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Activated cyclopropanes in the synthesis of five-membered carbocycles and heterocycles

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Abstract. The conversion of functionalised cyclopropane compounds to derivatives of cyclopentane and five-membered heterocycles is described. Topics discussed include reaction conditions, the regio- and stereo-selectivity of the reactions depending on the type of substituents in the three-membered ring, and also the main procedures for obtaining appropriate cyclopropane substrates. The bibliography comprises 174 references.

I. Introduction

Although the history of the chemistry of cyclopropane compounds stretches back more than a hundred years[1] the extensive use of this class of compounds as intermediates in organic synthesis began not much more than thirty years ago. Owing to the development of carbene methods for converting olefins to cyclopropane and to other effective approaches to the construction of a three-membered carbon ring,[2-8] various functional derivatives of cyclopropane have become accessible and in addition many synthetically useful reactions that involve opening of a three-membered ring have been found.[2,5-15]

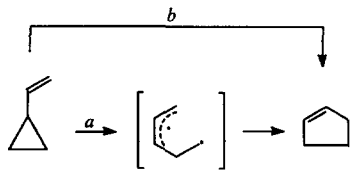
The main problem in using cyclopropane compounds in organic synthesis lies in securing high selectivity for two types of reaction: the formation and opening of a three-membered ring of carbon atoms. In many instances the nature of the substitution in the ring presupposes the possibility of both the straightforward production of the corresponding cyclopropane derivative and also chemo- and regio-selective cleavage of one of the three carbon–carbon bonds. A large amount of data has already been accumulated on the effect of substituents on the geometry of a three-membered carbon ring[16-21] and its energy characteristics.[16,20-24] Rules for predicting variations in the carbon–carbon bond lengths in a cyclopropane ring have been summarised:[20] π-electron-acceptor substituents, and also π- and σ-electron-donor substituents, that occur in a favourable conformation with respect to the cyclopropane ring cause lengthening of the adjacent bonds and shortening of the opposite bond whereas σ-electron-acceptor substituents have the opposite effect. Bearing in mind the normally observed direct correlation between the length of a carbon–carbon bond and its tendency to rupture, and also the predominant influence on this process of the π-electronic effects of substituents in a 'bisectrix' conformation for electron acceptors and a 'perpendicular' conformation for electron donors,[7,16,21] we may expect preferential rupture of the bonds in the ring that are adjacent to such substituents. Many experimental data are compatible with these conclusions,[7-12,15,16,25] so enabling us, in many instances, to make a reliable prediction of the results of possible conversions of 'activated cyclopropanes' and to design synthesis schemes involving them effectively. In the present review published data on the conversion of activated cyclopropanes to cyclopentane derivatives and five-membered heterocycles containing one hetero-atom (one of the best developed areas of the use of cyclopropanes in organic synthesis) are arranged systematically.

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II. Synthesis of five-membered carbocyclic compounds

The most important approach to the construction of five-membered carbocycles on the basis of cyclopropane precursors is the vinylcyclopropane–cyclopentene rearrangement.[26,27] The thermal version of this rearrangement[27] is usually effected at temperatures above 250 °C and can take place by a biradical mechanism (*a*)[28] or a concerted mechanism (*b*).[26-31]

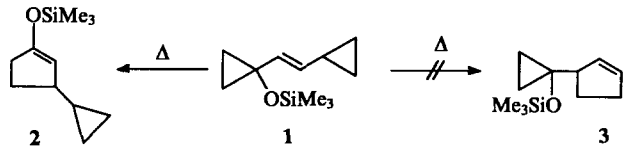


Considerable progress has also been achieved in the development of methods for synthesising cyclopentane systems using intra- and inter-molecular cyclisations, such as [3 + 2]-cycloaddition and intramolecular ring formation, with one or two carbon atoms from a cyclopropane ring incorporated in the newly generated cyclic system.[9-15,32-35]

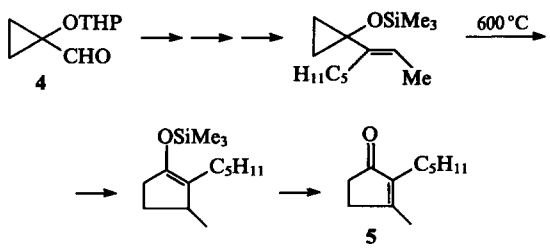
1. The vinylcyclopropane–cyclopentene rearrangement

Electron-donor substituents in the three-membered carbon ring, in either geminal or vicinal positions with respect to the vinyl group, considerably facilitate the occurrence of this rearrangement.[26] For example, the activating effect of a trimethylsiloxy group on the opening of a cyclopropane ring to which it is attached is clearly illustrated by the thermal

rearrangement of 1-(2-cyclopropylvinyl)-1-trimethylsiloxycyclopropane **1** which gives 3-cyclopropyl-1-trimethylsiloxycyclopent-1-ene **2** exclusively, but none of the isomeric compound **3**.[36]

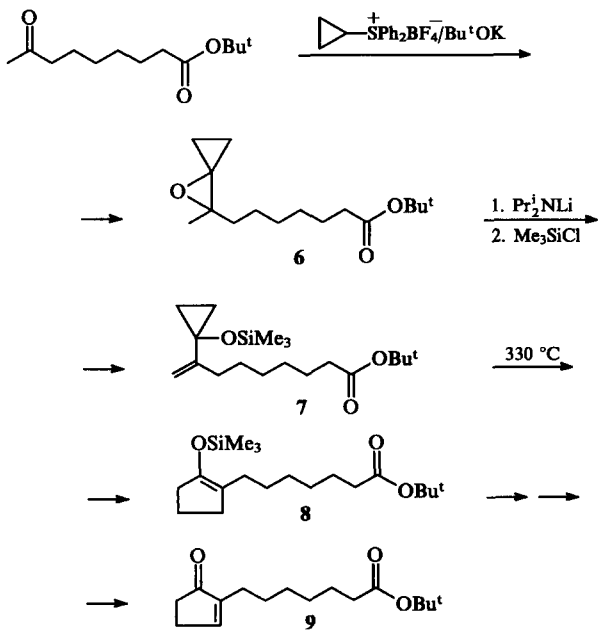


Several ways of obtaining substituted 1-trimethylsiloxyvinylcyclopropanes have currently been developed, starting from accessible hemiacetals of cyclopropanone,[12] oxaspiropentanes,[37] silyl ethers of enols,[38] 1-hydroxycyclopropylcarbonyl compounds[39] and certain other substrates.[40] This has enabled methods for synthesising different types of the cyclopentane system, including a number of natural compounds, to be proposed.[36,39,41-43] The methodology of the production of 2,3-disubstituted cyclopentenones starting from the available 1-tetrahydropyranyloxy-1-formylcyclopropane **4** can be followed using as an example the synthesis of dihydrojasmone **5** (with a total yield of 61%).

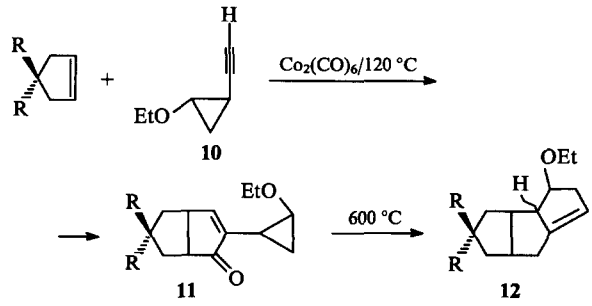


THP = tetrahydropyranyl.

