The Chemistry of Cyclopropanols

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Contents

Oleg G. Kulinkovich was born in Estonia in 1948. He graduated from the Belorussian State University in Minsk in 1971. After obtaining a doctoral degree in organic chemistry in 1975 under the supervision of Professor I. G. Tishchenko, he performed his research permanently in Minsk. He received the Doctor of Science (D.Sc.) degree in 1987 for his work on the chemistry of halogenated cyclopropyl ketones. Since 1991, he has been Head of Department of Organic Chemistry at the Belorussian State University. His research interests center on organic synthesis, including the development of new catalytic and noncatalytic synthetic methods based on transformations of strained organic or organometallic compounds.

I. Introduction

Cyclopropanol and its derivatives are carbocyclic homologues of enols, and there is an obvious similarity in chemical properties between these classes of compounds due to the well-known "unsaturated" character of the cyclopropane ring. Although cyclopropanols are usually less reactive than their olefinic "relatives", their chemical properties are more diverse than those of enols or enolates. Cyclopropanols are able to undergo synthetically useful transformations with retention or cleavage of the strained three-carbon ring. In the latter case, cyclopropanols act formally as equivalents of homoenolates (C^1-C^3 cyclopropane ring cleavage) or corresponding allylic derivatives (C^2-C^3 ring cleavage).

Cyclopropanol was first synthesized in 1942 by Cottle and co-workers.[1,2] The development of cyclopropanol chemistry in the past decades has been quite fruitful, and these compounds occupied their own niche in synthetic practice as useful intermediates in organic synthesis[3−11] and as substances which are capable of possessing important kinds of biological activity.[12−16] The present review is written for the purpose of reflecting recent achievements in the areas of synthesis and synthetic applications of cyclopropanols. It may be regarded as a supplement to the earlier review by Gibson and De Puy.[5]

II. Synthesis of Cyclopropanols

For the purpose of this review, it is convenient to divide the methods of preparation of cyclopropanols into sections according to the structure of substrate and mode of creation of the cyclopropane ring. These methods — cyclopropanation of enols, enolates, or carboxylic acid derivatives with formation of two carbon−carbon bonds of the cyclopropane ring; intramolecular ring-closure reactions of homoenolates and other precursors; and interconversion of cyclopropane derivatives — are often complementary. As a consequence, numerous cyclopropanols of various structures have been prepared for use as synthetic intermediates, for biological testing, or for other practical purposes.

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A. Cyclopropanation of Enols and Carboxylic Acid Derivatives

Cyclopropanation of enol derivatives, especially that of trialkylsilyl enol ethers, by carbene or carbenoid reagents is the most widely used method for the preparation of O-substituted cyclopropanols[17−33] and has been reviewed extensively.[20,24,26−28,30−33] In the past two decades, this approach has also been extended to the preparation of cyclopropanols. Cyclopropanation of carboxylic acid derivatives with reagents which supply two carbon atoms for the formation of a cyclopropane ring has also been developed as an effective alternative approach to cyclopropanols.

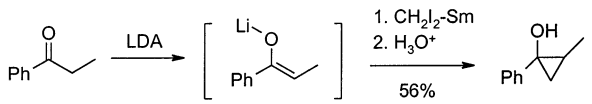
1. Enol Derivatives

Cyclopropanation of metal enolates with zinc or samarium carbenoids constitutes a direct route to cyclopropanols.[21,33−40] Imamoto and co-workers found that deprotonation of ketones with strong bases and treatment of the generated enolates with $CH_2I_2-SmI_2$ or CH_2I_2-Sm led to 1-substituted cyclopropanols in good yields.[37] The cyclopropanation of enolates using these reagents proceeded in a highly regioselective manner; thus, for example, propiophenone treated with lithium diisopropylamide (LDA), and then with $CH_2I_2-SmI_2$, gave *cis*-2-methyl-1-phenylcyclopropanol (**1**) in moderate yield (Scheme 1).[35]

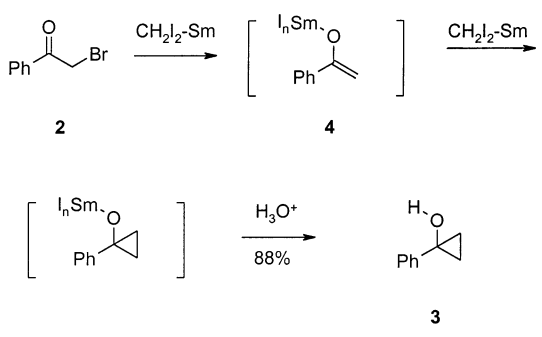
In a similar way, α-halo ketones (e.g., **2**) have been converted into the corresponding cyclopropanols (e.g., **3**) in moderate to good yields by simple treatment with diiodomethane and samarium.[37] In this case also, the key step of the reaction is a Simmons−Smith-type cyclopropanation of the corresponding samarium enolate **4** (Scheme 2).

It is noteworthy that cyclopropanols are also produced when CH_2I_2-Sm is treated with 1,2-diaroylcycloalkanes.[37] This reaction involves cleavage of the carbon−carbon bond between the two acyl groups, followed by cyclopropanation of the intermediate samarium enolates. In the case of 1,2-dibenzoylcyclopropane (**5**) or 1,2-dibenzoylcyclopentane, the corresponding bis-cyclopropanols (i.e., **6** from **5**) were formed as single stereoisomers (Scheme 3).

Scheme 1

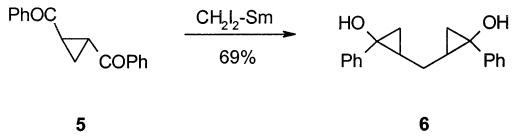


Scheme 2[a]

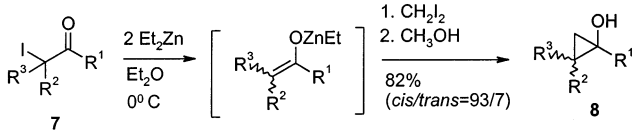


[a] $n = 1$ or 2.

Scheme 3



Scheme 4



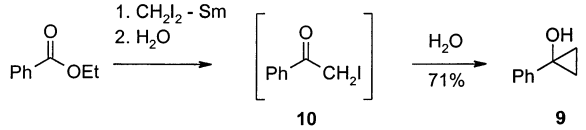
R^1	R^2	R^3	cis:trans	Yield (%)
CH_3	n-C_8H_{17}	H	93:7	82
n-C_6H_{13}	C_5H_{11}	H	87:13	93
	$(CH_2)_{10}$	H	>99:<1	58
C_6H_5	CH_3	H	n. d.	34
i-C_3H_7	$(CH_2)_7CH=CH_2$	H	51:49	65
H	CH_3	n-C_9H_{19}	57:43	92
H	$(CH_2)_5$			38

Zinc enolates prepared by reaction of α-iodoketones with diethylzinc or reaction of α,*β*-unsaturated ketones with lithium trialkylzincates are also effectively converted into the corresponding cyclopropanols under the Simmons−Smith cyclopropanation conditions (Scheme 4).[41] For example, α-iodoketone **7** was converted into cyclopropanol **8** in good yield and with high cis-stereoselectivity by treatment with $CH_2I_2-Et_2Zn$. High cis-stereoselectivity was observed for the preparation of 1,2-disubstituted cyclopropanols from aliphatic α-iodoketones, and the reaction of α-iodoketones, which bear a carbon−carbon double bond, led under these conditions to products of chemoselective cyclopropanation of the enolate moiety (Scheme 4).[41]

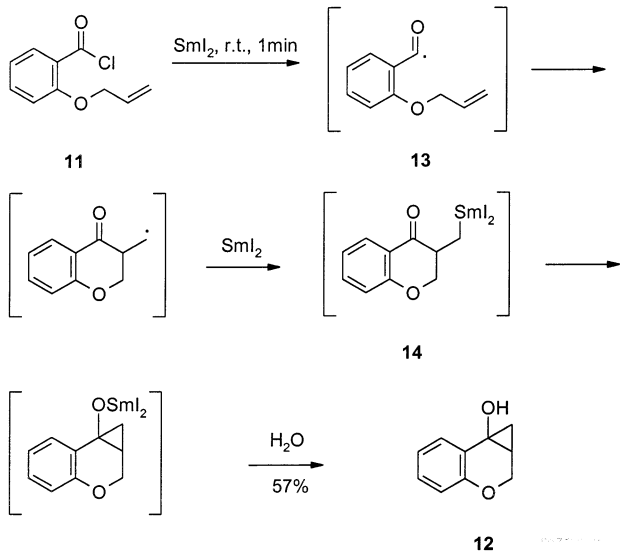
2. Carboxylic Acid Derivatives

Imamoto and co-workers developed a one-pot synthesis of cyclopropanols from carboxylic acid derivatives via tandem one-carbon homologation using the CH_2I_2-Sm reagent.[37] Benzoic acid derivatives were studied in this transformation systematically, and better yields of cyclopropanol **9** were obtained using $PhCOOEt-CH_2I_2-Sm$ in a molar ratio of 1:3:4 (Scheme 5). The authors suggested that the reaction proceeds through formation of an α-iodoketone intermediate **10**, followed by its cyclopropanation in the same way as that of bromoketone **2** (Scheme 2).

