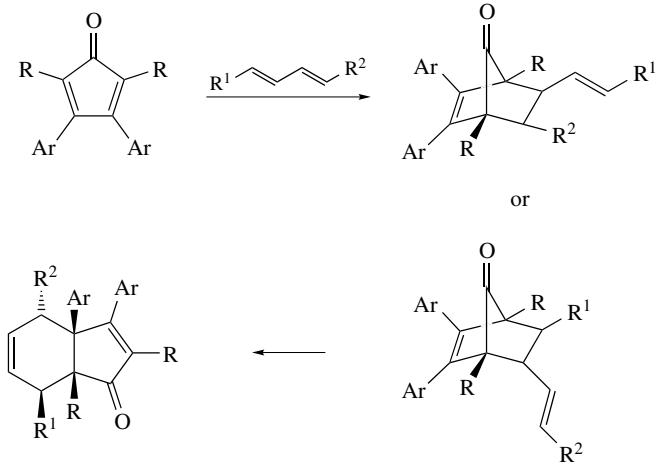


(**93**) (**94**)

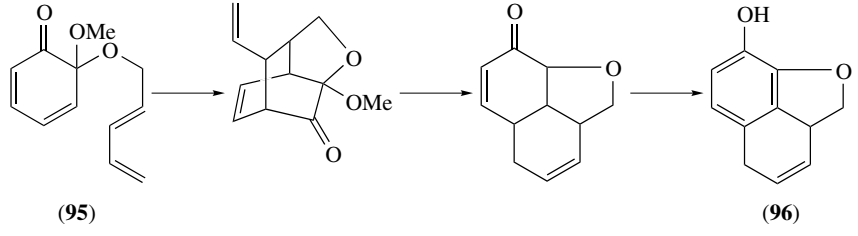
SCHEME 37

hexa-1,2,4,5-tetraene, and hexa-1-en-5-yne, has been undertaken.[153] In each case the mechanism was predicted to be concerted through an aromatic transition state. The effect of deuterium substitution on the positional equilibrium and rate of the Cope rearrangement of barbaralone-*d*(1) has been investigated[154] by ^{1}H and ^{13}C dynamic NMR spectroscopy. It has been proposed that every transition state should be accompanied by a bond-excited state with a similar structure, the properties of which should in principle be measurable by spectroscopic methods and can thus constitute a source of information about the transition state. This idea has been demonstrated computationally through the example of the degenerate Cope rearrangement of semibullvalene.[155] The effects of substituents on the degenerate Cope rearrangement of semibullvalenes and barbaralones have been reviewed,[156] and the mechanism of the Cope rearrangement in halobullvalenes in solution and in the solid state has been investigated by NMR techniques.[157]

It has been established[158] that the course of the sequential pericyclic reaction of cyclopentadienones with acyclic conjugated alkadienes depends on the reaction temperature, thermal treatment at low temperatures affording 3a,4,7,7a-tetrahydroinden-1-one derivatives by way of a Cope rearrangement (see Scheme 38). Roman *et al.*[159] have developed an efficient stereoselective synthesis of enantiomerically pure 1-nitrotricyclo[5.2.2.0^{2,6}]undeca-3,8-dienes via a tandem consecutive asymmetric Diels–Alder–Cope rearrangement (see Scheme 39). Adducts



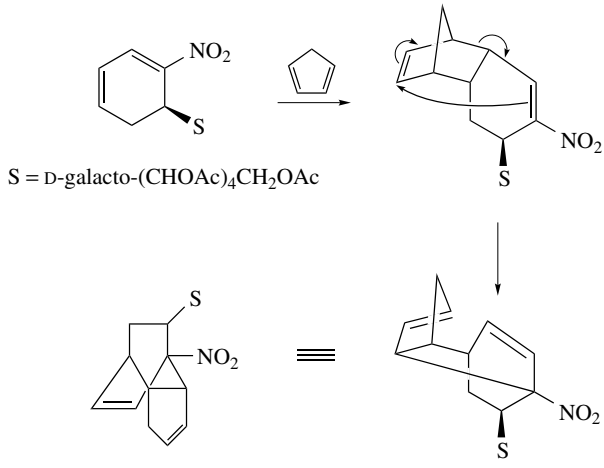
SCHEME 38



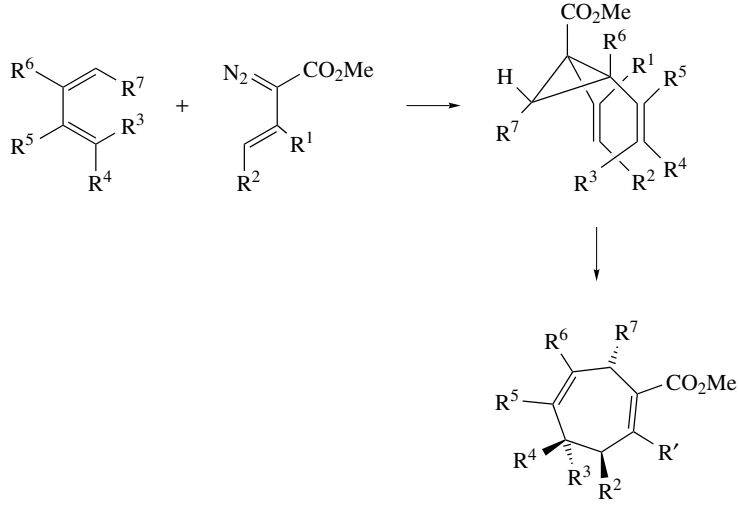
(**95**) (**96**)

of the intramolecular Diels–Alder reaction of *o*-benzoquinone monoketals, viz. (**95**), have been rapidly converted via Cope rearrangements to naphthofurans (**96**) and phenanthrofurans related to (−)-morphine.[160] Catalytic amounts of bis(benzonitrile)palladium(II) chloride have been found[161] to enhance the Cope rearrangement of germacranolides to elemanolides.

Rhodium(II) (*N*-dodecylbenzenesulfonyl)prolinate has been found to act as an effective catalyst for the enantioselective decomposition of vinyldiazoacetates to *cis*-divinylcyclopropanes. Combination of this process with a subsequent Cope rearrangement has resulted[162] in a highly enantioselective synthesis of a variety of cycloheptadienes containing multiple stereogenic centres (see Scheme 40). The tandem



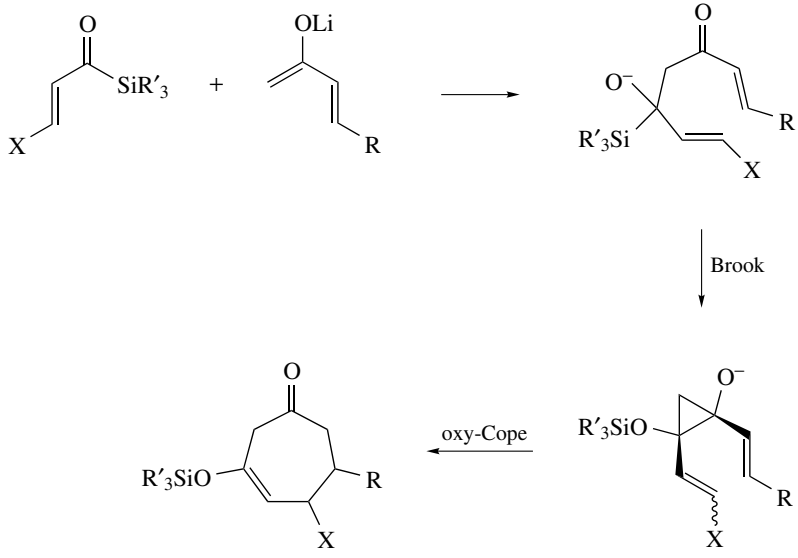
SCHEME 39



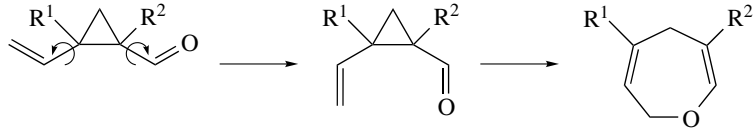
SCHEME 40

cyclopropanation–Cope rearrangement sequence has been used to synthesise members of the tremulane sesquiterpenes.[163] A useful and mechanistically interesting 3 + 4-annulation methodology has been reported for the stereo-controlled construction of highly functionalized cycloheptenone derivatives. The reaction has been presented[164] as an anionic oxy-Cope reaction of a 1,2-divinylcyclopropanediol intermediate generated via a Brook rearrangement of the 1,2-adduct of a lithium enolate (see Scheme 41). The prototypical 1,2-*cis*-vinylcyclopropanecarbaldehyde to 2,5-dihydrooxepin hetero-Cope type rearrangement (see Scheme 42) has been studied[165] by density functional theory. Divinylcarbinols of the type (**97**) have been found to undergo oxy-Cope rearrangement very rapidly at low temperatures although the rearrangement was found to proceed in a reversible manner. It appears[166] that the return to alkoxide can materialize only as long as the enolate anion has its oxygen atom oriented up towards the methano bridge as in (**98**). However, such a structure is thermodynamically unstable relative to its oxygen-down form (**99**).

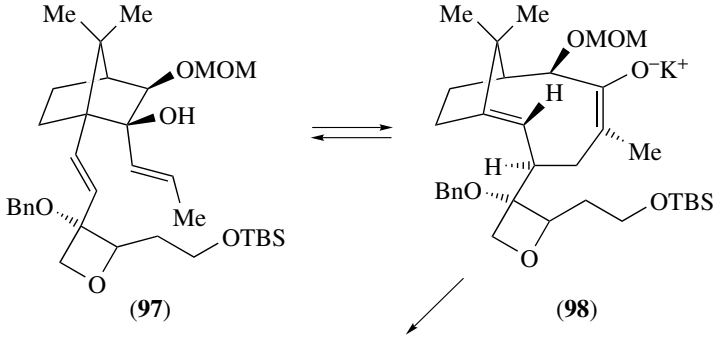
NMR and kinetic studies have been carried out[167] on the antibody-catalysed oxy-Cope rearrangement of hexadiene (**100**) to aldehyde (**101**). An aromatic oxy-Cope rearrangement involving a benzene ring [see (**102**) → (**103**)] has been observed to



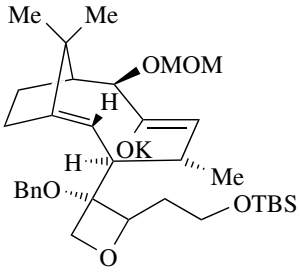
SCHEME 41



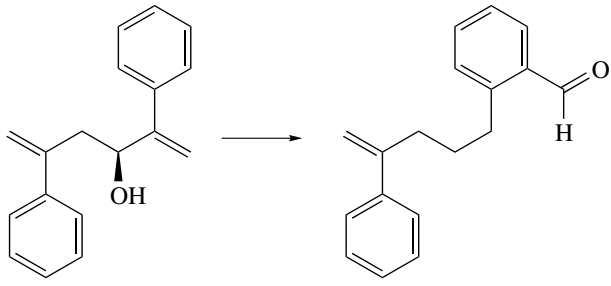
SCHEME 42



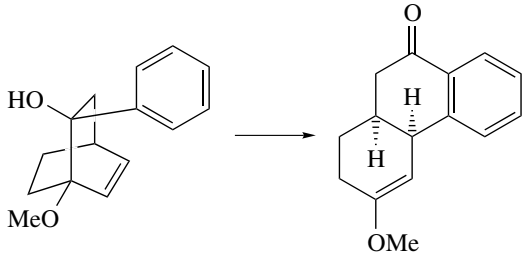
(**97**) (**98**)



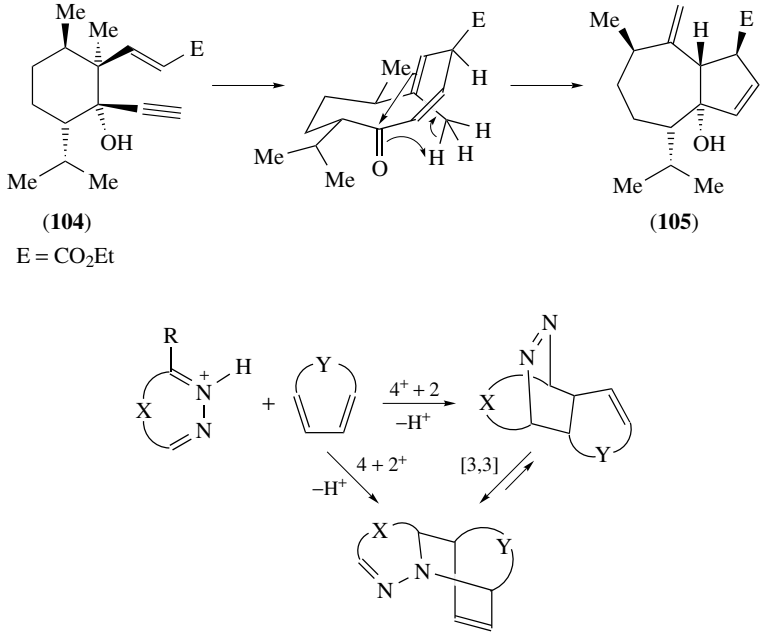
(**99**)



(**100**) (**101**)



(**102**) (**103**)

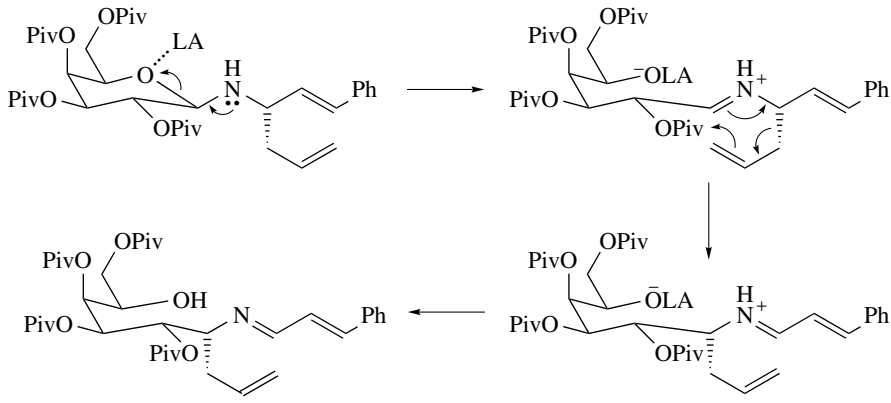


SCHEME 43

take place[168] when 1-methoxy-2-arylbicyclo[2.2.2]oct-5-en-2-*exo*-ols are treated with potassium hydride in THF. The thermally allowed oxy-Cope rearrangement of the optically active ethynyl alcohol (**104**) has been used[169] to construct the functionalized hydrazulenoid skeleton (**105**). A short, stereoselective synthesis of the C(1)−C(10) polyol fragment of nystatin A has been achieved[170] using a highly selective and efficient oxy-Cope rearrangement of a chiral unprotected aldol product as the key step, and a stereoselective synthesis of the natural product (+)-lasiol has been carried out in a similar manner using a silyloxy-Cope rearrangement of a chiral aldol product.[171] It has been demonstrated for the first time[172] that an anion-accelerated oxy-Cope rearrangement can produce strained medium-ring compounds from larger, less strained carbocycles.

The first unambiguous glimpse of the heteroatomic modulation of oxyanionic Cope rearrangement rates has been described[173] in the context of paclitaxel synthesis. Recent calculations have indicated[174] that anionic oxy-Cope substrates react via a concerted pathway, whereas anionic amino-Cope substrates react via a stepwise, heterolytic cleavage pathway. It has been demonstrated[175] that, in the acid-catalysed 4 + 2-cycloaddition between cyclic azines and 1,3-dienes, both partners may play the role of the diene or the dienophile, depending on particular structural features. Moreover, it has been shown that the thermal or acid-catalysed interconversion of isomeric 4 + 2-cycloadducts definitely occurs by a Cope rearrangement and not by a 4 + 2-cycloreversion (see Scheme 43). 3-Alkylideneindolin-2-ones have been prepared from propargylbenzotriazoles via

a selective nucleophilic reaction of an allene dianion followed by a 3-aza-Cope rearrangement,[176] and the reaction of 1-methyl-1-cyanohydrazones with methyl trifluoromethanesulfonate was found to afford 2-(methylamino)-1-methylimidazoles as their triflic acid salts. The authors[177] have proposed that this transformation involves the formation of the 1-cyano-1,2-dimethyl ene-hydrazine derivative which undergoes a 1,3,4-triaza-Cope rearrangement *in situ*. Chain-extended amino sugar derivatives have been synthesized[178] via the stereo-controlled Lewis acid-catalysed aza-Cope rearrangement of *N*-glycosylhomoallylamines (see Scheme 44). The anionic amino-Cope rearrangement of a series of 3-amino-1,5-diene substrates has been achieved[179] at low temperatures by using butyllithium to generate the lithium anion. The absolute stereochemistry of the major product has been predicted from simple transition-state models, the major enantiomer being produced from a chair-like conformation of the substrate with the amine component occupying a pseudo-equatorial orientation. High asymmetric induction has also been achieved in the anionic amino-Cope rearrangement of 3-amino-1,5-dienes by using β-amino alcohol auxiliaries.[180]



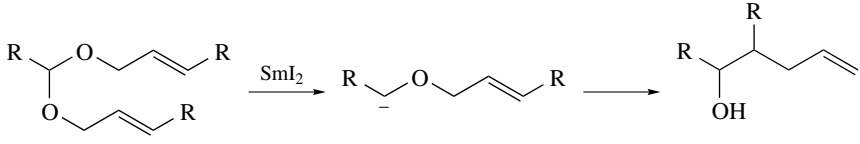
SCHEME 44

[2,3]-Migrations

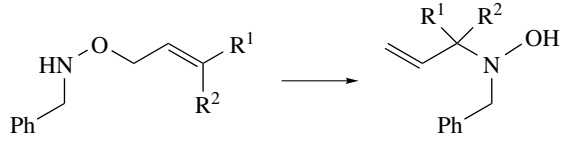
The tactical combination of Diels–Alder reactions with [2,3]-sigmatropic rearrangements, as well as the one-pot version of these tandem processes, have been used to create unusual structures with high efficiency.[181] The influence of the relative stereochemistry of the epoxide and benzyloxy functionalities present in *cis*- and *trans*-1-benzyloxy-3,4-epoxycyclopentanes on the tandem epoxide–allylic alcohol [1,2]/[2,3]-Wittig rearrangement has been studied,[182] together with the Wittig rearrangement of the intermediate alcohols. The study has shown that the reaction involving the *cis*-epoxybenzyl ether has a strong preference for [1,2]-rearrangement with retention whereas, in contrast, the rearrangement of the intermediate alcohol leads to a 9:1 mixture of [2,3]-products. A chiral non-racemic base-promoted [2,3]-Wittig rearrangement of a series of (allyloxymethylbenzene)tricarbonylchromium(0)

complexes has been reported to proceed with remarkably high enantioselectivity.[183] The *N,N*-diethylcarbamoyl group has been shown to act as an efficient director in the (−)-sparteine-mediated enantioselective [2,3]-Wittig rearrangement of *o*-substituted benzyl allyl ethers,[184] and the [2,3]-sigmatropic rearrangement of α-propargyloxyacetic acids has been achieved[185] by the use of a BuLi–(−)-sparteine complex. Tomooka *et al.*[186] have demonstrated that a chiral bis(oxazoline) system is effective as an external ligand for the enantioselective [2,3]-Wittig rearrangement of (*E*)-crotyl propargylic ethers. An asymmetric synthesis of the chiral β-lactone precursor of the HMG–CoA synthase inhibitor L-659,699 has been described.[187] It involves, as the key step, an asymmetric [2,3]-Wittig rearrangement to control the stereogenic centres at the ring carbons. It has been reported[188] that diallyl acetals (**106**) undergo reductive cleavage of an allyloxy group by SmI_2 to generate α-allyloxy carbanions (**107**), which can be transformed by a [2,3]-Wittig rearrangement into homoallylic alcohols (**108**). A novel [2,3]-sigmatropic rearrangement whereby *N*-benzyl-*O*-allylhydroxylamines (**109**) are transformed into the corresponding *N*-allylhydroxylamines (**110**) has been described, and evidence for the intramolecular nature of the process has been presented.[189] The diastereoselective formation of a 2,8-dioxabicyclo[3.2.1]octane skeleton has been accomplished[190] from methyl acetoacetate through the generation and [2,3]-rearrangement of a bicyclic oxonium ylide (see Scheme 45). Apparently, this is the first example of an exocyclic [2,3]-shift from an acetal-derived oxonium ylide.

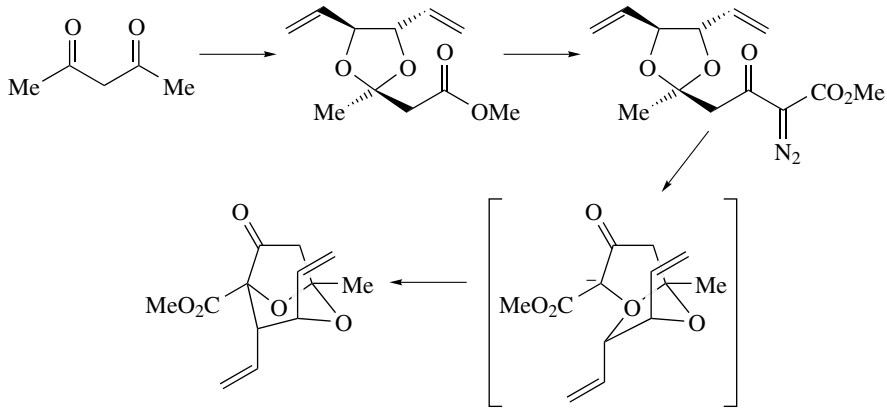
A study of the mechanism of the rearrangement of a tertiary amine oxide to the *O*-substituted hydroxylamine has been carried out by the semiempirical AM1 method.[191] The use of prolinol as a chiral auxiliary has allowed the formation of single diastereomeric amine *N*-oxides from *N*-allyl prolinol derivatives. However, on warming, these amine oxides were found to undergo the [2,3]-Meisenheimer rearrangement with only low stereoselectivity.[192] The Meisenheimer rearrangement of allyl *N*-oxides has been used[193] as a route to initiators for nitroxide-mediated free-radical polymerizations. A detailed study of the [2,3]-Meisenheimer rearrangement of 2-vinylazetidine *N*-oxides has been undertaken.[194] A competitive study of the Meisenheimer rearrangement in a substrate tertiary amine with allylic and propargylic



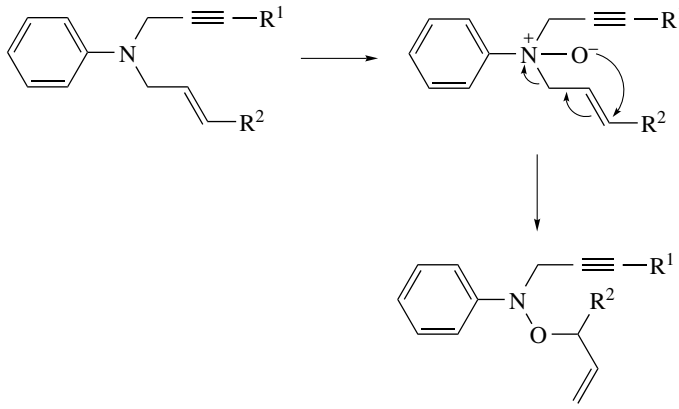
(**106**) (**107**) (**108**)



(**109**) (**110**)



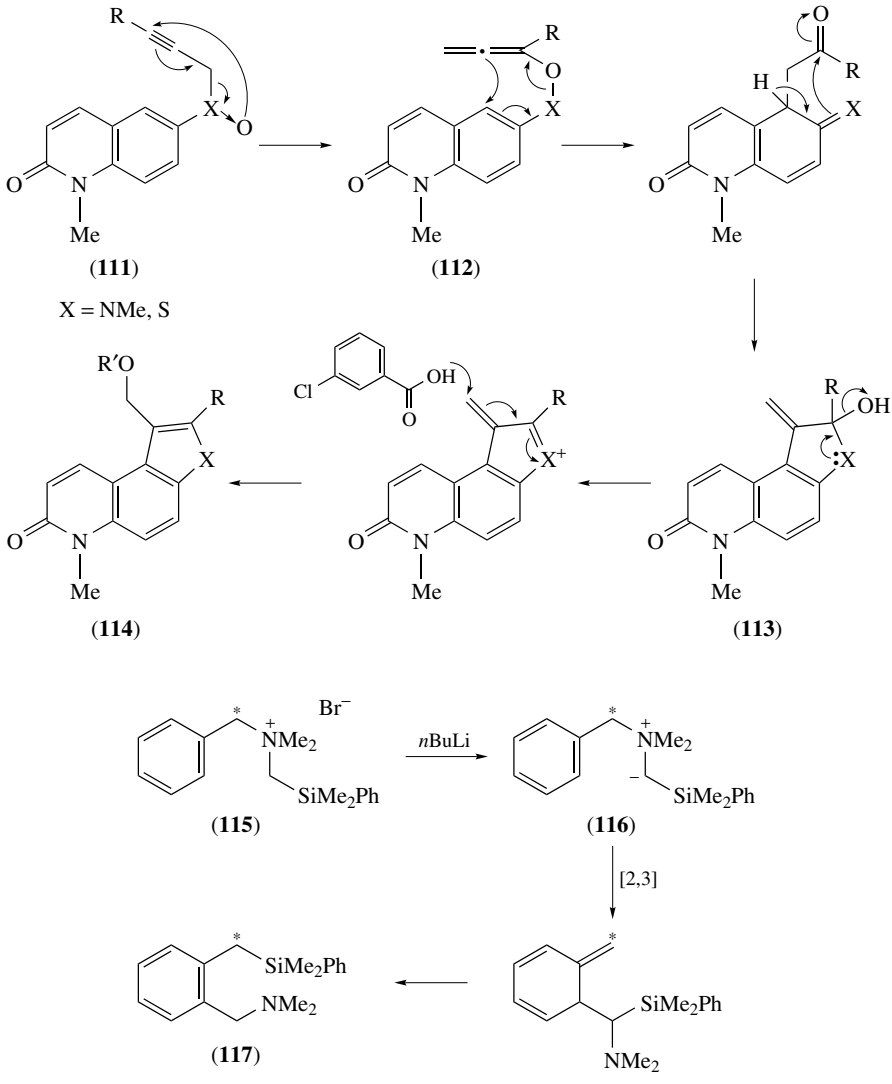
SCHEME 45



SCHEME 46

moieties has shown[195] that the rearrangement of the allyl aryl amine moiety is preferred over the rearrangement of the allyl propargyl amine oxide moiety (see Scheme 46). Several derivatives of pyrrolo-[196] and thieno-[3,2-*f*]quinolin-7-ones[197] have been synthesized. Formation of the products has been explained by invoking a [2,3]-sigmatropic rearrangement of the *N*-oxide or sulfoxide (**111**) in a manner similar to a Meisenheimer rearrangement to give an intermediate (**112**) which undergoes a [3,3]-sigmatropic rearrangement followed by ketol formation to give (**113**). Acid-catalysed allylic rearrangement of (**113**) gives the final product (**114**). A similar methodology has been used[198] to prepare a number of pyrrolo[3,2-*d*]pyrimidine derivatives from the corresponding 5-[*N*-[4-(aryloxy)but-2-ynyl]-*N*-ethylamino]-1,3-dimethyluracils.

It has been shown that the tri-*n*-butyltin group can control the diastereoselection of an aza-[2,3]-Wittig rearrangement,[199] and the silicon-assisted aza-[2,3]-Wittig rearrangement of crotyl-type amines has been used to furnish each diastereoisomer of the

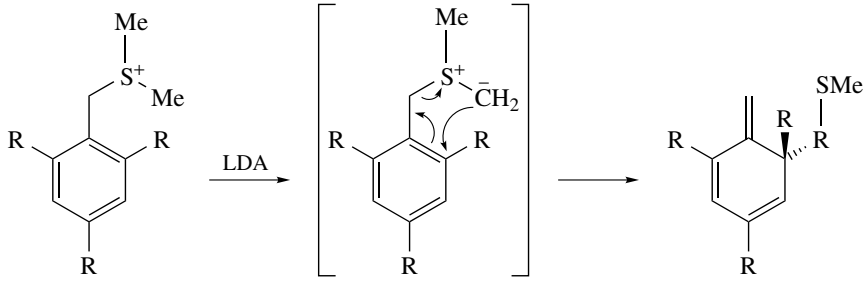


SCHEME 47

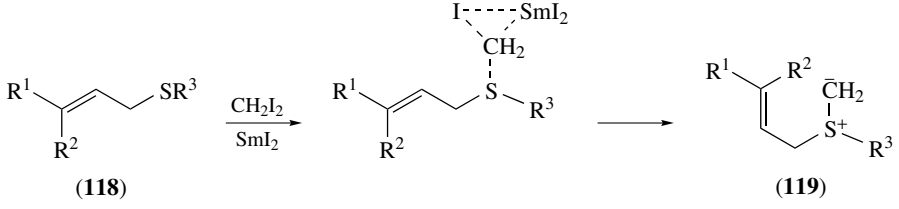
product homoallylic amines in good yield.[200] A number of ketene dithioacetals have been found to react readily with aziridine to afford the corresponding *N*-vinylaziridines which undergo an iodine ion-assisted ring expansion to produce pyrrolines.[201] Investigations into the aza-[2,3]-Wittig rearrangement of *N*-alkyl-*N*-allyl-α-amino esters have demonstrated[202] that the rearrangement of tertiary amines with Lewis acids is less effective than the [2,3]-Stevens rearrangement using ylides generated from quaternary ammonium salts. Both approaches, however, have been shown to have potential for the formation of novel, substituted allylglycine esters. The application of ^{13}C NMR spectroscopy and ^{13}C-labelled benzylammonium salts to the study of the rearrangements of

ammonium benzylates has revealed[203] that the ylide (**116**) generated from *N*-benzyl-N,*N*-dimethyl-*N*-[(dimethylphenylsilyl)methyl]ammonium bromide (**115**) and BuLi affords N,*N*-dimethyl-2-[(dimethylphenylsilyl)methyl]benzylamine (**117**) via a [2,3]-shift in the silylmethylide followed by subsequent [1,4]-silicon and [1,2]-hydrogen shifts (see Scheme 47).