The conversion of the keto-group in esters of 8-oxononanoic acid to a vinylcyclopropane group is accomplished via the intermediate formation of the corresponding oxaspiropentane **6**, isomerisation of the epoxide ring, and then silylation of the hydroxyl group. Thermal rearrangement of the resultant substituted trimethylsiloxycyclopropane **7** gives an ester of an enol **8** that is readily converted to the 2-substituted cyclopentenone **9**, which is used as a precursor of homoprostaglandins.[44] The use of cyclic ketones as the initial substrates enables the corresponding condensed systems to be synthesised.[33]

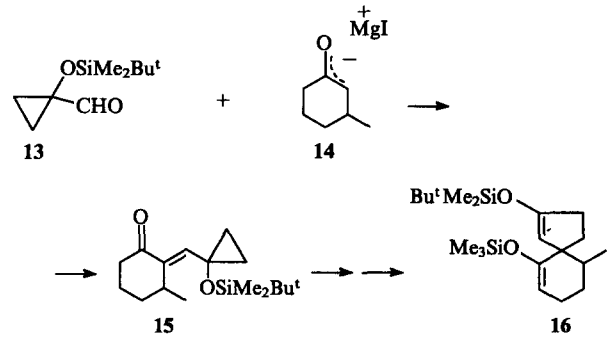


A combination of the cycloaddition of the dicobalt hexacarbonyl complex of the cyclopropylalkyne **10** to olefins and the vinylcyclopropane–cyclopentene isomerisation of the resultant cycloaddition products **11** makes it possible to carry out successive fusion of cycloalkenes to form tricyclic systems **12**.[45]

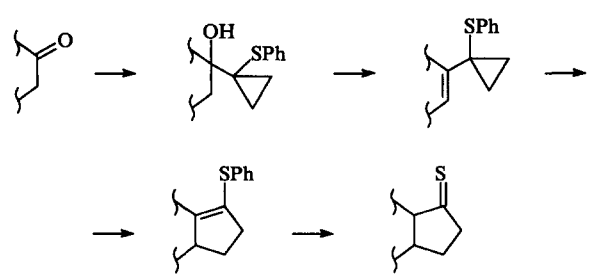


R = H, Me.

The *tert*-butyldimethylsilyl ether of 1-hydroxy-1-formylcycloproane **13** can be used for the synthesis of substituted vinylcyclopropane systems by a Wittig reaction or an aldol condensation.[47] For example, if the enolate anion **14**, which is obtained by the copper-iodide-catalysed addition of methylmagnesium iodide to cyclohex-2-enone, is captured by the aldehyde **13** the corresponding ketol is obtained and after its dehydration the siloxyvinylcyclopropane **15** can be isolated in a 73% yield (based on the aldehyde **13**). After a trimethylsilylation stage and vinylcyclopropane–cyclopentene rearrangement, **15** is converted to the spirocyclic derivative **16**.[47]

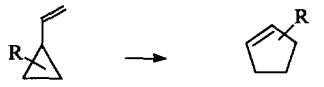


The main limitations of the methods described above for constructing cyclopentane systems on the basis of 1-oxo-substituted vinylcyclopropanes are usually due to difficulties in obtaining the latter. There is therefore considerable interest in the possible use of available 1-(phenylthio)cyclopropyllithium reagents for the introduction of a cyclopropane fragment into ketonic substrates.[48-50] For the formation of a cyclopentane ring the successive stages are indicated in a general form by the following scheme:[51,52]



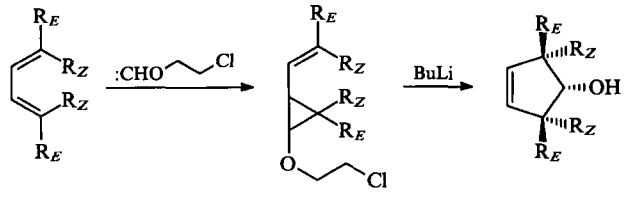
The yields are high at each of these stages and the vinylcyclopropane–cyclopentene rearrangement of 1-(phenylthio)-cyclopropyl derivatives takes place at even lower temperatures than in the case of the corresponding oxo-compounds.[27]

Electron-donor substituents in position 2 of the vinylcyclopropanes facilitate the thermal rearrangement of these compounds to a greater extent than the same substituents in position 1.[53–55]

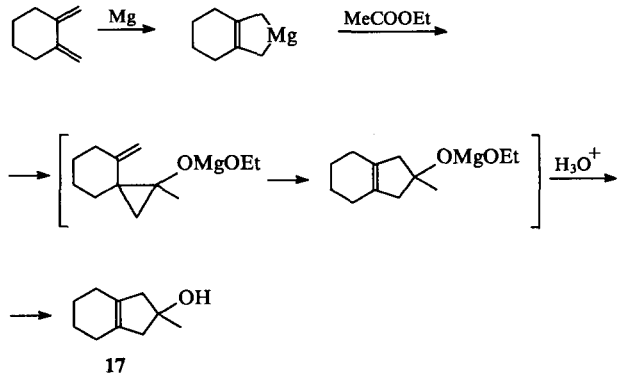


R	E_a/kcal mol^{-1}
H	49.7
1-OMe	44.7
2-OMe	38.7
2-NMe$_2$	31.1

When there are anionic substituents present in the ring the vinylcyclopropane–cyclopentene rearrangement takes place at room temperature or below.[56,57] In this case the reaction is by and large highly selective [4 + 1]-ring formation[57] whereas in the usual versions the rearrangement often takes place with only moderate stereoselectivity.[58]

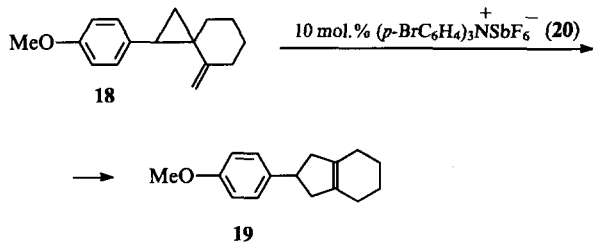


An alternative version involving the conversion of 1,3-dienes to the corresponding 3-cyclopentenols was proposed recently.[59] An example of this is the production of the bicyclic derivative **17** by treatment of the magnesium complex of 1,2-bis-(methylene)cyclohexane with esters followed by rearrangement of the resultant magnesium alkoxides of vinylcyclopropanols, which also occurs under exceptionally mild conditions.



17

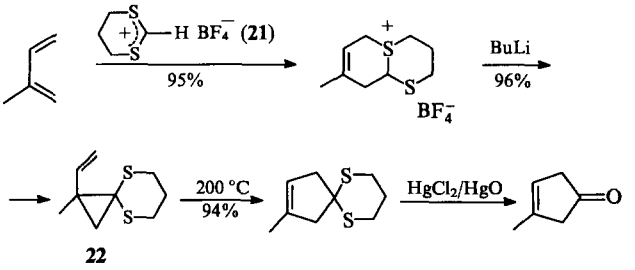
Ring expansion in vinylcyclopropane systems containing electron-donor substituents can also be expedited by the previous one-electron oxidation of the hetero-atom, an example being rearrangements of *p*-anisyl-substituted vinylcyclopropanes.[60] Thus in the presence of catalytic quantities of the one-electron oxidant **20**, rearrangement of **18** to the bicyclic derivative **19** will occur in 5 min at room temperature, with an 86% yield.



18

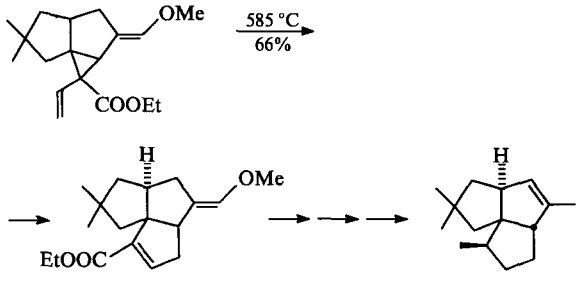
19

The 1,3-dithienium tetrafluoroborate **21** can also be used as a source of the single-carbon component in [4 + 1]-ring formation processes proceeding via a stage in which the corresponding activated vinylcyclopropane **22** is formed.[61]



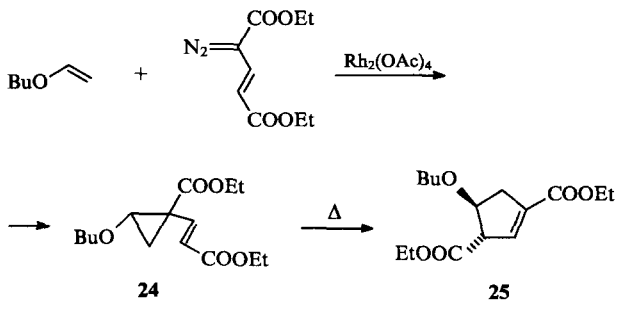
22

There are many examples of rearrangements of vinylcyclopropanes containing acceptor substituents in the ring; these usually occur under more mild conditions than the rearrangements of the corresponding unsubstituted compounds (see Refs 26 and 32). An example of the use of this type of rearrangement in the synthesis of natural compounds is the key stage in the construction of the non-linear tricyclic pentalene system **23**.[62]