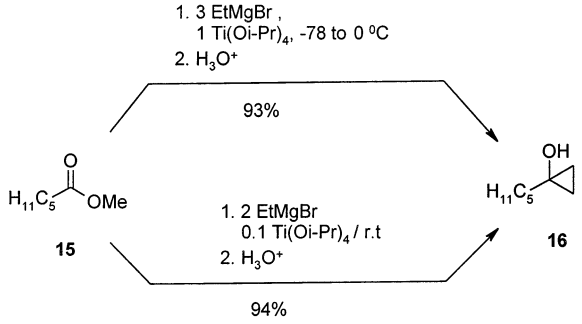
Scheme 5



Scheme 6



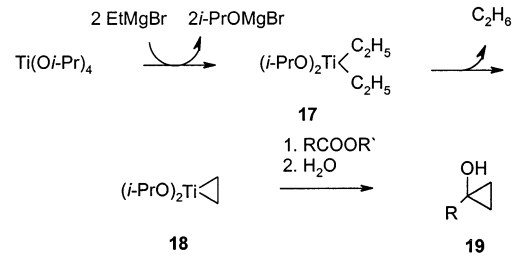
Scheme 7



The effective transformation of *o*-allyloxybenzoic acid chlorides (e.g., **11**) into the respective bicyclic cyclopropanols (e.g., **12),** mediated by samarium diiodide, was developed by Kagan and co-workers.[34] A possible reaction mechanism involves formation of an acyl radical intermediate **13**, which adds intramolecularly to the vinylic double bond, and the three-membered ring is formed by means of an intramolecular cyclization of γ-oxoorganometallic species **14** (Scheme 6). The authors did not exclude the possibility of a carbene mechanism in the cyclopropanation stage.

Kulinkovich and co-workers have disclosed a simple and efficient method for the preparation of cyclopropanols from carboxylic esters.[42] Addition of esters to a mixture of 1 equiv of titanium(IV) isopropoxide and 3 equiv of ethylmagnesium bromide at low temperature afforded 1-alkylcyclopropanols in good to excellent yields. This novel efficient transformation was also performed in a catalytic version, with the order of reagents mixing being inverted; i.e., the organomagnesium compound was added to the mixture of carboxylic ester and titanium(IV) isopropoxide.[43] In this case, the reaction can be performed at room temperature, and only 2 equiv of the Grignard reagent is needed to consume the ester. Thus, methyl hexanoate **15** gave 1-pentylcyclopropanol **16** in both noncatalytic[42] and catalytic reaction versions[43] in virtually the same yields (Scheme 7). The use of higher homologues of ethylmagnesium halides led to

Scheme 8



the corresponding *cis*-1,2-disubstituted cyclopropanols.[44−48] Corey and co-workers reported enantioselective preparation of 2-phenyl-1-methylcyclopropanol from ethyl acetate and (2-phenylethyl)-magnesium bromide in the presence of titanium bistaddolates, with an enantiomeric excess of up to 78%.[48]

Mechanistically, this reaction was rationalized[42,43] by assuming the formation of the thermally unstable diethyltitanium intermediate **17**, which rapidly undergoes β-hydride elimination[49] to give ethane and titanacyclopropane **18**. The latter acts as a 1,2-dicarbanionic equivalent in reaction with carboxylic esters, producing a 2-fold alkylation of the alkoxycarbonyl group, leading to cyclopropanols **19** (Scheme 8). A theoretical study on the mechanism of the carboxylic ester cyclopropanation[42,43] has been recently reported.[50]

On the basis of experimental data on the titanium-mediated reaction of allylic alcohol derivatives with ethylmagnesium bromide,[51] slight modifications of the original mechanism[42,43] of the carboxylic ester cyclopropanation have been proposed,[52] i.e., that the carbon−carbon bond formation in the titanacyclopropane−ester complex **20** is initiated by addition of EtMgBr, and that an ate-complex **21** is formed as a reactive intermediate (Scheme 9).

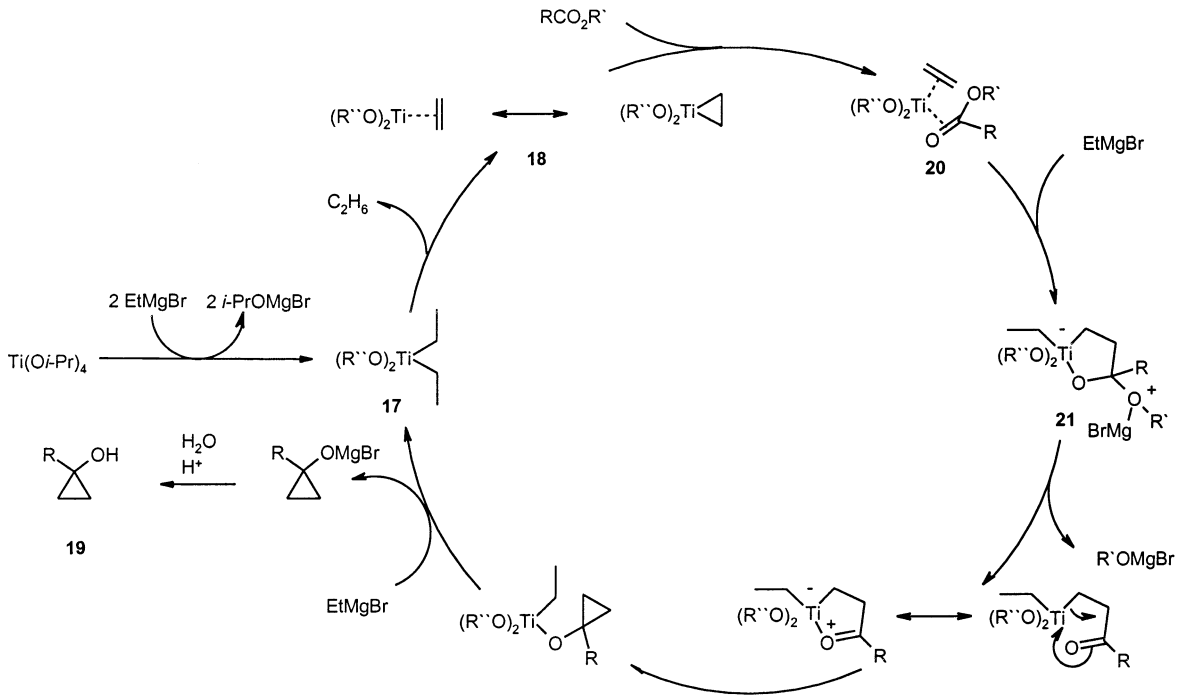
The same research group has elaborated also an alternative approach to substituted cyclopropanols.[53,54] Thus, *trans*-1-methyl-2-phenylcyclopropanol (**22)** was prepared in a moderate yield by cyclopropanation of ethyl acetate with ethylmagnesium bromide in the presence of an excess of styrene and a catalytic amount of titanium tetraisopropoxide (Scheme 10).[53]

It was suggested[53] that the key organometallic intermediate in this transformation is phenyl-substituted titanacyclopropane **23**, which is formed as a result of olefin−ligand exchange in the titanacyclopropane molecule (titanium(II)−olefin complex) **18** (Scheme 11).

To facilitate ligand exchange, the Sato[55] and Cha[56−58] groups proposed the use of more sterically hindered titanacyclopropane intermediates generated from isopropyl-,[55] *n*-butyl-,[56] cyclohexyl-,[57] or cyclopentylmagnesium bromide.[58] For example, intramolecular cyclopropanation of the unsaturated ester **24** by the olefin-exchange reaction led to the bicyclic alcohol **25** in an acceptable yield (Scheme 12).[59]

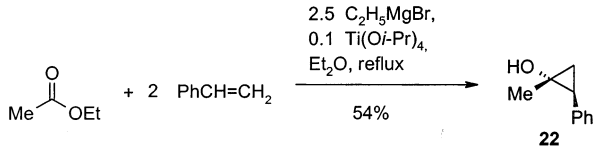
Stereoselective formation of *cis*-cyclopropanol **26** was observed in the course of the titanium-mediated cyclopropanation of homoallyl 2-alkenoate **27** (Scheme 13). A good yield of the product **26** was obtained in this case, whereas intramolecular cyclopropanation of conjugated alkyl esters gave the corresponding

Scheme 9[a]

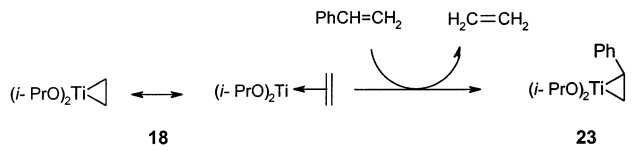


[a] R″ = *i*-Pr or R′.