It has been established[204] that the thia-Sommelet dearomatization leading to the formation of hexatrienes containing quaternary stereogenic centres can be achieved in excellent yield by deprotonation with LDA (see Scheme 48). Allylic sulfides (**118**) have been transformed into homoallylic sulfides (**120**) with complete allylic inversion by treatment with SmI_2 and CH_2I_2. The reaction is considered[205] to involve addition of a samarium carbenoid to a divalent sulfur leading to the formation of a sulfonium ylide (**119**) which rearranges to the homoallylic sulfide. A rearrangement of *O,O*-silylketene acetals (**121**) leading to the γ-thiomethylation of butenoic acid derivatives has been reported. The process has been explained[206] by invoking the [2,3]-sigmatropic rearrangement of the intermediate ylide (**122**) to give

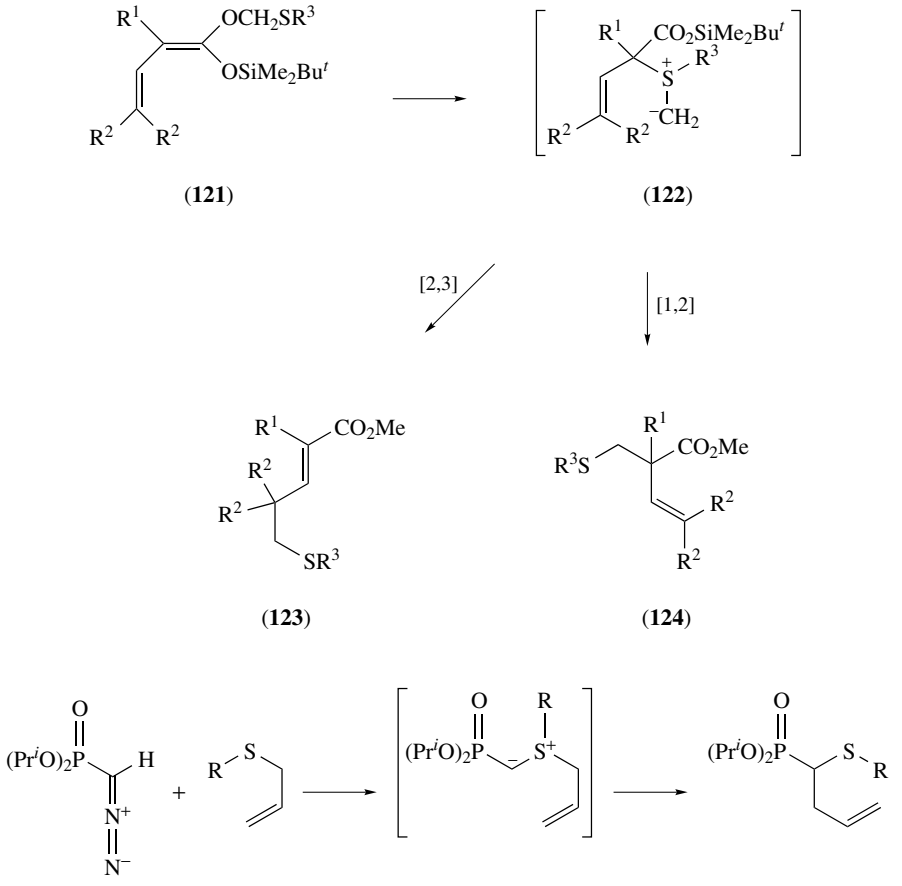


SCHEME 48



(**118**) (**119**)

(**120**)



SCHEME 49

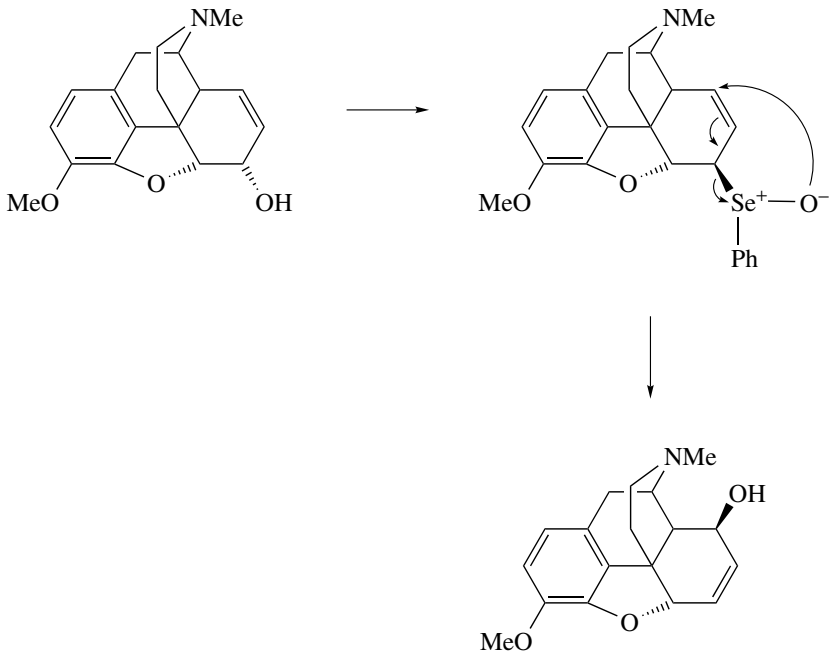
the γ-alkylated product (**123**). Alternatively, a [1,2]-shift analogous to the Stevens rearrangement leads to the α-substituted product (**124**), the major product in the case of phenylthiomethyl esters. New nine-membered heterocyclic compounds, 6,7,9,10-tetrahydro-4*H*-thieno[3,2-*f*][1,4]oxathionine and 4,7,8,10-tetrahydro-5*H*-thieno[2,3-*f*][1,4]oxathionine, have been synthesized[207] by [2,3]-sigmatropic rearrangements of the *S*-methylides generated by the fluoride ion-induced desilylation of 3-(2-thienyl)-4-[(trimethylsilyl)methyl]-1,4-oxathianium triflate and the (3-thienyl)-analogue, and 1,3,4,5,6,11a-hexahydro-(7*E*)-2-benzothionine has been obtained[208] in a similar manner by the fluoride ion-induced desilylation of *trans*-2-phenyl-1-[(trimethylsilyl)methyl]tetrahydrothiopyranium perchlorate. The reaction of diisopropyl diazomethylphosphonate with allylic sulfides in the presence of a catalytic amount of copper(II) acetylacetonate or rhodium acetate dimer, has been shown to afford[209] the corresponding α-phosphorylated γ,δ-unsaturated sulfides, presumably by way of a [2,3]-sigmatropic rearrangement of the intermediate sulfonium ylide (see Scheme 49). This reaction has been successfully extended to

α-vinyltetrahydrothiophene and dipropargyl sulfide. A theoretical study of the sulfenate–sulfoxide rearrangement has indicated[210] that a biradical mechanism is the lowest energy pathway and therefore the most likely mechanism for this rearrangement.

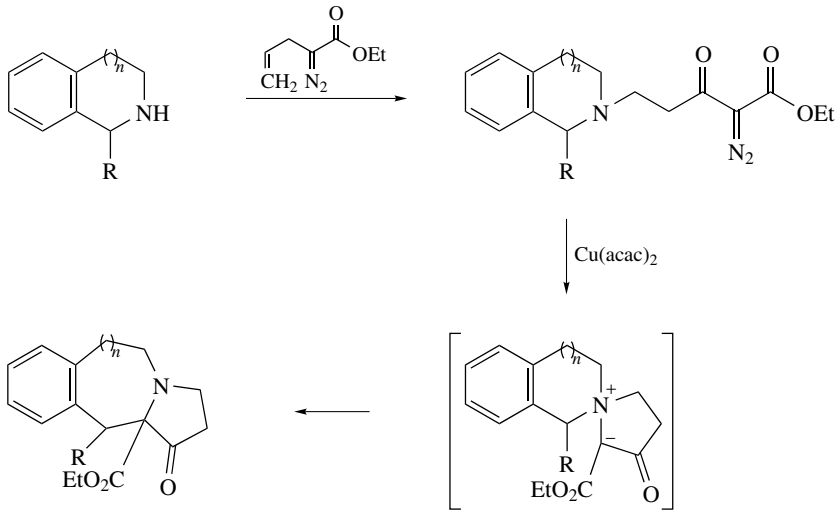
A [2,3]-sigmatropic rearrangement using selenium intermediates has been used[211] in a recent stereospecific synthesis of pseudocodeine (see Scheme 50).

Miscellaneous

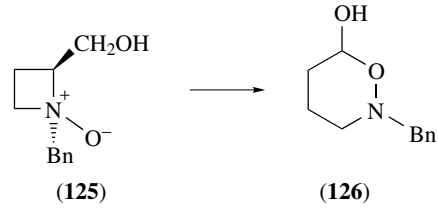
Theoretical calculations have been performed[212] for the Stevens rearrangement of phosphorus and arsenic ylides ($ZH_2MCH_2 \rightarrow H_2MCH_2Z$; Z = H, CH_3, $CH{=}CH_2$, SiH_3 and GeH_3; M = P or As), and ammonium ylides derived from the Cu(II)-catalysed decomposition of α-diazocarbonyl compounds tethered to tertiary amines have been found[213] to undergo a benzylic Stevens [1,2]-rearrangement to afford tetrahydroisoquinolines and benzazepines containing fused five-membered rings (see Scheme 51). The rearrangement of *N*-benzyl-2-hydroxymethylazetidine *N*-oxide (**125**) to the novel tetrahydrooxazine (**126**) in warm CH_2Cl_2 has been rationalized either as a Cope-type elimination followed by tautomerism of the enol to an aldehyde and lactol formation, or as a [1,2]-rearrangement.[214] The first phosphorothiolate to mercaptophosphonate [1,2]-sigmatropic rearrangement has been described[215] and used to prepare a new (mercaptomethylene)diphosphonate (see Scheme 52).



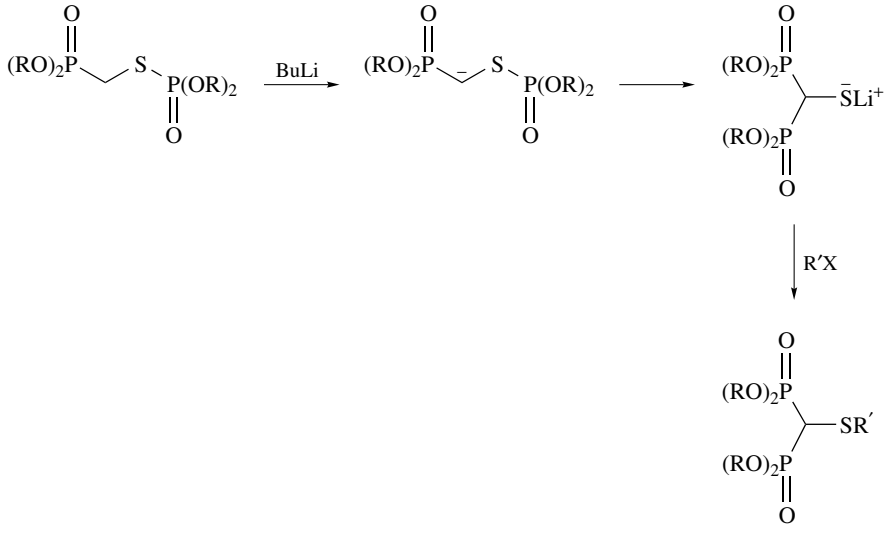
SCHEME 50



SCHEME 51



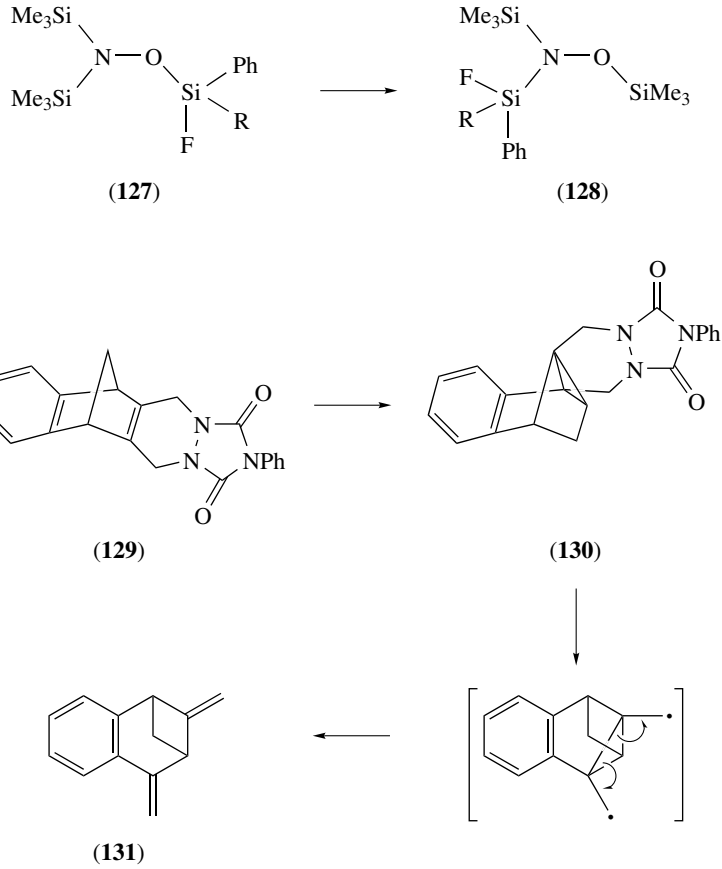
(**125**) (**126**)



SCHEME 52

An irreversible dyotropic rearrangement of fluoro-substituted tris(silyl)hydroxylamines (**127**) → (**128**) has been reported[216] and *ab initio* and density functional calculations for model compounds have confirmed the dyotropic course of this rearrangement.[217]

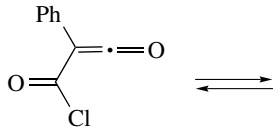
The photochemical di-π-methane rearrangement of quinoxalinobarrelenes has been studied,[218] and the novel hydrocarbon 8,10-dimethylidenetricyclo[7.1.1.$0^{2,7}$]undeca-2,4,6-triene (**131**) has been synthesized[219] by triplet-sensitized di-π-methane rearrangement of the norbornadiene derivative (**129**) and hydrolysis of the resulting urazol (**130**) (see Scheme 53). A method involving an oxa-di-π-methane rearrangement has been developed[220] to introduce appropriate substituents at both bridgehead positions of a bicyclo[2.2.2]oct-5-en-2-one leading to a formal total synthesis of modhephene, a propellane-type triquinane sesquiterpene. The oxa-di-π-methane rearrangement of bicyclo[2.2.2]oct-5-en-2-one and bicyclo[2.2.1]hept-5-en-2-one has also been induced by the external heavy-atom cation effect within a zeolite.[221]



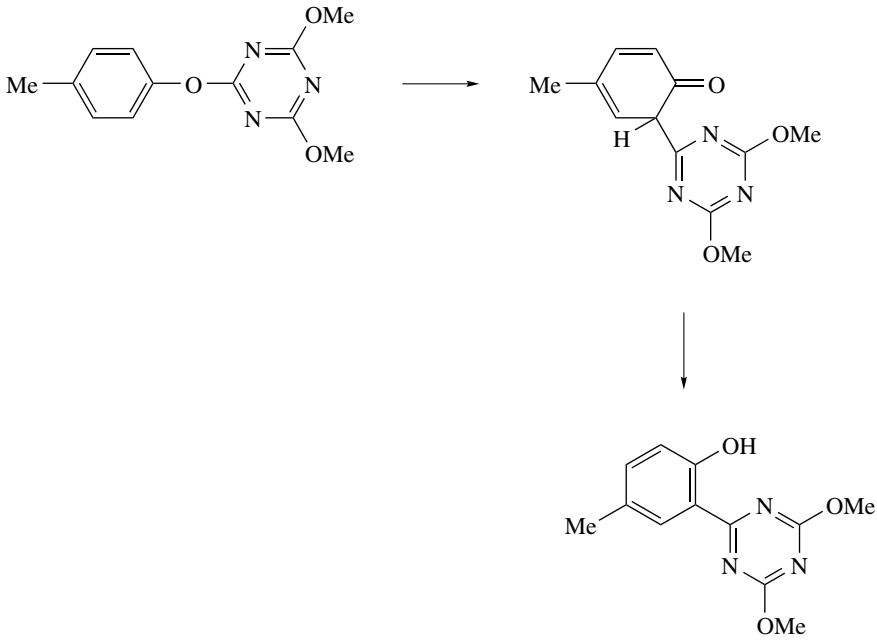
SCHEME 53

It has been shown[222] that [1,3]-dialkylboryl shifts in cyclononatetraenyl systems are facile and are slightly favoured over [1,2]-shifts. Apparently, neither Woodward–Hoffmann rules nor the 'least motion principle' alone can be used for the prediction or rationalization of large-ring sigmatropic migrations. Adequate analyses require a combination of dynamic NMR techniques and high-level *ab initio* calculations. α-Oxo ketenes have been found to undergo a degenerate thermal rearrangement by a [1,3]-shift of the acyl substituent.[223] Imidoyl-ketenes have been converted into α-oxo ketenimines by a similar rearrangement, while ^{13}C NMR spectroscopy has shown[224] that chlorocarbonyl(phenyl)ketene undergoes a degenerate [1,3]-shift of chlorine [see (**132**) $\rightleftarrows$ (**133**)].

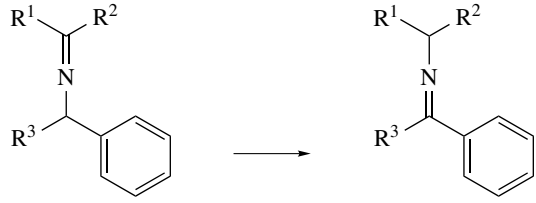
Theoretical considerations based on the tunnel-effect theory have shown[225] that in the intramolecular [1,3]-sigmatropic hydrogen shift in the photo-Fries rearranged intermediate of 2,4-dimethoxy-6-(*p*-tolyloxy)-*s*-triazine, the hydrogen atom migrates directly to the carbonyl oxygen without being enhanced by the basic catalytic action of the adjacent triazine ring (see Scheme 54). The ruthenium (II)-catalysed



(**132**) (**133**)



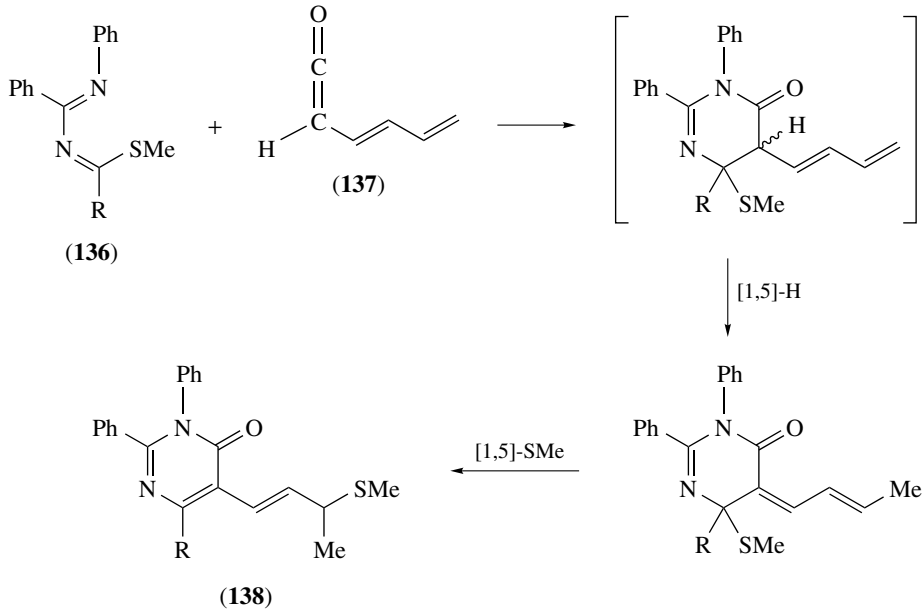
SCHEME 54



(**134**) (**135**)

isomerization of imines via a [1,3]-hydrogen shift [see (**134**) → (**135**)] has been described.[226] A convenient asymmetric synthesis of both (*R*)-(−)- and (*S*)-(+)-2-benzyl-2-hydroxycyclohexanones starting from racemic 2-benzyloxycyclohexanone and the chiral auxiliary 1-phenylethylamine has been reported.[227] The route involves a [1,3]-sigmatropic shift and a new diastereoselective α-iminoamine rearrangement of a 2-benzyl-2-iminocyclohexanamine substrate. The photochemical [1,3]-stannyl rearrangement of allylic stannanes has been investigated[228] in some detail, and a pentacoordinate *t*-alkoxy-1,2-oxastannetanide, considered to be formed by a novel tin [1,3]-migration from carbon to oxygen involving the formation of an oxetane ring and subsequent tin–carbon bond cleavage, has been obtained[229] from the treatment of a bis (β-hydroxyalkyl)stannane with potassium hydride in THF in the presence of 18-crown-6. Under the influence of potassium hydride, bicyclo[3.2.1]oct-6-en-2-ols have been found to undergo a [1,3]-sigmatropic shift to afford 8-*endo*-hydroxybicyclo[3.3.0]oct-2-en-4-ones.[230] It has been observed[231] that hydride reduction of the 2(*Z*)- and 2(*E*)-isomers of methyl and *t*-butyl 3-methyl-4-phenylthioheptenoates is accompanied by [1,3]-migration of the phenylthio group in both cases. The rhodium(I)-catalysed regioselective ring expansion of allenylcyclopropanes into methylenecyclopentenes has been achieved.[232] A stereochemical investigation of the thermal isomerization of 1-ethenyl-7-*exo*-phenylbicyclo[4.1.0]heptane to 7-phenylbicyclo[4.3.0]non-1(9)-ene has indicated[233] that vinylcyclopropane to cyclopentene rearrangements occur through diradical structures that allow for some conformational flexibility before a transition-state region of the potential-energy surface is reached.

A density functional theory computational approach has been used[234] to investigate the [1,5]-hydrogen shift in (*z*)-penta-1,3-diene. *Ab initio* calculations of the activation barriers to proton transfer in nitrogen derivatives have been computed and these values used to show that the proton transfer in pyrazole is formally a [1,5]-hydrogen shift.[235] The novel photochemical rearrangement of 1,3-diaryl-1,2-dihydropentalenes to the 1,5-dihydropentalenes has been viewed[236] as a photo-induced [1,5]-hydrogen shift. Tandem [1,5]-hydrogen and [1,5]-thiomethyl shifts have been invoked[237] to explain the formation of 5-butenylpyrimidones (**138**) from the reaction of 1,3-diazabuta-1,3-dienes (**136**) with butadienylketene (**137**) (see Scheme 55). *trans*-1,2,3,3a,4a,5,6,7-Octaphenyl-3a*H*, 4a*H*-dicyclopenta[*b,e*] [1,4] dithiin has been prepared by thionation of 2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one. A pathway involving dimerization and subsequent [1,5]-phenyl migration has been proposed[238] for the transformation.



SCHEME 55

The mechanism of the degenerate [5,5]-sigmatropic rearrangements of 5,5a,10,10a-tetrahydroheptalene and (*z, z*)-decatetraene-1,3,7,9 has been explained. A stepwise diradical mechanism has been predicted for both reactions.[239]

Electrocyclic Reactions

Density functional theory and MC-SCF calculations have been applied to a number of pericyclic reactions including cycloadditions and electrocyclizations.[240] It has been established[241] that the transition states of thermally allowed electrocyclic reactions are aromatic. Apparently they not only have highly delocalized structures and large resonance stabilizations, but also strongly enhanced magnetic susceptibilities and show appreciable nucleus-independent chemical-shift values.

The molecular mechanisms for the ring openings of various cyclopropanone systems in the gas phase have been studied[242] at the PM3 semiempirical level and shown to be disrotatory processes, while an experimental study of the stereomutation of 1,1-difluoro-2-ethyl-3-methylcyclopropane has confirmed[243] the predicted preference for disrotatory ring opening and ring closure for this system.

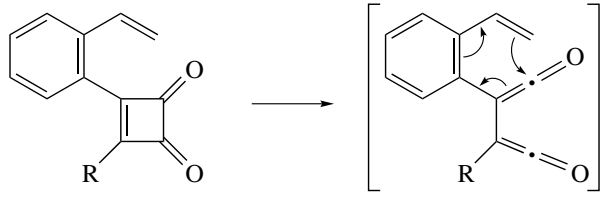
Spin-coupled theory has been used to study the changes that occur in the electronic wavefunction as a system moves along the intrinsic reaction coordinate for the case of the conrotatory and disrotatory pathways in the electrocyclization of cyclobutene to *cis*-butadiene.[244] Against intuitive expectations, conrotatory opening of cyclobutenes was found to be promoted by pressure.[245] *Ab initio* MO and density functional calculations have indicated[246] that the ring opening of the cyclobutene

radical cation follows two competitive pathways. The reported double 1,2-addition of alkenyl, cycloalkenyl and alkynyllithium reagents to squarate esters and subsequent 4π conrotatory ring openings and 8π conrotatory cyclizations has constituted an expedient method for producing polycyclic products of considerable structural complexity.[247] An unprecedented intramolecular cyclization of an intermediate bioketene (**140**) has been invoked[248] to account for the thermal rearrangement of substituted cyclobutanediones (**139**) to substituted naphthofuranones (**141**).

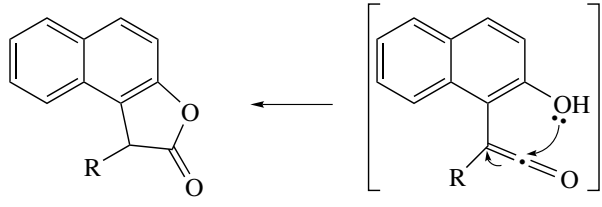
Upon exposure to UV light, α-tropolone methyl ether (**142**), included within chirally modified Y zeolite, has been found to undergo 4π-electron disrotatory electrocyclic ring closure to afford[249] the bicyclic photo-isomer (**143**).

Several 4-aminocyclopent-1-enes have been prepared[250] in two steps from conjugated dienes via the corresponding 2-alkenylcyclopropylamines and their thermal rearrangement.

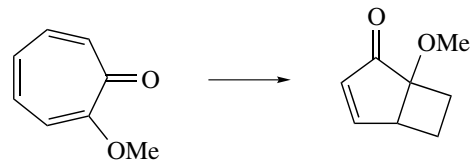
Ketenimines (**144**), generated from α-substituted benzophenone 1-acetamidoethylidenehydrazones with a mixture of triphenylphosphine, carbon tetrachloride and triethylamine in dichloromethane (Appel's conditions), have been used[251] to synthesize a variety of 1,2,4-triazole-fused heterocycles (see Scheme 56). Mechanistically, the



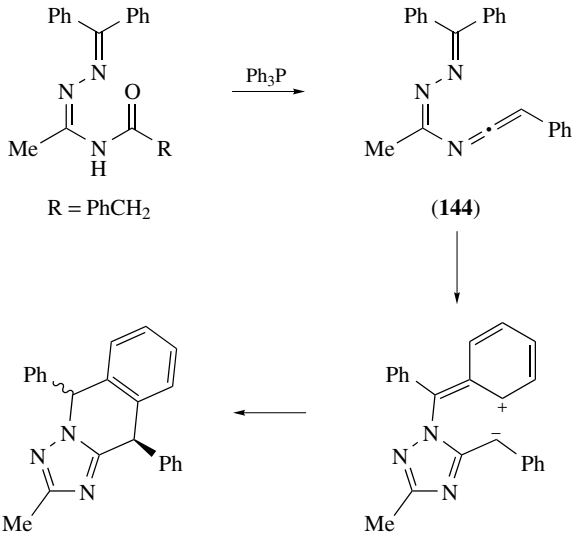
(**139**) (**140**)



(**141**)

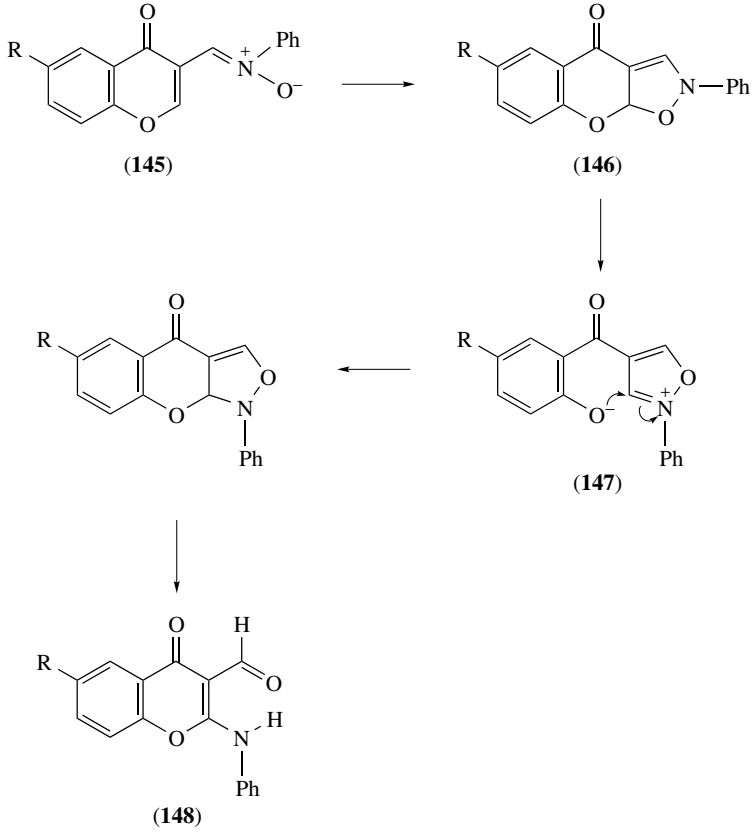


(**142**) (**143**)



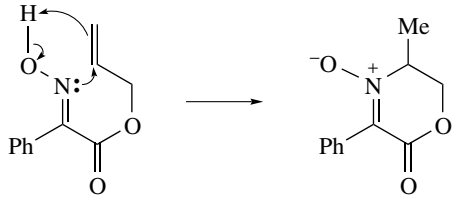
R = $PhCH_2$ (**144**)

SCHEME 56



formation of 2-(*N*-phenylamino)-4-oxo-4*H*[1]benzopyran-3-carboxaldehydes (**148**) as major products from *C*-(4-oxo-4*H*[1]-benzopyran-3-yl)-*N*-phenyl nitrones (**145**) on heating the latter in benzene, has been rationalized[252] in terms of an initial 1,5-electrocyclization to give intermediate (**146**) which is converted into the chromone ring-opened intermediate (**147**) which, after recyclization followed by a [1,5]-hydrogen shift, affords (**148**).

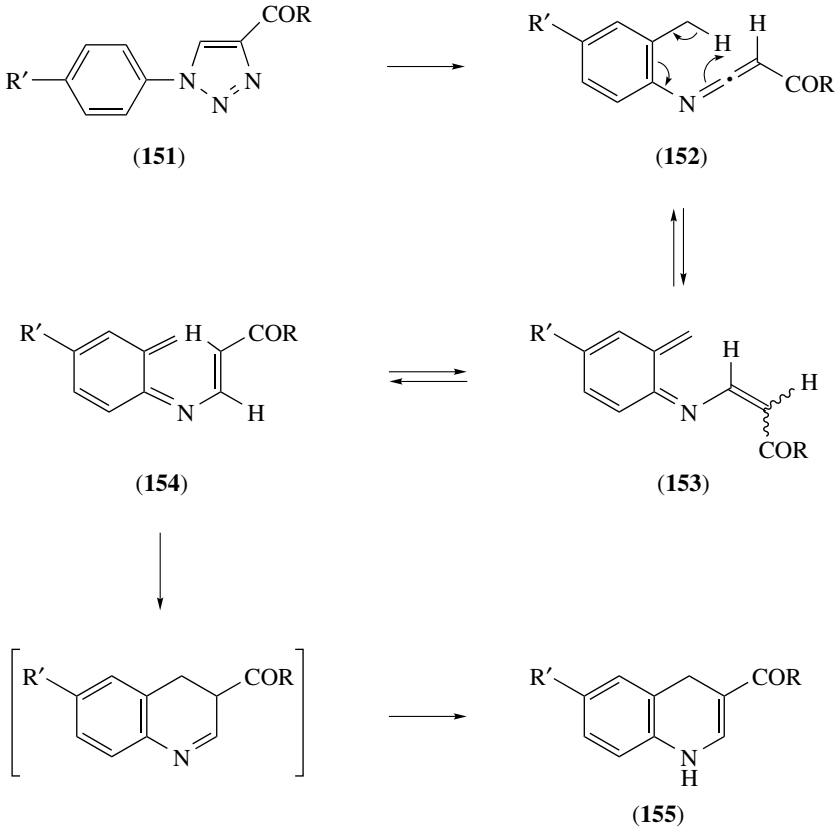
The formation of cyclic nitrones (**150**) from ω-alkenyl oximes (**149**) has been shown to proceed via a concerted pericyclic mechanism.[253] Kinetic and computational studies have provided evidence for the involvement of a novel pseudo-pericyclic electrocyclization in the conversion of *o*-vinylphenyl isocyanates into quinolin-2-ones.[254] Such reactions have also provided evidence of torquoselectivity in a 6π system. Flash vacuum thermolysis of triazoles (**151**) has been found to afford dihydroquinolines (**155**), presumably by generation of α-oxoketenimines (**152**) which can undergo a [1,5]-hydrogen shift to the *o*-quinoid imines (**153**)/(**154**) and subsequent electrocyclization[255] (see Scheme 57).