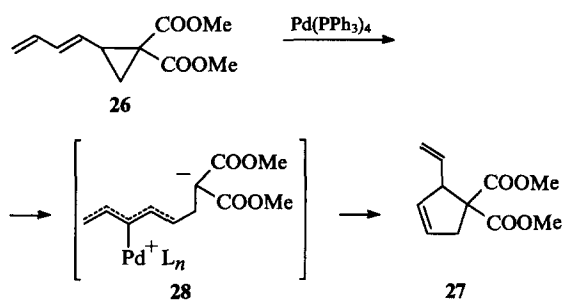
23

Compounds containing *p*-electron-donor and π-acceptor substituents in vicinal positions in the cyclopropane ring undergo the vinylcyclopropane–cyclopentene rearrangement particularly easily.[26,63] For example, the butoxyvinylcyclopropane **24**, unlike compounds with a similar structure that contain no alkoxy substituent, is unstable under chromatographic conditions and when its distillation is attempted it undergoes a smooth rearrangement to give the substituted cyclopentene **25** (total yield 61%).[63]

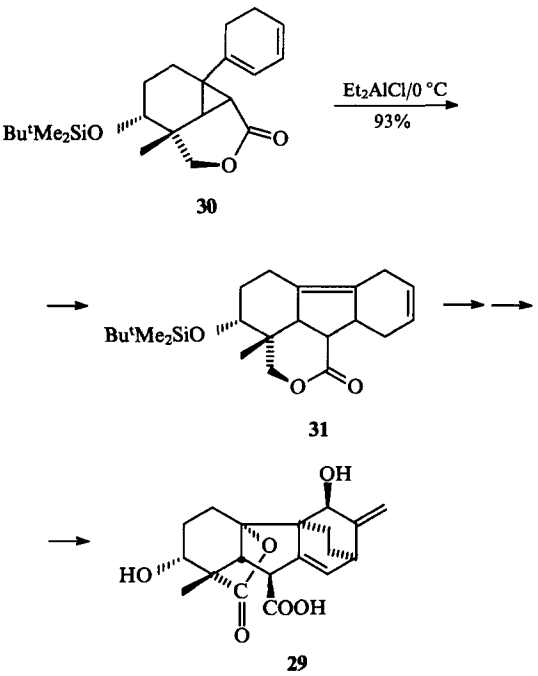


24 **25**

The presence of carbonyl substituents linked to the cyclopropane ring enables catalytic variants of the vinylcyclopropane–cyclopentene rearrangement to be carried out.[26,64–70] For example, the butadienylcyclopropane **26**, which contains two activating methoxycarbonyl groups, undergoes rearrangement to the corresponding vinylcyclopentene **27** at 50 °C (with an 87% yield) in the presence of catalytic quantities of $Pd(PPh_3)_4$. With other acceptor substituents the rearrangement can take place at even lower temperatures.[71] It is proposed[71] that the reaction occurs via nucleophilic attack by Pd^0 on the diene group to form the zwitter-ion **28**.

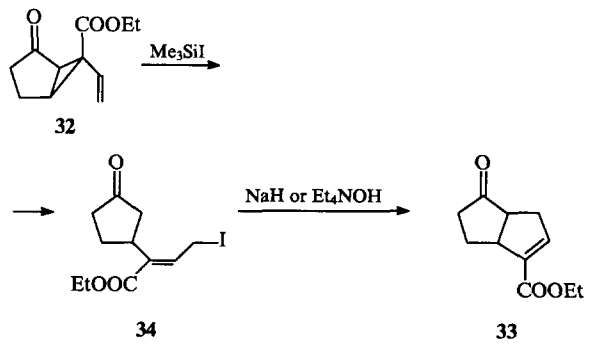


An extremely effective catalyst of the rearrangement of vinylcyclopropanes containing an ester function is diethylaluminium chloride.[66–88] It has been used to synthesise the tricyclic system of antheridic acid (**29**) (see Refs 67 and 68) via a stage in which the lactone **30** undergoes rearrangement to **31**, whereas an attempt to achieve this conversion by heating was unsuccessful.

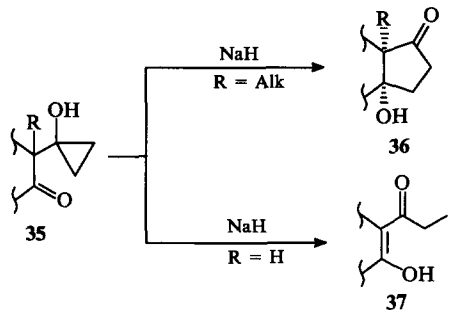


2. Other reactions that are accompanied by intramolecular cyclisation

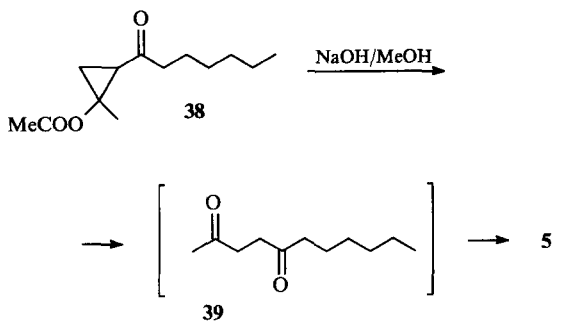
Complementary to the single-stage versions of the vinylcyclopropane–cyclopentene rearrangement considered above are procedures in which expansion of the ring in activated cyclopropanes to the corresponding cyclopentane derivatives is often accomplished by using consecutive heterocyclic ring opening and closure reactions, which are usually achievable in two or more stages. For example, conversion of the vinylcyclopropane derivative **32** to the bicyclanone **33** can be carried out under exceptionally mild conditions by opening the three-membered ring (which is activated by acceptor substituents) with trimethyliodosilane and then carrying out cyclisation of the iodoketone product **34** under the action of strong bases.[72,73]

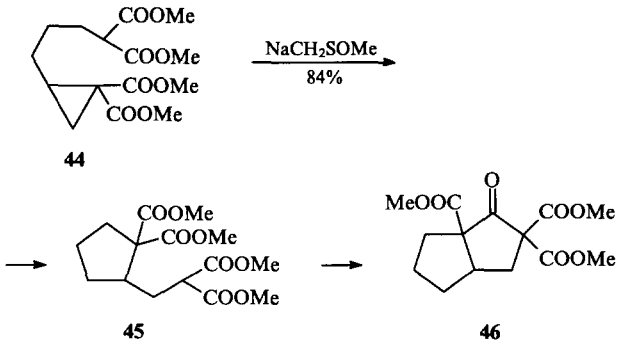


The ketone **32**, as well as a number of its analogues, are easily accessible and are readily formed by the reaction of the corresponding unsaturated cyclic ketones with the lithium dienolates of esters of α-bromocrotonic acid or its derivatives. In general, a sequence of conversions of cycloalkenones to the corresponding bicyclic derivatives is an effective method of [3 + 2]-ring formation which has been used successfully to synthesise a number of natural compounds.[72–74] A new variant of [3 + 2]-ring formation that has been developed recently for the synthesis of steroids[75] is based on intramolecular capture of the homoenolate anion that is generated when the cyclopropane ring in the 1-(2-ketoalkyl)cyclopropanols **35** is opened by the action of sodium hydride,[75–77] forming the corresponding cyclopentanols **36** or products obtained from them in further reactions. When a hydrogen atom is present in the position α to the carbonyl group and to the three-membered ring isomerisation to the ethyl ketones **37**, which is normal for substituted cyclopropanols, is observed.[76]