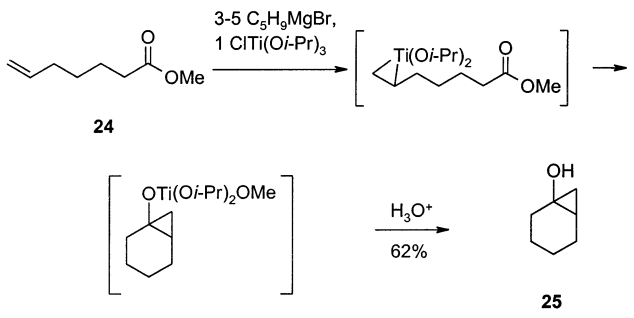
Scheme 10



Scheme 11



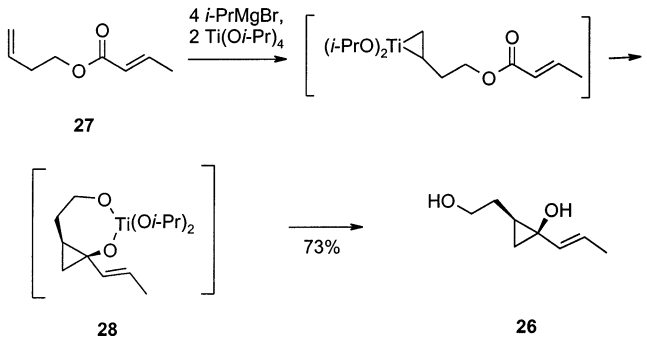
Scheme 12



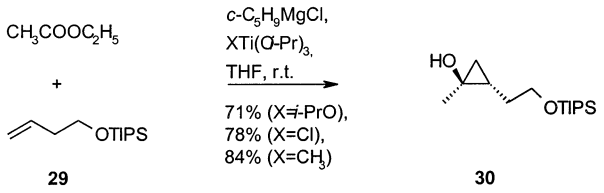
cyclopropanols in poor yields. In this conversion, the high diastereoselectivity observed in the product *cis*-isomeric diol **26** was explained by assuming the formation of a bicyclic titanate intermediate **28**.[60,61]

Recently, an evaluation of the reactivity of several titanium alkoxides and aryloxides was conducted in the titanium-mediated cyclopropanation of methyl cyclohexanecarboxylate, as well as in the hydroxycyclopropanation of 1-tri(isopropylsiloxy)-3-butene (**29**) with ethyl acetate, leading to cyclopropanol **30**

Scheme 13



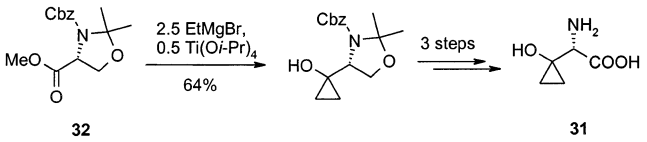
Scheme 14



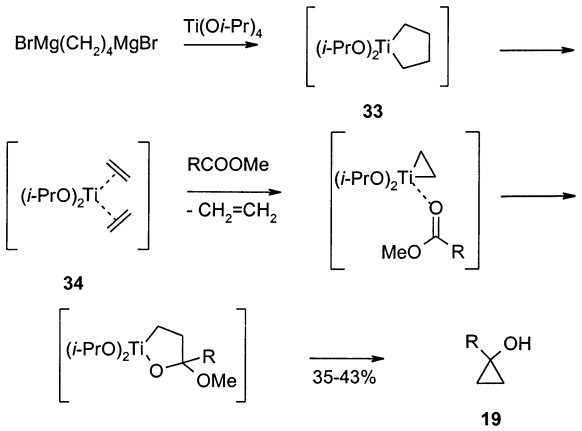
(Scheme 14).[62] The yields of the products[42,43] were found to be insensitive to the structure of the titanium alkoxides or aryloxides, whereas chlorotitanium triisopropoxide and/or methyltitanium triisopropoxide proved to be the reagents of choice for modification of the hydroxycyclopropanation of olefins.[62]

Preparation of enantiomerically pure (*S*)-cleonine **31**, a key component of the antitumor−antibiotic cleomycin, starting from (*R*)-serine, is a recent example of the use of this reaction in a natural product synthesis.[63] Formation of the cyclopropanol fragment of (*S*)-cleonine **31** was achieved by cyclopropanation of the ester group in methoxycarbonyl-substituted

Scheme 15



Scheme 16[a]



[a] R = C_3H_7, C_4H_9, or C_5H_{11}.

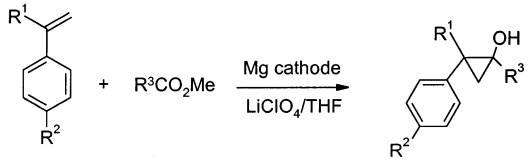
oxazolidine **32** (Scheme 15). Numerous carboxylic esters successfully underwent intermolecular or intramolecular cyclopropanation using titanacyclopropane reagents. This work has been reviewed recently.[64−68]

1-Substituted cyclopropanols were formed in moderate yields when carboxylic esters were treated with 1,4-di(bromomagnesium)butane in the presence of titanium(IV) isopropoxide.[68] This transformations is thought to involve a rearrangement of the titanacyclopentane intermediate **33** into the respective bisethylenic complex **34**, which is then converted into 1-substituted cyclopropanol **19** (Scheme 16) in the manner described above (Scheme 9).

Hydroxycyclopropanations of styrenes by carboxylic esters has also been carried out under electrochemical conditions.[69] The reaction proceeds stereoselectively on a magnesium cathode and affords *trans*-aryl-substituted cyclopropanols **35** in good yields (Scheme 17). Treatment of magnesium complexes of 1,2- bis(methylene)cyclohexane with carboxylic esters at low temperature also resulted in formation of cyclopropanol derivatives.[70,71]

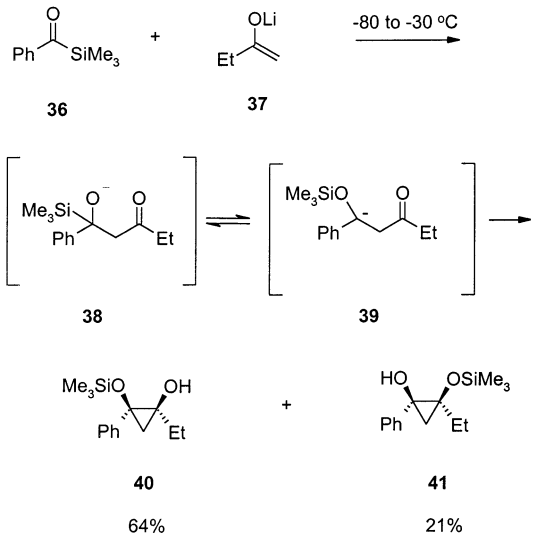
An interesting and useful alternative for generation of species which act as 1,2-dicarbanionic equivalents has been found recently,[72−74] as exemplified by the reaction of benzoyltrimethylsilane (**36**) with lithium enolate **37**. This reaction involves a Brook rearrangement of the initial 1,2-adduct **38**, followed by intramolecular cyclization of carbanion **39**. Cyclopropanols **40** and **41** were thus prepared in good yields as a mixture of isomeric silyl ethers (Scheme 18). In the reaction of acylsilanes with ester enolates, cyclopropanol products were not obtained, and this was explained by acceleration of the Brook rearrangement by the more electrophilic ketone carbonyl group relative to the ester carbonyl group.[73]

Scheme 17



R^1	R^2	R^3	Yield (%)
H	H	Me	71
H	H	Et	67
H	H	i-Pr	55
Me	H	Me	94
Me	Me	i-Bu	82
Me	Me	Me	96

Scheme 18



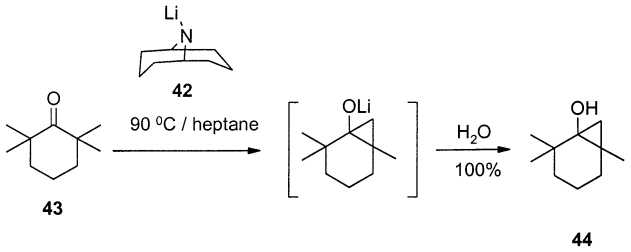
B. Intramolecular Ring Closure and Ring Contraction

An important method for preparing cyclopropanols is based on ring closure of oxygen-functionalized organic compounds. Among these reactions, intramolecular nucleophilic addition to the carbonyl group and nucleophilic 1,3-elimination have found the most widespread preparative applications. Some important preparative procedures to obtain cyclopropanols are based on intramolecular cyclization involving C^2-C^3 bond formation.