(**149**) (**150**)

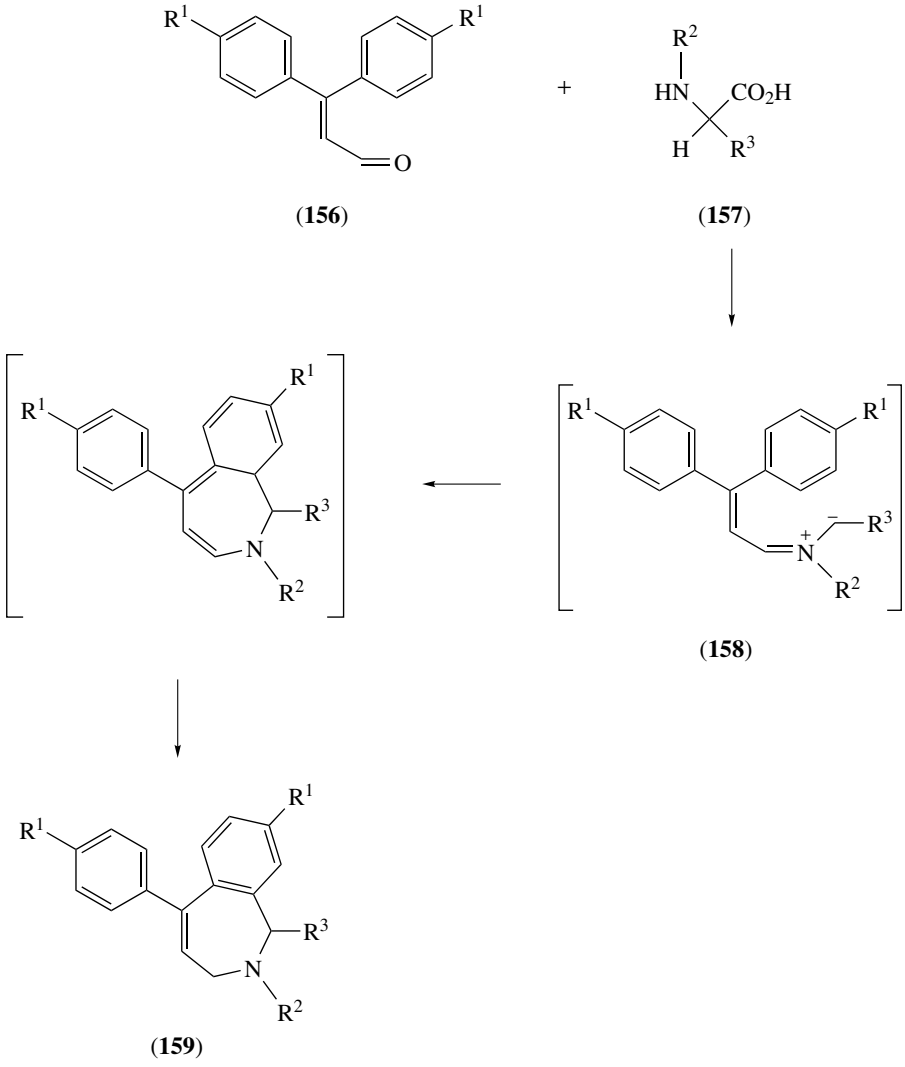
Non-stabilized $\alpha,\beta:\gamma,\delta$-unsaturated azomethine ylides (**158**), generated by the decarboxylation method from 3,3-diarylpropenals (**156**) and secondary amino acids (**157**), have been found[256] to undergo [1,7]-electrocyclization followed by a [1,5]-hydrogen shift, to yield 2,3-dihydro-1*H*-2-benzazepines (**159**).

The intramolecular 4 + 2-cycloaddition of conjugated ynones, e.g. (**160**), has been shown[257] to produce, initially, highly strained heterocyclic allenes (**161**) which undergo an unusual rearrangement leading to polycyclic furans (**162**) (see Scheme 58). The dimeric derivatives of 1,1,2,2-tetraethynylethene, viz. (**163**), have been found to undergo an unexpected rearrangement to a permethylenated cycloocta-1,5-diyne (**164**) in the presence of acid. Formation of (**164**) has been rationalized[258] by assuming a cascade mechanism consisting of electrocyclic or radical reactions. In the first step, thermal cleavage of the carbon–carbon bonds in both dioxolane rings occurs by a conrotatory 12π-electrocyclic ring opening. A formal intramolecular $4\pi + 4\pi$-cycloaddition between the central butatriene units of the intermediate would finally result in the formation of the strained cycloocta-1,5-diyne system. The photochemical reaction of a series of enediynes to yield a cyclization product identical to that which would be expected from a thermal Bergman rearrangement has been reported.[259] Reaction coordinates have been computed[260] for the Bergman cyclization of hex-3-en-1,5-diyne and neutral and protonated 3-azahex-3-en-1,5-diyne.



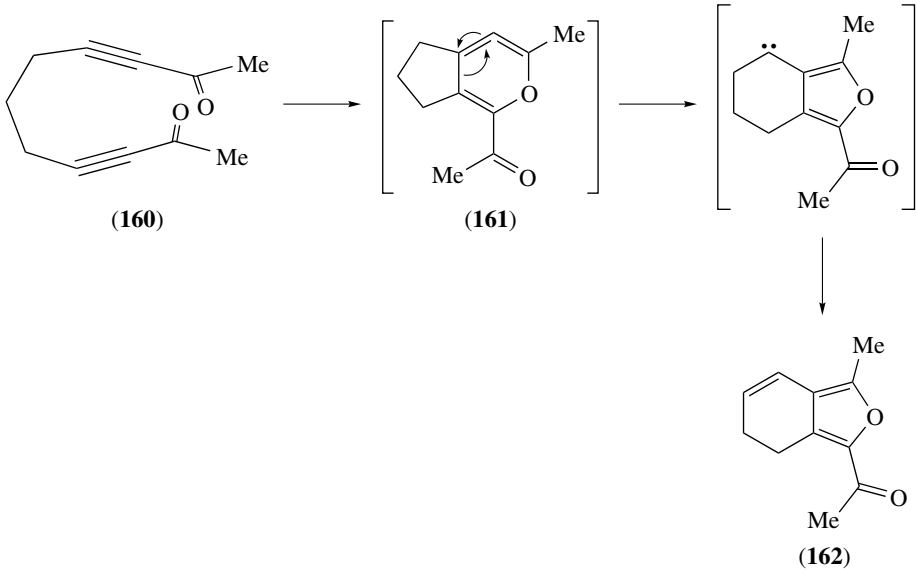
SCHEME 57

The ruthenium-catalyzed Alder ene addition of alkenes and alkynes has provided a powerful new method for the construction of complex organic molecules.[261] The ene reaction between propene and various enophiles has been examined[262] by *ab initio* methods. The transition structures were all found to be cyclic and the reactions found to be concerted. The complex *trans*-[Ru(salen)(NO)(H_2O)]$^+$ has been found to catalyse the ene reaction between activated enophiles and alkenes to yield homoallylic alcohols by a stepwise process.[263] High enantioselectivity has been achieved[264] in the ene reactions of *n*-butylglyoxylate to α-methylstyrene using multi-component titanium catalysts, while bidentate bis(oxazolinyl)Cu(II) complexes have been established[265] as highly selective catalysts for the glyoxylate–ene reaction. Scandium trifluoromethanesulfonate has been found to act as an efficient catalyst for both intra- and intermolecular carbonyl-ene reactions.[266] Not surprisingly, different cyclization products have been obtained in the ene cyclization of 5-methyl-2-(1-methylethyl)-hex-5-enal when different Lewis acids are used.[267] A facile and diastereoselective route to various chiral β-amino acids has been developed[268] using the carbonyl–ene reaction of



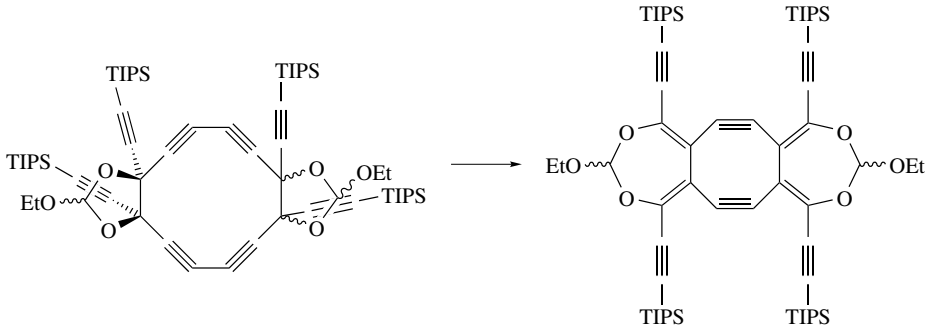
N-tritylaziridine-2-(*S*)-carboxaldehyde. The application of a novel, sequential, trans-acetalation oxonium ene cyclization has delivered[269] a stereoselective synthesis of the *C*-aromatic taxane skeleton, and a combinatorial sequence of the regioselective propiolate–ene, catalytic enantioselective epoxidation and carbonyl–ene cyclization reactions has been used[270] to complete the synthesis of the A-ring of a vitamin D hybrid analogue.

Allenic esters (**165**) have been found[271] to undergo a retro-ene reaction on flash vacuum thermolysis above 800 °C to give unsubstituted vinylketene together with formaldehyde or acetaldehyde (see Scheme 59).

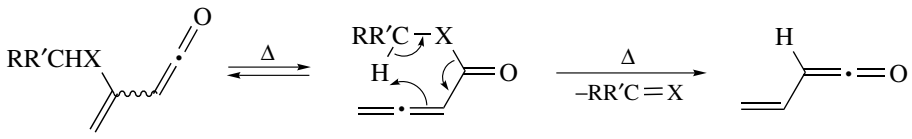


(**160**) (**161**) (**162**)

SCHEME 58



(**163**) (**164**)



(**165**)

X = O or NMe

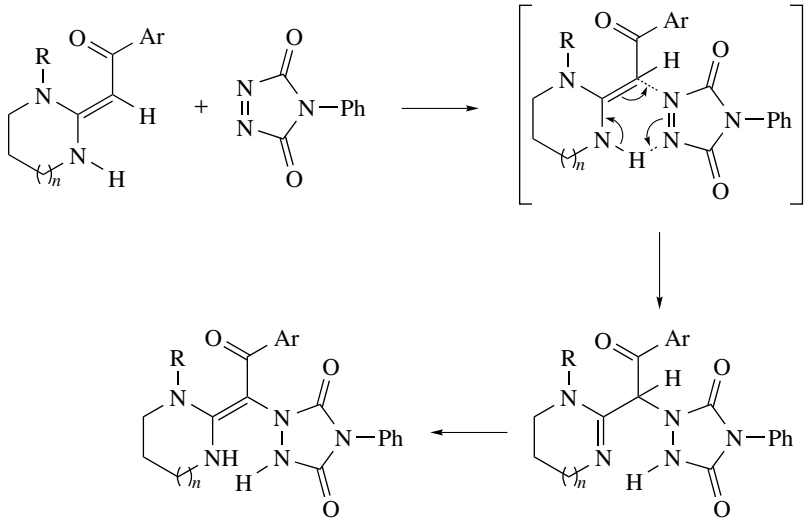
SCHEME 59

A novel stereoelectronic effect rather than intramolecular hydrogen bonding or steric congestion has been shown to determine the *threo*-diastereoselectivity in the ene reaction of singlet oxygen with an electron-poor allylic alcohol and its ethers.[272] The effect of solvent polarity on the photo-oxygenation of 2,4-dimethylpenta-1,3-diene has been studied. The differences observed in the ene and 4 + 2-cycloaddition reactions in different solvents have been explained[273] by competition between a concerted and a perepoxide mechanism. Dramatic diastereoselectivity differences have been observed in the asymmetric ene reactions of triazolinediones and singlet oxygen with chiral 2,2-dimethyloxazolidine derivatives of tiglic acid. These differences have been rationalized[274] in terms of the differences in steric demand of the singlet oxygen and triazolinedione enophiles rather than electronic factors. It has been shown for the first time that the phenyl ring of styrene substrates can dictate the *syn/anti* stereochemistry in their ene reactions with singlet oxygen and triazolinediones. The authors[275] have proposed that a favourable interaction of the enophiles with the phenyl ring directs the orientation of perepoxide or aziridinium imide. Recent studies[276,277] have shown that the ene reactions of triazolinediones with chiral allylic alcohols exhibit high *threo*-diastereoselectivity in non-polar solvents, whereas in polar solvents the diastereoselectivity was shown to decrease substantially. These results support a favourable interaction occurring between the hydroxyl group of allylic alcohols and triazolinediones in the transition state of aziridinium imide formation. This steering effect occurs either between the negatively charged nitrogen during the formation of the aziridinium imide where the triazolinedione is placed *syn* to the hydroxyl, or between the carbonyl group of the triazolinedione and the hydroxyl, in the transition state where the enophile is placed *anti* to OH. These studies have further substantiated the mechanistic equivalence between triazolinedione and singlet oxygen enophiles. Convenient syntheses of 1-deoxy-*neo*-inositol and 1-deoxy-*myo*-inositol have been achieved[278] using ene reactions of singlet oxygen. Heterocyclic ketene aminals bearing a secondary enamine moiety have been found to undergo an efficient aza–ene reaction with 4-phenyl-1,2,4-triazolin-3,5-dione[279] (see Scheme 60).

The diastereofacial selective imine–ene reactions with α-imino esters prepared from (−)-8-phenylmenthyl glyoxylate have provided[280] an efficient entry to the asymmetric synthesis of α-amino acids, and a Lewis acid-mediated intramolecular imine–ene reaction has been used for the key spirocyclization step in a recent synthesis of (−)-perhydrohistrionicotoxin.[281] Asymmetric azo–ene reactions have been effected using the chiral azo–enophile, di-(−)-(1R,2S)-2-phenyl-1-cyclohexyldiazenedicarboxylate.[282]

Ene reactions of Pummerer-type reaction intermediates have been used as key steps in the synthesis of both pellitorine[283] and trichonine.[284]

The effect of ring substituents on the rate constants, deuterium kinetic isotope effects and Arrhenius parameters for ene-additions of acetone to 1,1-diphenylsilane have been explained[285] in terms of a mechanism involving fast, reversible formation of a zwitterionic silene–ketone complex, followed by a rate-limiting proton transfer between the α-carbonyl and silenic carbon. A study[286] of the thermal and Lewis acid-catalysed intramolecular ene reactions of allenylsilanes with a variety of

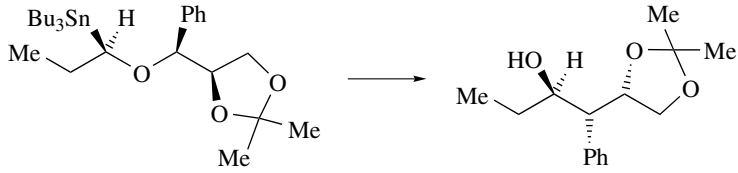


SCHEME 60

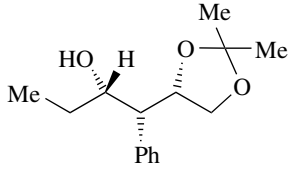
enophiles has shown that, in all cases studied, the cycloaddition reactions were stereoselective. The results of the Lewis acid-catalysed ene reactions of allylic silenes and stannanes with methyl propiolate have been described.[287] They indicated clearly that the chemoselectivity of these reactions was extremely dependent on the identity of the metallic group and the nature of the ene and enophile. Diels–Alder and ene reactions of ethenes $Me_2M{=}C(SiMe_3)_2$ [M = Si, Sn, Ge] have been shown to take place both regio- and stereo-selectively and the results have been explained[288] by the $\pi-\pi^*$ energy differences, the double-bond polarities and the M–C bond energies. A highly diastereoselective synthesis of (−)-erythrodiene has been achieved using an intramolecular Pd-catalysed zinc–ene reaction as the key step.[289] Applications of the phospha–ene reaction to the synthesis of different classes of organophosphorus compounds have been reviewed.[290]

Anionic Rearrangements

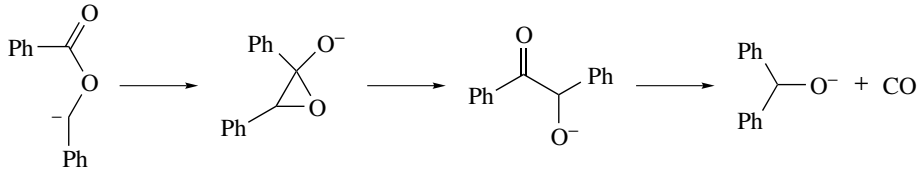
The mechanism of [1,2]-methyl Wittig migration in the free and lithiated anionic methoxymethide model system has been discussed.[291] The study has provided, on the one hand, a picture of the free anion processes taking place in the gas phase and, on the other hand, two extreme descriptions of ionic association relevant to the condensed phase. It has been reported[292] that in the [1,2]-Wittig rearrangement of enantio-defined stannanes such as (**166**), the normal tendency for the α-oxylithium species to undergo an inversion of configuration [see (**166**) → (**167**)] can be suppressed and even overturned by the chelation effect [see (**166**) → (**168**)]. Experimental evidence has been provided[293] to suggest that a cyclization–Wittig-type [1,2]-migration best accounts for the rearrangement of deprotonated benzyl benzoate to the diphenylmethoxide anion and carbon monoxide. Thus cyclization of $PhCO_2^-CHPh$ yields deprotonated



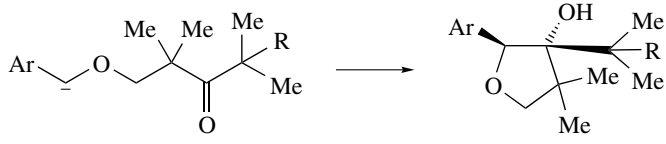
(**166**) (**167**)



(**168**)



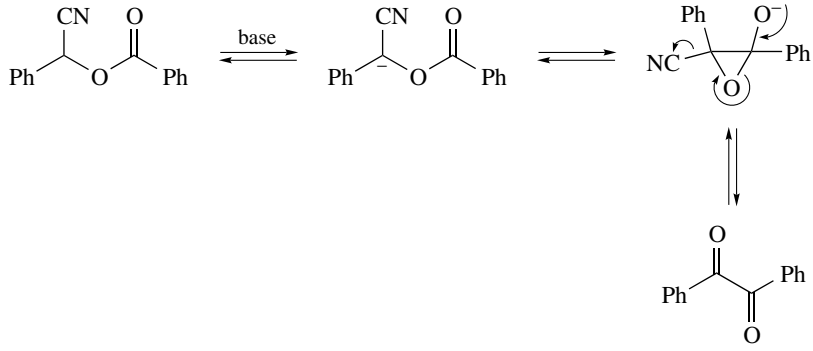
SCHEME 61



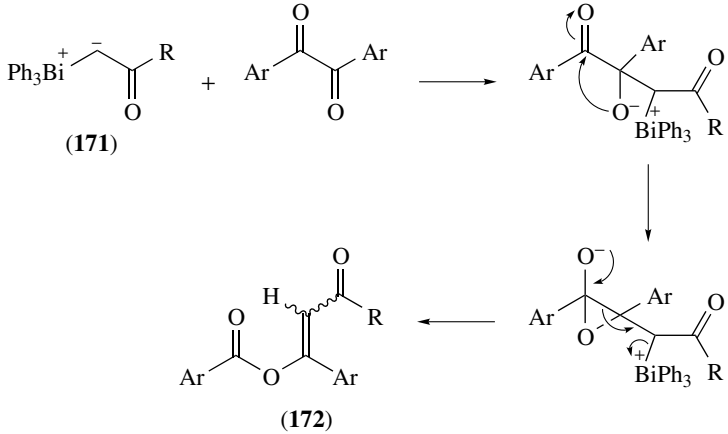
(**169**) (**170**)

diphenylhydroxyoxirane which undergoes ring opening to afford deprotonated deoxybenzoin which then dissociates via an anionic [1,2]-Wittig-type rearrangement (see Scheme 61).

It has been shown[294] that the α-carbanion of an alkyl benzyl ether such as (**169**) undergoes nucleophilic addition to a carbonyl moiety existing in the same molecule [see (**170**)] without Wittig rearrangement or protophilic decomposition. The mechanism shown in Scheme 62 has been postulated[295] to account for the formation of benzil from *O*-benzoylbenzaldehyde cyanohydrin in a reversible base-catalysed reaction. Triphenylbismuthonium 2-oxoalkylide (**171**), generated *in situ* from the corresponding oxonium salt and base, has been shown to react with 1,2-diketones to yield *O*-aroyl enolates of unsymmetrical 1,3-diketones (**172**) via a carbon to oxygen migration of



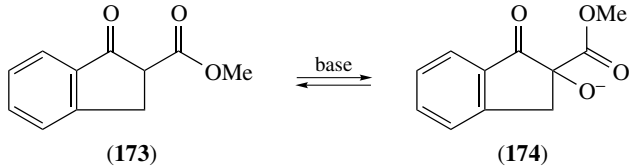
SCHEME 62



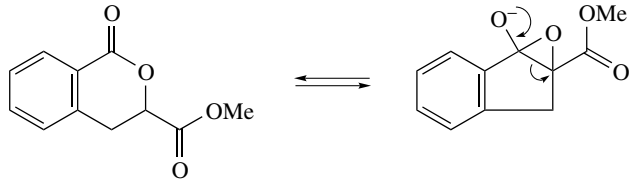
SCHEME 63

the aroyl moiety[296] (see Scheme 63). This type of carbon–carbon bond construction based on 1,2-carbonyl migration is unprecedented in ylide chemistry. It has been proposed[297] that the formation of products such as (**176**) from the oxidation of 1,3-dicarbonyl compounds of the type (**173**) with (camphorylsulfonyl)oxaziridines involves initial generation of the α-alkoxy-β-keto ester anion (**174**) which rearranges via the alkoxy epoxide (**175**). Wasabidienone A (**178**) has been synthesized[298] via a novel rearrangement reaction of an acyl group from carbon to the β-hydroxy oxygen on a cyclohexadienone ring (**177**).

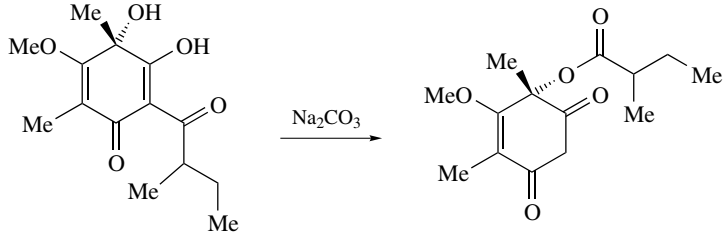
The formation of fluorinated α-hydroxy-β-imino esters (**180**) by treatment of fluorinated imino ethers (**179**) with lithium 2,2,6,6-tetramethylpiperidide has been reported.[299] A possible explanation for this interesting intramolecular rearrangement is proposed in Scheme 64. Acyclic imides derived from primary benzylic amines and amino acid esters have been found to undergo a novel nitrogen to carbon acyl migration via a base-generated carbanion to yield the corresponding α-amino



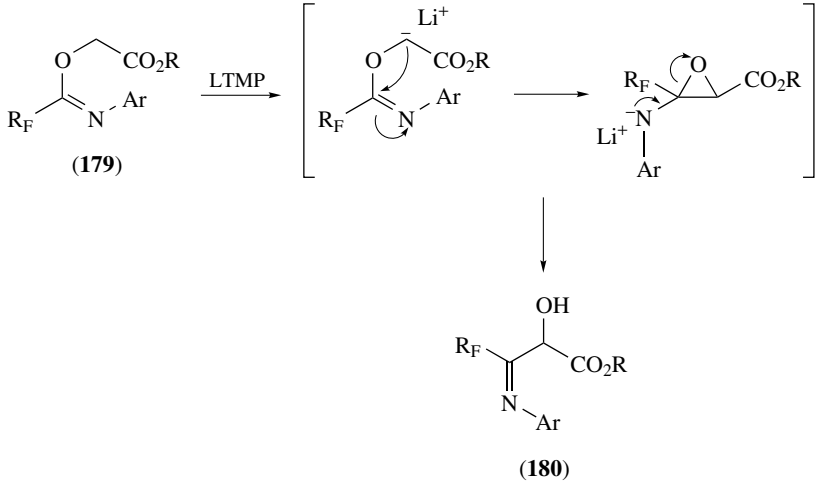
(**173**) (**174**)



(**176**) (**175**)

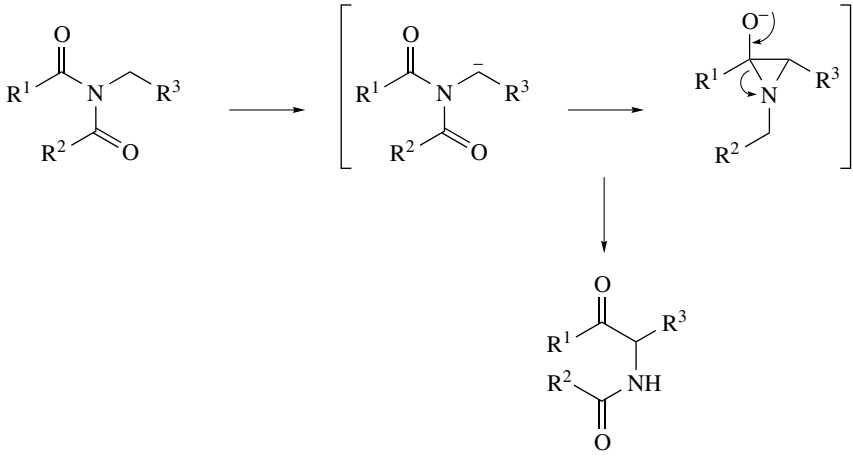


(**177**) (**178**)

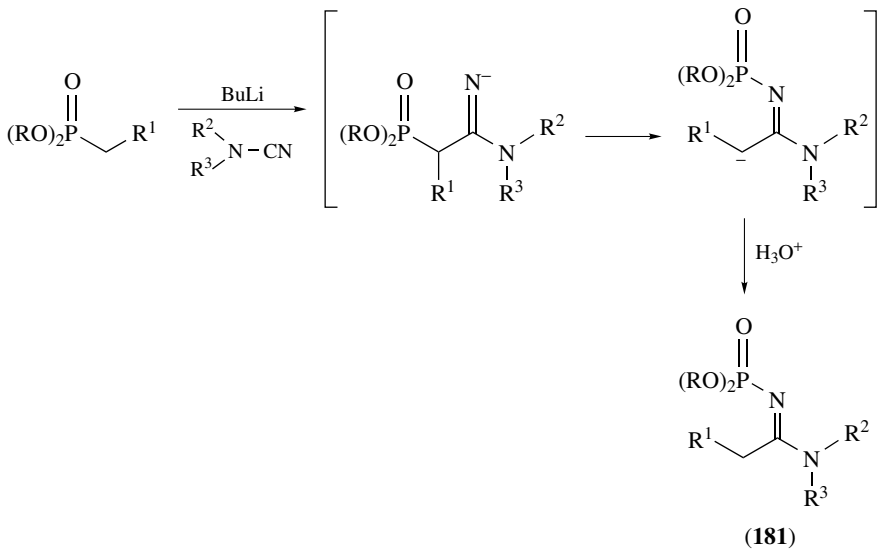


(**179**) (**180**)

SCHEME 64



SCHEME 65



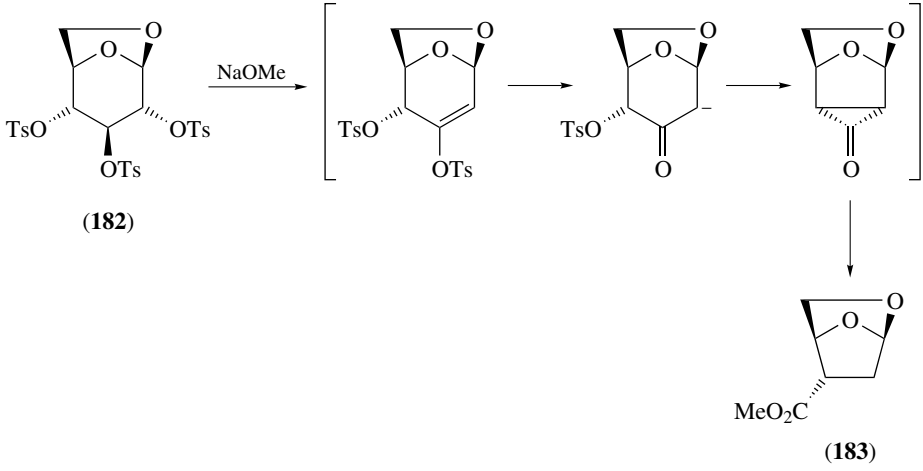
(**181**)

SCHEME 66

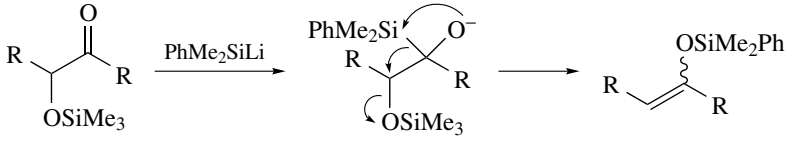
ketones.[300] A possible mechanism for the transformation is outlined in Scheme 65. A new type of [1,2]-rearrangement of a toluenesulfonyl group from nitrogen in azoles to the neighbouring carbon has been initiated[301] by treatment with *n*-butyllithium. *N′*-Phosphorylated amidines (**181**) have been synthesized[302] by the reaction of lithiated alkyl phosphonates with *N,N*-dialkylcyanamide via an unprecedented carbon-to-nitrogen migration of the phosphoryl group (see Scheme 66). A novel electrophilic rearrangement involving the migration of an alkoxycarbonyl group from carbon to a nitrogen anionic centre has been reported.[303]

Recent applications of the Favorskii rearrangement have been reviewed.[304] A PM3 semiempirical study has been undertaken of the molecular mechanism for the Favorskii rearrangement of α-chlorocyclobutanone. The results indicated that, although two competitive reaction mechanisms can exist, viz. the semibenzilic acid and the cyclopropanone rearrangement, the former appears to be the energetically favorable pathway *in vacuo* and in solution.[305] Electrochemically reduced polyhalo ketones have been found to react with amines and phenols to afford the corresponding α,β-unsaturated amides and esters in an electrochemically induced Favorskii rearrangement.[306] A variety of iridolactones have been synthesized using a stereoselective Favorskii rearrangement as the key step.[307] α-Hydroxy ketones have been prepared from the corresponding α-nitro ketones under aqueous basic conditions by a novel transformation which has been explained[308] by a double S_N2 reaction which proceeds via a Favorskii-like cyclopropanone intermediate. 3-Methoxycarbonyl-1,5-anhydro-β-D-*erythro*-pentafuranose (**183**) has been obtained[309] by a tandem elimination–Favorskii rearrangement by treating 2,3,4-tri-*o*-tosyl-1,6-anhydro-β-D-glucopyranose (**182**) with sodium methoxide (see Scheme 67).

Silyl enol ethers have been prepared[310] via a Brook rearrangement from the reaction of phenyldimethylsilyllithium with α-silyloxy ketones (see Scheme 68). The comparison of the rate of the base-catalysed Brook rearrangement in β-substituted



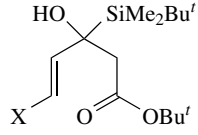
SCHEME 67



SCHEME 68

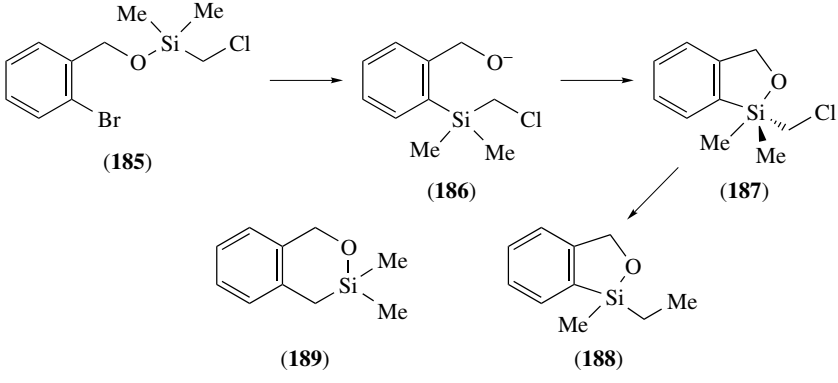
α-silylallyl alcohols (**184**) has been used[311] as a tool for the assessment of the α-carbanion-stabilizing ability of the β-substituent. 3-Trimethylsilylprop-2-yn-1-ol has been prepared[312] from 1-trimethylsiloxy-3-bromomagnesiumprop-2-yne by an unusual 1,4-migration of the trimethylsilyl group from oxygen to carbon, and a recent approach to the C(33)–C(38) fragment of amphotericin B and nystatin has involved a retro-(1,4)-Brook rearrangement and the stereoselective manipulation of the resulting allylsilane.[313] Treatment of 3-[(silyloxy)methyl]furans and thiophenes with *n*-butyllithium has provided[314] 2-silylated-3-(hydroxymethyl)furans and thiophenes via an intramolecular 1,4-oxygen to carbon silyl migration, and a new method which involves the regioselective lithiation of various 2-silylated-3-(hydroxymethyl)furans has been described[315] for the preparation of 2,4- and 3,4-disubstituted furan rings. Treatment of chloromethylsilane (**185**) with *t*-butyllithium has been shown to yield oxasilacyclopentane (**188**), believed to arise via rearrangement of γ-oxidosilane (**186**), followed by methyl migration.[316] Aryl migration would have given oxasilacyclohexane (**189**). The preference for methyl migration in (**185**) suggests that migration is favoured by an apical position of the migrating group in a trigonal bipyramid intermediate (**187**).