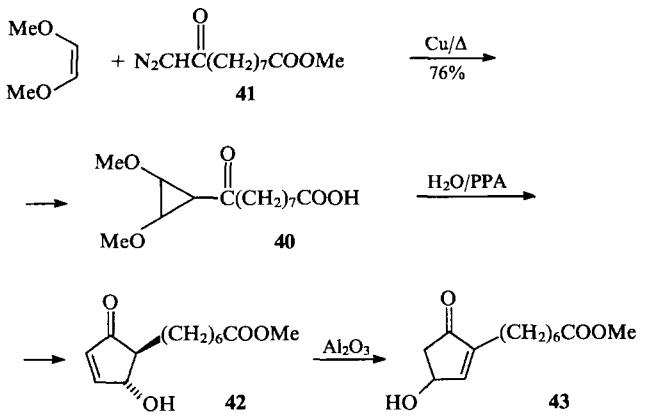


Carbonyl derivatives of cyclopropane with electron-donor substituents in a vicinal position will undergo solvolytic ring opening reactions under exceptionally mild conditions to give the corresponding 1,4-dicarbonyl derivatives or their latent forms.[7,11,25] These compounds are, as is well known, one of the most effective sources for obtaining substituted cyclopentenones by intramolecular cyclisation;[35] this provides a basis for using a sequence of such transformations in the development of effective methods for synthesising a number of cyclopentane derivatives.[78–81] For example, the reaction of the acetoxycyclopropyl ketone **38** with sodium hydroxide gives an 83% yield of dihydrojasmone **5** via the formation of the diketone **39** as an intermediate.[78]

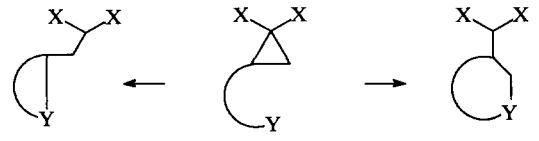




The dimethoxycyclopropyl ketone **40**, which is produced by the reaction of *cis*-1,2-dimethoxyethylene with the diazoketone **41**, will react with polyphosphoric acid in aqueous acetone in a single stage to give the hydroxycyclopentenone **42**, owing to the solvolytic opening of the cyclopropane ring, intramolecular aldolisation, and the elimination of methanol. Isomerisation of **42** on basic aluminium oxide gives the cyclopentanone **43** which is a well known key intermediate in the synthesis of PGF_1.[79]



Methods for synthesising cyclopentane structures with one or two carbon atoms from the initial cyclopropane incorporated into the five-membered ring have been developed to a considerably lesser extent than the reactions for expanding a three-membered carbon ring that have been discussed above (see Refs 9, 34, and 35). Of the two alternative versions of nucleophilic opening of an activated cyclopropane ring, called spirocyclisation and fused cyclisation respectively, spirocyclisation is kinetically preferred.[82]



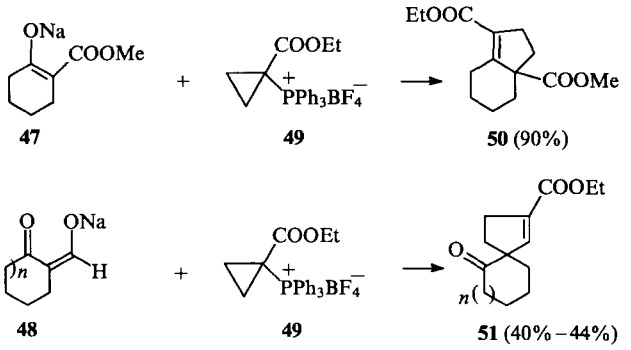
spirocyclisation fused cyclisation

For example, the reaction of the cyclopropane tetraester **44** with $NaCH_2 \cdot SO \cdot Me$ in dimethyl sulphoxide at room temperature gives the thermodynamically more stable cyclopentane tetraester **45** which undergoes smooth cyclisation to the bicyclo[3,3,0]octanone derivative **46** when the temperature is raised.[82]

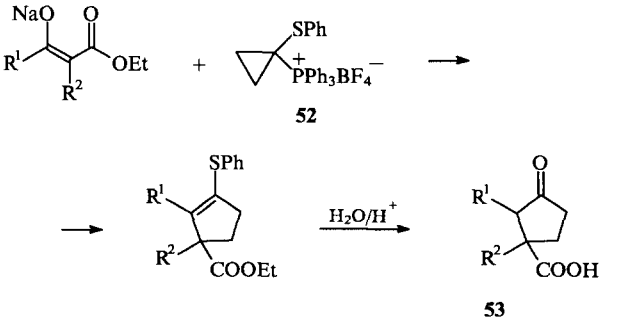
It was established in the same work that spirocyclisation is kinetically preferred in the formation of a four-membered ring but under conditions where there is thermodynamic control the corresponding cyclopentane derivatives can also be obtained.

3. Intermolecular ring formation reactions

The approaches to the synthesis of cyclopentane structures relying on intermolecular reactions of activated cyclopropanes that are known at the present time are based on the strategy of [3 + 2]-ring formation. For example, tetracyanoethylene forms the relevant cyclopentane adducts with donor or donor-acceptor cyclopropanes.[25] However this method has not achieved significant use in synthesis because it is not flexible enough. Another approach uses a series of homo-Michael addition reactions of enolate anions to cyclopropane derivatives doubly activated by acceptor substituents and intramolecular condensation.[83-91] For example, the sodium enolates of α-methoxycarbonylcyclohexanone **47** (data from Ref. 84) or the α-formylcycloalkanones **48** (data from Ref. 85) react with 1-(ethoxycarbonyl)cyclopropyltriphenylphosphonium tetrafluoroborate **49** to give condensed **50** or spiran **51** derivatives respectively. The latter approach has been used successfully in the synthesis of a number of natural sesquiterpenes.[85]

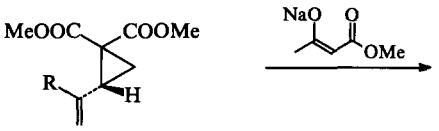


The use of [1-(phenylthio)cyclopropyl]triphenylphosphonium tetrafluoroborate **52** as the Michael acceptor opens up a simple route to substituted 2-carboxycyclopentanones **53**.[86,87]

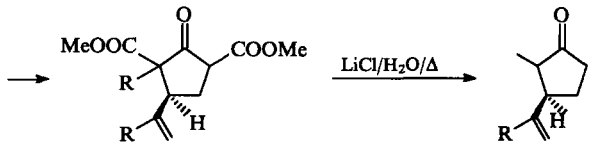


R^1, R^2 = H, Me, Ph, CH_2Ph.

Similar transformations of the *R*-dimethyl-2-vinylcyclopropane-1,1-dicarboxylate **54** have been used as a basis for developing effective approaches to the complete asymmetric synthesis of certain steroids[88,89] and prostaglandins.[90] A key stage in the construction of a cyclopentane ring in these schemes is the stereospecific opening of the ring in **54** by enolates based on derivatives of malonic or acetoacetic ester as, for example, in the production of the enantiomerically pure vinylcyclopentanones **55**.[91]

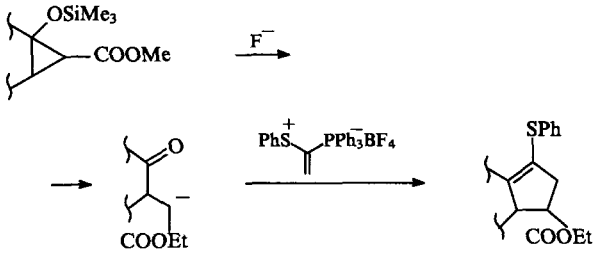


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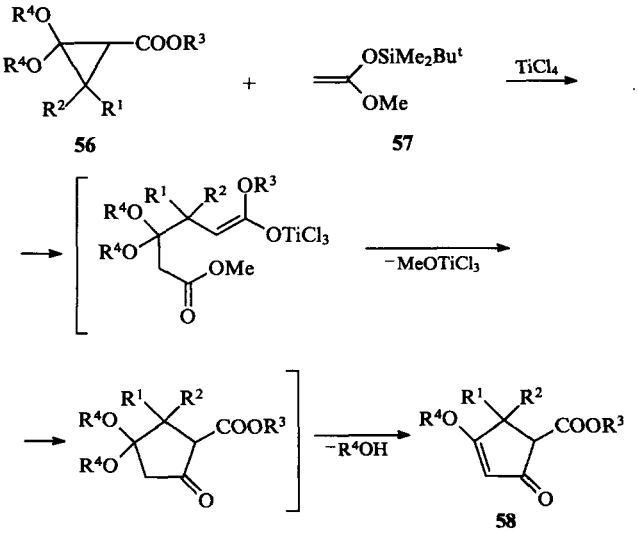