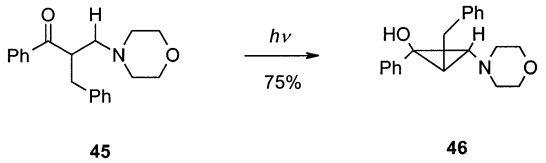
1. Aldehydes and Ketones

Intramolecular cyclization of homoenolates is a convenient way to obtain cyclopropanols. The use of homoenolates with carbanion-stabilized substituents does not generally give positive results, due to the low stability of the corresponding donor−acceptor cyclopropanes (for reviews, see refs 31, 75−77). In contrast, nonstabilized alkali metal homoenolates usually undergo rapid cyclization into the respective

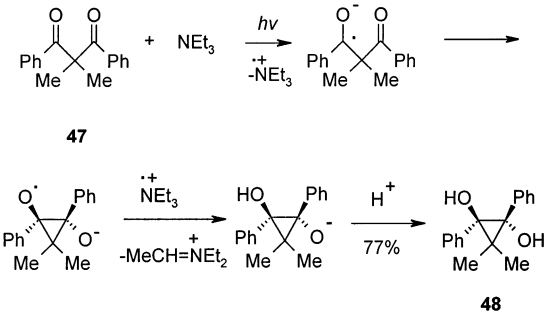
Scheme 19



Scheme 20



Scheme 21



cyclopropanolates, but this conversion is often accompanied by formation of significant amounts of byproducts.[78−81] Direct metalation of non-enolizable ketones and aldehydes by *N*-lithiobicyclo[3.3.1]nonane (**42**) allowed suppression of the side reactions; for example, 2,2,6,6-tetramethylcyclohexanone (**43**) was converted into the corresponding cyclopropanol **44** in quantitative yield (Scheme 19).[81]

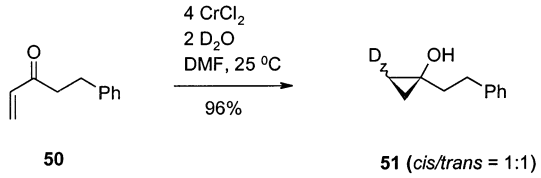
Intramolecular hydrogen abstraction in photoexcited β-*N*,*N*-dialkylaminopropiophenones leads to hydrogen transfer from the β-carbon to the carbonyl oxygen, resulting in the formation of hydroxy biradicals that can undergo cyclization to form 2-dialkylaminocyclopropanols.[82−85] Photocyclization of **45** proceeded regioselectively, involving the β-aminomethylene hydrogen, and resulted in stereoselective formation of 2-benzyl-substituted cyclopropanol **46** in good yield (Scheme 20). In the presence of oxygen, UV irradiation of β-aminopropiophenones yielded the products resulting from ring-opening reactions of the corresponding 2-aminocyclopropanols.[82−84]

α,β-Unsaturated ketones and β-substituted aromatic 1,3-diketones were utilized in photochemical cyclopropanol formation by C^1-C^3 bond closure.[86−88] UV irradiation of dibenzoyl ketone **47** in the presence of triethylamine led to the formation of *trans*-1,2-cyclopropanediol **48** in good yield.[86] A mechanism involving single electron transfer between the exited diketone and the ground-state amine, followed by the anion radical rearrangement, was proposed (Scheme 21). Product **48** was also obtained for the reaction with samarium diiodide.[86] α,β-Unsaturated aldehydes and ketones, as well as 1,3-dicarbonyl compounds, have been also reduced in the same manner into the corresponding 1,2-cyclopropanediols when treated with metallic zinc or other reducing agents.[86,89−92]

Scheme 22

R^1	R^2	Yield (%)
n-C_4H_9	H	32
c-C_6H_{11}	H	63
$CH_3CH_2C(CH_3)_2$	H	69
H	n-C_6H_{13}	51
H	CH_3	0
H	C_6H_5	0
n-C_5H_{11}	n-C_4H_9	0

Scheme 23



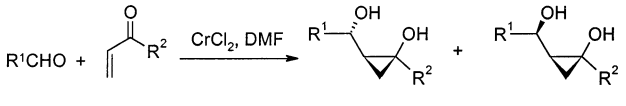
Stevenson and co-workers observed formation of *trans*-cyclopropanols **49** when α,β-unsaturated aldehydes were treated with $CrCl_2$ in the presence of catalytic amounts of $NiCl_2$.[93] This reaction appears to be general for 2-substituted acroleins (Scheme 22); however, in the case of 2-butylacrolein, the pinacol dimer was formed as the main product (45%).

Recently, Takai and co-workers[94] found that the presence of water is necessary to promote cyclopropanol formation in the reaction of α,β-unsaturated aldehydes and ketones under the reducing conditions using $CrCl_2$. In these experiments, however, a catalytic amount of the nickel salt did not affect the transformation. Treatment of enone **50** with a mixture of excess $CrCl_2$ and D_2O in dimethylformamide gave cyclopropanol **51** in high yield with 89% deuterium incorporation (Scheme 23).

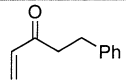
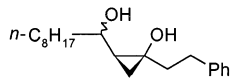
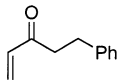
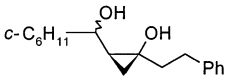
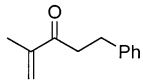
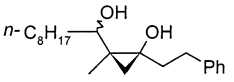
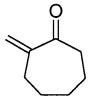
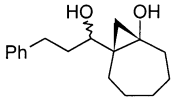
These workers also discovered a cross-coupling reaction of aldehydes **52** with α,β-unsaturated ketones **53**, promoted by $CrCl_2$, to give 2-hydroxyalkylcyclopropanols **54**.[94] Stereoisomers **A** and **B** were produced diastereoselectively out of four possible diastereomers (Table 1).

The mechanism proposed for this interesting reaction explains its high cis−trans stereoselectivity and includes one-electron reduction of the enone **53** with chromium(II), giving the corresponding enolate radical **55**, which undergoes reaction with the aldehyde **52** to give a cross-coupling intermediate **56**. Reduction of the radical **56** with chromium(II), followed by

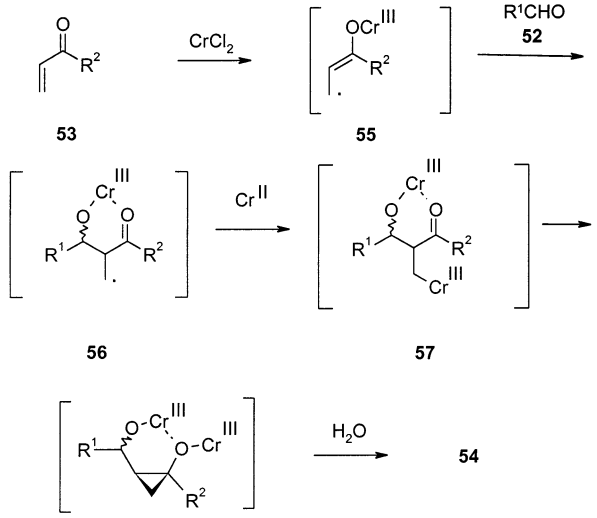
Table 1. Preparation of Cyclopropanols by Cross-Coupling Reactions of α,β-Unsaturated Ketones and Aldehydes with $CrCl_2$ [94]



52 53 54 A 54 B

Entry	R^1	Enone	Product	Yield (%)	54A:54B
1	n-C_8H_{17}			93	58:42
2	c-C_6H_{11}			89	79:21
3	n-C_8H_{17}			78	91:9
4	$Ph(CH_2)_3$			54	85:15

Scheme 24

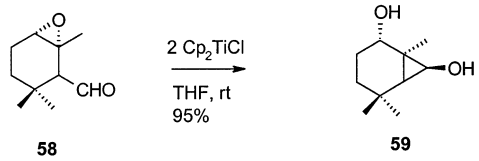


intramolecular cyclization of chromium homoenolate **57**, gives the cyclopropanols **54** (Scheme 24).[94]

Reduction of epoxycarbonyl compounds with dicyclopentadienyltitanium chloride led directly to hydroxyalkyl-functionalized cycloalkanols in high yields.[95] For example, highly efficient and stereoselective cyclization of β,γ-epoxyaldehyde **58** into bicyclic cyclopropanol **59** was realized (Scheme 25).