Recent applications of the Ramberg–Bäcklund rearrangement to the synthesis of bioactive target molecules have been reviewed.[317] Under Ramberg–Bäcklund conditions, *exo*-6-bromo-*syn*-7-bromo(chloro)methylsulfonyl-*endo*-6-phenylbicyclo[3.1.1]-heptane has been shown to yield *anti*-6-hydroxy-7-methylene-*syn*-6-phenylbicyclo-[3.1.1]heptane along with 3-oxa-2-phenyl-5-thiatricyclo[4.4.0.0^{2,7}]decane S,S-dioxide, the product of an unusual heterocyclization.[318] In contrast to trichloromethyl sulfoxides which undergo base-induced β-elimination of chloroform to produce sulfines, the corresponding sulfones have been found to undergo an unusually

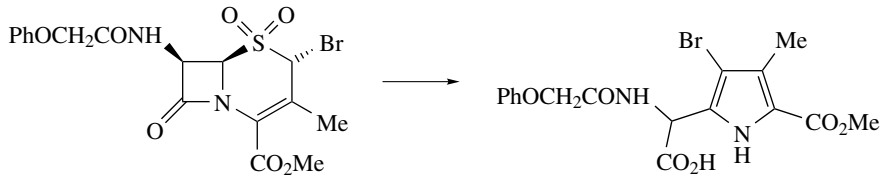


(**184**)

X = SPh, $SiMe_3$



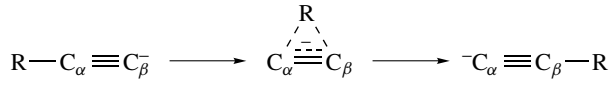
(**185**) (**186**) (**187**) (**189**) (**188**)



(**190**) (**191**)

facile Ramberg–Bäcklund rearrangement with the formation of dichloromethylene products.[319] A new route to *exo*-glycals, which starts from *S*-glycoside dioxides and utilizes a variant of the Ramberg–Bäcklund rearrangement has been described.[320] An unusual Ramberg–Bäcklund-like rearrangement followed by bromination has been invoked[321] to explain the formation of a bromopyrrole derivative (**191**) from α-bromocephem sulfone (**190**) in acetonitrile solution.

Density functional theory has been used to study the rearrangement of the fulminate anion to the cyanate anion. The study has shown that the transformation proceeds via an oxazirinyl anion intermediate.[322] The activation barriers of the 1,2-migrations of various groups (R) in acetylide anions [(**192**) → (**193**)] have been calculated[323] with *ab initio* methods. The barrier for the rearrangement was found to depend on the capability of R to form a hypervalent-type bonding for which its ability to accomplish negative hyperconjugation as well as its polarizability are important. The carbanionic ring enlargement of (halomethylene)cyclobutanes to 1-halocyclopentenes has been extended to the fluoro analogues. Experiments with labelled substrates have shown that, in general, the larger the halide and the higher the reaction temperature, the greater the preference for double migration over single migration as a mechanistic pathway.[324] Chemical evidence has been obtained[325] for the first time to support a cyclopropane ring migration on the periphery of a cyclic polyenide, during the butyllithium-mediated rearrangement of tricyclo[5.3.1.$0^{1,7}$]undeca-2,4,9-triene to tricyclo[6.3.0.$0^{1,3}$]undeca-5,7,9-triene, the sole product of the reaction.



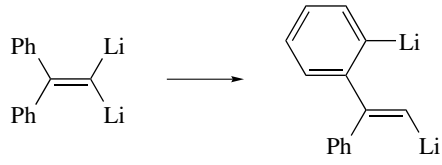
(**192**) (**193**)

A recent study has indicated[326] that the skeletal rearrangement step in the B_{12}-catalysed isomerization of methylmalonyl-CoA to succinyl-CoA occurs not by a radical pathway but by an anionic or organocobalt pathway. A computational study of the isomerization of allyl alcohol into homoallyl alcohol by lithium amide has pointed to[327] a process proceeding via a transition state in which the proton is half transferred between carbon and nitrogen in a hetero-dimer. 1,1-Dilithio-2,2-diphenylethene (**194**), accessible from 1,1-dibromo-2,2-diphenylethene by double bromine–lithium exchange, has been found[328] to undergo an intramolecular rearrangement to (*E*)-1-lithio-2-(2-lithiophenyl)-2-phenylethene (**195**), while the intermolecularity of

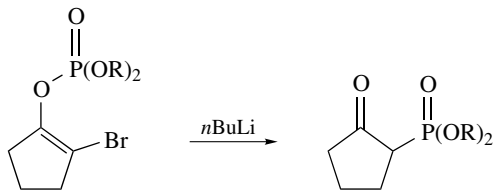
the rearrangement of 3,4-dilithio-2,5-dimethylhexa-2,4-diene to the cross-conjugated 2,5-dimethylhexadienediyl anion has been established.[329]

A new strategy has been developed[330] for the preparation of β-keto-phosphonates (**197**) via a halogen metal exchange-induced 1,3-phosphorus migration of 2-bromovinyl phosphates (**196**). The *ortho*-directing properties of the (aryloxy)tetrazole functionality, and the subsequent anionic 1,3-migration of *ortho*-lithiated (aryloxy)tetrazoles (**198**) to provide 5-(hydroxyaryl)-1-phenyl-1*H*-tetrazoles (**199**) have been demonstrated for the first time.[331] It has been proposed[332] that the base-catalysed rearrangement of 3-halocoumarins to benzofuran-2-carboxylic acids proceeds by rate-determining fission of the carbon–halogen bond following formation of a relatively unstable carbanion intermediate formed by intramolecular nucleophilic attack on the vinyl group by the phenoxide anion (see Scheme 69).

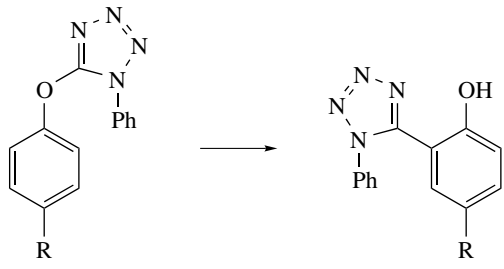
An ^{18}O-labelling investigation of the oxygen to sulfur transposition in the base-catalysed rearrangement of *o*-benzoyl-*N*-(diphenylphosphinothioyl)hydroxylamine (**200**) to (**201**) has been undertaken.[333] The labelling results are outlined in Scheme 70 although further evidence is required to substantiate the mechanism



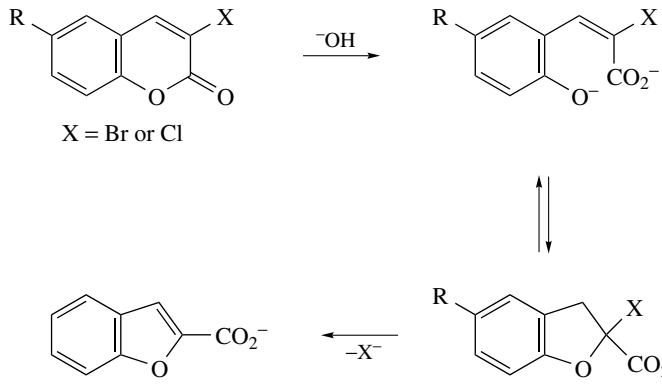
(**194**) (**195**)



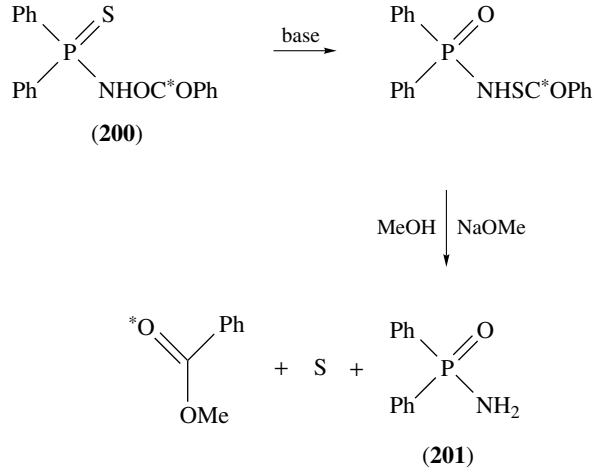
(**196**) (**197**)



(**198**) (**199**)



SCHEME 69

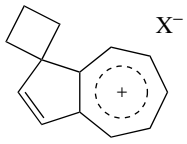


SCHEME 70

of this unusual rearrangement. The *o*-mesyloxime derivatives of ring- and side-chain-substituted 3-phosphonomethylcyclohexenones have been found to undergo a basic aluminium oxide-promoted Neber rearrangement to yield the corresponding vinyl aminocyclohexenonealkylphosphonates, regioselectively.[334] A synthetic route involving a key Neber rearrangement has been described[335] for the preparation of both [1-^{13}C]- and [1-^{15}N]-2-amino-4-phenylbutanoic acids.

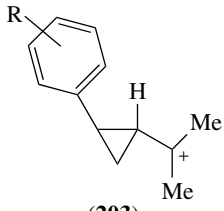
Cationic and Related Rearrangements

A theoretical *ab initio* study of the interconversion of isobutonium ions has been carried out.[336] The 1,1-trimethylene-1*H*-azulenium ion (**202**) has been prepared and its chemical behaviour has been shown[337] to be different from that of its three-membered ring homologue. The solvolysis of 1-[*trans*-2-(*m*- or *p*-substituted phenyl)

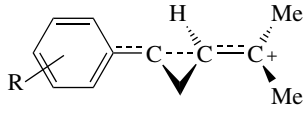


(**202**)

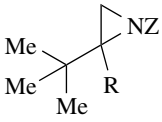
X = BF_4, PF_6



(**203**)

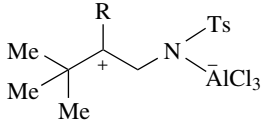


(**204**)

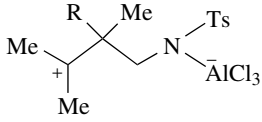


(**205**)

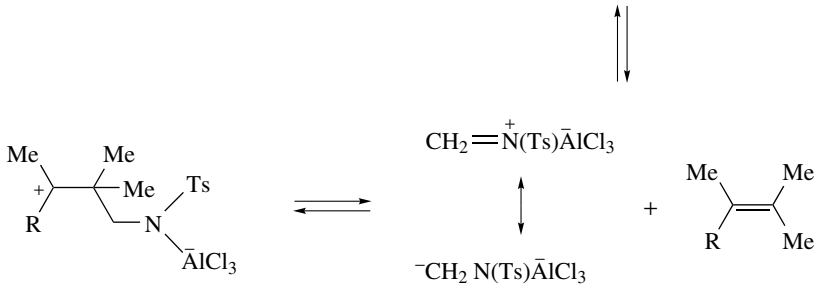
R = Bn, Ph
Z = Ts



(**206**)

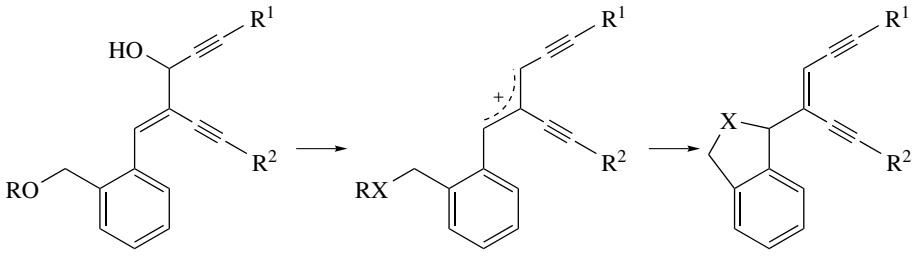


(**207**)

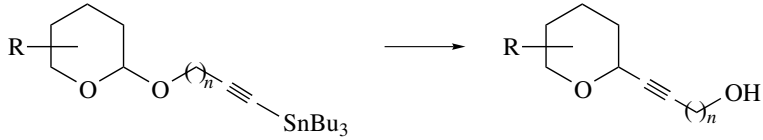


(**209**) (**208**)

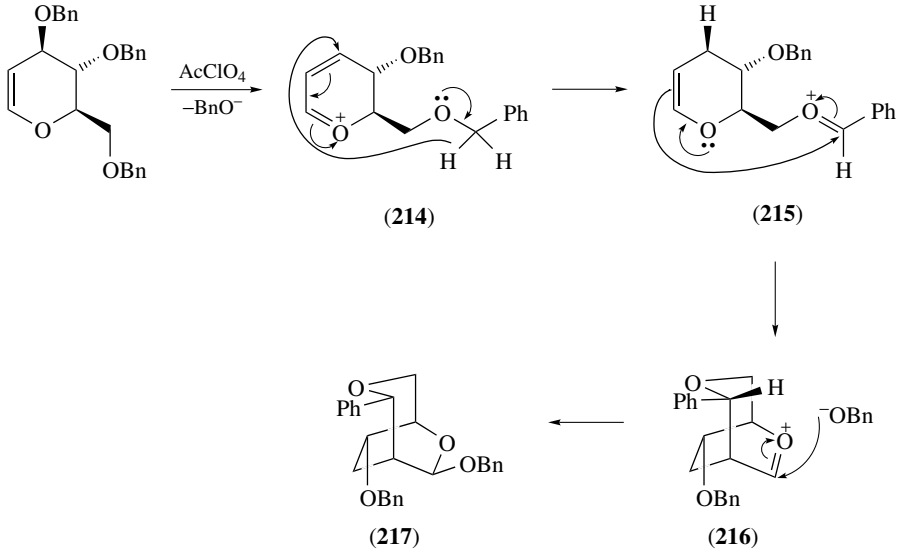
cyclopropyl]-1-methylethyl *p*-nitrobenzoates in 80% aqueous acetone has been shown to proceed via two independent reaction pathways.[338] One intermediate is the correspondent cyclopropylmethyl cation (**203**) and the other is the homoallylic cation (**204**). Aluminium-induced ring cleavage of 2-*t*-butyl-1-tosylaziridines (**205**) has been shown to yield a number of products which can be explained by invoking[339] the generation of carbocations (**206**), which on neopentyl rearrangement afford (**207**) whose β-cleavage generates (**208**) and an alkene. The intermediate then recombines with the alkene at either double-bond carbon, resulting in reversal of the cleavage, or in a formal 1,2-shift to give (**209**). The mechanism of the acid-induced racemization and regioisomerization of *o*-methylated (*S*)-*trans*-hex-4-en-3-ol and (*R*)-*trans*-hex-3-en-2-ol has been investigated in the gas phase at pressures high enough to allow complete thermalization of the reaction intermediates. The study[340] has provided a first comparative analysis of the intrinsic factors governing acid-catalysed racemization of optically active alcohols, and suggests the involvement of intramolecular



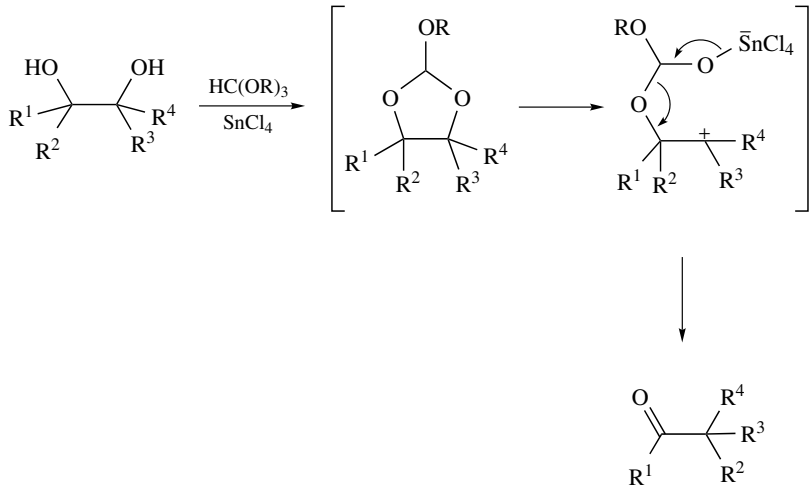
SCHEME 71



processes and the intermediacy of two distinct hydrogen-bonded complexes, wherein the CH_3OH molecule is coplanarly coordinated to the in-plane hydrogens of the 1-methyl-3-ethylallyl moiety. A good example of the control of regiochemistry associated with nucleophilic addition to allylic cations has been demonstrated.[341] Thus the regio-controlled allylic rearrangement of substrates such as (**210**) has proved successful in the synthesis of a number of 2,5-dihydro-2-benzofuryl-*cis*-enediynes (**211**; X = O) and their sulfur analogues (**211**; X = S) (see Scheme 71). Stereo-controlled routes to 2,3-dihydro-4*H*-pyran-4-ones by the Hg(II)-catalysed rearrangement of 1-alkynyl-2,3-epoxy alcohols in acidic media have been reported.[342] A general method for the introduction of carbon-linked substituents adjacent to the heteroatom in pyran ring systems via the Lewis acid-mediated oxygen to carbon rearrangement of a variety of different anomerically linked carbon-centred nucleophiles has been described. Thus treatment of alkynyl tributylstannane tetrahydropyranyl (and tetrahydrofuranyl) ether derivatives such as (**212**) has been found to effect an efficient anomeric oxygen to carbon rearrangement[343] leading to carbon-linked alkynol products (**213**). A further extension of this methodology, encompassing silyl enol ethers as the anomerically linked carbon nucleophile has also been reported,[344] and the strategy has been used to achieve a total synthesis of (+)-goniodiol.[345] An unprecedented 1,6-hydride shift has been observed[346] during acetyl perchlorate treatment of tri-*O*-benzyl-D-glucal (see Scheme 72). Formation of the observed product (**217**) has been rationalized via initial generation of the conjugated oxacarbenium ion (**214**). An intramolecular 1,6-hydride shift then regenerates the glycal producing a benzylic oxacarbenium ion (**215**). Cyclization through attack of the vinyl ether affords, after trapping of the oxacarbenium ion (**216**) with benzyl alcohol, the observed acetal (**217**). The acid-catalysed rearrangement of 1-hydroxy-2,3,4,4a-tetrahydro-9*H*-xanthen-9-ones has been shown



SCHEME 72

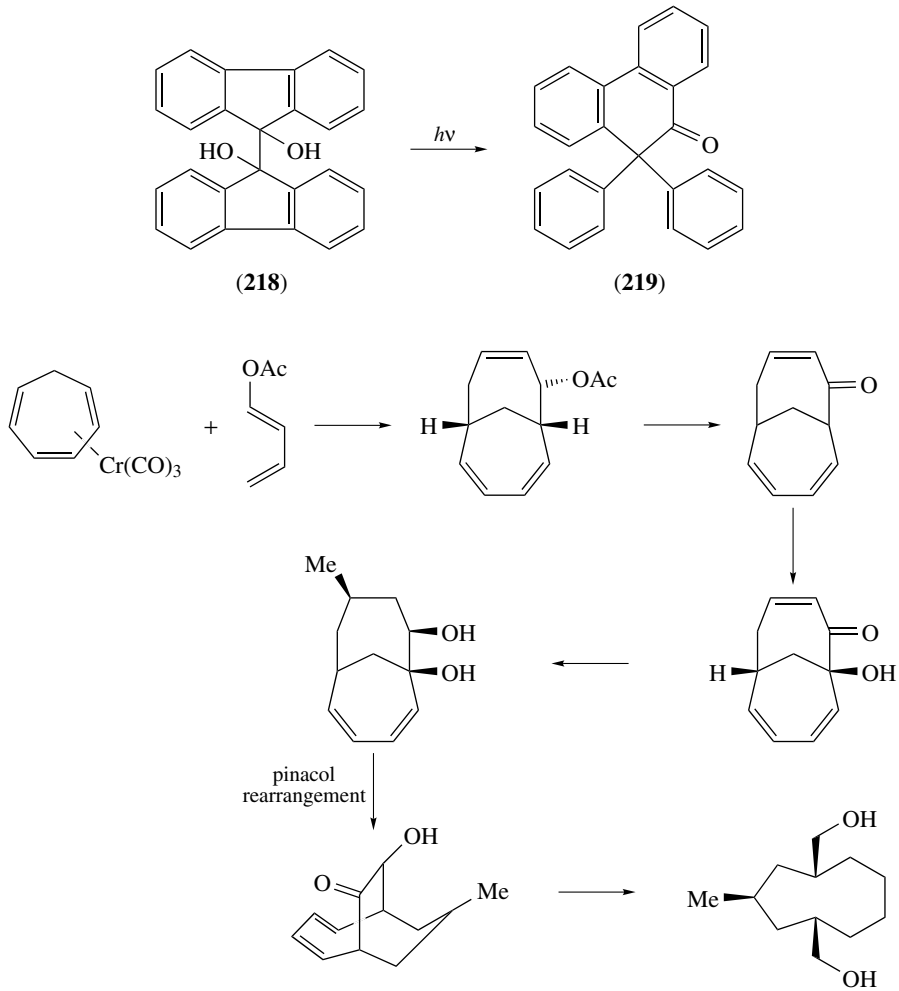


SCHEME 73

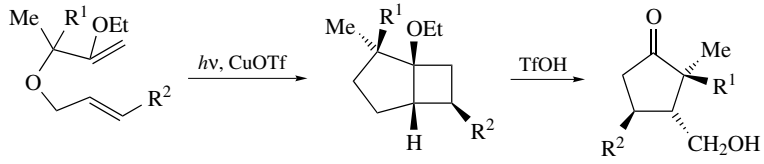
to yield 1-alkoxy- or 1-alkylidene-1,2,3,4-tetrahydro-9*H*-xanthen-9-ones and/or 3,4-dihydro-9*H*-xanthen-9-ones, depending on the conditions employed.[347]

The MNDO method has been employed[348] to study the acid-catalysed rearrangement of propylene 1,2-glycol. Propanaldehyde was found to be the major product with a small amount of acetone also being produced. The solid-state pinacol rearrangement of 1,1,2-triphenylethane-1,2-diol has been performed over various solid

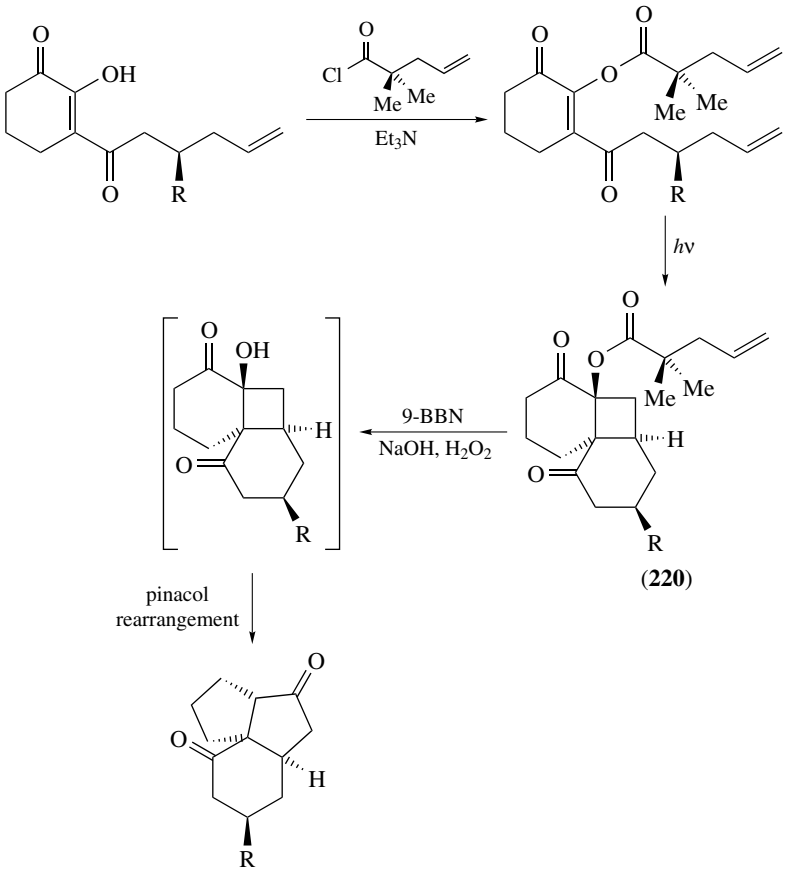
acids,[349,350] and pinacol has been converted into pinacolone and 2,3-dimethylbuta-1,4-diene at relatively mild temperatures over metal-substituted aluminophosphate molecular sieves.[351] An efficient pinacol rearrangement, mediated by trialkyl orthoformate, has been developed[352] (see Scheme 73). It has been shown[353] that a pinacol rearrangement occurs during photo-excitation of 9, 9′-bifluorene-9, 9′-diol (**218**). The reaction proceeds via initial C−O bond heterolysis to give a substituted 9-fluorenyl cation, which undergoes rearrangement and deprotonation to yield spiro[9*H*-fluorene-9, 9′(10′-OH)phenanthren]-10′-one (**219**). A novel chromium(0)-promoted $6\pi-4\pi$-cycloaddition–pinacol rearrangement strategy that delivers substituted nine-membered carbocycles with complete control of substituent stereochemistry has been described,[354] as shown in Scheme 74. An interesting stereo-controlled approach to highly substituted



SCHEME 74

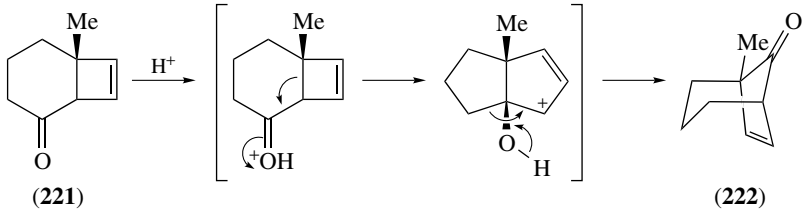


SCHEME 75

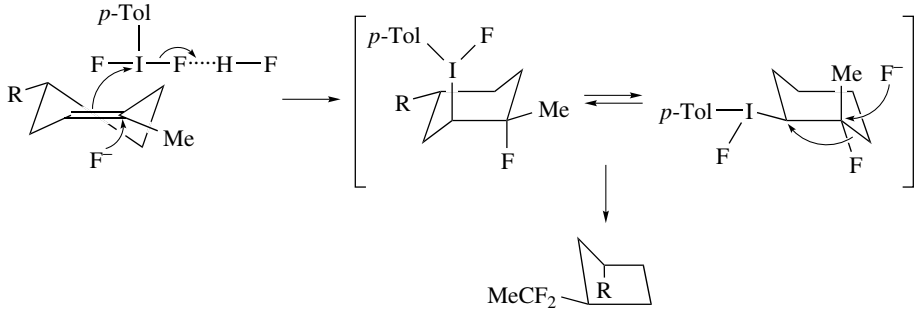


SCHEME 76

cyclopentanones[355] has involved as a key step the stereoselective copper(I)-catalysed photo-cycloaddition of dienes followed by a stereospecific pinacol–pinacolone rearrangement of the resulting cyclobutane derivative (see Scheme 75). A novel vinyl pivalate protecting group, which can be removed either oxidatively or reductively as dictated by the sensitivity of the molecule in question, has been developed. It has been exploited[356] to effect a novel pinacol-type rearrangement of intramolecular photo-cycloadducts such as (**220**) in high yield (see Scheme 76).



SCHEME 77

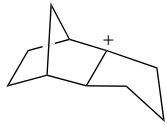


SCHEME 78

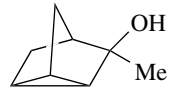
Mono- and bi-cyclic cyclopentanes, known precursors of variety of sesquiterpenes, have been prepared[357] by the acid-catalysed rearrangement of 1-methylcyclobutylmethanols. An acid-catalysed rearrangement (see Scheme 77) has been found to afford a practical method for converting a bicyclo[4.2.0]octene system (**221**) into a bicyclo[3.2.1]octene framework (**222**) in a recent synthesis of verrucarol.[358]

The thallium trinitrate-mediated ring contraction of *trans*-decal-2-ones has opened up a new route to the hydrindane system,[359] and fluorinative ring contraction of cyclic alkenes to afford difluorocycloalkanes has been induced by iodotoluene difluoride and Et_3N–HF. A possible mechanism[360] is shown in Scheme 78. The double bond of the cyclohexene ring is attacked by iodotoluene difluoride activated by HF from the axial direction, followed by the addition of a fluoride ion from the *trans* direction. Reductive elimination of iodotoluene from the resulting adduct, ring contraction and the addition of the fluoride ion to the carbocation stabilized by fluorine then take place to give the ring-contracted difluorinated product.

The reaction of different substituted 2-norbornanones with triflic anhydride in the presence of nitriles has been carried out in order to study the factors that influence the different reaction possibilities of 2-norbornyl carbocations.[361] The chemistry of 2-norbornyl cations with spiro-annellated cyclobutane rings has been found to deviate strongly from that of the cyclopropane analogues.[362] A cyclobutane ring spiro-annellated to the 6-position does not undergo ring expansion, whereas a cyclopropane ring does. On the other hand, a cyclobutane ring spiro-annellated to the



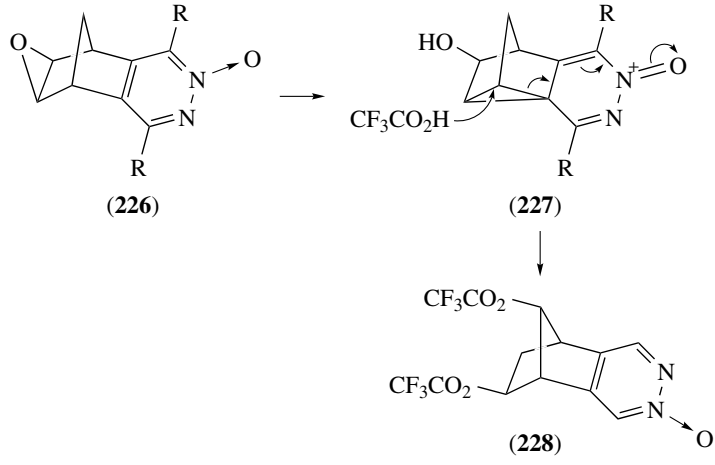
(**223**)



(**224**)

(**225**)

3-position expands readily giving rise to a uniquely *endo*-selective tertiary cation (**223**), whereas an analogously positioned cyclopropane ring remains intact. The main product of the acid-catalysed hydrolysis of 3-methyl-3-nortricyclanol (**224**) has been identified[363] as *endo*-2-methyl-exo,exo-norbornane-2,5-diol (**225**). Acid hydrolyses of 2-*exo*-arylfenchyl alcohols have been found to afford the corresponding cyclofenchones as the kinetic products. These on prolonged treatment with acid are converted into Wagner–Meerwein products via equilibration with the stabilized fenchyl carbocations. These stabilized, sterically unhindered carbocations are proposed to react with water to give 2-*endo*-arylfenchyl alcohols that are stereoelectronically set up for a Wagner–Meerwein rearrangement. The presence of *ortho* substituents on the aryl ring hinders the Wagner–Meerwein rearrangement through decreased resonance stabilization of the carbocation and steric encumbrance to attack by external nucleophiles. However, when the *ortho* substituent itself is a nucleophile, the barrier to Wagner–Meerwein rearrangement is overcome and the authors[364] have suggested that this is due to internal trapping of the carbocation from the *exo*-side to give a reactive intermediate that is stereoelectronically predisposed to concerted bond migration. Epoxide (**226**), on treatment with trifluoroacetic acid, has been found to undergo a regioselective ring opening, followed by a Wagner–Meerwein-type rearrangement, to give the 6,9-bis(trifluoroacetoxy) derivative (**228**). The intermediacy of the 2*H*-pyridazinium ion (**227**) has been invoked[365] for the transformation. The possibility of the intervention of a 2*H*-pyrazinium ion to account for the formation of the skeletally



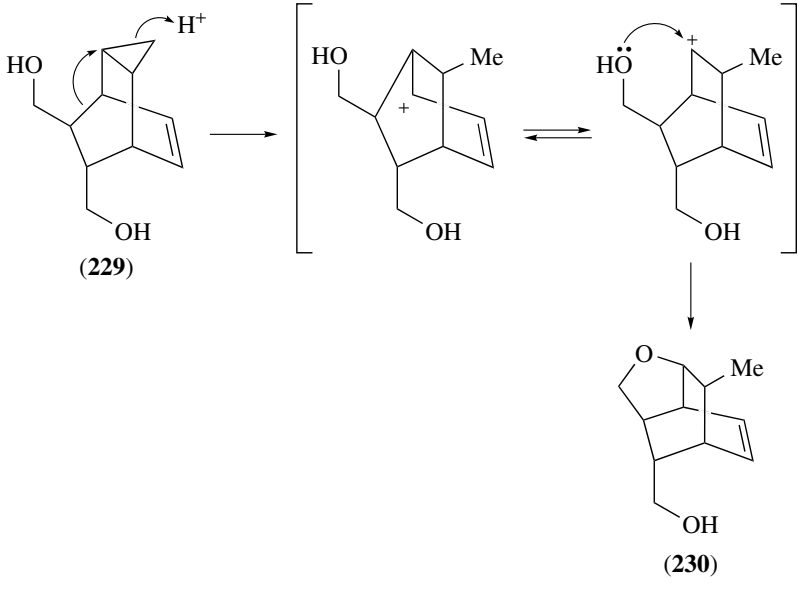
(**226**)

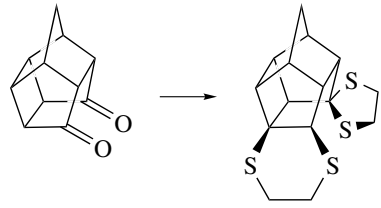
(**227**)

(**228**)

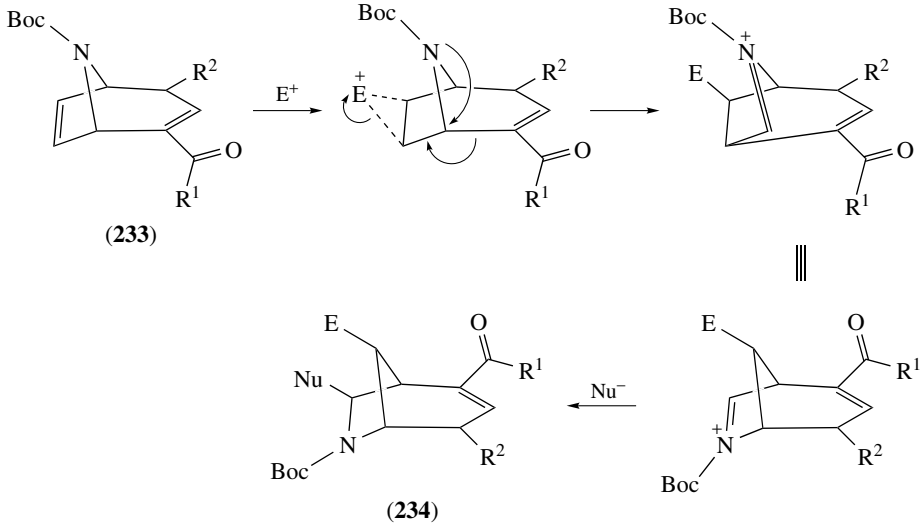
rearranged products, observed during the reaction of norbornadiene-fused pyrazines and their benzo derivatives with bromine, has also been discussed.[366] A recent study[367] has shown that oxabicyclo[2.2.1]norbornadienes, when reacted with Lewis acids, are rearranged to 6-hydroxyfulvenes or 4-phenylphenols. The course of the reaction, which is highly selective, was found to depend exclusively on the nature of the Lewis acid used.