R = H, Me. **55**

The possible simultaneous generation of a carbanion centre and a carbonyl function by the action of fluoride ions on adducts of an ethoxycarbonylcarbene with silyl ethers of enols[25] provides a basis for developing an alternative strategy for [3 + 2]-ring formation.[92-94]



[3 + 2]-Cycloaddition of the donor-acceptor cyclopropanes **56** to the *tert*-butyldimethylsilylacetal of keten **57** is catalysed by titanium tetrachloride, resulting in the formation of derivatives of 3-alkoxycyclopentenones **58** with yields of 28% – 75%.[95]



56 **57**

58

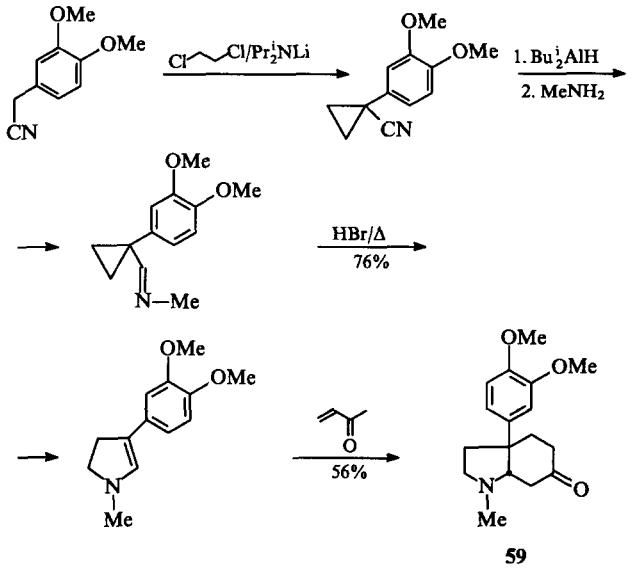
R^1 – R^4 = Me, Et.

III. Synthesis of five-membered heterocycles

The number of publications devoted to the conversion of activated cyclopropane compounds to five-membered heterocycles is considerably greater than the number concerned with the production of cyclopentane derivatives from such compounds. However there are, to our knowledge, no papers in which data on the use of activated cyclopropanes in the synthesis of heterocycles are arranged especially systematically although there are a number of reviews devoted to particular aspects of this subject.[6,7,9,11,96]

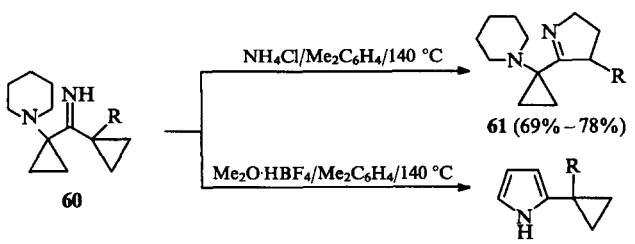
1. Ring expansion reactions in hetero-analogues of vinylcyclopropanes

The ring expansion reactions that have been studied most extensively are those in carbonyl and heterocarbonyl cyclopropane derivatives and a number of effective preparative methods for synthesising five-membered heterocycles have been developed on their basis. For example, the acid-catalysed rearrangement of cyclopropylketimines is one of the most flexible methods for obtaining 2-pyrrolines with various degrees of substitution (see Ref. 96). The use of this reaction for the synthesis of alkaloids is illustrated by the simple scheme for obtaining (±)-mesembrine **59**.[97-99]



59

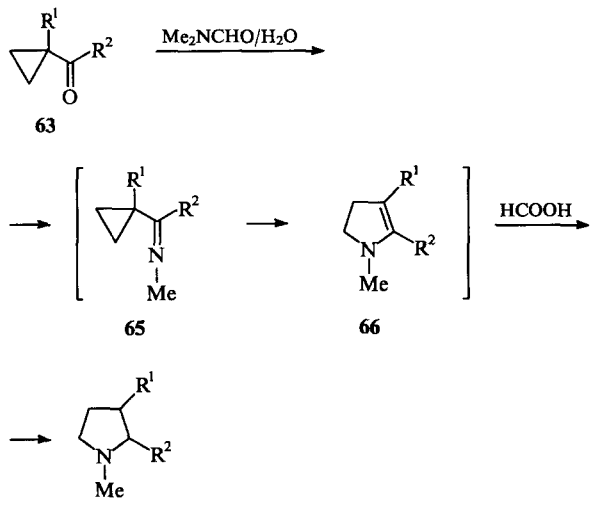
The hetero-substituents in the cyclopropane ring have an appreciable effect on the course of the reaction but this effect is not always in accord with their effect on the thermal vinylcyclopropane–cyclopentene rearrangement.[100-103] For example, the thermolysis of the di(cyclopropyl)ketimines **60** in boiling xylene in the presence of ammonium chloride gives the pyrrolines **61** as a result of opening of the cyclopropane ring that has no piperidine substituent.[102]



R = H, SPh. **62** (32% – 42%)

The use of the dimethyl etherate of tetrafluoroboric acid as an acid catalyst gives the opposite result as regards selectivity of opening of the three-membered ring. The rearrangement of the di(cyclopropyl)ketimines **60** now gives the pyrrole derivatives **62** owing to opening of the three-membered carbon ring that has the electron-donating piperidyl substituent. These differences are attributed to the greater role of the nitrogen atom of the piperidyl radical in stabilisation of the positive charge in the transition state when an acid with a weakly nucleophilic tetrafluoroborate counter-ion is used as a catalyst.[103]

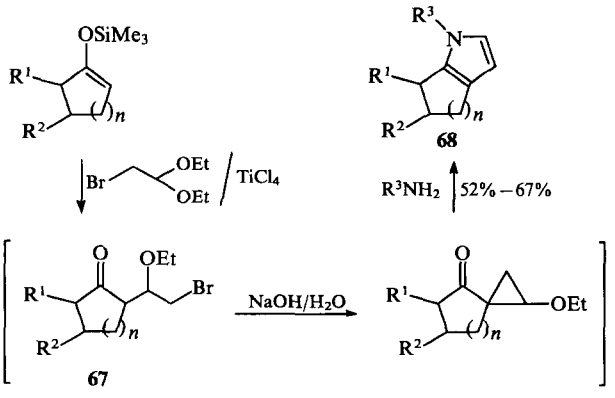
Cyclopropylimines often act as intermediates in the ring expansion reactions of cyclopropane carbonyl compounds with primary amines. For example, boiling the cyclopropyl ketones **63** in dimethylformamide in the presence of magnesium chloride gives the pyrrolidines **64**.[104] It is likely that the reaction proceeds via the formation of intermediate cyclopropylimines **65** and their rearrangement to substituted pyrrolines **66** which are reduced *in situ* by formic acid to give the final products.



63 **65** **66** **64** (31%–72%)

R^1 = H, Ph; R^2 = Alk, cyclo-Alk, Ar.