Intramolecular reductive cyclization of β-halogen-substituted carbonyl compounds was also performed effectively under the action of samarium(II) iodide as a reducing agent.[34,96−98] In that way, a one-pot method for the preparation of 1-substituted cyclopropanols was developed by treatment of commercially available ethyl β-bromopropionate with 1 equiv of organomagnesium or organolithium reagents in

Scheme 25



58 59

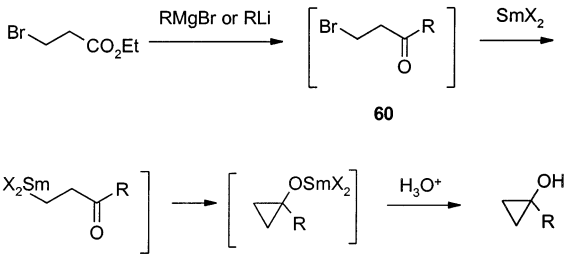
the presence of 2 equiv of SmI_2 in a THF/hexamethylphosphoramide (HMPA) mixture (or samarocene without HMPA) via the intermediate formation of β-bromoketones **60** (Scheme 26).[96]

In contrast to homoenolates of the alkali metals mentioned above, as well as those of magnesium, samarium, and zinc, which are rapidly transformed into the respective cyclopropanolates, β-stannyl aldehydes and ketones may be transformed into cyclopropane compounds only by treatment with Lewis acids.[99−106] Thus, titanium(IV) chloride induced an effective intramolecular cyclization of β-stannyl ketone **61** to yield 1-hexylcyclopropanol (Scheme 27).[101]

Cyclopropanol formation is not typical also for β-silyl-carbonyl compounds.[107,108] However, as shown by Fleming and co-workers,[107] intramolecular addition becomes possible if the electrofugal properties of the silyl group are enhanced by intramolecular participation of electron donor group, as exemplified by the transformation of an hemiacetal **62** into cyclopropanol **63** upon treatment with sodium hydride (Scheme 28).

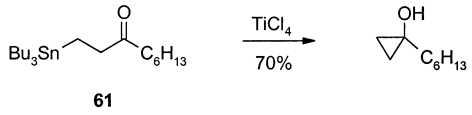
A practical method for the preparation of 1-hydroxycyclopropane carboxylic acid **64**, which is used as a convenient starting compound for the synthesis of many cyclopropanol derivatives,[7] is based on the conversion of 1,2-bis(trimethylsiloxy)cyclobutene (**65**) (easily available from succinic esters by acyloin condensation)[109−113] into 1,2-cyclobutanedione (**66**),

Scheme 26

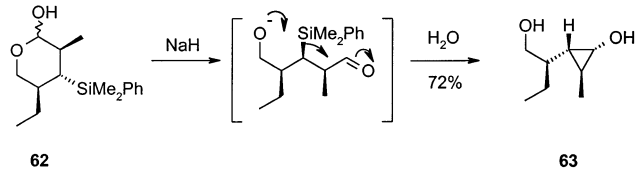


RMgBr or RLi	SmX_2	Yield (%)
C_4H_9MgBr	SmI_2	99
C_4H_9MgBr	Cp_2Sm	85
$(CH_3)_2CHMgBr$	SmI_2	85
$(CH_3)_2CHMgBr$	Cp_2Sm	40
c-$C_6H_{11}MgBr$	SmI_2	95
$(CH_3)_3SiCH_2$	SmI_2	95
C_6H_5MgBr	SmI_2	99
4-$CH_3C_6H_4MgBr$	SmI_2	85
4-$CH_3C_6H_4MgBr$	Cp_2Sm	95
4-$CH_3OC_6H_4MgBr$	SmI_2	70
trans-C_6H_5CH=$CHMgBr$	SmI_2	95
trans-C_6H_5CH=$CHMgBr$	Cp_2Sm	85
C_4H_9Li	SmI_2	30
C_6H_5Li	SmI_2	88

Scheme 27



Scheme 28

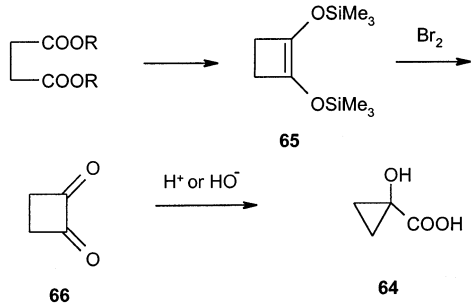


followed by an acid- or base-induced ring-contraction reaction (Scheme 29).[112−117] Similar transformations of chiral 2-alkyl-substituted succinic esters allow the preparation of the corresponding optically active 2-methylcyclopropanols.[9,118,119]

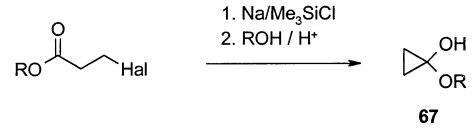
2. Carboxylic Acids Derivatives

β-Halogen carboxylic esters and amides are the starting compounds used most frequently for the synthesis of cyclopropanols by intramolecular ring-closure reactions.[7,109,120−122] Alkoxycyclopropanols **67** were prepared in this way more than 30 years ago and were used in various types of nucleophilic reactions as cyclopropanone equivalents (Scheme 30).[109,120−124]

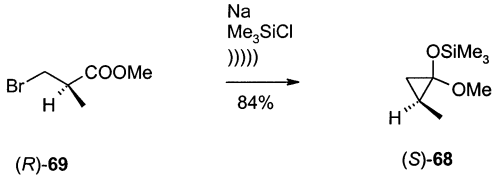
Scheme 29



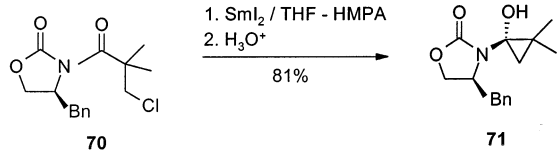
Scheme 30



Scheme 31



Scheme 32



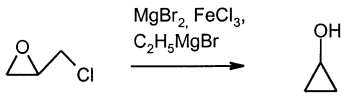
The original procedure for the preparation of 1-alkoxycyclopropanols **67** proposed by Rühlmann[109] was substantially improved and simplified by application of sonication.[111] Secondary and branched β-halogen carboxylic esters also underwent smooth reactions under these conditions, and the chirality of the β-bromoester was completely retained in this transformation, as proved by conversion of cyclopropanol silyl ether (*S*)-**68** back to the starting bromide (*R*)-**69** (Scheme 31).[111] Utilization of zinc metal in place of sodium metal as a reducing agent was also effective for the transformation of allyl iodopropionates into the corresponding cyclopropanone acetals.[121]

Samarium diiodide-promoted cyclization of chiral β-chloro-substituted amides led to functionalized optically active cyclopropanols in high yield and high diastereomeric excess. Although cyclization of β-chloroamide **70** by sodium trimethylchlorosilane under sonication (Scheme 31)[111] afforded mostly unreacted starting material and a mixture of unidentified products, SmI_2-promoted cyclization of **70** gave exclusively 1-aminocyclopropanol derivative **71** in good yield (Scheme 32).[97]

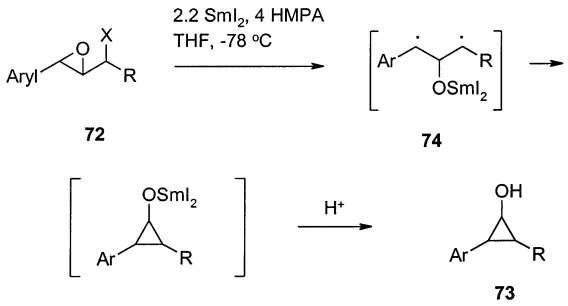
3. Alcohols

Methods for assembling a cyclopropane ring containing an appropriate alcohol via C^2-C^3 bond for-

Scheme 33

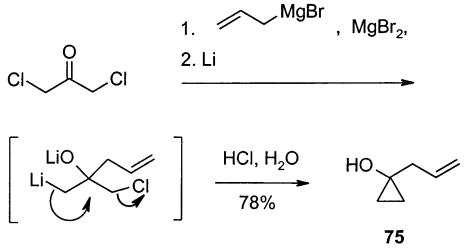


Scheme 34



Ar	R	X	Yield (%)
Ph	H	Br	75
Ph	H	I	70
4-MeOC$_6$H$_4$	H	Br	65
Ph	Ph	Br	70
Ph	Me	Br	80

Scheme 35

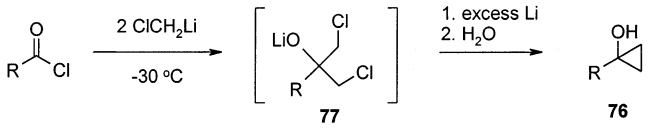


mation are rare, especially compared to those involving C^1-C^2 or concerted C^1-C^2/C^1-C^3 (C^2-C^3) bond formation. Nevertheless, the first synthesis of the parent cyclopropanol was achieved by this approach by treatment of epichlorohydrine with magnesium bromide, ferric chloride, and ethylmagnesium bromide (Scheme 33).[1,2]

Subsequently, this approach was improved to afford cyclopropanols in better yields and higher purity.[5,125−128] Thus, aryl-substituted α-halo epoxides **72** were recently found to undergo reaction with SmI_2 in the presence of HMPA to give cyclopropanols **73**. In the absence of HMPA, the corresponding allyl alcohols were formed. Allyl alcohols were also obtained by treatment of alkyl α-haloepoxides with SmI_2, regardless of the presence or absence of HMPA. The authors proposed that formation of the cyclopropane ring proceeded via the biradical intermediate **74** (Scheme 34).