A new cationic rearrangement of a dibenzobicyclo[2.2.2]octadiene alcohol into a fused anthracene has been described.[368] An *ab initio* study of the mechanism of the bromination of benzobicyclooctadiene has been reported.[369] The study proposes that the stereoselectivity of the reaction is best accommodated by an asynchronous concerted electrophilic addition of bromine across carbon atoms 1 and 3 and that it proceeds via an ion-pair transition structure in which the Wagner–Meerwein portion of the reaction has already occurred. The electrophilic-induced opening of a cyclopropyl ring with concerted intramolecular addition of a hydroxymethyl group in a number of tricyclo[3.2.2.0^{2,4}]nonene alcohol derivatives [see (**229**) → (**230**)] has been studied[370] with a view to establishing a procedure for the formation of the tetrahydrofuran ring in the diterpenoid harringtonolide. Acid-catalysed transformations of homodrin and its epoxide have been reported,[371] and several novel products have been obtained from the thermolysis of [4.3.1]propellanes.[372] A novel tetrathio cage compound (**232**) has been obtained[373] in good yield from the Lewis acid promoted reaction of pentacyclo[5.4.0.^{2,6}0.^{3,10}0^{5,9}]undecane (**231**) with excess ethanedithiol. A direct and flexible entry to 6-azabicyclo[3.2.1]octanes (**234**) has been achieved[374] by a facile cation-induced rearrangement of 8-azabicyclo[3.2.1]octa-2,6-dienes (**233**) (see Scheme 79). The unusual isomerization reaction of the sterically congested adamanylideneadamantanes (**235**) has been shown[375] to proceed via a two-step mechanism in





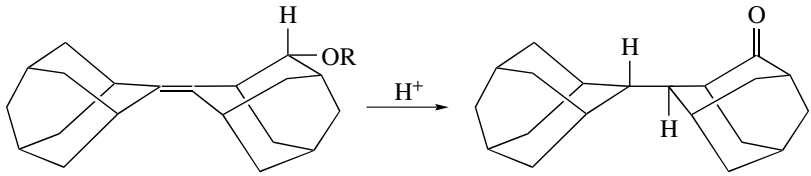
(**231**) (**232**)



(**233**)

(**234**)

SCHEME 79

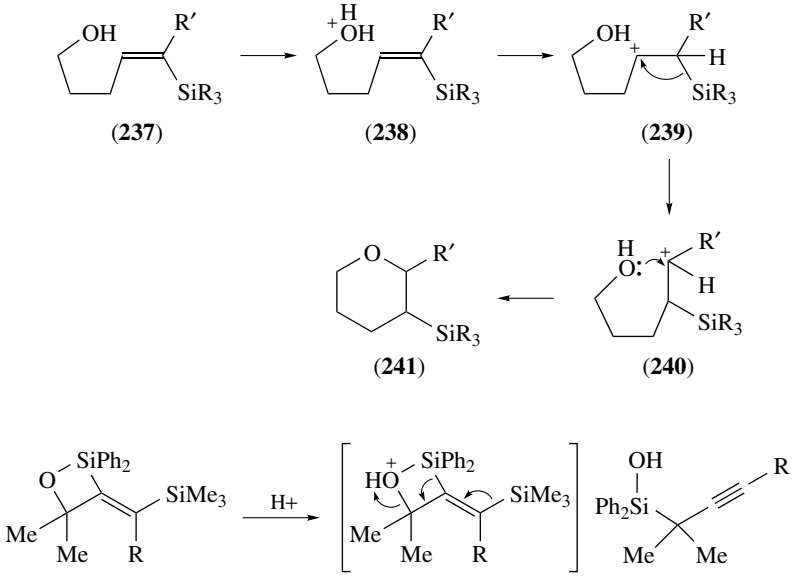


(**235**) (**236**)

R = H or OAc

which protonation of the double bond by an external acid is followed by a rate-determining intramolecular 1,4-hydride transfer to give (**236**). A detailed study of the mechanism of the solvolysis of 2-adamantyl azoxytosylate has been undertaken.[376]

Equilibrium geometries of the nine low-energy isomers in the $SiC_3H_9^+$ system and the transition states for their interconversion have been studied[377] by MO methods. It has been reported[378] that the acid-catalysed cyclization of vinylsilanes (**237**) gives

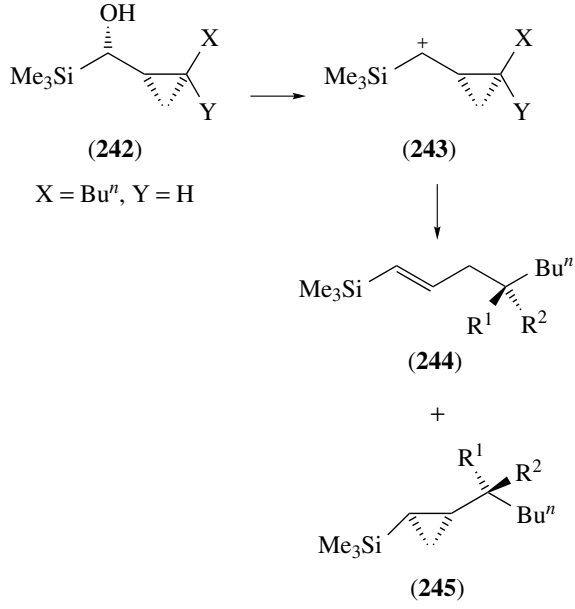


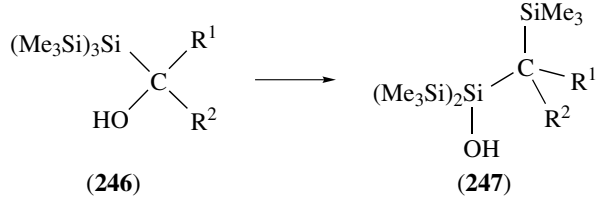
SCHEME 80

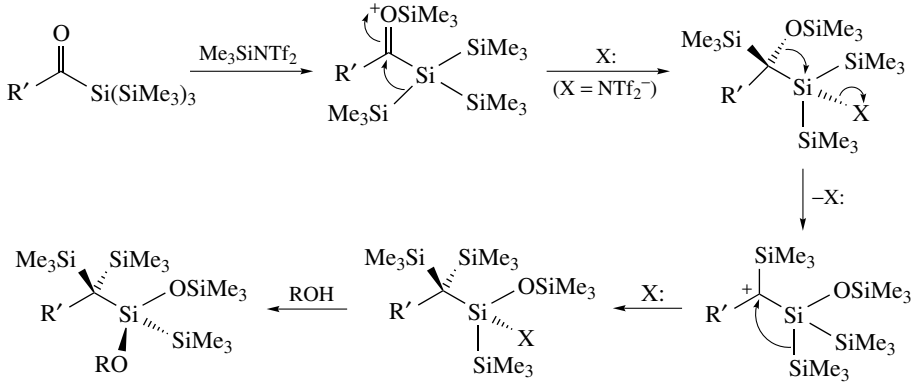
the tetrahydropyrans (**241**) with high *trans*-selectivity. A plausible mechanism for the formation of (**241**) involves attachment of a proton to the hydroxyl group of (**237**) to form the oxonium ion (**238**), shift of the proton from the oxygen atom to the α-carbon, and a 1,2-silyl migration of the β-silyl carbocation (**239**) to yield another β-silyl carbocation (**240**). Intramolecular attack of the oxygen from the side opposite to the silyl group will then give *trans*-(**241**). A highly stereospecific skeletal rearrangement involving a *syn*-1,2-silyl shift and the elimination of a trimethylsilyl group has been invoked[379] to account for the formation of enantiomerically enriched propargylsilanes (and allylsilanes) from the reaction of oxasilacycloalkanes with acid (see Scheme 80). Acidic treatment of the (1S,1′S,2′R)-α-hydroxycyclopropylsilane (**242**) has been found to yield, via the unprecedented α-silyl cation (**243**), a mixture of rearranged products which are composed of the ring-opened (*S*)-vinylsilane (**244**), the tandem (1,2)-carbon–carbon bond migration product, (1S,2R,1′S)-silylcyclopropane (**245:** $R^3 = H$, $R^4 = OH$) and its 1′R isomer (**245;** $R^3 = OH$, $R^4 = H$), respectively.[380]

In the presence of strong acids, 1-hydroxyalkyltris (trimethylsilyl) silanes (**246**) have been found[381] to isomerize by a 1,2-trimethylsilylhydroxy exchange to afford trimethylsilylmethylsilanols (**247**). The reaction of acylpolysilanes with silylbistriflimides has been found[382] to lead to novel silanols via a pathway involving two 1,2-migrations of trimethylsilyl groups from silicon to carbon and one migration of a R_3SiO unit from carbon to silicon (see Scheme 81).

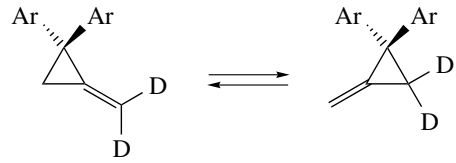
A detailed comparison of the rearrangement of 1,3-radical cations and carbocations derived from tricyclo [3.3.0.$0^{2,4}$] octanes has shown (by electron-transfer oxidation and protonation, respectively) that electronic substituent effects on the diyl sites profoundly influence the regioselectivities of the Wagner–Meerwein 1,2-shifts. The


OH
X
Y
Me3Si
(242)
X = Bu^n, Y = H
(243)
Bu^n
R1
R2
(244)
+
(245)

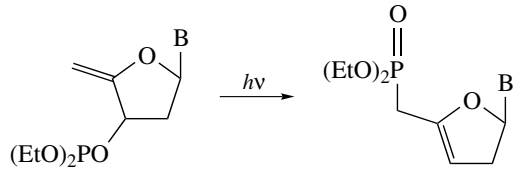

(Me3Si)3Si
R1
C
HO
R2
(246)
SiMe3
(Me3Si)2Si
OH
(247)


O
R′
Si(SiMe3)3
Me3SiNTf2
+OSiMe3
SiMe3
Si
Me3Si
X:
(X = NTf2−)
OSiMe3
–X:
ROH
RO
X

SCHEME 81



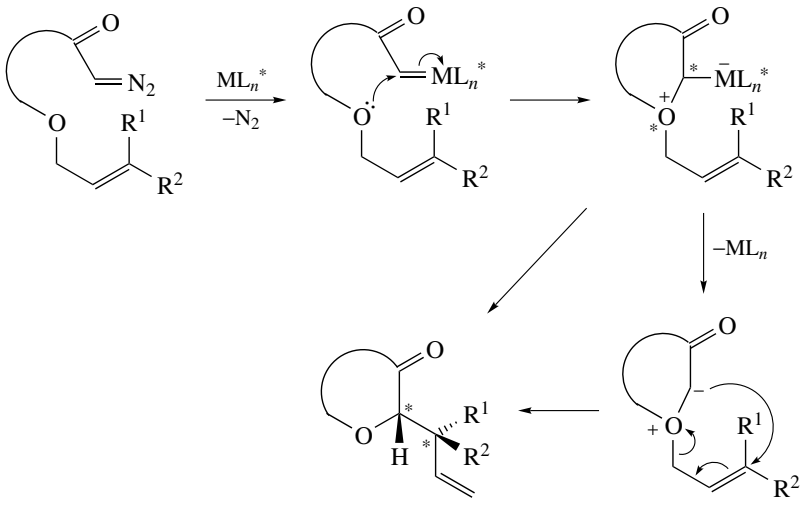
(**248**) (**249**)



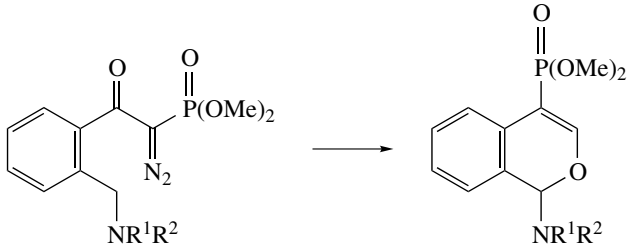
(**250**) (**251**)

regioselectivity of the electron-transfer oxidation has been rationalized[383] in terms of a qualitative MO interaction diagram, whereas that of the protonation is considered to follow the relative stability of the initially formed carbocation. *Ab initio* computational studies of methanethiol and dimethyl sulfide radical cations have demonstrated[384] that both of these groups of compounds have similar decomposition paths that involve rearrangement and fragmentation of initially formed radical cations. Two different types of intermediates, a bisected trimethylenemethane cation radical and a diradical have been directly observed[385] during the photochemical electron-transfer degenerate methylenecyclopropene rearrangement, (**248**) → (**249**). The recently discovered photochemical single electron-transfer-induced rearrangement of allyl phosphites (**250**) has been applied[386] to the preparation of allyl phosphonates (**251**). A number of persistent dihydrobenzofuranyl cations have been investigated by ^{1}H NMR and UV–visible spectroscopy and by cyclic voltammetry, and for the first time a selective and high-yield rearrangement proceeding via radical dications has been unambiguously established.[387]

A density functional study has been made of the competition between the Wolff rearrangement and 1,2-hydrogen shift in β-oxy-α-diazocarbonyl compounds.[388] A report has appeared[389] which shows that five- and six-membered acyclic ethers can be prepared enantioselectively from achiral diazo ketones, using chiral copper complexes as catalysts (see Scheme 82). A highly efficient protocol for the chain elongation of fluorenylmethoxycarbonyl-protected α-amino acids by a Ag^+-catalysed ultrasound-promoted Wolff rearrangement of the corresponding α-diazo ketones has been described.[390] The Wolff rearrangement of diazo ketones derived from *N*-*p*-tolylsulfonyl-protected α- and β-amino acids has been investigated.[391] Several different reaction pathways, including direct carbene N–H insertion, appear to be possible, depending on the nature of the *N*-protecting group, the substrate structure and the solvent. The thermolysis of α-diazo-β-keto-phosphonates (**252**) has been shown to afford 1-(disubstituted)-amino-1*H*-2-benzopyrans (**253**) which can be transformed into 1*H*-2-benzopyran derivatives by the action of various nucleophilic reagents. The extension of this reaction to pyridine and thiophene α-diazo-β-ketophosphonate



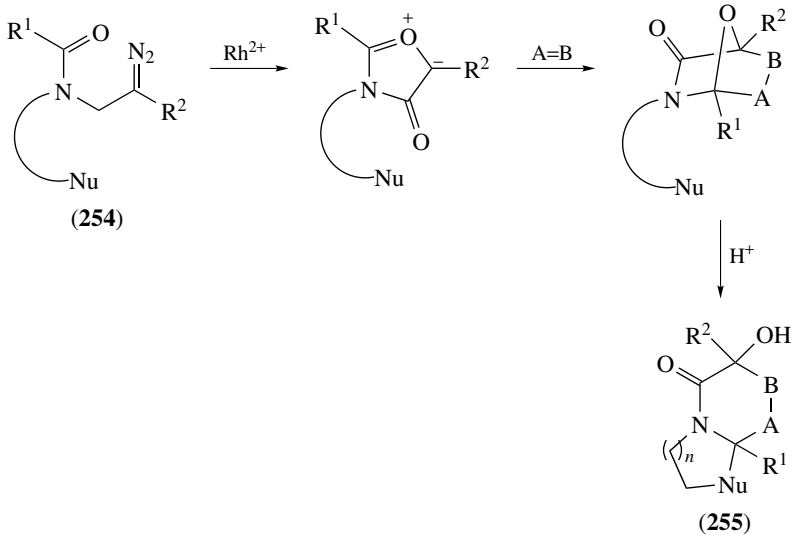
SCHEME 82



(**252**) (**253**)

analogues has also been described.[392] Starting from simple acyclic diazo imides (**254**) a domino carbenoid cyclization–4 + 2-cycloaddition–cationic π-cyclization protocol has been developed[393] for the construction of complex nitrogen poly-heterocycles of the type (**255**) (see Scheme 83).

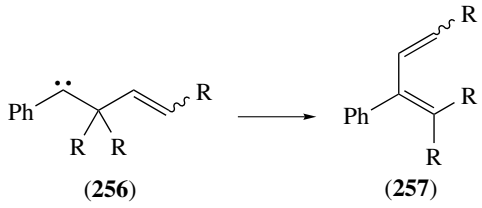
The rearrangement of dimethylcarbene to propene has been studied[394] by laser flash photolysis and *ab initio* MO theory, and substituent effects at the migration origin on the rate of rearrangement of several alkylchlorocarbenes have been studied.[395] It has been shown that the Arrhenius curvature observed for the rate constants of the 1,2-hydrogen rearrangement of benzylchlorocarbene in hydrocarbon solvents is due mainly to competitive intermolecular chemistry.[396] Absolute rate constants and activation parameters have been presented[397] for the 1,2-hydrogen and 1,2-acetyl migrations of a family of alkylacetoxycarbenes, while absolute rate constants detected for 1,2-carbon and 1,2-hydrogen migrations of cyclobutyl-, cyclopentyl-, benzocyclobutenyl-,

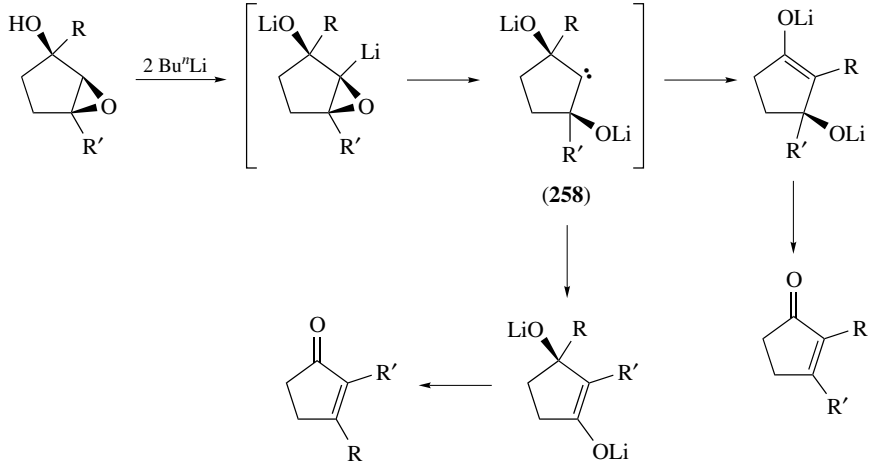


SCHEME 83

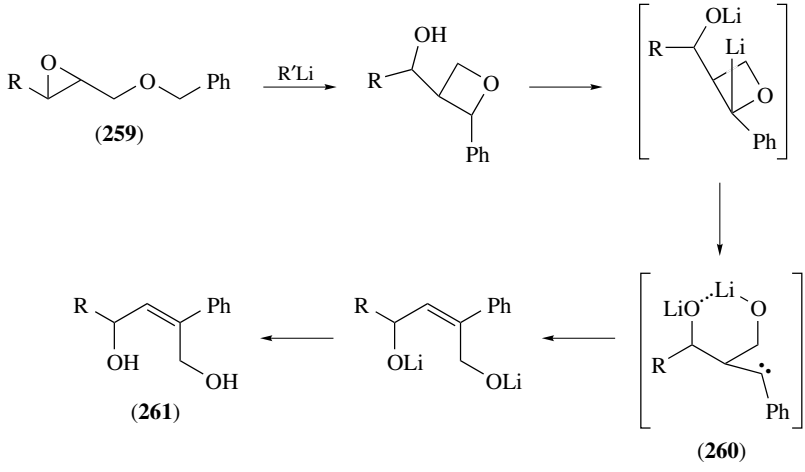
and various benzocyclopentenyl-carbenes have revealed[398] that phenyl carbon migrations are preferred to alternative 1,2-carbon shifts. It has been observed[399] that 1,2-vinyl shifts of 1-phenylbut-3-arylidenes [(**256**) to (**257**)] proceed with retention of configuration. A theoretical study of the adamantene and protoadamantene systems has been undertaken,[400] and adamantylchlorocarbene and its ring-expanded product chlorohomoadamant-3-ene have been characterized[401] by matrix isolation spectroscopy combined with DFT calculations. The latest results on the metal-induced 1,2-alkyl shifts in cyclic *syn* α-hydroxy epoxide systems have been reported.[402] They have shown that the reaction proceeds via a carbenoid intermediate (**258**) which can rearrange along two distinct intramolecular carbenoid insertion routes to yield two regioisomeric α,β-unsaturated ketones (see Scheme 84). A carbene-type intermediate (**260**) has been invoked[403] to account for the unusual base-promoted rearrangement of (*E*)-1-benzyloxy-2,3-epoxyalkanes (**259**) to allylic alcohols (**261**) (see Scheme 85).

A bis(dithia-dication) dimer has been proposed[404] as an intermediate in the remote oxygen migration reactions of 1,4-bis(methylthio)benzene and its derivatives (see

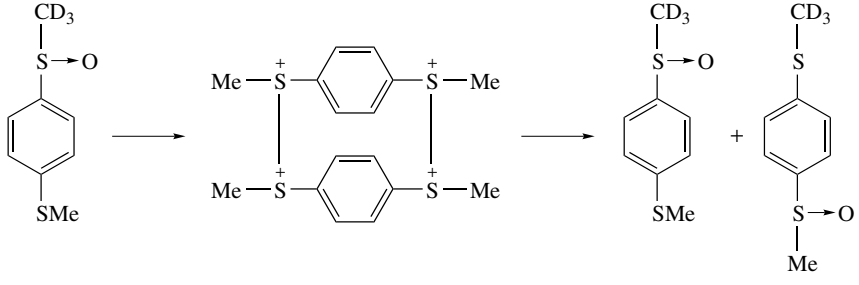




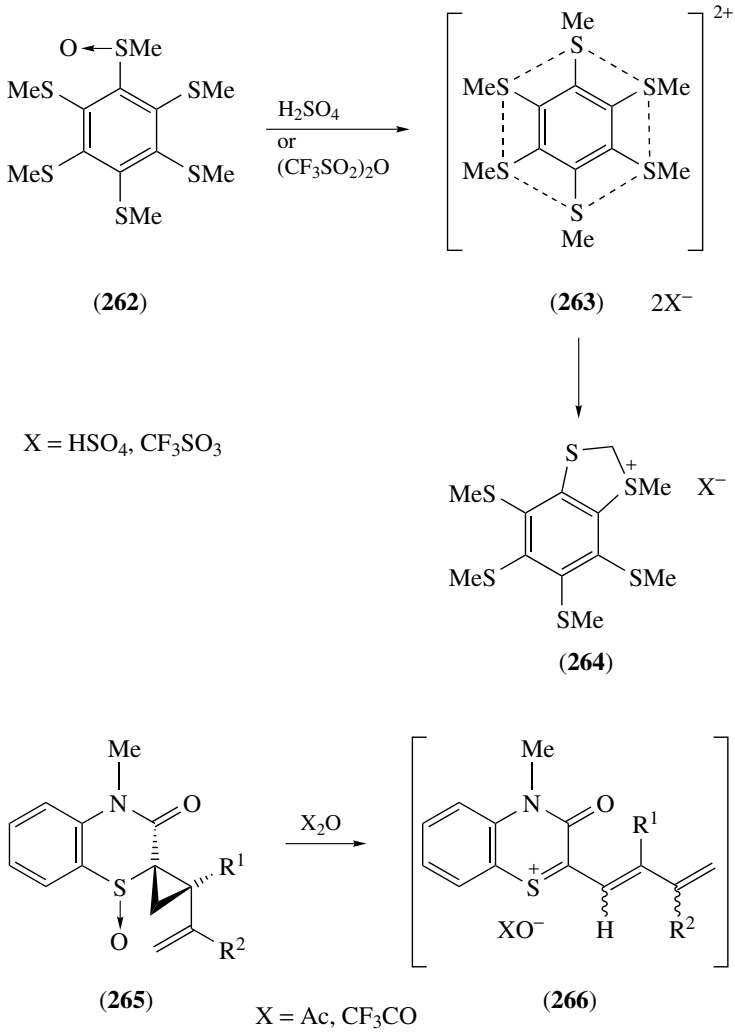
SCHEME 84



SCHEME 85

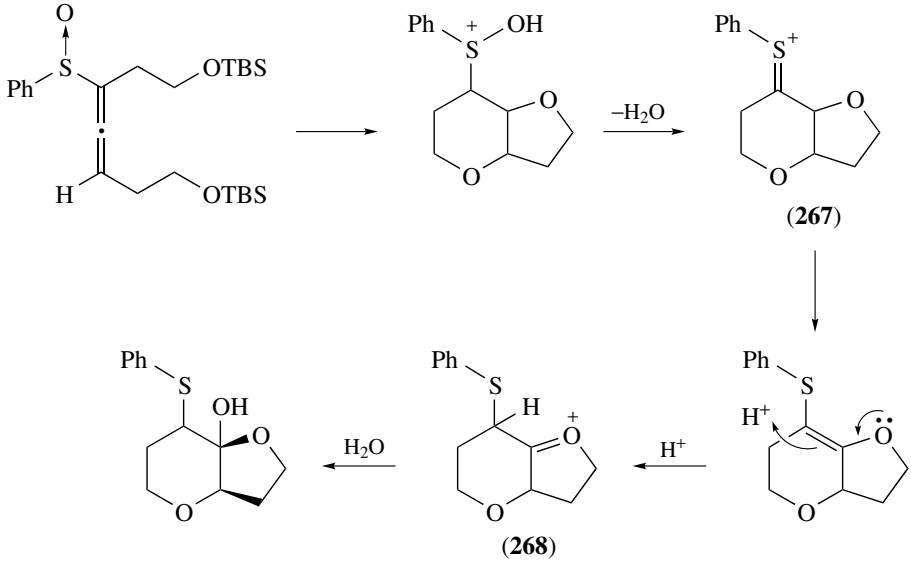


SCHEME 86



Scheme 86), and a σ-delocalized hexathia dication (**263**) is considered[405] to be the most stable intermediate for the Pummerer-type rearrangement of (**262**) into (**264**). The Pummerer reaction of 2-vinylcyclopropyl sulfoxides (**265**) has been shown to proceed via butadienyl thionium ions (**266**) by the proton abstraction from the 2′-methyl group or the cyclopropane ring, to yield cyclic dienes or acyclic dienols.[406] Benzyl 2-(hydroxymethyl)phenyl sulfoxides on treatment with *p*-toluenesulfonic acid monohydrate have been found to undergo a Pummerer-type rearrangement to afford benzaldehydes. The reaction was found to proceed via an oxosulfonium salt as an intermediate.[407] The potential of both additive and vinylogous Pummerer reactions of amido sulfoxides for the preparation of nitrogen-containing heterocycles has

been demonstrated.[408] A new synthesis of the 1,4-dioxahydrindane ring system has been reported[409] using a novel double deprotective-double cyclization rearrangement sequence mediated by aqueous HF. The process is considered to involve fluoride-induced desilylation of both silyl ethers followed by an acid-catalysed double cyclization and finally a Pummerer-type rearrangement, in which the sulfoxide moiety becomes protonated and undergoes subsequent dehydration to give thionium ion (**267**). A deprotonation and subsequent protonation then produces oxonium ion (**268**) which is trapped with water (see Scheme 87).



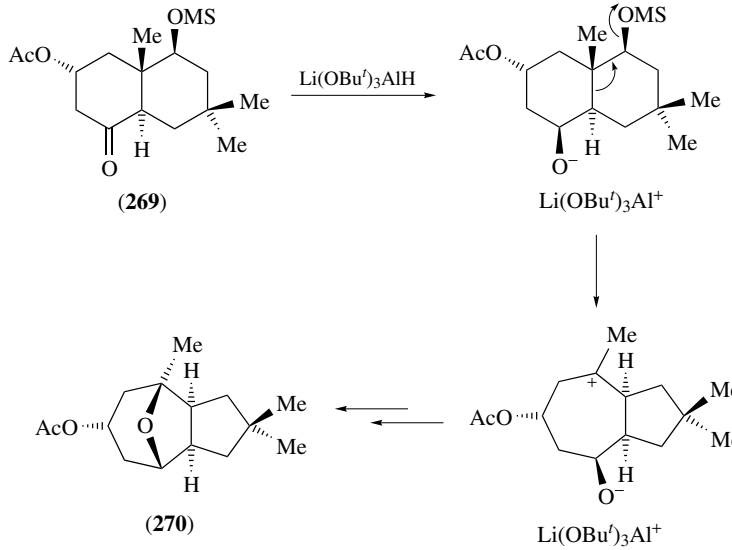
SCHEME 87

The mechanism of phenylseleno-etherification of unsaturated alcohols, which involves seleniranium cationic intermediates, has been studied[410] by the semiempirical molecular orbital MNDO–PM3 method.

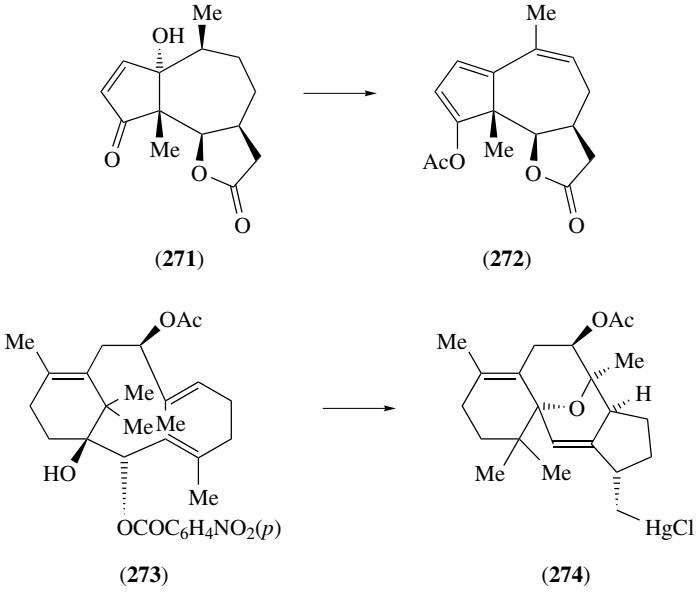
Rearrangements in Natural-product Systems

A comparison has been made[411] of various monoterpenoid rearrangements catalysed by either zirconium phosphates or by zirconium organo-substituted phosphonates, and acid-catalysed rearrangements of α-trans- and β-cis-3,4-epoxycaranes have been described.[412] It has been observed[413] that on exposure to Li $(OBu^t)_3AlH$, perhydronaphthalene-1,4-diol monosulfonate ester (**269**) rearranges to the 11-oxatricyclo-[5.3.1.0.2,6]undecane derivative (**270**) (see Scheme 88).