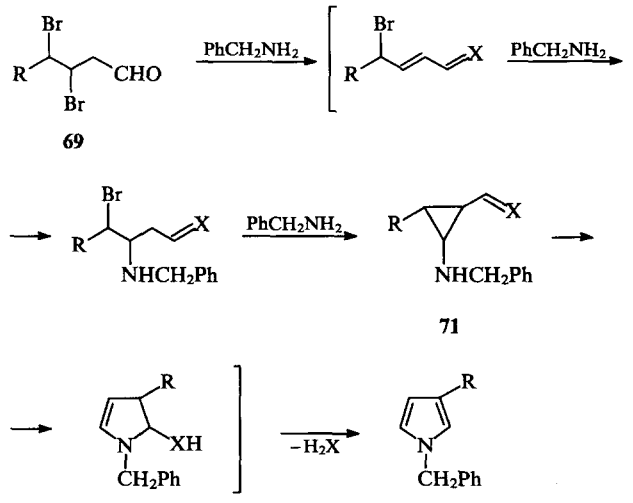
Cyclopropylcarbonyl compounds with electron-donor substituents in a β position to the carbonyl group will react with primary amines under mild conditions to give the corresponding pyrrole derivatives.[105–108] A convenient preparative method for obtaining this type of activated cyclopropane is 1,3-dehydrohalogenation of accessible 3-bromo-2-alkoxypropyl ketones.[105,106] The use of the cyclic ketones **67** as initial substrates in this reaction enables pyrrole derivatives condensed with cyclopentane and cyclohexane rings **68** to be synthesised.[106]



67 **68**

R^1, R^2 = H, Bu; R^3 = H, Me, CH_2Ph; n = 1, 2.

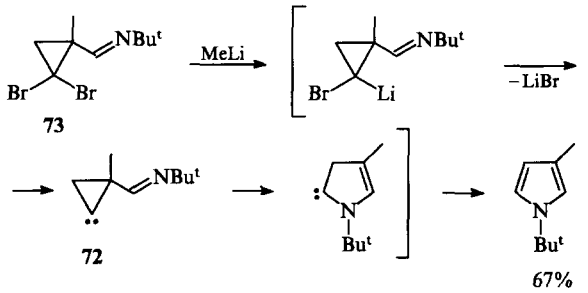
A similar approach was used in a convenient scheme for converting β,γ-dibromoaldehydes **69** to the inaccessible 3-alkyl-β-benzylpyrroles **70**.[108,109] The rearrangement of the linear carbon-carbon skeleton of the initial aldehyde **69** to give the branched structure of the 3-alkyl-pyrrole **70** is effected via the intermediate formation of the donor-acceptor cyclopropanes **71** by closure of the three-membered ring initiated by a Michael addition.



69 **71** **70**

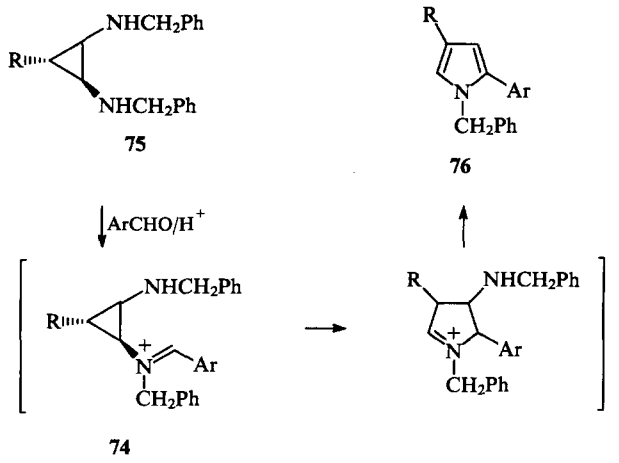
R = Alk; X = O, NCH_2Ph.

The role of the activating electron-donor substituent in the β position to the imine function can, at least formally, be performed by the lone pair of electrons of the carbene centre in the intermediate **72** which is formed when the dibromocyclopropylimine **73** is converted to 1-*tert*-butyl-3-methylpyrrole by the action of methyllithium.[110,111]



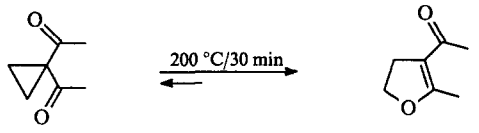
73 **72** 67%

Aza-analogues of vinylcyclopropanes in which the nitrogen atom is directly bonded to the three-membered ring are also able to undergo rearrangement to pyrrole derivatives.[112,113] In the case of the activated cyclopropanes **74**, which are intermediate products of the reaction of the 1,2-diaminocyclopropanes **75** with aromatic aldehydes, the rearrangement proceeds smoothly at room temperature to give the 2-arylpyrroles **76** as final products.[113]



R = H, Me.

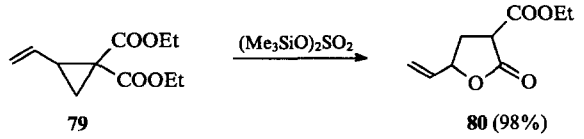
Rearrangements of cyclopropylcarbonyl compounds to give furan derivatives have been studied more thoroughly and there are many examples of their use in synthesis (see Refs 7, 11, 23, and 114). Formylcyclopropane[115] and acetylcyclopropane[116] undergo rearrangement reversibly in the gas phase at 400–500 °C to form 2,3-dihydrofuran and 2,3-dihydro-5-methylfuran respectively. The reaction is accompanied by the irreversible formation of a number of by-products and is of no preparative importance. On the other hand, 1,1-diacetylcyclopropane **77** will isomerise at 200 °C to give a high yield of the dihydrofuran **78**.[117,118]



77 **78** (92%)

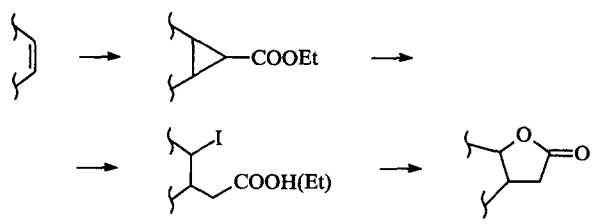
Other 1-acylcyclopropanes with electron-acceptor substituents in the α position to the acyl group undergo a similar isomerisation.[118,119]

Cyclopropanecarboxylic acid[120] and its derivatives[121–124] isomerise in the presence of various acid catalysts to give the corresponding γ-butyrolactones. The best yields of the final products are obtained by opening the three-membered ring in the carbonyl-substituted cyclopropanes using organosilicon reagents such as trimethyliodosilane or bis(trimethylsilyl) sulfate.[125] For example, treating 1,1-bis(ethoxycarbonyl)-2-vinylcyclopropane **79** with bis(trimethylsily) sulfate in 1,2-dichloroethane gives an excellent yield of the butyrolactone **80**.[126]

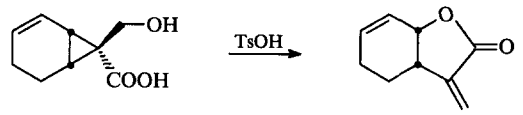


79 **80** (98%)

Other 1-carbonyl-substituted cyclopropanecarboxylates will also enter into reaction; the thermodynamically more stable butyrolactones with predominant inversion of the configuration of the reaction centre are formed.[126] A reaction in two stages, viz. opening the ring in the cyclopropanecarboxylic ester with trimethyliodosilane and closure of the lactone ring, is an effective method for converting olefins to γ-butyrolactones.[127]

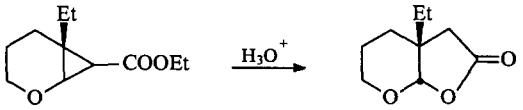


The use of 1-hydroxymethyl-,[128,129] 1-halogenomethyl-,[129] and 1-dialkylaminomethyl-substituted cyclopropanecarboxylate esters[130] enables α-methylene-γ-butyrolactones to be obtained. The regio-selectivity of the reaction is determined by the type of substituents in positions 2 and 3 of the three-membered ring.[128,129] For example, the rearrangement of the cyclopropylcarbinol substrate **81** to the lactone **82** takes place owing to rupture of the carbon–carbon bond in the cyclopropane ring that is adjacent to the double bond[128] whereas for the corresponding methoxyl analogue the reverse selectivity is observed.[129]



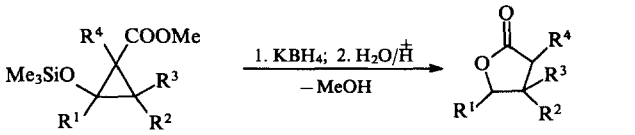
81 **82** (89%)

Cyclopropylcarbonyl compounds undergo rearrangement to furan derivatives especially easily when electron-donor substituents are present in the β position of the cyclopropane ring.[25] One of the most effective approaches to the synthesis of this type of substrate involves formation of the cyclopropane from esters of enols of diazocarbonyl compounds.[11,14,25,130] In certain instances not only the carbonylcyclopropanes are formed in these reactions but also the corresponding dihydrofurans. The latter may be obtained by 1,3-dipolar cycloaddition of ketocarbenes to olefins or isomerisation of the initially formed cyclopropane derivatives.[131–136] A typical example of this type of transformation is the synthesis of the bicyclic lactone **83** which is used as a key intermediate in the synthesis of certain indole alkaloids.[134] The cyclopropane precursor **84**, which is obtained from β-ethyldihydropyran, undergoes rearrangement to the lactone **83** smoothly when it is heated with dilute sulfuric acid.