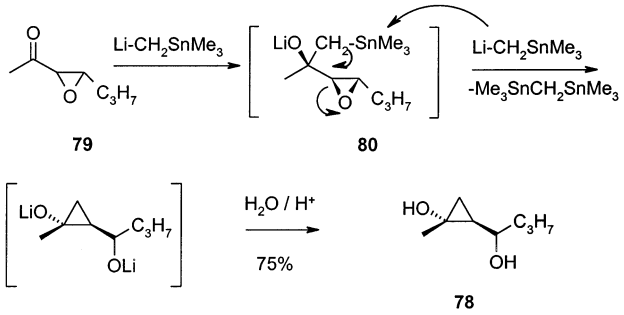
Barluenga and co-workers developed a method to prepare 1-substituted cyclopropanols (e.g., **75)** by treatment of 1,3-dichloroacetone with a mixture of a Grignard reagent, anhydrous magnesium bromide, and an excess of lithium powder (Scheme 35).[126] This procedure is an alternative variant of the cyclopropanol preparation from 1,3-dichloroacetone and Grignard reagents in the presence of $FeCl_3$, which was previously developed by De Puy and co-workers.[129]

Scheme 36



R	Yield, %	R	Yield, %
c-C$_3$H$_5$	45	C$_2$H$_5$OCH$_2$	50
n-C$_3$H$_7$	37	C$_6$H$_5$	80
c-C$_4$H$_7$	65	*c*-C$_6$H$_{11}$	40
n-C$_4$H$_9$	42	4-CH$_3$OC$_6$H$_4$	63

Scheme 37



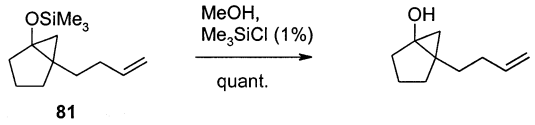
Later, a similar approach was used for the preparation of 1-substituted cyclopropanols **76** from acid chlorides which were treated with in situ-generated chloromethyllithium at −78 °C, followed by treatment with excess lithium powder between −78 and −30 °C.[127] In the case of butanoyl chloride, when the reaction mixture was hydrolyzed before the lithiation step, the corresponding dichloromethyl carbinol **77** (R = *n*-C_3H_7) was isolated in moderate yield (Scheme 36).

Reaction of trialkylstannylmethyllithium with α-chloro or α,β-epoxy ketones also leads to formation of substituted cyclopropanols.[130] α,β-Epoxy ketones underwent reaction more cleanly, and 2-hydroxybutyl cyclopropanol **78** was thus obtained from epoxy ketone **79** in good yield using 2 equiv of the organometallic reagent (Scheme 37). This transformation is believed to proceed through nucleophilic addition of trialkylstannyllithium to the carbonyl group, followed by 1,3-elimination of the organometallic intermediate **80**. The latter step is induced by nucleophilic attack of another equivalent of trialkylstannyllithium at the tin atom.[130]

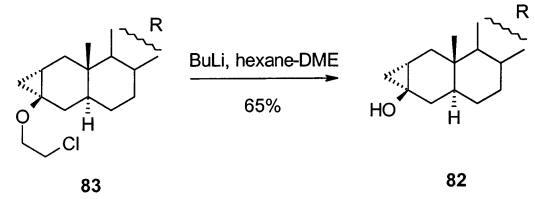
C. Transformations of Three-Carbon Ring Precursors

It is sometimes more convenient to prepare cyclopropanols starting from readily available O-substituted cyclopropane derivatives, such as esters or ethers. Attachment of functional groups to the cyclopropane rings by substitution reactions has been also performed successfully.

Scheme 38

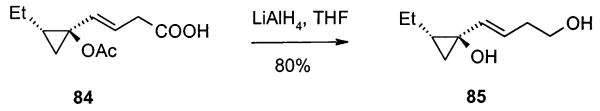


Scheme 39[a]



[a] R = $C_{16}H_{30}$ (cholestane).

Scheme 40



1. O-Substituted Cyclopropanes

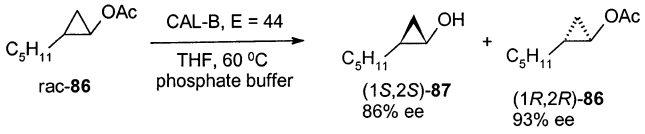
Cleavage of trimethylsilyl ethers is a particularly convenient method for the preparation of cyclopropanols from easily available[20,24,28,30−33] O-silylated precursors, a reaction which may be performed under neutral or slightly acidic conditions.[3,22,96,131−139] For example, a strained bicyclic silyl ether **81** was smoothly deprotected by treatment with methanol in the presence of $ClSiMe_3$ (Scheme 38).[135,136]

Cleavage of the carbon−oxygen bond in cyclopropyl ethers has also been used for the preparation of cyclopropanols.[4,140−145] For example, cyclopropanocholestanol **82**, an inhibitor of cholesterol oxidase, was obtained in a satisfactory yield by cleavage of the carbon−oxygen bond in β-chloroethyl ether **83** with butyllithium (Scheme 39).[144] Compound **83** was prepared by cyclopropanation of the corresponding enol ether under Simmons−Smith conditions. An alternative general preparation of β-chloroethyl cyclopropyl ethers is that reported by Schöllkopf, in which β-chloroethoxycarbene is trapped with an alkene.[4,142]

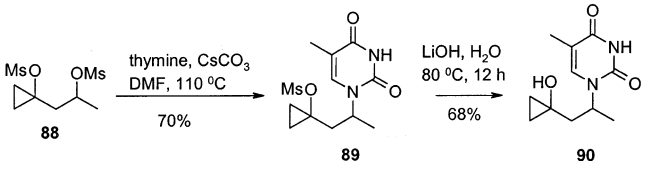
Cyclopropyl tetrahydropyranyl ethers and other acetal derivatives are generally cleaved without complications under mild acidic conditions.[3,5,115,146,147] Hydrolysis of cyclopropyl esters, which may be obtained in high yield by Baeyer−Villiger oxidation of cyclopropyl ketones, often does not proceed smoothly, and better yields were obtained by De Puy and coworkers when the deacylation was performed by trans-esterification or by treatment with methyllithium or lithium aluminum hydride.[3,5] The latter conditions, for example, were successfully used for the conversion of the cyclopropane ester **84** into the corresponding alkenylcyclopropanol **85** (Scheme 40).[148]

The parent cyclopropanol of high purity was obtained by enzymatic hydrolysis of cyclopropyl acetate at neutral pH using commercially available hydrolases.[149] Another reaction involving enzymes involves the lipase-catalyzed trans-esterification of bicyclo[*n*.1.0]alkan-1-yl chloroacetates, leading to products in moderate to excellent ee's. Higher enantioselectivity in enzymatic hydrolysis was generally observed for bicyclohexane derivatives (enantiomeric ratio between 40:1 and 420:1).[135,136] Among 16 hydrolases investigated, *Candida antarctica* B lipase was most effective for enzymatic resolution of racemic 2-pentylcyclopropyl acetate **86**, to afford (1*S*,2*S*)-cyclopropanol **87** and (1*R*,2*R*)-acetate **86** (Scheme 41).[150]

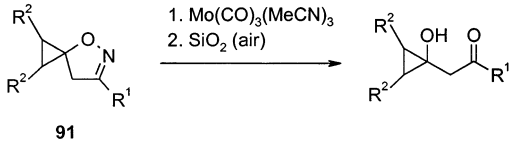
Scheme 41



Scheme 42



Scheme 43



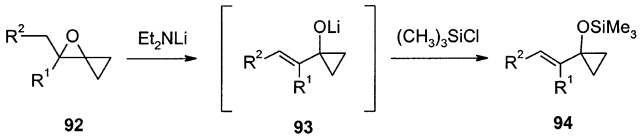
R^1	R^2	Yield (%)
Ph	H	72
Ph	$(CH_2)_4$	73
$PhCH_2$	H	59
n-C_6H_{13}	H	79
$MeO_2CC(CH_3)_2$	H	53

The methanesulfonyl group has been used for concomitant activation of a primary or secondary hydroxyl group, and for protection of the tertiary hydroxy group attached to the cyclopropane ring.[152] For example, reaction of thymine with bis-mesylate **88** gave cyclopropyl mesylate **89**, which after deprotection with LiOH at elevated temperatures afforded the cyclopropanol **90**, a potential antiviral agent (Scheme 42).