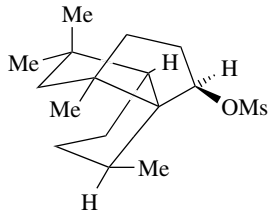
Parthenin (**271**) has been found to undergo a skeletal rearrangement with the introduction of acetate functionality[414] [see (**272**)] upon treatment with $Ac_2O–H_2SO_4$. An



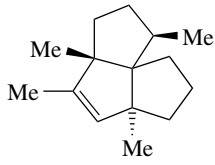
SCHEME 88



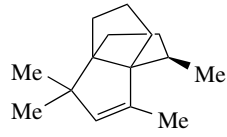
unexpected rearrangement–transannular cyclization product (**274**) has been obtained[415] on treatment of bicyclo[9.3.1]pentadecatriene (**273**), a precursor of taxol, with mercuric triflate. A Wagner–Meerwein rearrangement of rings B and C of the clovane skeleton has been explored[416] by deuterium labelling of 9 α-bromo-2β-methoxyclovane. The formation of isocomene (**276**) and modhephene (**277**) in the solvolytic rearrangements



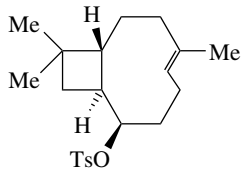
(**275**)



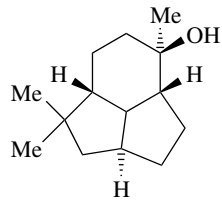
(**276**)



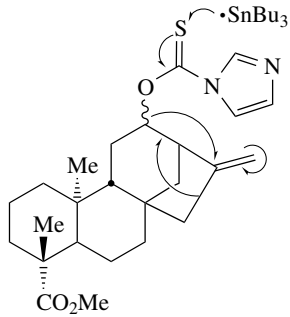
(**277**)



(**278**)



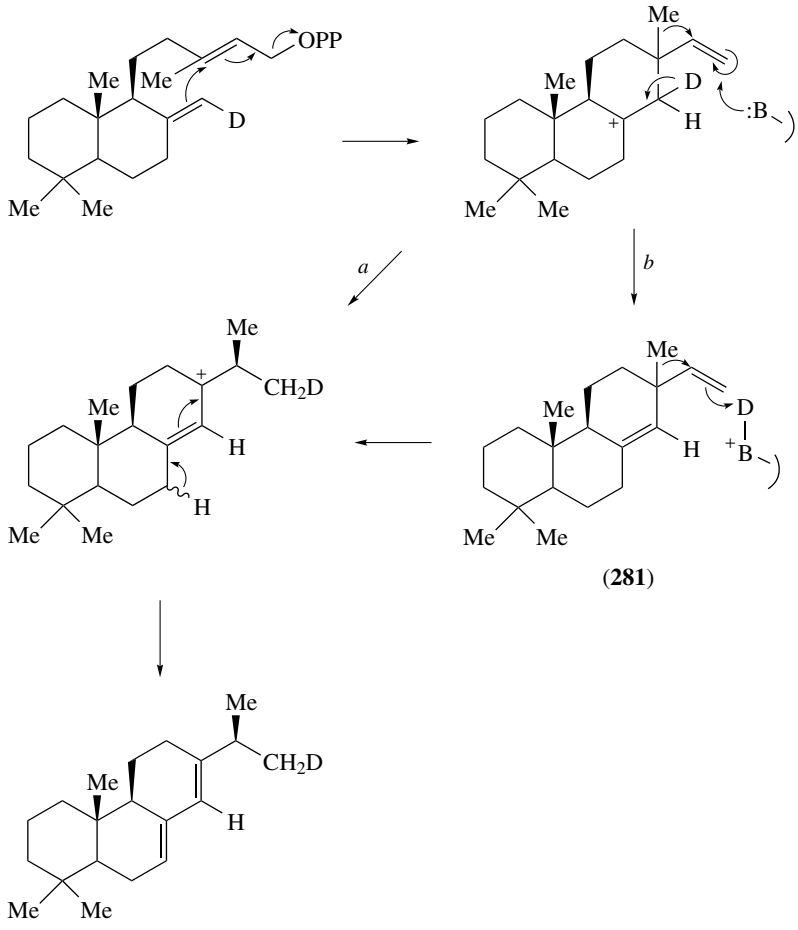
(**279**)



(**280**)

of silphinyl mesylates (**275**) and from the acid-catalysed conversion of silphinene, has provided[417] experimental precedent for the biogenetic linkage of these triquinane sesquiterpenes. 15-Norcaryophyllen-8-β-yl tosylate (**278**) has been found to undergo a stereospecific rearrangement–cyclization to 12-nor-8α-presilphiperfolan-9-β-ol (**279**) upon solvolysis in aqueous acetone. Although the ring bond that participates in the cyclobutylcarbinyl–cyclopentyl rearrangement is unknown, the reaction has provided a chemical precedent for a biogenetic connection between caryophyllene and the presilphiperfolanols.[418]

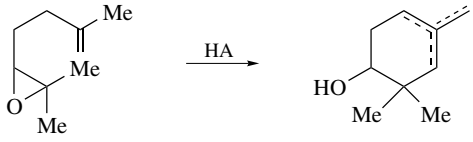
It has been shown[419] that isomerization of the exocyclic allylic system of the five-membered ring D of kaurenols depends on the orientation of the C(15) hydroxyl group. The total synthesis of methyl atis-16-en-19-oate, a tetracyclic diterpenoid possessing a bicyclo[2.2.2]octane skeleton, has been accomplished[420] using a homoallyl-homoallyl radical rearrangement process of methyl 12-hydroxykaur-16-en-19-oate monothioimidazolide (**280**) as the pivotal step. Two plausible mechanisms have been presented[421]



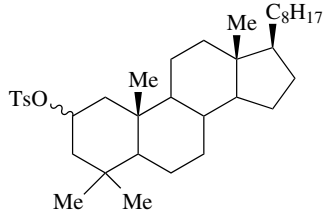
SCHEME 89

(see Scheme 89) for the novel cyclization-rearrangement of (+)-copalyl diphosphate to (−)-abietadiene which is catalysed by recombinant cyclase from *Abies grandio*. However, further research is required to elucidate whether the mechanism involves an intramolecular C(14) to C(16) hydrogen-transfer pathway (path *a*), or an enzyme-mediated proton elimination to form a pimara-8(14),15-diene intermediate (**281**) that incorporates the proton at C(16) (path *b*). The structure of a naphthalene derivative obtained by rearrangement of 13-methoxytotara-5,8,11,13-tetraen-7α-ol has been revised[422] to 5-(5′-isopropyl-6′-methoxy-2′-methyl-1′-naphthyl)-2-methylpent-2-ene.

The involvement of a common concerted mechanistic pathway for the acid-catalysed cyclization of 5,6-unsaturated oxiranes, viz. (**282**) to (**283**), in chemical and enzymatic systems has been demonstrated,[423] and indeed, theoretical evidence has been produced[424] to show the participation of a concerted mechanism for oxirane cleavage and A-ring formation in oxidosqualene cyclization. Further



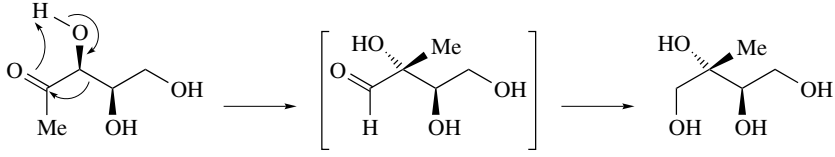
(**282**) (**283**)



(**284**)

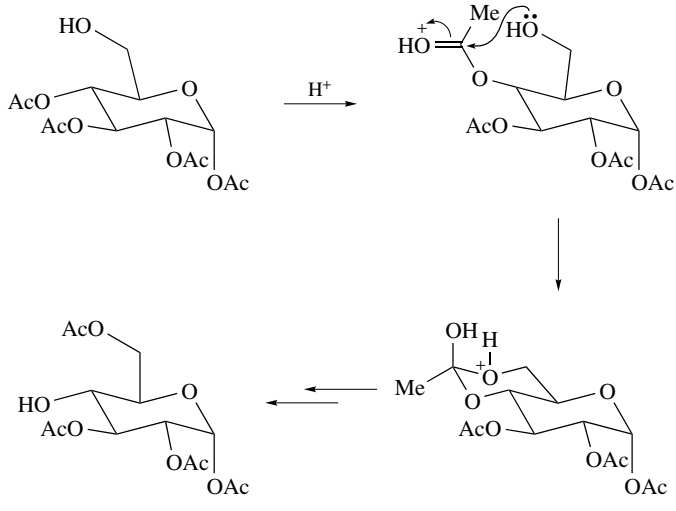
evidence has been obtained[425] to suggest that the polycyclization reaction by oxidosqualene–lanosterol cyclase proceeds via the expansion of a five- to a six-membered ring for C-ring formation of lanosterol. 6-Methyl-3-isopropyl-A,19-dinorcholesta-6,8,10(5)-triene has been identified as a new by-product from the acid-catalysed reaction of 4,4-dimethylcholest-5-en-3-one. A novel enone-benzene rearrangement has been invoked[426] to account for the formation of this product. A number of 4-hydroxyestrogens have been prepared by the thermal rearrangement of steroidal 4,5-epoxides.[427] Sigmatropic and/or contact-ion-pair processes have been invoked[428] to explain the observed rearrangement products obtained on the acetolysis of the epimeric tosylates (**284**). Pinacol rearrangements of 2α,3β,19α-trihydroxyurs-12-triterpenoids have been studied,[429] the peracid-induced oxidative rearrangement of bauerenyl acetate has been investigated,[430] and a novel oxidative skeletal rearrangement of ring A of lupenone has been described.[431] The rearrangement of steroidal α, β-unsaturated pyridine *N*-oxides with acetic anhydride has been shown to afford diastereoisomeric 20-acetoxy-17-picolyl-16-androstene derivatives.[432]

It has been established[433] that the leaves of *Liriodendron tulipifera* convert 1-deoxy-D-xylulose (**285**) into 2-*C*-methyl-D-erythritol (**286**) via a skeletal rearrangement (see Scheme 90) reminiscent of the formation of terpene precursors from 1-deoxy-D-xylulose 4-phosphate. An esterase-catalysed regioselective 6-deacylation of

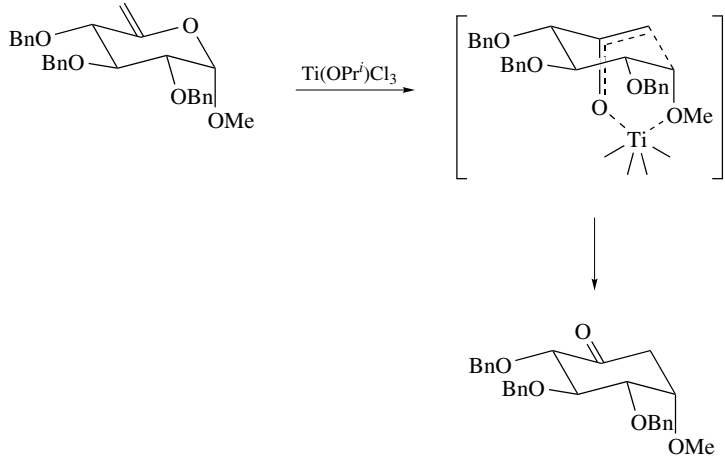


(**285**) (**286**)

SCHEME 90

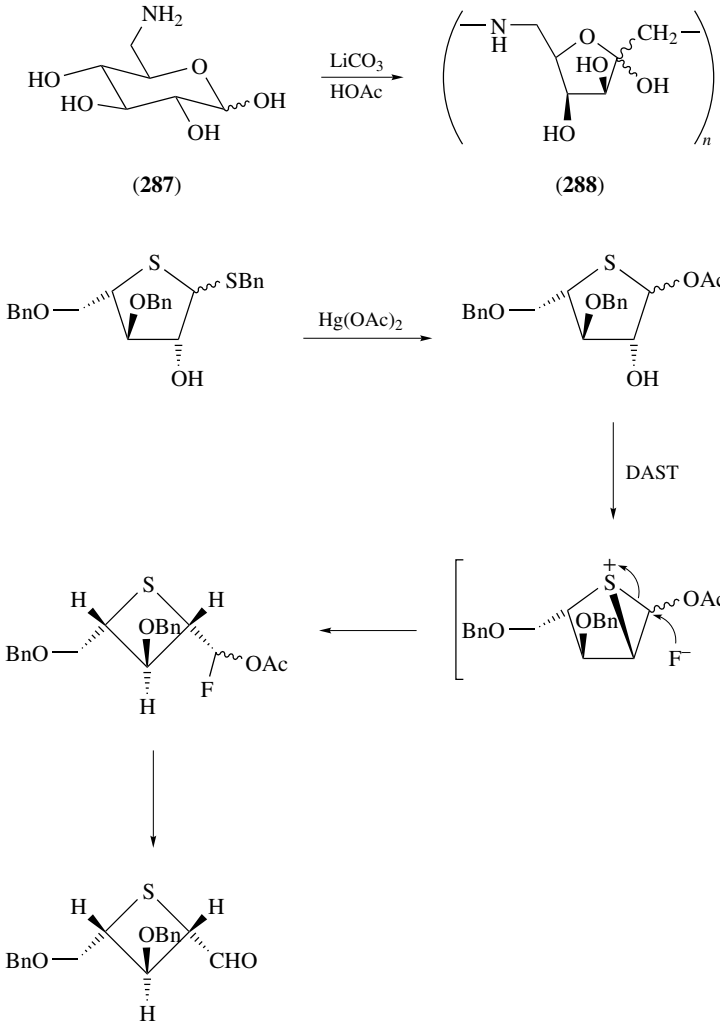


SCHEME 91



SCHEME 92

hexopyranose peracetates has been reported. Moreover, utilization of the propensity of acyl groups to migrate under acidic conditions (see Scheme 91) has ultimately made possible the conversion of C(6) partially acylated monosaccharides into the corresponding C(4) deprotected species, thus providing a simple method for the regiospecific deprotection of the C(4) position of hexopyranosides.[434] A novel stereoselective approach to polyhydroxylated cyclohexanones has been described,[435] starting from benzylated 6-deoxy-hex-5-enopyranosides and promoted by titanium(IV) (see Scheme 92). 2,3-Unsaturated mono- and di-saccharide glycosylglycerol derivatives have been obtained in good yields by the Lewis acid-catalysed allylic

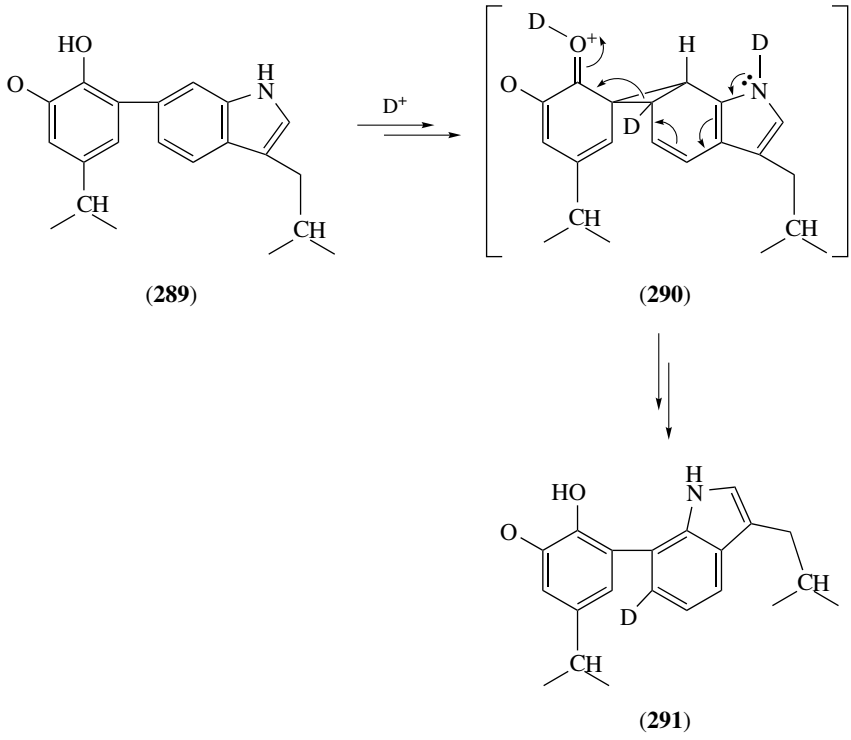


SCHEME 93

rearrangement reaction of various glycals with glycerol derivatives[436] and other *O*-nucleophiles.[437] The synthesis of a new aminopolysaccharide (**288**) having an amino-ketose structure, has been achieved[438] utilizing the thermal polymerization of 6-amino-6-deoxy-D-glucose (**287**) in the presence of acetic acid. The novel Lewis acid-catalysed rearrangement of a sugar-base hybrid to afford an anhydronucleoside has been reported,[439] and the attempted intermolecular addition of malonyl radicals to 1′, 2′-unsaturated nucleosides has been found to lead to furanones.[440] An unusual ring contraction–rearrangement has been observed[441] during the attempted fluorination of thiofuranose derivatives with diethylaminosulfur trifluoride (DAST). Scheme 93

outlines the proposed mechanism for this transformation which is considered to proceed by the regioselective opening of a transient episulfonium ion.

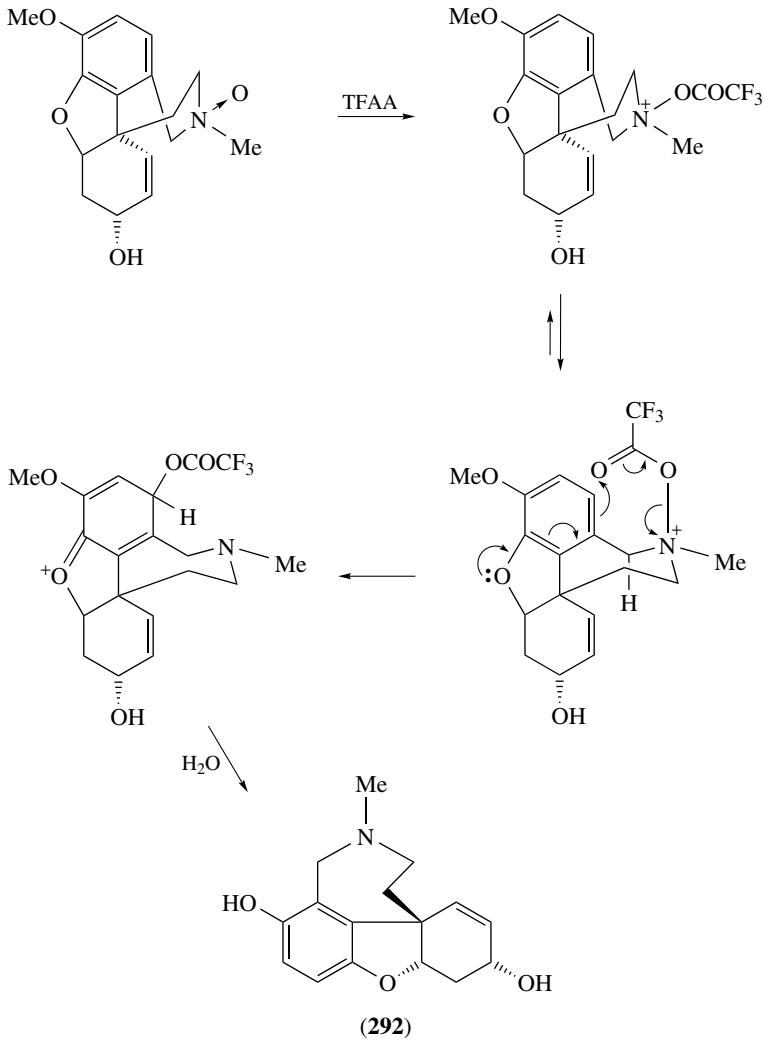
The observed acid-catalysed conversion of complestatin (**289**) into chloropeptin L (**291**) has been envisioned[442] as proceeding through a cyclopropyl intermediate (**290**) (see Scheme 94). An intramolecular oxygen-transfer reaction illustrated in Scheme 95 has been proposed[443] to explain hydroxylation of the aromatic nucleus, viz. formation of (**292**), during the course of a modified Polonovski reaction on galanthamine.



SCHEME 94

Rearrangements Involving Electron-deficient Heteroatoms

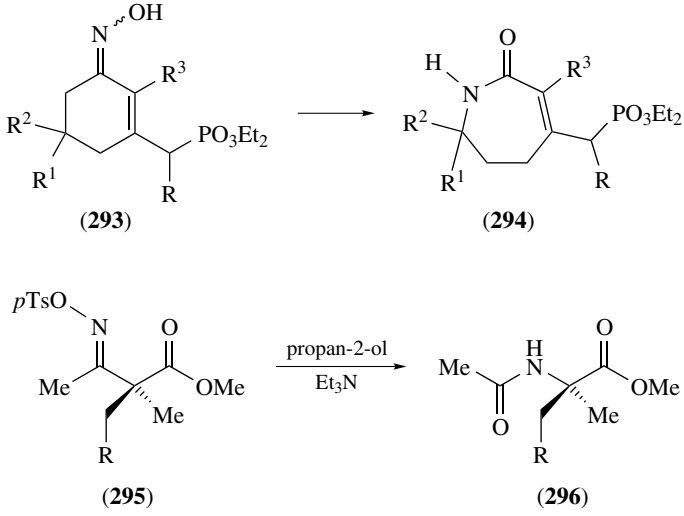
An *ab initio* study of the effects of both substituents and solvents on the Beckmann rearrangement has been undertaken[444] and the potential-energy surfaces corresponding to the Beckmann rearrangement of a series of aliphatic and cyclic alkanone oximes have been explored[445] using density functional theory. The vapour-phase Beckmann rearrangement of cyclohexanone oxime to ϵ-caprolactam, catalysed by mesoporous molecular sieves, has been studied,[446] and a weakly acidic borosilicate has also been utilized[447] as a catalyst in the above reaction. The non-catalytic Beckmann rearrangement of cyclohexanone oxime to ϵ-caprolactam in supercritical water has been reported,[448] and a comparison has been made of the Beckmann rearrangement of



(**292**)

SCHEME 95

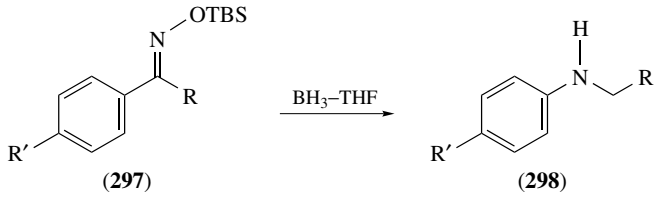
oximes with different molecular sizes over a series of β-zeolites containing different Brønsted acid sites.[449] A facile and efficient synthetic procedure for the Beckmann rearrangement of oximes using aluminium chloride in the absence of solvent has been developed,[450] and the Beckmann rearrangement of 1-indanone oxime using aluminium chloride has been reported.[451] Lactams (**294**), resulting from the regioselective migration of the C(6)-methylene ring-carbon atom, have been obtained[452] from the Beckmann rearrangement of the oximes of 3-phosphonoalkylcyclohexenones (**293**). A convenient method for the preparation of a bicyclo[3.3.3]undecane derivative via the Beckmann rearrangement of bicyclo[3.3.2]decan-9-one has been described,[453] and a novel method for the synthesis of fully protected chiral α,α-disubstituted α-amino



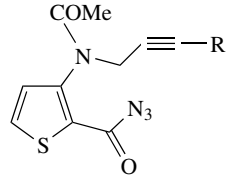
acids via a Beckmann rearrangement has been developed[454] [see (**295**) to (**296**)]. The syntheses of 6-*O*-methylazithromycin and its aza-ketolide analogue have been achieved[455] by carrying out the Beckmann rearrangement of the readily available 9(*E*)-6-*O*-methylerythromycin oxime. The reduction of aromatic and cyclic *O*-(*t*-butyldimethylsilyl) aldoximes and ketoximes with various reducing agents has been investigated and an attempt has been made to explain the effect of substituents on the novel rearrangement [(**297**) to (**298**)] that occurs with a borane–tetrahydrofuran complex.[456]

A re-evaluation of the Hofmann rearrangement in electron-deficient systems has been undertaken.[457] A detailed study of the discrete intermediates, and the sensitivity of the intermediates and products to reagents and to each other in the Hofmann rearrangement of *N*-α-tosylasparagine, has led to a process that produces 2-(*S*)-(tosylamino)-β-alanine on a large scale.[458]

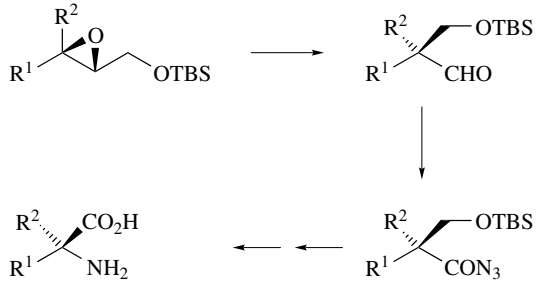
It has been demonstrated that the thermal reaction of a series of alkynyl- or alkenoyl-containing acyl azides such as (**299**) involves competition between intramolecular azide cycloaddition and a Curtius rearrangement. Apparently the substituent R plays a key role in determining the competition between the two possible routes.[459] It has been shown[460] that a silicon group situated at the β-position with respect to an acyl azide group enhances the rate of the Curtius rearrangement by a factor of three, whereas a γ-silyl substituent has a marginal influence. These observations have lent support to the proposition that, during the concerted intramolecular rearrangement of an acyl azide to an isocyanate, an electron-deficient centre at the migration origin is created. An efficient route for the asymmetric synthesis of α,α-disubstituted α-amino acid derivatives, starting from readily available epoxy silyl ethers, has been developed[461] using the Curtius rearrangement as a key step (see Scheme 96).



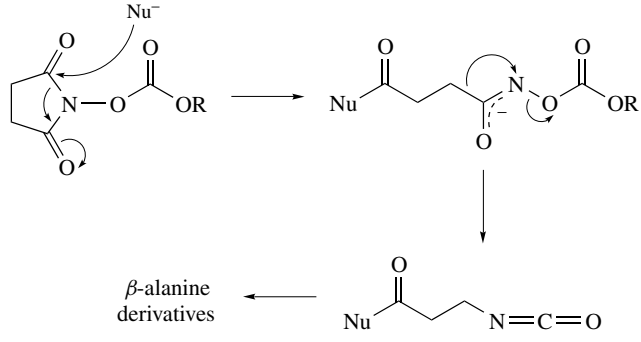
(**297**) (**298**)



(**299**)



SCHEME 96

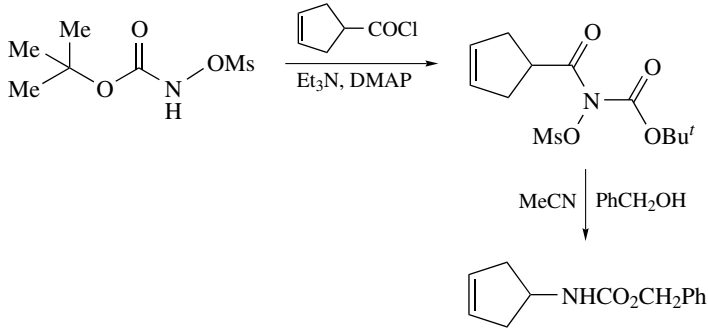


SCHEME 97

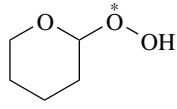
The neutral alkali metal salts of benzohydroxamic acids have been found to undergo an unprecedented rearrangement to *N*,*N*′-diarylureas.[462] A side reaction, producing β-alanine derivatives by way of a Lossen rearrangement, has been observed to accompany the hydrolysis of alkyl succinimidyl carbonates[463] in basic aqueous buffers (see Scheme 97). The development of a modified Lossen rearrangement, whereby

N-(*t*-butyloxycarbonyl)-*O*-methanesulfonylhydroxamic acids have been converted into protected amines in good yield, has been described[464] (see Scheme 98).

A successful synthesis of the tetrahydropyran-protected hydroperoxide (**300;** 1-^{18}O) using the Baeyer–Villiger strategy has been reported.[465] Experimental evidence has been obtained[466] to support the fact that, in the Baeyer–Villiger oxidation and Criegee rearrangement, a stereoelectronic effect directs the migratory aptitude, and it is the bond antiperiplanar to the dissociating peroxide bond that always migrates, even when it is electronically disfavoured from doing so.



SCHEME 98

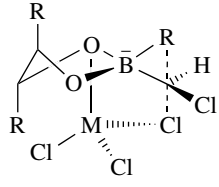


(**300**)

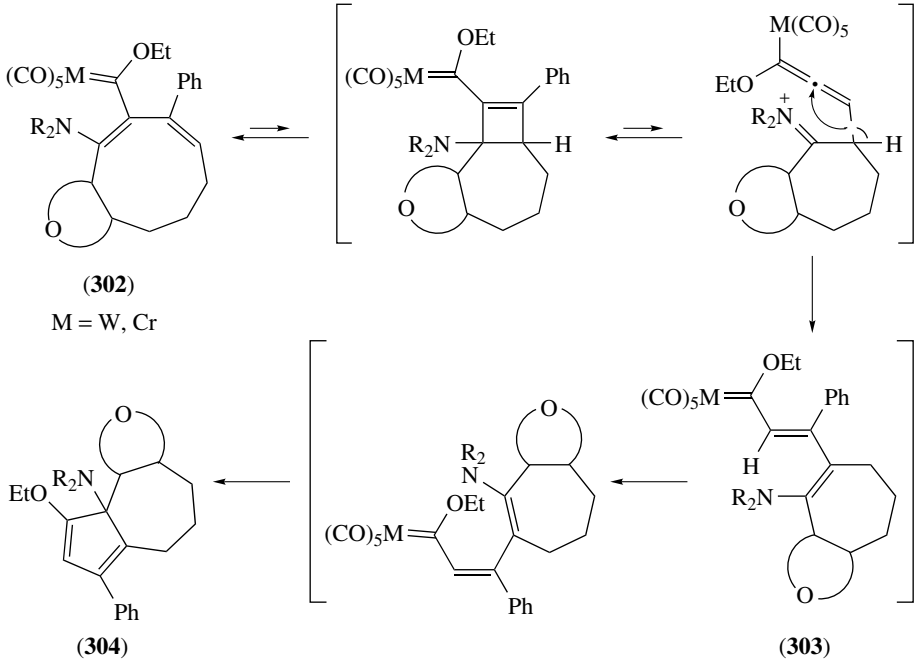
$^{*}O = {}^{18}O$

Rearrangements Involving Organometallic Compounds

An *ab initio* investigation of the transition state for the Lewis acid-associated migration of an alkyl group from boron to an α-dichloro-carbon in a non-racemic boronic ester has been carried out.[467] The calculated transition state has shown that it is important to have the non-participating chlorine atom *anti* to the metal, e.g. as in (**301**). The



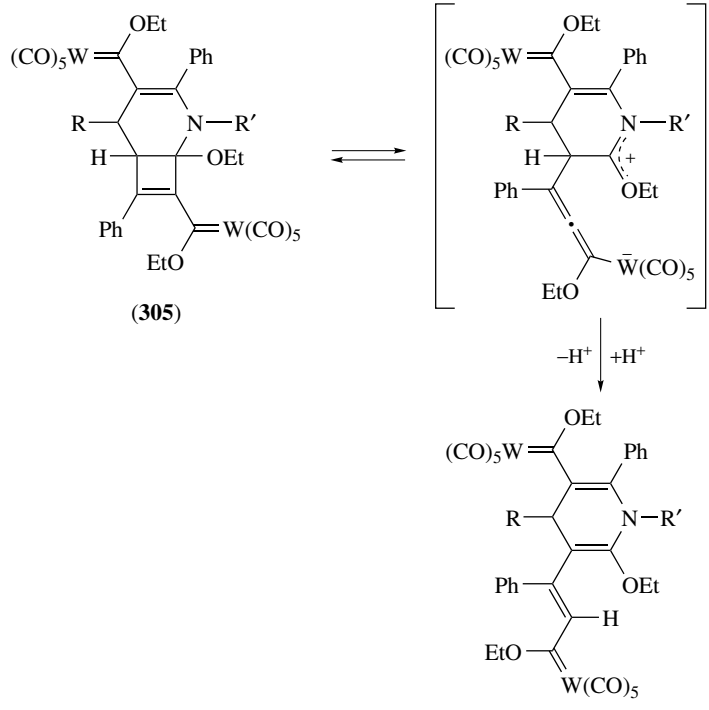
(**301**)

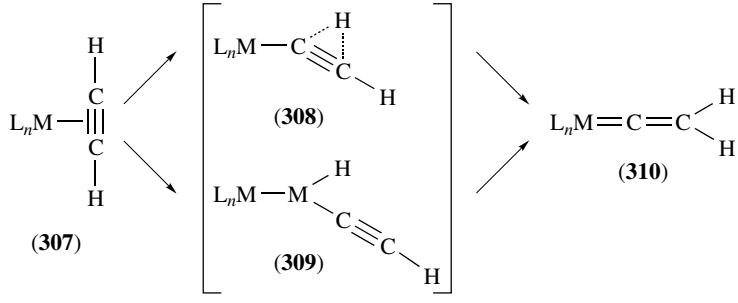


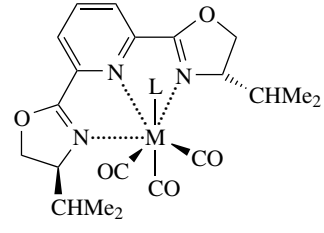
SCHEME 99

stereoselectivity is then dictated by placing the metal on the least-hindered side of the oxygen, *trans* to the R group of the ester. This combination places the Lewis acid in the sterically least hindered position.