84 **83** (93%)

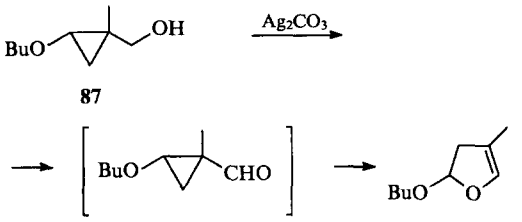
In certain instances, under the reaction conditions used, the hydroxylactones formed initially undergo dehydration to give the corresponding unsaturated lactones.[137] On the other hand, the reaction of the methyl 2-siloxycyclopropanecarboxylates **85** with potassium hydroborate in methanol enables the substituted saturated γ-butyrolactones **86** to be synthesised in a different way in a one-step procedure with a high yield. This multi-stage procedure evidently includes initial desilylation of **85** by potassium methoxide (generated *in situ* from potassium hydroborate and methanol), opening of the activated cyclopropane ring to form the corresponding 4-oxoalkanoates, their reduction and lactonisation.[138]



85 **86** (78%–95%)

R^1–R^4 = Alk, cyclo-Alk, Alkenyl.

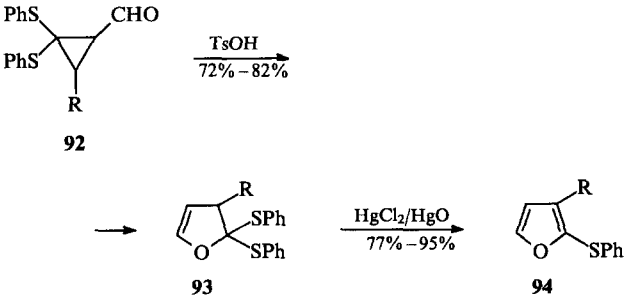
2-Oxy-substituted cyclopropyl ketones and aldehydes are considerably less stable and will undergo rearrangement to the corresponding dihydrofurans smoothly in the presence of acid catalysts or *in situ*.[131,133,139-141] For example, oxidation of the butoxycyclopropylcarbonyl **87** with silver carbonate on a zeolite gives a high yield of the dihydrofuran **88**, probably via the intermediate formation of the corresponding aldehyde **89**.[139,140] The reaction is of a general nature and in some instances the corresponding activated cyclopropanecarbaldehydes and cyclopropyl ketones can be identified.[139-141]



Cyclopropanes in which the three-membered ring has two geminal acceptor[132,135] or donor substituents and a substituent of the opposite type in a third position[142,143] will undergo rearrangement to dihydrofuran derivatives under very mild conditions. For example, in solutions of derivatives of 2-methoxycyclopropanecarboxylic acids **90** in dimethyl sulfoxide an equilibrium with the corresponding dihydrofurans **91** is established rapidly even at room temperature. The rearrangement typically takes place with retention of the stereochemical configuration at the reaction centre[132] (see also Ref. 136).

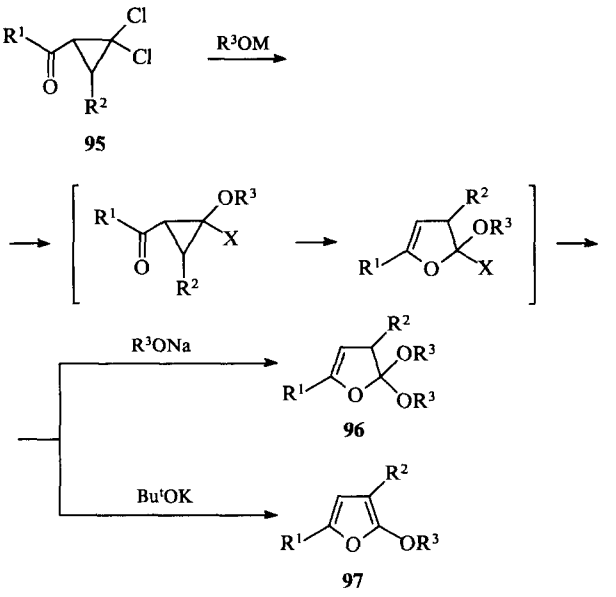


In the presence of catalytic quantities of *p*-toluenesulfonic acid the *gem*-di(phenylthio)cyclopropanecarbaldehydes **92** isomerise to the 3-substituted 2,2-di(phenylthio)-2,3-dihydrofurans **93** rapidly at room temperature and the latter can readily lose thiophenol to form the phenylthiofurans **94**.[144,145] Note that *gem*-di(phenylthio)cyclopropyl ketones with a similar structure isomerise smoothly under the same conditions to give acyclic products.[146]



R = Me, Ar.

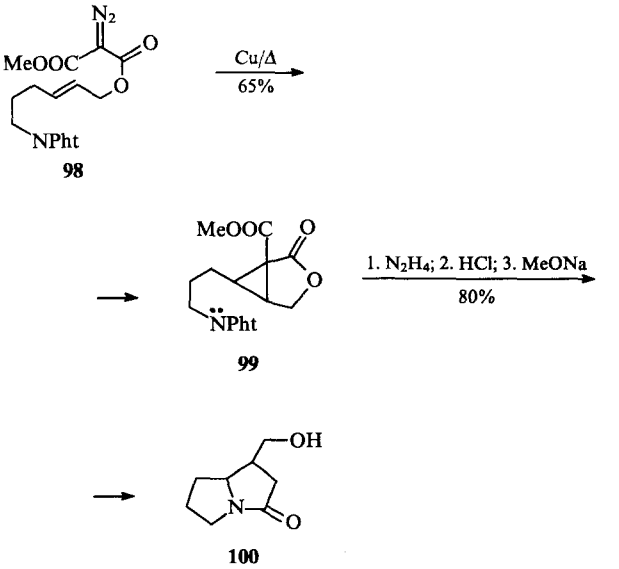
Nucleophilic substitution of the halogen atoms in 1-acyl-2,2-dichlorocyclopropanes **95** by reaction with alkali metal alkoxides leads directly to 2,2-dialkoxy-2,3-dihydrofurans **96**[147-150] or substituted 2-alkoxyfurans **97**,[151] depending on the type of alkoxide and the reaction conditions. 2-Dialkylaminofurans can be obtained by a similar scheme of reactions.[152]



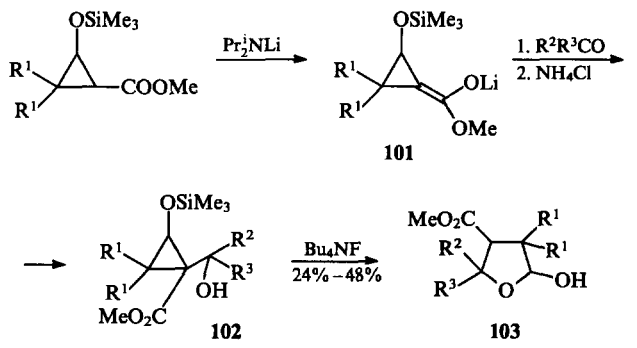
R[1], R[2] = Alk, Alkenyl, Ar; R[3] = Alk; M = Na, K; X = Cl, OR[3].