A two-step sequence involving nitrile oxide cycloaddition of alkylidenecyclopropanes and subsequent N−O cleavage has been shown to give 1-(2-oxoalkyl)cyclopropanols.[153,154] Thus, selective N−O reductive cleavage of oxazolines **91** proceeded smoothly under the action of $Mo(CO)_3(MeCN)_3$ and silica gel (Scheme 43). The use of silica gel and air atmosphere was mentioned to be essential for this conversion.[154]

A flexible way to obtain alkenylcyclopropanols is nucleophilic ring opening of the oxirane ring in oxaspiropentanes[141,155] which, in turn, may be prepared by epoxidation of cyclopropylidenes,[7,156,157] by nucleophilic addition of 1-lithio-1-bromocyclopropanes to ketones,[158,159] or by cyclopropanation of carbonyl compounds with diphenylsulfonium cyclo-

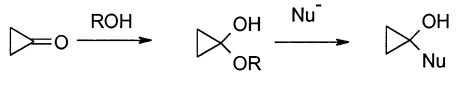
Scheme 44



92 93 94

R^1	R^2	Yield (%)
CH_3	C_6H_{13}	96
	$(CH_2)_3$	94
	$(CH_2)_5$	91

Scheme 45



95 96 97

propylide.[155,160−162] Treatment of oxaspiropentanes **92** with lithium diethylamide led to unstable 1-vinylcyclopropanol alcoholates **93**, which were directly derivatized with trimethylchlorosilane to give 1-alkenylcyclopropanol silyl ethers **94** in good yields (Scheme 44).[141]

Reactions proceeding through direct nucleophilic substitution at the cyclopropane ring carbon are rarely observed.[163] In contrast, nucleophilic addition to the carbonyl group of cyclopropanone **95** proceeds extremely easily; for example, reaction with alcohols immediately gives hemiacetals **96**.[5,10,120−122] Although cyclopropanones are labile and cannot serve as convenient precursors for the preparation of cyclopropanols, it has been shown that cyclopropanone hemiacetals **96** may act as cyclopropanone equivalents in a wide variety of nucleophilic reactions.[5,120−122] The alkoxy group of hemiacetals **96** or the respective magnesium salts[164] is easily displaced by nucleophiles, including C−H acidic compounds, Grignard reagents, and silyl enol ethers, to form the corresponding cyclopropanols **97** (Scheme 45).[5,120−122,165]

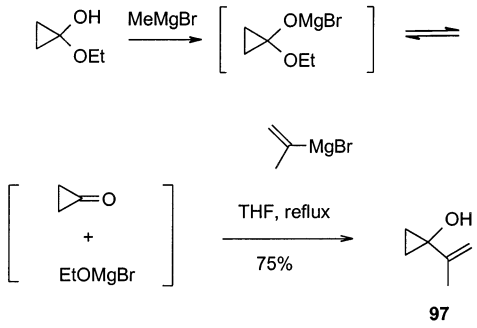
Owing to the easy availability of cyclopropanone hemiacetals **96** and the usually good yields obtained in their reactions with nucleophiles, this methodology continues to be one of the most useful ones for the synthesis of cyclopropanols. For example, the magnesium salt resulting from treatment of cyclopropanone ethyl hemiacetal with 1 equiv of methylmagnesium bromide undergoes reaction with 2-propenylmagnesium bromide to give propenylcyclopropanol **97** in good yield (Scheme 46).[166]

Furthermore, substituted cyclopropanones generated in situ from α-bromoketones possessing a tertiary carbon atom in an α-position (e.g., **98)** undergo reaction with diethylsodium malonate to form the respective cyclopropanols (e.g., **99**) in moderate yields (Scheme 47).[167]

2. Other Cyclopropane Precursors

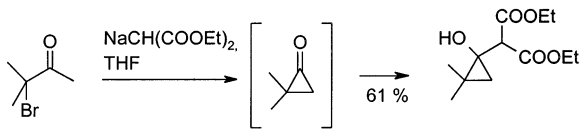
Methylenecyclopropanes with electron-acceptor substituents at the double bond, being strong Michael acceptors, may be effectively used as precursors for

Scheme 46



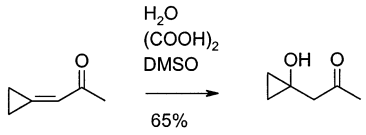
97

Scheme 47



98 99

Scheme 48



100 101

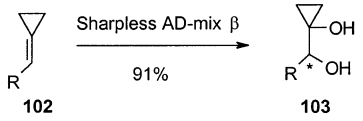
the preparation of cyclopropanols.[167,168] Conia and coworkers found that α-cyclopropylidene ketones and aldehydes show high reactivity in 1,4-addition reactions with different nucleophiles.[168−170] For example, nucleophilic addition of water to cyclopropylidene acetone **100** in the presence of oxalic acid gave acetonylcyclopropanol **101** in moderate yield (Scheme 48).[168]

Addition reactions to nonactivated double bonds of alkylidenecyclopropanes have been also successfully used for the preparation of cyclopropanols.[171−174] The Sharpless asymmetric hydroxylation of cyclopropylidenmethylarenes **102** provides the diols **103** in moderate to good yields and ee up to 98% when AD-mix β was used (Table 2).[174]

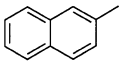
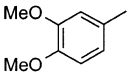
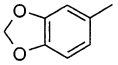
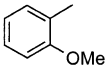
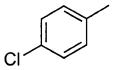
The dye-sensitized photooxygenation of alkylidenecyclopropanes at low temperature with singlet oxygen leads to hydroperoxides via an ene reaction.[171] The latter were reduced with triphenylphosphine into the corresponding 1-alkenylcyclopropanols in about 60% yield. Cyclopropyl-substituted alkylidenecyclopropane **104** was also successfully used in this type of transformation (Scheme 49).

Reaction of cyclopropylmagnesium halides with oxygen affords low yields of cyclopropanols.[175] The oxygenation proceeds more smoothly when cyclopropyllithium[176] and cyclopropylboron compounds are used.[177−191] The Brown oxidation, realized by treatment of the cyclopropylboronic acid derivative **105** with hydrogen peroxide in the presence of sodium hydroxide, led to cyclopropanol **106**, together with small quantities of acyclic carbonyl compounds. No formation of these byproducts was observed when sodium perborate was used as the oxidizing agent and the reaction time was controlled carefully (Scheme 50).[184]

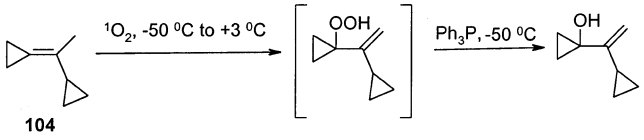
Table 2. Asymmetric Dihydroxylation of Aryl Cyclopropylidenemethylarenes[174]



102 103

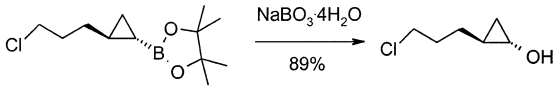
Entry	R	AD-mix α		AD-mix β	
		Yield, %	% ee	Yield, %	% ee
1		64	79	68	90
2		76	0	90	70
3		66	47	67	75
4		50	67	55	76
5		51	71	42	89
6		33	70	47	87

Scheme 49



104

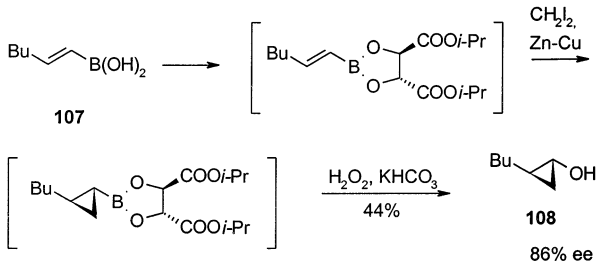
Scheme 50



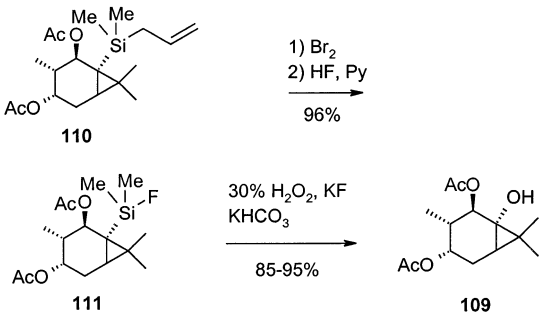
105 106

An enantioselective preparation of optically active cyclopropanols has been achieved using chiral cyclopropylboronic esters as precursors.[150,177,188,190] The latter were effectively prepared by asymmetric cyclopropanation of 1-alkenylboronic esters.[188,192] For example, esterification of *trans*-1-hexenylboronic acid (**107**) with 1 equiv of (+)-diisopropyl tartrate, followed by the Simmons−Smith cyclopropanation and oxidation with hydrogen peroxide, gave *trans*-(−)-2-butylcyclopropanol (**108**) in 44% overall yield and good enantiomeric excess (Scheme 51). Better yields[184,185] but lower selectivity[188] were obtained in palladium-catalyzed cyclopropanation with diazomethane. The stereoselectivity of the cyclopropanation step was improved by using (2*R*,3*R*)-1,4-dimethoxy-1,1,4,4-tetraphenyl-2,3-butanediol as a chiral auxiliary additive. Moreover, this auxiliary strongly facilitated chromatographic separation of the