2-Aminocyclonona-1,8-dienyl carbene complexes (**302**) in solution have been found to undergo ring contraction of the nine-membered ring to give (2-amino-cycloheptenyl)alkenyl carbene complexes (**303**) which are subsequently transformed into tetrahydroazulenes (**304**) by elimination of the metal unit[468] (see Scheme 99), and (cyclobutenyl)carbene tungsten complexes (**305**) have been shown to rearrange to 1-tungstahexa-1,3,5-trienes (**306**) by ring opening of the cyclobutene ring and subsequent [1,3]-hydrogen migration.[469] It has been reported[470] that the d^2[{*p*-Bu^t-calix[4]-(O_4)}W] fragment assists a variety of ethylene rearrangements which are very similar to those often supposed to occur on metal oxides. Such rearrangements are driven by light, acids, and bases, or occur under reducing conditions. Quantum-mechanical calculations have shown that[471] that two energetically nearly degenerate pathways are possible for the rearrangement of tungsten–acetylene complexes (**307**) to the energetically higher lying vinylidene complexes (**310**). The direct [1,2]-hydrogen migration was found to proceed via a transition state (**308**) which has a non-planar C_2H_2 moiety. The alternative pathway involves the alkynyl(hydrido)metal complex (**309**). Complexes of the chiral bis(oxazoline) 2,6-bis[(4*S*)-isopropyloxazoline-2-yl]pyridine (**311;** M = Mo or W), in which the ligand is restricted to a bidentate bonding mode, have been found to be

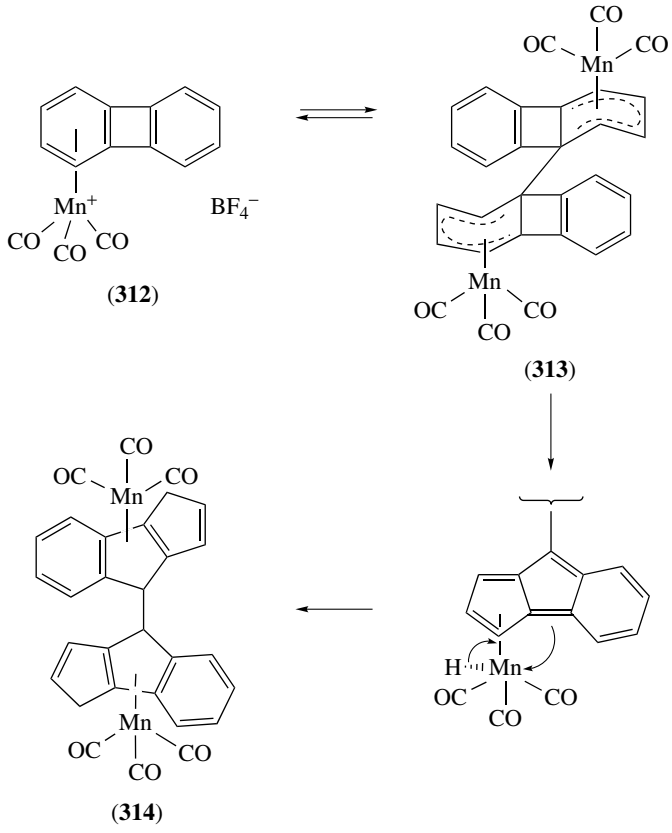

OEt
(CO)5W
Ph
R
N
R′
H
OEt
Ph
W(CO)5
EtO
(305)
OEt
(CO)5W
Ph
R
N
R′
H
Ph
OEt
W(CO)5
EtO
−H+
+H+
OEt
(CO)5W
Ph
R
N
R′
Ph
OEt
H
EtO
W(CO)5
(306)


H
LnM
C
C
H
(307)
LnM
C
H
C
H
(308)
LnM
M
H
C
C
H
(309)
LnM
C
C
H
H
(310)

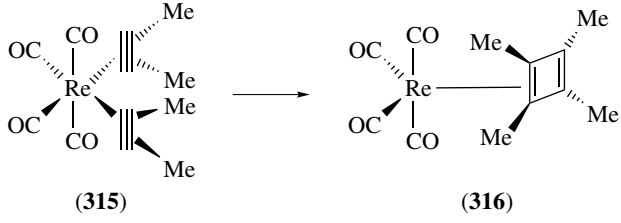

O
N
N
L
CHMe2
O
N
M
OC
CO
CO
CHMe2
(311)

fluxional, with exchange occurring between the pendant and coordinated oxazoline rings. The energetics and mechanism of the rearrangement have been studied in detail[472] by one- and two-dimensional NMR techniques.

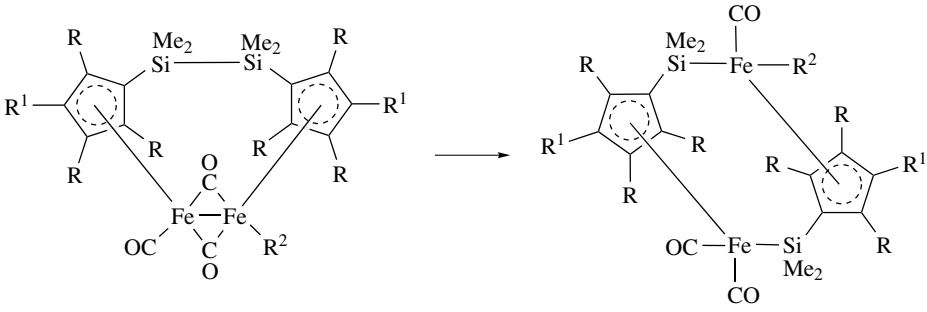
Reduction of (**312**) has been found to afford the dimer (**313**) which upon heating rearranged to yield the unprecedented di(benzopentalene) complex (**314**). The regio- and stereo-specificity of the conversion (**313**) into (**314**) implies a metal-mediated pathway for the process[473] (see Scheme 100). The first observable *cis*-bis(alkyne)cyclobutadiene rearrangement [see (**315**) to (**316**)] has been reported.[474]



SCHEME 100



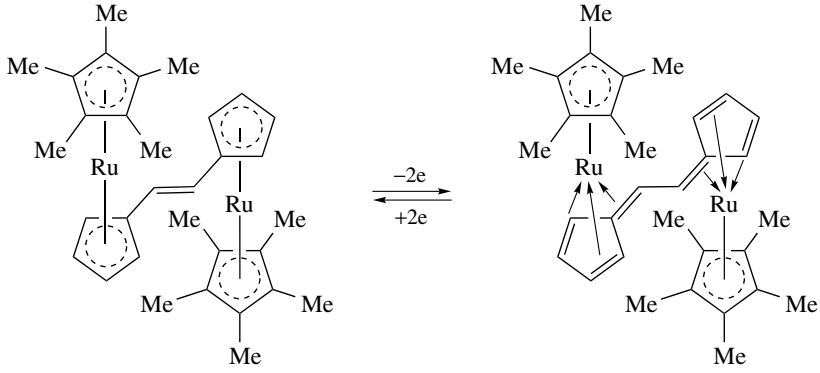
The binuclear iron complexes (**317**) have been found to undergo a thermal rearrangement[475,476] to afford the complexes (**318**), which were evidently formed via a metathesis between Si−Si and Fe−Fe bonds in (**317**). A similar rearrangement has been observed[477] in a disilyl-bridged bis(cyclopentadienyl)tetracarbonyldiruthenium complex. Unprecedented and stable ($\eta - \eta^6 : \eta^6$-pentafulvadiene)diruthenium complexes (**320**) have been prepared[478] from a two-electron oxidation of *trans*-1,2-bis(ruthenocenyl)ethylenes (**319**), and dimethyl analogues have been similarly obtained from *trans*- and *cis*-1,2-dimethyl-1,2-bis(ruthenocenyl)ethylenes.



(**317**) (**318**)

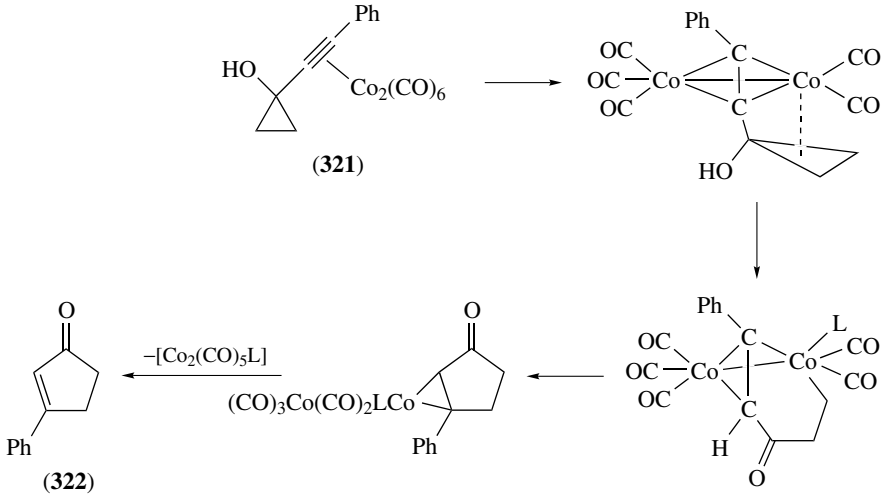
R, R^1 = Me; R^2 = CO

R = H; R^1 = Bu^t; R^2 = $P(OPh)_3$

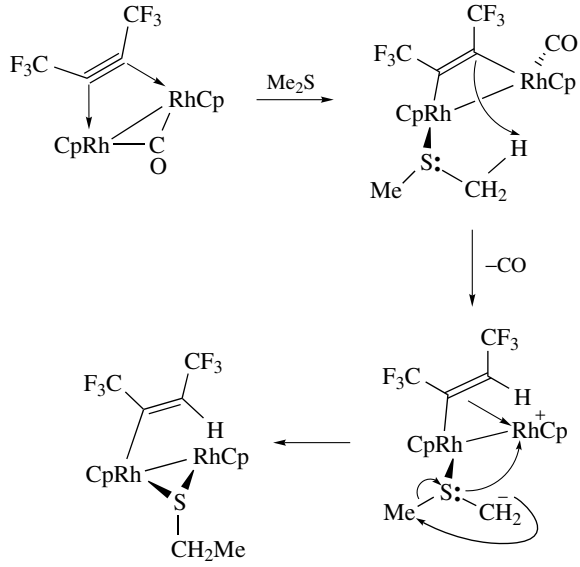


(**319**) (**320**)

A hitherto unknown type of rearrangement of 1-(1-alkynyl)cyclopropanols (**321**) to cyclopent-2-en-1-ones (**322**) mediated by octacarbonyldicobalt[479] and hexacarbonyldicobalt[480] complexes has been described. A possible pathway for the transformation is outlined in Scheme 101. A β-proton transfer accompanied by a metal-mediated Stevens rearrangement, which converts a coordinated dimethylsulfane

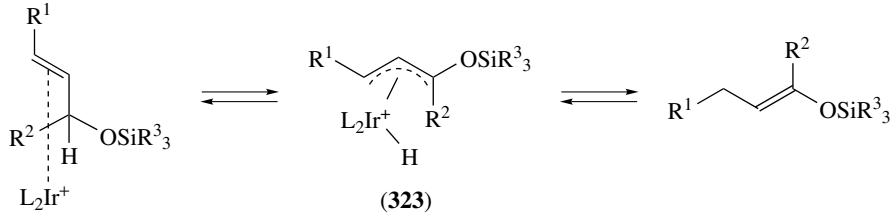


SCHEME 101



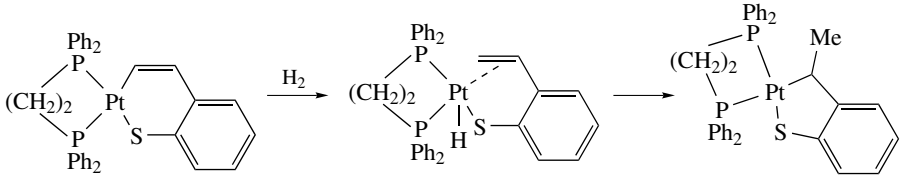
SCHEME 102

to a bridging ethanethiolate group (see Scheme 102), has been invoked[481] to account for the observed rearrangement of organic chalcogenides on a rhodium–rhodium bond. The iridium-catalysed isomerization of allyl silyl ethers has been rationalized[482] as proceeding through the oxidative addition of an allylic C–H bond to the iridium(I) metal centre, giving a *syn*-π-allyliridium complex (**323**) which selectively leads to the *E*-isomer (see Scheme 103).

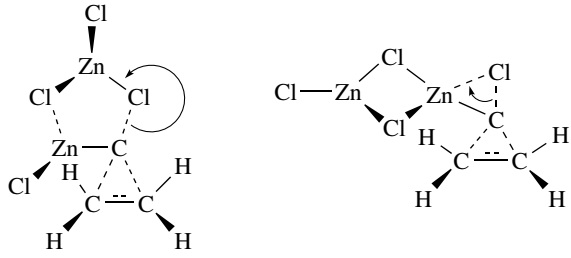


(**323**)

SCHEME 103



(**324**) (**325**) (**326**)



(**327**) (**328**)

A σ-*S*-bonded π-alkene (η^3) intermediate (**325**) has been invoked to account for the hydrogenation of the thiaplatinacycle (**324**) to the complex (**326**) in which two hydrogens have been added and a hydrogen shift has occurred.[483] When coordinated to neutral and cationic palladium(II) and platinum(II) centres, the diphosphine 2,3-bis(diphenylphosphino)propene, on treatment with benzylamine, was found to undergo isomerization to coordinated *cis*-1,2-bis(diphenylphosphino)propene[484] rather than the expected nucleophilic addition to the double bond.

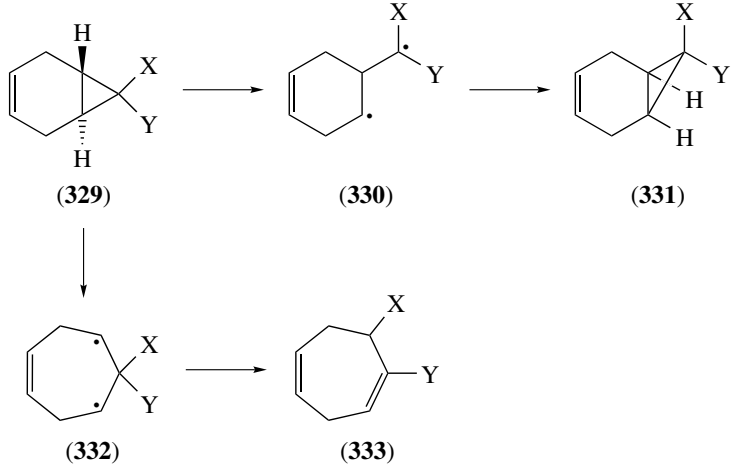
Metallation–demetallation of new multi-porphyrinic [2]rotaxanes in which a gold(III)-porphyrin is part of the ring, has been found to induce a complete changeover of the molecule.[485]

With the aid of density functional theory, the $ZnCl_2$ acceleration of the Simmons–Smith reaction of ethylene and allyl alcohol has been investigated.[486] A pathway involving direct Lewis acid acceleration of the leaving halogen atom (**327**) was found to be a more facile process than the more popular pathway involving 1,2-chlorine migration (**328**).

It has been established[487] that dimers of monofunctional tetrabutyldistannoxanes of the general formulae $[R_4Sn_2X_2O]_2$ rearrange rapidly in solution by an intradimeric dynamic process.

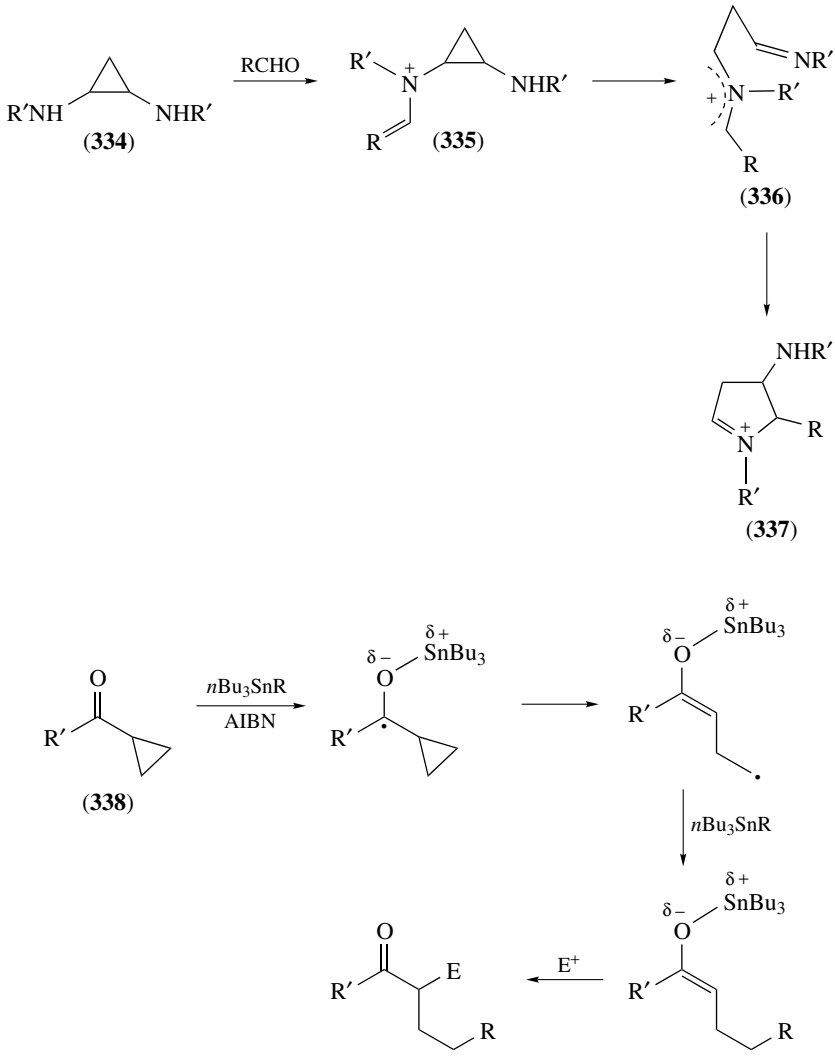
Rearrangements Involving Ring Opening

A study has been made[488] of the ring opening of methyl- and phenyl-substituted 1,1,2-trihalocyclopropanes to acetylenic acetals under a variety of reaction conditions. The thermal rearrangements of *trans*-bicyclo[4.1.0]hept-3-ene with halogen substituents at the 7-position have been examined.[489] Thermolysis of the dichloride (**329;** X, Y = Cl) led to the formation of the *cis*-fused isomer (**331;** X, Y = Cl) by a mechanism which appeared to involve initial cleavage of either the bridgehead or peripheral bond of the three-membered ring and ring closure of the corresponding biradical (**330;** X, Y = Cl). On the other hand, heating the dibromide (**329;** X, Y = Br) resulted in a cycloheptadiene product (**333;** X, Y = Br) which presumably arose via a [1,3]-shift of a bromine atom in the intermediate (**332;** X, Y = Br) generated by cleavage of the bridgehead bond. The formation of pyrroles from the reaction of 1,2-cyclopropanediamines (**334**) with aldehydes has been explained[490] by ring expansion of an intermediate monoiminium ion of the type (**335**) via the azomethine ylides (**336**), to yield the dihydropyrrolinium ion (**337**). It has been shown[491] that the reaction of a cyclopropyl ketone (**338**) with tributyltin radical produces a tin(IV) enolate separated from a carbon-centred radical by a methylene unit, entities which allow for reactions with both electrophiles and radicophiles (see Scheme 104). A theoretical study of the thermal isomerization of buta-1,3-diene to but-2-yne has indicated[492] that a pathway via 1-methylcyclopropene is more energetically favourable than that via a two-step hydrogen-shift process, and a theoretical study of the thermally induced ring opening of substituted cyclopropenes has supported the proposal that alkyl-substituted singlet vinylidenes are intermediates in the process.[493]



(**329**) (**330**) (**331**)

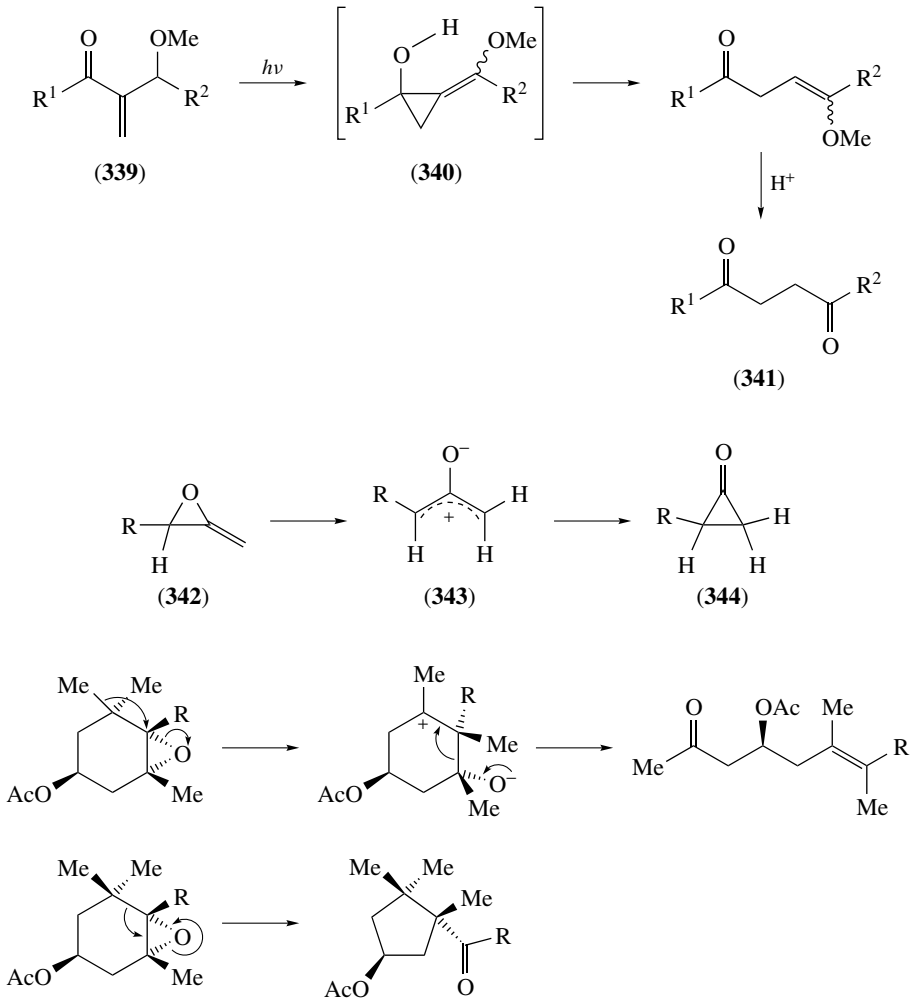
(**332**) (**333**)



SCHEME 104

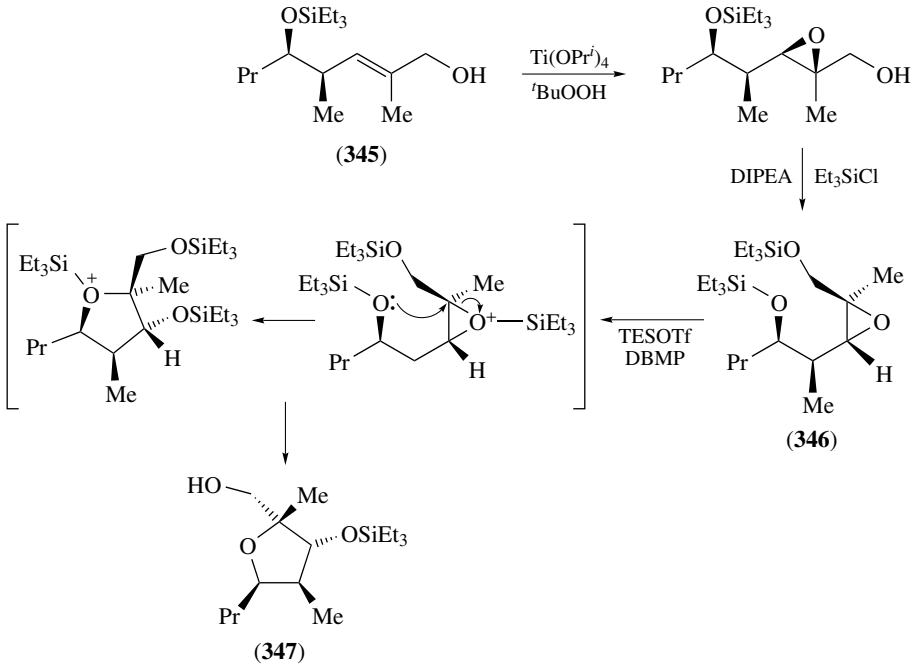
Hydroxymethylenecyclopropanols (**340**) have been shown[494] to be intermediates in the photochemical rearrangement of α,β-unsaturated carbonyl compounds (**339**) to 1,4-dicarbonyl compounds (**341**). The products are eventually obtained by double tautomerization of the enol and cyclopropanol portions of (**340**).

The rearrangements of 3-methylbut-1-ene oxides[495] and 1,2-epoxybut-3-ene[496] on lithium phosphate have been studied, and a detailed theoretical study of the rearrangement of allene oxide (**342**) to cyclopropanone (**344**), which shows that the transformation proceeds via an intermediate oxyallyl (**343**), has been presented.[497] It has been shown that aldehydes, ketones, and cyclic ethers are all produced

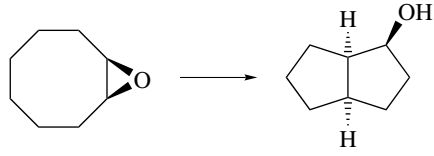


SCHEME 105

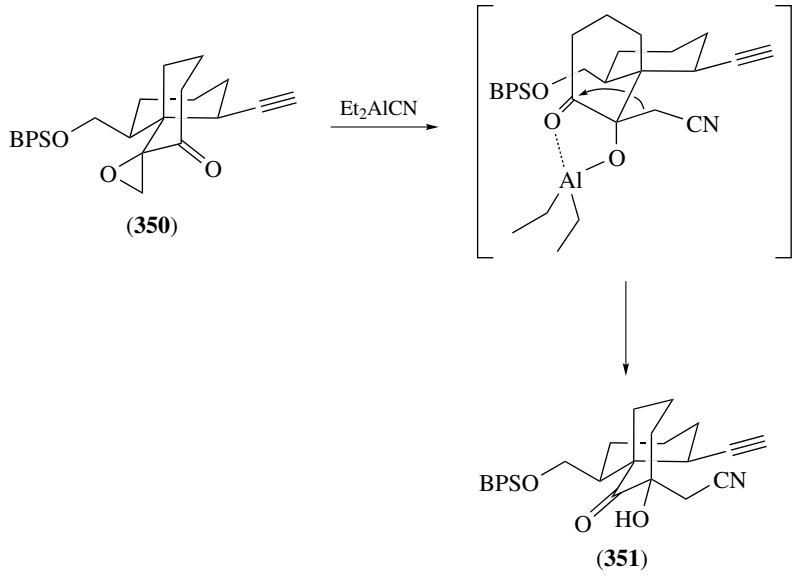
when phenyloxiranes are treated with a clay,[498] while novel acyclic tetrasubstituted olefinic and cyclopentyl end-groups of carotenoids have been obtained[499] by the Lewis acid-promoted stereoselective rearrangement of the epoxide end-group of 5,6-epoxycarotenoids (see Scheme 105). A joint *ab initio* and experimental study of the gas-phase Payne rearrangement has been undertaken.[500] A novel preparative route to a series of tetrahydrofuran-2-methanols (**347**), bearing substituents at all four carbon atoms of the ring, has been described.[501] These compounds have been prepared by the diastereoselective epoxidation of the (*E*)- and (*Z*)-allylic alcohols, e.g. (**345**), silylation of the alcohol to afford the epoxy silyl ether (**346**) and Lewis acid-catalysed rearrangement of (**346**) (see Scheme 106). The isomerization of cycloalkene- and bicycloalkene-derived achiral epoxides [e.g.



SCHEME 106



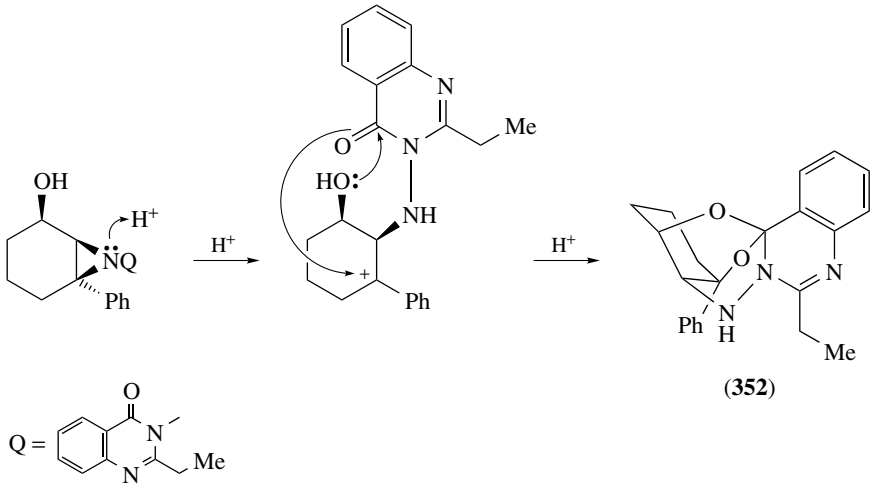
(**348**) to (**349**)] has been achieved[502] by enantioselective α-deprotonation, while a new enantioselective synthesis of *cis*-protected 4,5-dihydroxycyclohex-2-enones from cyclohexa-1,4-diene, via a chiral base-mediated reaction of *meso*-cyclohexene oxides to allylic alcohols followed by oxidation, has been described.[503] Photolysis of *exo*-3,6,7-trioxotricyclo[3.2.2.0^{2,4}]nonane has been found to produce a number of rearrangement products. The authors[504] have proposed that most of these products are the result of initial homolytic cleavage of the C−O bond of the epoxide ring, which does not occur on thermolysis. A new reductive rearrangement of allylic epoxy alcohols to 1,3-diols has been reported,[505] and a tandem epoxide cleavage−1,2-alkyl migration resulting from the hydrocyanation of an α-epoxy ketone has been described.[506] Thus hydrocyanation of (**350**) resulted in regioselective ring opening of the epoxide and subsequent 1,2-cyanomethyl migration to yield the transposed α-hydroxy-ketone (**351**) (see Scheme 107).