2. Other intramolecular cyclisation reactions

Intramolecular nucleophilic ring opening reactions in activated cyclopropanes also provide an effective approach to the production of five-membered heterocycles.[7,9,11,15,25] The intramolecularity factor has an additional activating effect on the opening of the three-membered ring[9] and the main problem in using this approach in directed synthesis is to obtain appropriate cyclopropane derivatives that contain suitable nucleophilic centres in the substituents. This approach has been used successfully in the synthesis of natural compounds,[9] particularly in the stereospecific synthesis of certain alkaloids where one of the stages involves intramolecular formation of cyclopropane from the multiple bond in **98**. The removal of the shielding phthalimide (NPht) group in the resultant cyclopropane derivative **99** using hydrazine hydrate leads to the formation of the key bicyclic product **100** due to spiro-opening of the cyclopropane ring with inversion of the configuration of the reaction centre.[153]

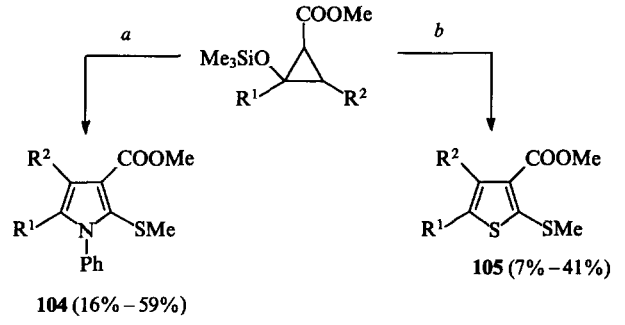


An alternative method of introducing nucleophilic substituents into activated cyclopropanes involves alkylation of deprotonated derivatives of a cyclopropanecarboxylic acid by using suitable substrates.[154-158] For example, the reaction of the ester enolates **101**, which are readily generated from methyl 2-siloxycyclopropanecarboxylates by the action of lithium diisopropylamide, with carbonyl compounds gives the trifunctional derivatives **102**. The latter are unstable and are converted, either spontaneously or by the action of desilylating agents, to the lactols **103** which are readily convertible to the corresponding tetrahydrofuran or γ-butyrolactone derivatives.[155]



R^1_2 = Me_2, $-(CH_2)_5-$; R^2, R^3, = H, Me, Ph, $-(CH_2)_5-$.

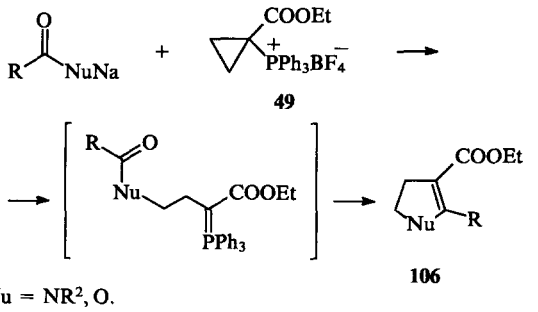
The use of hetero-analogues of carbonyl compounds, such as phenyl isothiocyanate and carbon disulfide, as electrophiles opens up a route to the corresponding derivatives of pyrrole **104** [158] and thiophen **105**.[156,157]



a — 1. Pr^i_2NLi, 2. PhNCS, 3. MeI, 4. CF_3COOH;
b — 1. Pr^i_2NLi, 2. CS_2, 3. MeI, 4. CF_3COOH
R^1, R^2 = Alk, cyclo-Alk.

3. Intermolecular hetero-ring formation reactions

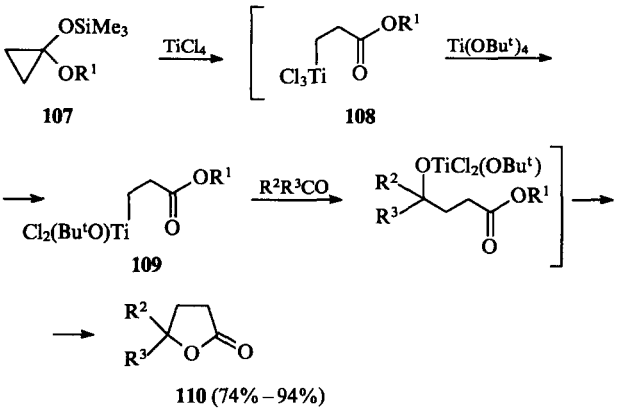
The synthesis of five-membered heterocycles by means of intermolecular hetero-ring formation, like that of cyclopentane derivatives (see above), is based on [3 + 2]-ring formation reactions. 1-Ethoxycarbonylcyclopropyltriphenylphosphonium tetrafluoroborate **49** will react with α-carbonyl-containing nucleophiles to give the corresponding five-membered heterocyclic compounds **106**. The stages in the reaction are nucleophilic opening of the three-membered carbon ring (which is doubly activated by the electron-acceptor substituents) and then olefination of the carbonyl group.[159-163]



Nu = NR^2, O.

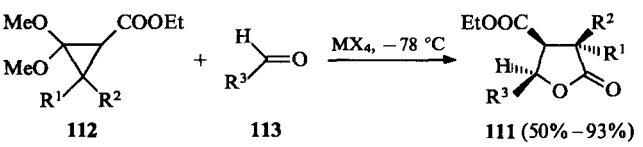
The reaction of anions of cyclic imides with the phosphonium salt **49** opens up a means of obtaining bicyclic lactams with a bridgehead nitrogen atom.[159,160,162]

The cyclopropanone acetals **107**, which are doubly activated by electron-donor substituents, are suitable precursors of homoenolate anions[40,164,165] which react with carbonyl compounds to give derivatives of γ-hydroxycarboxylic acids or γ-butyrolactones.[166,167] In the homoenolate anions an intramolecular back reaction with the carbonyl group is favoured to a considerable extent by the entropy factor and hence for the reaction with an external electrophile to take place a substantial gain in enthalpy is required. It is known that in reactions with carbonyl compounds titanium and zinc homoenolates of esters satisfy these conditions.[164,167] The addition of 0.5 equiv. of tetra(*tert*-butoxy)titanium to the trichlorotitanium homoenolate **108**, which is obtained by the reaction of the silylacetal of cyclopropanone **107** with titanium tetrachloride, gives an alkoxide derivative **109** that is more reactive than the initial enolate **108**. The reaction of **109** with ketones does not stop at the stage where the corresponding γ-oxyesters are formed but leads to their cyclisation *in situ* to give the γ-lactones **110**.[167-170]



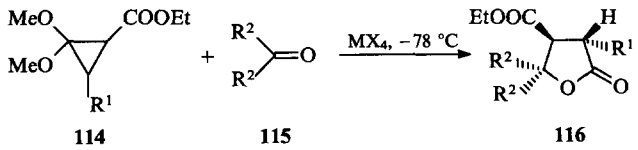
R^1 = Alk; R^2, R^3 = Alk, cyclo-Alk, Ar.

Cyclopropanes containing donor and acceptor substituents simultaneously are able to enter into a similar condensation with aldehydes and ketones in the presence of titanium tetrachloride, giving γ-hydroxyketones and dihydrofurans respectively.[168-170] There are also reports of the diastereoselective synthesis of *cis*-3,4-disubstituted γ-lactones **111**[171,172] and *cis*-3,4-disubstituted-γ-lactams[172] using the Lewis-acid-catalysed reaction of 2,2-dialkoxy-3,3-dialkylcyclopropanecarboxylic esters **112** with aldehydes **113** and *N*-toluenesulphonylaldimines respectively.[173]



R^1, R^2, R^3 = Alk; MX_4 = $TiCl_4$, $TiBr_4$, or $SnBr_4$.

The reaction of 2,2-dialkoxy-3-alkylcyclopropanecarboxylic esters **114** with symmetrical ketones **115** under the same conditions gives *cis*-2,3-disubstituted lactones **116**, also with high selectivity.[173]



114 **115** **116**

R^1, R^2, R^3 = Alk.

* * *

It is clear from the data presented in this review that the methods for synthesising five-membered carbocycles and heterocycles using activated cyclopropanes as intermediates are in many instances highly flexible and stereoselective. Since there are simple and effective methods for obtaining cyclopropane compounds of different structures, including individual optical isomers,[174] it is safe to say that these methods for synthesising cyclic compounds are undoubtedly of preparative importance. The majority of the publications are concerned with ring expansion reactions in vinylcyclopropanes and their oxa- and aza-analogues, and also other types of intramolecular cyclisation, as these have been used extensively to obtain five-membered rings. However the use of reactions that entail intermolecular [3 + 2]- and [4 + 1]-ring formation is no less promising.

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