(**350**)

(**351**)

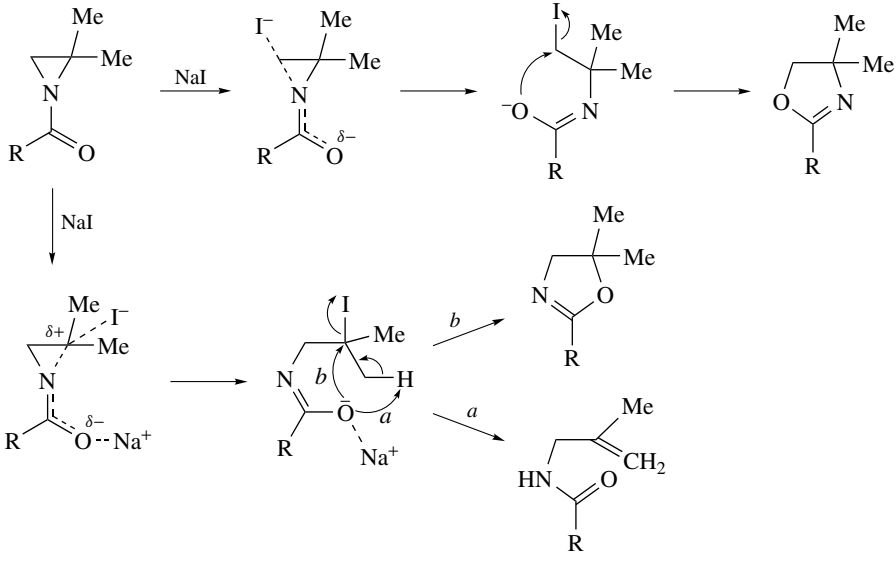
SCHEME 107



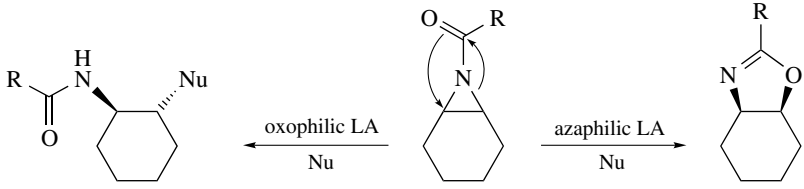
(**352**)

SCHEME 108

The aza-Payne rearrangement and its use as a synthetically valuable equilibration process has been reviewed.[507] Unusual diazadioxabicyclo[2.2.2]octanes (**352**) have been obtained by the acid-catalysed rearrangement of *N*-quinazolinonyl- and *N*-phthalimido-aziridines derived from 3-phenylcyclohex-2-enol.[508] A probable mechanism is outlined in Scheme 108. *N*-Acyl-2,2-dimethylaziridines have been isomerized by sodium iodide into three isomers whose yields appear to depend



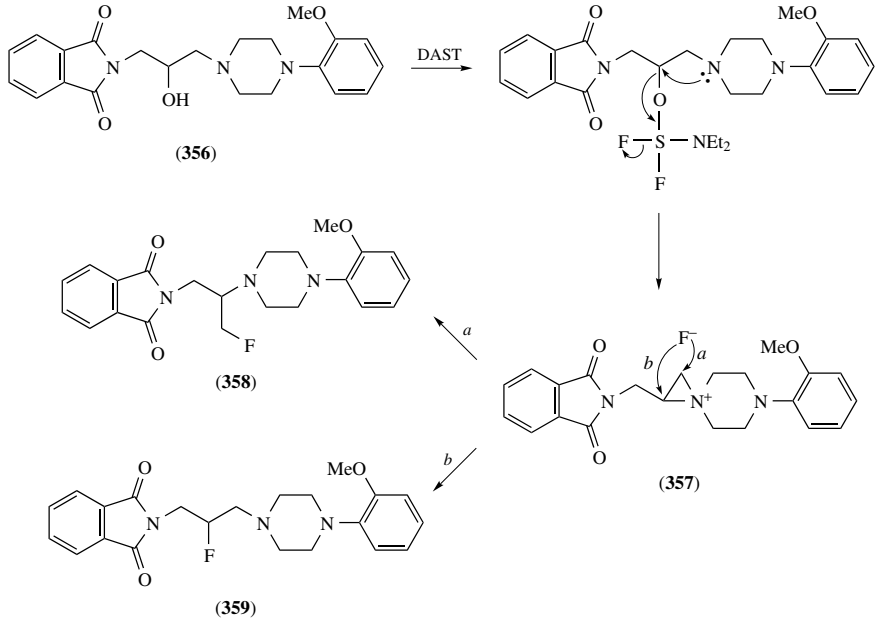
SCHEME 109



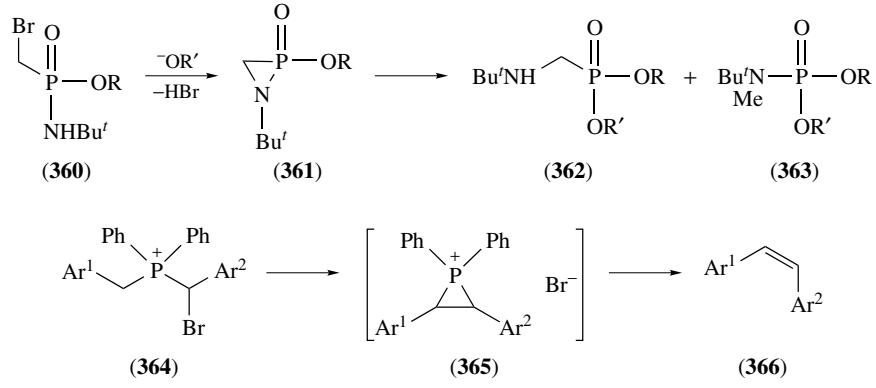
(**354**) (**353**) (**355**)

upon the electronic effect of the acyl group[509] (see Scheme 109), while it has been shown[510] that under certain conditions catalytic quantities of relatively oxophilic metals activate acylaziridines (**353**) predominantly toward external nucleophilic attack, yielding (**354**), whereas more azaphilic Lewis acids catalyse the oxazoline rearrangement to (**355**). Treatment of 1-phthaloylamino-3-[4-(2-methoxyphenyl)piperazin-1-yl]propanol (**356**) with DAST has been found to induce a 1,2-migration via a postulated[511] spiro-aziridinium intermediate (**357**) to yield *N*-[2-fluoromethyl-2-[4-(2-methoxyphenyl)piperazin-1-yl]ethylphthalimide (**358**) and *N*-[2-fluoro-3-[4-(2-methoxyphenyl)piperazin-1-yl]propylphthalimide (**359**) (see Scheme 110).

Methyl *P*-bromomethyl-*N*-*t*-butylphosphonamidate (**360**) has been found to rearrange upon treatment with methoxide to give dimethyl *t*-butylaminomethylphosphonate (**362**) and dimethyl *N*-*t*-butyl-*N*-methylphosphoramidate (**363**). The authors have proposed that the products are derived from an azaphosphiridine oxide intermediate (**361**) by nucleophilic attack at phosphorus and cleavage of the P−N or P−C bond, respectively.[512]



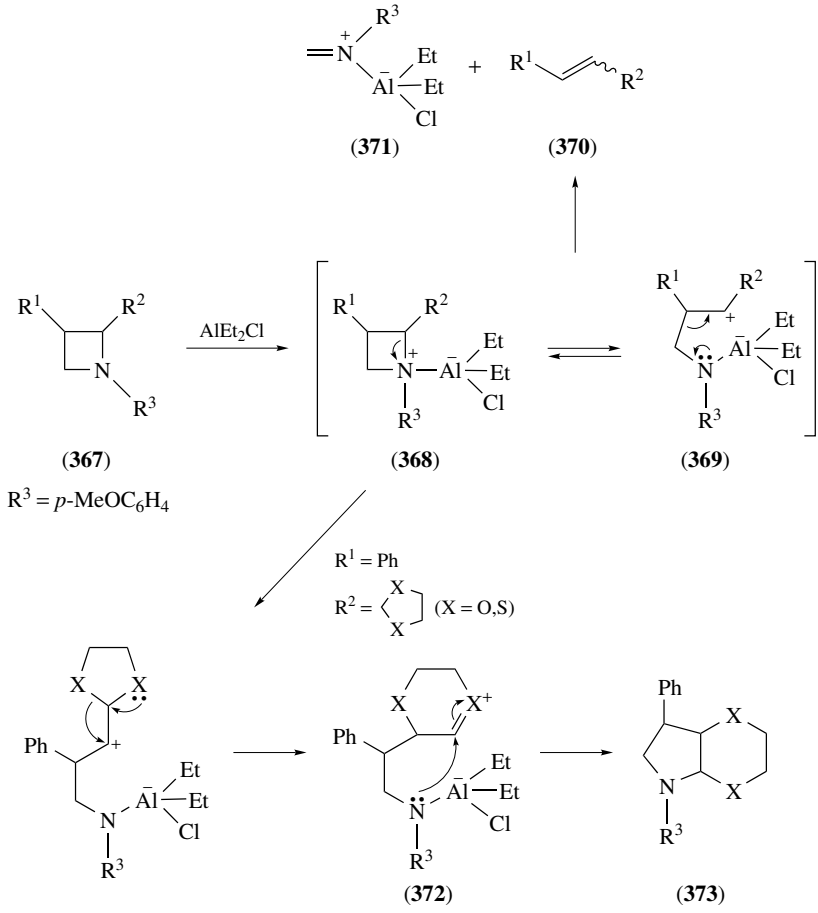
SCHEME 110



Treatment of (α-bromobenzyl)benzyldiphenylphosphonium salts (**364**) with amine bases has been shown to afford alkenes (**366**) with *Z*-selectivity. The reaction is believed to proceed[513] via an *epi*-phosphonium species (**365**) by a mechanism similar to that of the Ramberg–Bäcklund transformation.

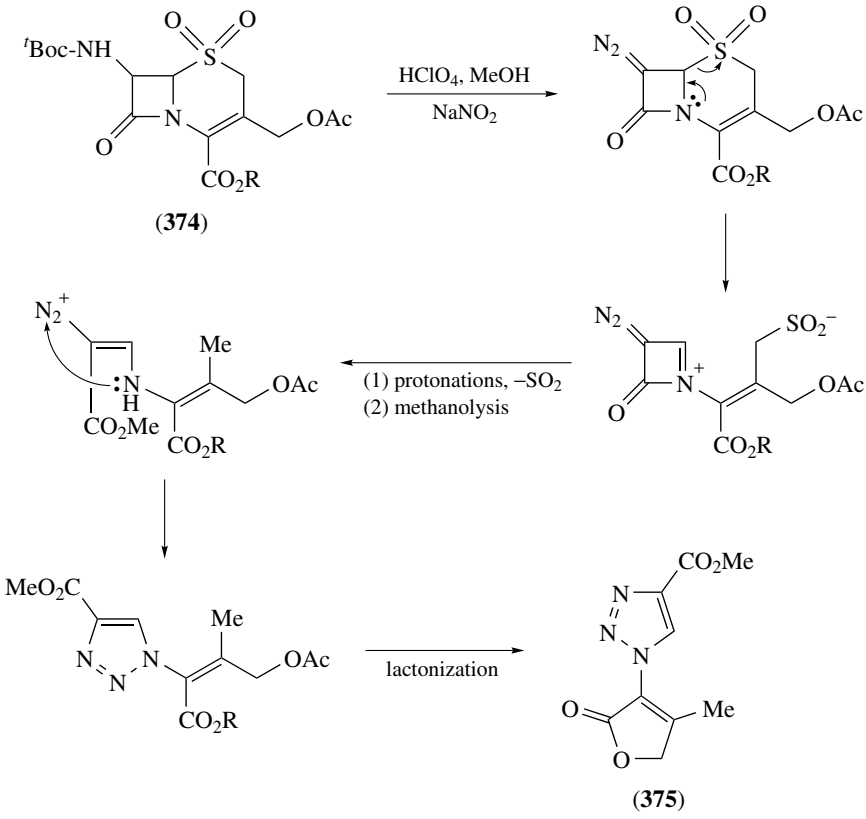
A novel ring-contraction reaction which proceeds via an *epi*-sulfonium ion intermediate has been reported[514] for the simple and regiospecific synthesis of mono- and symmetrically di-functionalized tetrathiamacrocycles, starting with the mono- or dichloro-substituted macrocycles that have one or two more ring atoms.

The formation of a highly strained transient cyclobutane which undergoes cleavage has been invoked[515] to account for the formation of three novel



SCHEME 111

tetracyclic structures formed on acid-catalysed treatment of 5-bromo-3-[1-allyl-2-(3,5-dimethoxyphenyl)ethyl]-2-cyanopyridine. New highly stereoselective fragmentation and rearrangement processes of the azetidine ring (**367**) have been discovered.[516] Plausible pathways for these processes are outlined in Scheme 111 where, as shown, the formation of alkenes (**370**) and fused pyrrolidines (**373**) is considered to occur by the initial coordination of the azetidine nucleus to $AlEt_2Cl$ to give intermediate (**368**). This coordination promotes C(2)−N(1) bond breakage to form zwitterion (**369**) which reacts through two different pathways depending on the nature of the group attached to C(2). For electron-donor aryl groups, the C(3)−C(4) bond breaks to yield the observed olefin (**370**) together with the iminium salt (**371**). The presence of an acetal or thioacetal group on C(2), however, promotes the conversion of intermediate (**368**) into a new carbocation (**372**) which is, in turn, trapped intramolecularly by the nitrogen atom to yield the double-rearranged product (**373**).

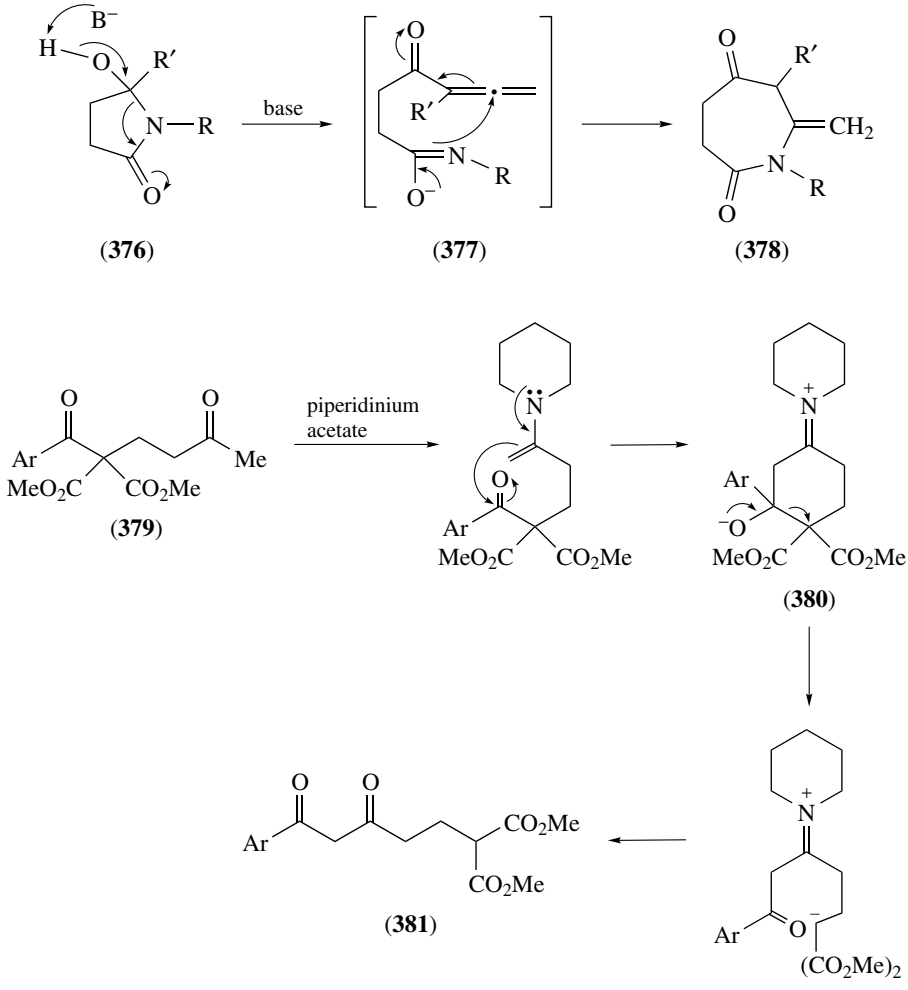


SCHEME 112

7-β-Amino-cephalosporin sulphones, generated *in situ* from the appropriate 7-β-*t*Boc-amino derivatives (**374**) and diazotized in a one-pot reaction in aqueous $HClO_4$–MeOH–$NaNO_2$, have been shown to rearrange exclusively to triazoles (**375**). The multi-step process postulated[517] for this transformation is shown in Scheme 112.

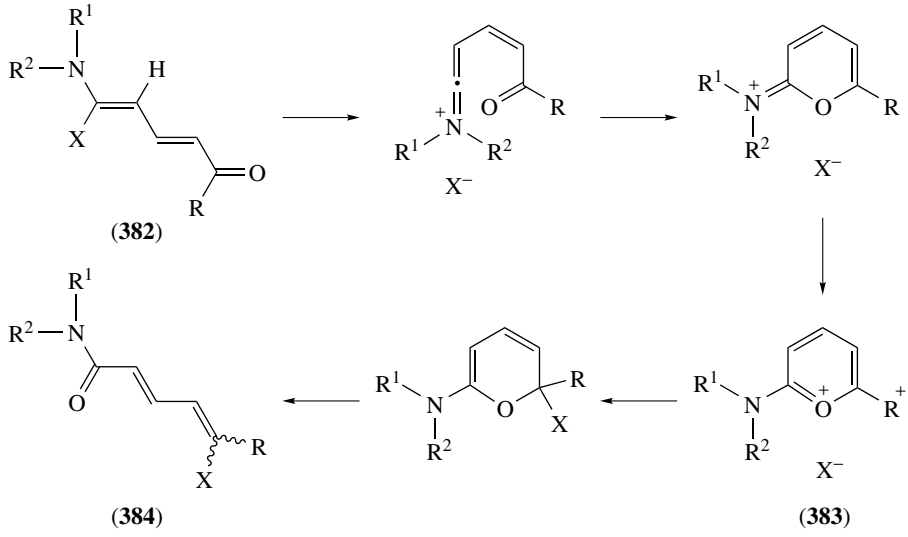
Dihydroxylation of carbapenems bearing an exocyclic vinyl sulfone at C(2) has been found to provide access to the corresponding 2-keto-3-hydroxycarbacephams.[518] In the presence of base, allenylic hydroxy-γ-lactams of the type (**376**) have been found to undergo ring expansion via generation of the conjugated allenyl ketone (**377**), followed by an intramolecular Michael-type addition of the resulting imidate anion to form a two-carbon atom ring-expanded lactam (**378**).[519]

The formation of 1-aryl-1,3-diketones (**381**) from the reaction of the corresponding 1-aryl-1,5-diketones (**379**) with piperidinium acetate has been explained[520] as outlined in Scheme 113 and involves a retroaldol-type reaction in intermediate



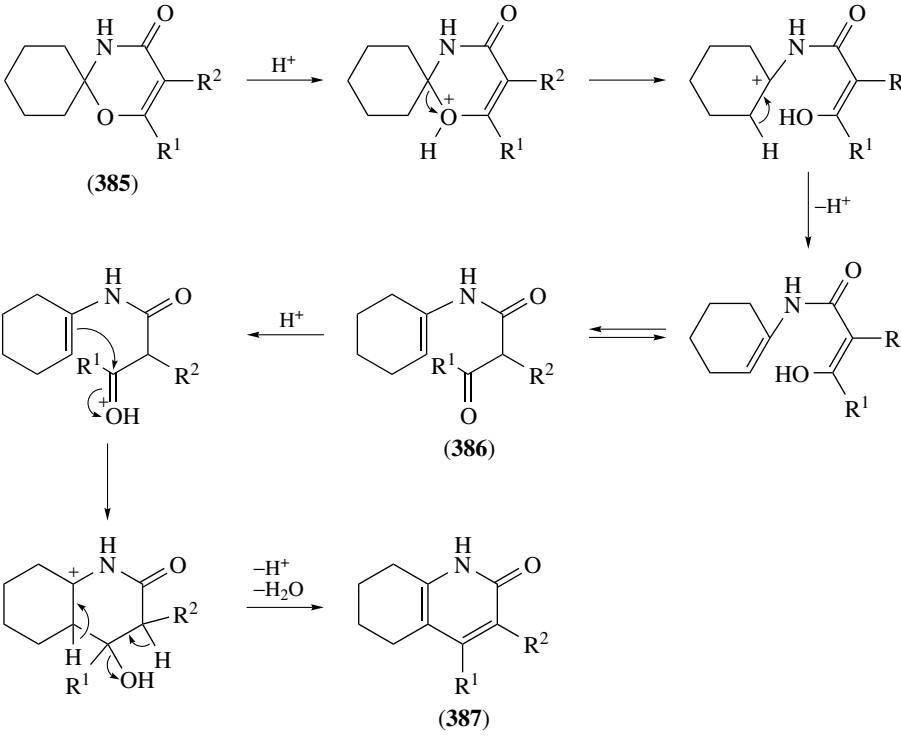
SCHEME 113

(**380**). Undoubtedly, formation of the delocalized malonate anion is the driving force for the carbon–carbon bond cleavage. 2-Aminopyrylium salts (**383**) have been proposed[521–523] as key intermediates in the postulated rearrangement of 5-amino-5-halopentadienals (**382**) to 5-halopenta-2,4-dienamides (**384**) (Scheme 114). 1-Oxa-5-azabicyclo[5.5]undec-2-en-4-ones (**385**) have been readily converted into tetrahydroquinolin-2-ones (**387**) in a one-step reaction involving anhydrous strong acid conditions. A plausible mechanism (see Scheme 115) involves initial ring opening promoted by acid catalysis to afford an enamide intermediate (**386**), which cyclizes to the tetrahydroquinolone ring system.[524]



(**382**) (**383**) (**384**)

SCHEME 114



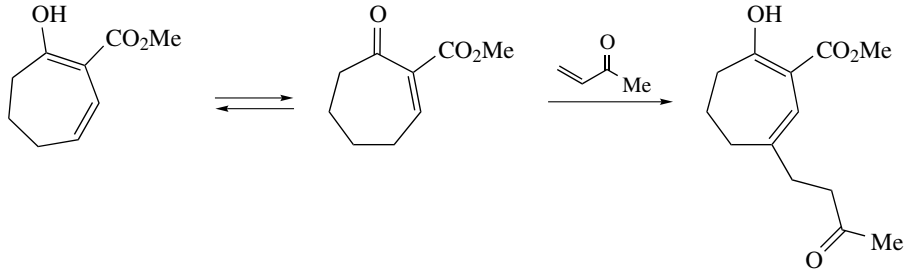
(**385**) (**386**) (**387**)

SCHEME 115

Isomerizations

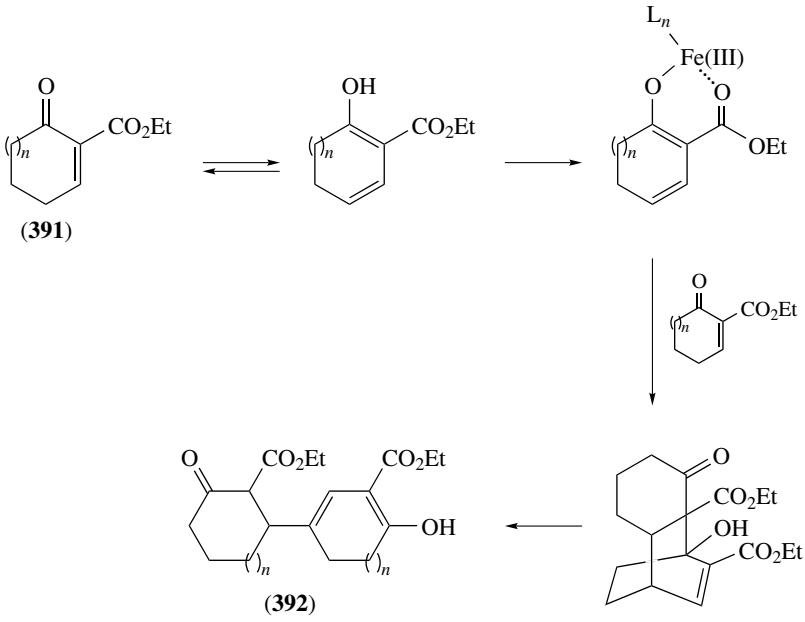
Tautomerism

A mechanistic study of acetophenone keto–enol tautomerism has been reported,[525] and intramolecular and external factors determining the enol-enol equilibria in the *cis*-enol forms of 1,3-dicarbonyl compounds have been analysed.[526] The effects of substituents, solvents, concentration, and temperature on the tautomerization of ethyl 3-oxobutyrate and its 2-alkyl derivatives have been studied,[527] and the keto–enol tautomerism of mono-substituted phenylpyruvic acids has been investigated.[528] Equilibrium constants have been measured[529] for the keto–enol tautomers of 2-, 3- and 4-phenylacetylpyridines in aqueous solution. A procedure has been developed for the acylation of phosphoryl- and thiophosphoryl-acetonitriles under phase-transfer catalysis conditions, and the keto–enol tautomerism of the resulting phosphoryl(thiophosphoryl)-substituted acylacetonitriles has been studied.[530,531] The equilibrium (**388**) $\rightleftarrows$ (**389**) has been catalysed by acid, base and by iron(III). Whereas base-catalysed conversion of (**388**) with methyl vinyl ketone yielded a Michael reaction product in the classical sense, iron(III) catalysis was found[532] to drive the Michael donor (**388**) to react in a vinylogous fashion to yield (**390**). A similar, formally vinylogous Michael reaction product (**392**), generated by a sequence of enone–dienol tautomerization, Diels–Alder, and retro-aldol reactions as outlined in Scheme 116, has been observed[533] during the iron(III)-catalysed dimerization of cycloalkenone-2-carboxylates (**391**).

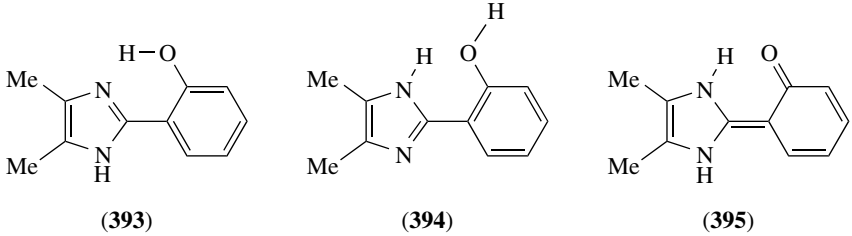


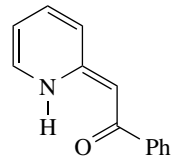
(**388**) (**389**) (**390**)

The various tautomers and rotamers of alloxan have been examined in detail by the MNDO method and it is predicted[534] that the keto form is most important in the gas phase, although in solution the monohydroxy forms are also thought to contribute. A mass spectral study has been used to investigate the enol–keto tautomeric equilibria of a series of substituted salicylaldehyde and 2-hydroxynaphthaldehyde Schiff bases.[535] In neutral, ethanolic solutions, the *cis*- and *trans*-enol forms of 4,5-dimethyl-2-(2′-hydroxyphenyl)imidazoles (**393**) and (**394**) have been found to exist in equilibrium in the ground state. However, in neutral aqueous solutions, the *trans*-enol and keto forms (**394**) and (**395**) were the only species detected.[536] Deuterium isotope effects on



SCHEME 116

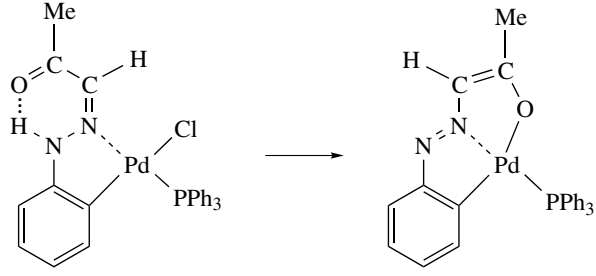




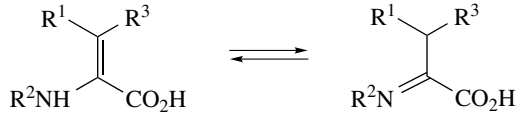
^{13}C chemical shifts have provided independent evidence to show that the enaminone structure (**396**) is the dominant tautomeric form in the enol–enaminone equilibrium of a series of α-heteroaromatic ketones.[537] Semiempirical and *ab initio* calculations on the relative stabilities of the different tautomers of 2,3-dihydroxypyrazine have shown[538] that the species exists predominantly as a dioxo tautomer in both the

solution and gas phase, while a comprehensive theoretical study of the tautomerism of the four isomeric hydroxypyridazine *N*-oxides as well as pyridazine-1,2-dioxide has been presented.[539] The tautomerism of the N(1)-methylated derivatives of uracil, thymine, and 5-bromouracil has been studied in order to analyse its implications in the mutagenicity of 5-bromouridine. The results of the study[540] have provided a basis for ruling out the involvement of non-canonical enol tautomers as the origin of the mutagenic properties. Studies have been reported on the tautomerism of 1-(2-pyrimidinyl)-3-methylpyrazolin-5-one derivatives[541] and 3(5)-ethoxycarbonyl-5(3)-hydroxypyrazole.[542] The significant influence of selenium on the structural properties of the nucleic acid base guanine has been demonstrated.[543]

The azo–hydrazo tautomerism of 1-phenylazo-4-naphthol and its isomers has been investigated by quantum chemical AMI and *ab initio* methods.[544] The syntheses of new palladacycles containing phenylhydrazones derived from 2-oxopropionaldehyde, benzoylformaldehyde, or butane-2,3-dione, in which the organic fragment acts as a bidentate monoanionic ligand in the hydrazo-keto form (**397**), have been described. Deprotonation of the NH group of these complexes has been shown to afford new palladacycles (**398**) in which the organic fragment acts as a terdentate bianionic ligand in the azo-enol form.[545]

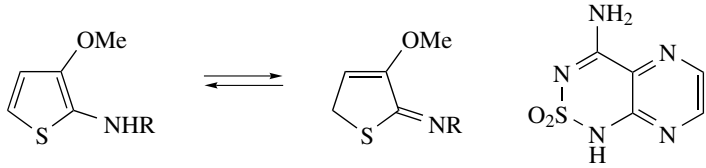


(**397**) (**398**)



(**399**) (**400**)

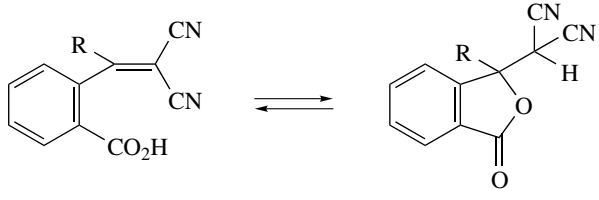
The prototropic tautomerism of 8-azaadenine has been studied[546] theoretically in both the gas phase and aqueous solution by means of *ab initio* methods. It has been shown[547] that dehydrovaline (**399**; R^1 = Me, R^2 = H, R^3 = Me), dehydrophenylalanine (**399**; R^1 = Ph, R^2, R^3 = H), and dehydropipecolinic acid [**399**; $R^1R^2 = (CH_2)_3$, R^3 = H] hydrolyse rapidly via the imine tautomer (**400**) even when the corresponding esters and sodium salts exist as the enamine tautomers. The 3-methoxy-substituted deriva-



(**401**) (**402**)

tives of (**401**; R = Me, Ph) have been reported as the first examples of amino–imino tautomerism in *N*-monosubstituted aminothiophenes.[548] A quantum chemical investigation of the tautomerism of 1,2,3- and 1,2,4-triazoles has been undertaken,[549] the tautomerism of nitrotriazoles has been investigated[550] by combined ^{1}H, ^{13}C and ^{15}N NMR spectroscopy, and the tautomerism of 3-amino-5-nitro-1,2,4-triazole has been studied[551] by *ab initio* MO calculations. A dynamic NMR study of the tautomerism of 2,2′-bisbenzimidazolyl in DMSO-d_6, and a mechanistic interpretation of the process based on a stepwise, single-proton transfer and formation of a zwitterionic intermediate, has been presented.[552] Semiempirical, density functional theory and *ab initio* methods have indicated[553] that, in the gas phase, the most stable tautomer of 4-aminopyrazino[2,3-*c*][1,2,6]thiadiazine 2,2-dioxide is (**402**). A detailed density functional study of the tautomerism of porphyrin and its seven isomers with an N(4)–metal coordination core has been carried out,[554] and the relative energies of different tautomers of inverted porphyrin, carbaporphyrin and certain related ring systems have been determined using geometry optimizations with non-local density functional theory.[555]

Ring–chain tautomerism in 2-acylbenzamides, 8-acyl-1-naphthamides, and 5-acyl-4-phenanthramides has been investigated[556] by IR and ^{1}H NMR spectroscopy. In all cases studied, the hydroxylactam or aminolactone was found to be the predominant species. Ring–chain tautomerism with slow interconversion has been observed[557] in solutions of 2-(2,2-dicyano-1-methylethenyl)benzoic acid and related compounds; see (**403**) ⇄ (**404**). The first examples of ring–chain tautomerism in 2-aryl-substituted imidazolidines have been observed,[558] and instances of ring–chain tautomerism in angularly substituted cycloalkane-fused tetrahydro-1,3-oxazines[559] and in the adducts of 6-nitroazolo[1,5-*a*]pyrimidine with methyl heterocycles[560] have been reported. The ring–chain tautomerism of some Schiff bases of 1-*p*-nitrophenylserinol has been quantitatively described.[561]



(**403**) (**404**)

The valence tautomerism of cobalt–quinone complexes in non-aqueous solvents has been investigated[562] by spectroscopic, electrochemical, and spectroelectrochemical methods, and it has been shown[563] that the cobalt (III) complex of a Schiff base diquinone ligand undergoes an entropy-driven valence tautomeric equilibrium in solution. A new interpretation of the valence tautomerism of 1,6-methano[10]annulenes and its application to fullerene derivatives has appeared.[564]

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