Scheme 51



Scheme 52



corresponding diastereomeric cyclopropylboronic esters.[186]

Replacement of an organosilyl group by a hydroxyl group[193−196] has also been successfully used in the preparation of cyclopropanols.[197−202] For example, the allyldimethylsilyl group served as a latent hydroxy group in the preparation of bicyclic cyclopropanol **109**.[197,198] Treatment of cyclopropylsilane **110** with bromine, followed by reaction with pyridinium hydrogen fluoride, gave fluorosilane **111**, which was then oxidized to give **109** in high yield (Scheme 52). Hydroxysilyl-substituted[199,200] and (1-phenylthiocyclopropyl)dimethylsilyl-substituted cyclopropanes[202] were also effectively oxidized into the corresponding cyclopropanols.

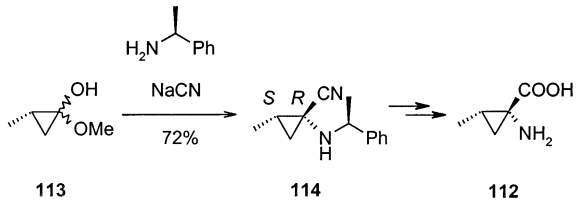
III. Reactions of Cyclopropanols

A. Reactions with Retention of the Three-Carbon Ring

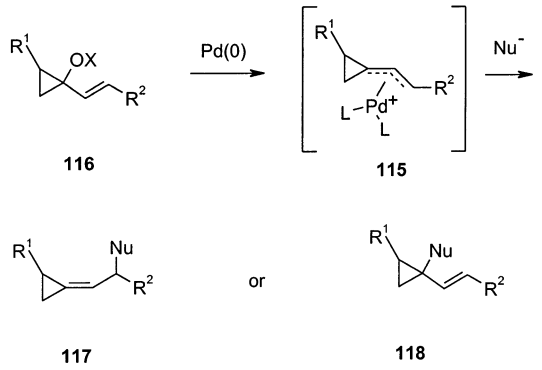
Reactions of cyclopropanols involving carbon−oxygen bond cleavage are often accompanied by cleavage of the cyclopropane ring. An important exception to this generally observed behavior occurs for cyclopropanols having a strong electron-donor substituent attached to the same carbon atom as the hydroxyl group; in such cases, nucleophilic displacement of the substituent usually proceeds quite easily.[5,7,10,122]

For example, simple syntheses of aminocyclopropane carboxylic acid[203,204] and some other methanoamino acids[205−207] may be achieved by starting with the corresponding 1-alkoxycyclopropanols (cyclopropanone hemiacetals). Thus, for the preparation of (1*R*,2*S*)-*allo*-norcoranamic acid **112**, chiral acetal **113** was used as a precursor. The latter could be prepared in three steps from commercially available (*S*)-methyl-2-hydroxymethylpropionate[111,203,208] or, alternatively, from dimethyl (*R*) [or (*S*)]-2-methylsuccinate.[118,119,209] The Strecker reaction of hemiacetal **113**

Scheme 53



Scheme 54[a]



[a] X = Ts or Ms.

with NaCN and (*S*)-α-phenylethylamine leads to the (*S*,*R*)-aminonitrile **114** as a mixture with its (*S*,*S*)-diastereomer (88:12). The major isomer **114** was separated and converted into *allo*-norcoranamic acid **112** by standard methods (Scheme 53).[206]

Nucleophilic displacement of the hydroxyl group in less active cyclopropanol derivatives may be successfully realized by activation of the leaving group. Thus, Salaün and co-workers found that 1-alkenyl cyclopropyl esters readily form π- or σ-1,1-ethyleneallylmetal complexes which afford cyclopropane derivatives.[15,61,119,166,208−218] Formation of allylmetal complexes **115** proceeded readily when the corresponding sulfonic esters **116** (mesylates or tosylates) were treated with catalytic amounts of palladium(0) species at room temperature. The former underwent regio- and diastereoselective substitution reactions to provide alkylidenecyclopropanes **117** or (1-alkenyl)cyclopropanes **118** (Scheme 54). [214,219]

In cases involving stabilized anions (enolates of malonic ester, β-dicarbonyl compounds, β-sulfonyl esters), the nucleophilic substitution led exclusively to the corresponding alkylidene cyclopropanes in very good yields (Table 3). The use of chiral phosphine ligands in the palladium catalyst provides chiral methylenecyclopropane derivatives with moderate ee (Table 3, entries 7 and 8). Regioselective O- and N-allylations of glycolates,[213,215] amines,[60,220] and amino acids[213,216] were also realized by reactions of the respective substrates with appropriate 1,1-ethyleneallylpalladium complexes.

On the other hand, palladium-catalyzed nucleophilic substitution reactions of sulfonates of vinylcyclopropanols **116** with nonstabilized nucleophiles (alkyl- and arylzinc chlorides,[166] metal hydrides,[169,209] and azides[60,61,208,220]) lead to the formation of 1-alkenyl-1-substituted cyclopropanes. For example, reaction of tosylate **116a** with phenylzinc chloride gave exclusively 1-ethenyl-1-phenylcyclopropane (**119**). The authors proposed the transfer of the phenyl group from zinc to palladium via a π-complex **115a**, in which palladium is positioned closer to the cyclopropyl carbon at the allylic moiety to give σ-complex **120**.[166] The latter undergoes a reductive Pd(0) elimination to give **119** (Scheme 55).

The synthetic utility of these transformations of 1-alkenylcyclopropanol derivatives was demonstrated by several natural product syntheses.[61,119,148,208,210−212] In a recent example, coronamic acid[148] and *allo*-coronamic acid **121**[61] were prepared via palladium(0)-catalyzed stereoselective azidation[208] of the corresponding mesylates (e.g., **122**) in the key step of the synthesis (Scheme 56).

Umpolung reactivity of the π-allylpalladium complex **115a** in the presence of 2 equiv of diethyl zinc was reported recently.[214] Under these conditions, the reaction with benzaldehyde led to the formation of alkylidenecyclopropane derivative **122** in high yield. The umpolung reaction probably proceeds via transmetalation of the π-allylpalladium intermediate **115a** with diethyl zinc into the allylzinc reagent **123** (Scheme 57). Regioselectivity of related reactions of π-3-alkylsilyl-1,1-dimethyleneallylpalladium complexes with aldehydes has been shown to be governed by electronic effects of the trialkylsilyl substituent.[214] Kasatkin and Sato have also found that 1,1-dimethyleneallyltitanium species, generated by treatment of the ethyl carbonate derivative of 1-vinylcyclopropanol with (η^2-propene)Ti(O*i*-Pr)$_2$, react with aldehydes and ketones to form alkylidenecyclopropanes.[221]

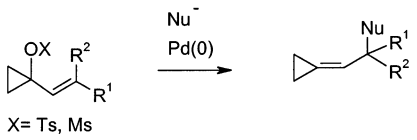
The well-known ability of a cyclopropyl group to stabilize an adjacent carbocation center also facilitates nucleophilic displacement of the hydroxyl group in 1-cyclopropylcyclopropanol and related compounds. This allowed Zefirov and de Meijere and their respective co-workers to develop convenient methods for the preparation of bicyclopropylidene **124** and its numerous derivatives.[222−230] These methods are based on the finding that 1-cyclopropyl-1-cyclopropanol (**125**) is effectively transformed into cyclopropyl bromide **126** under the action of a triphenylphosphine−bromine complex.[222,230] Since cyclopropanol **125** can be easily prepared by cyclopropanation of methyl cyclopropanecarboxylate with EtMgBr in the presence of titanium(IV) isopropoxide, and bromocyclopropane **126** is smoothly dehydrobrominated into **124**, this parent bicyclopropylidene is readily available in multigram quantities (Scheme 58).[224]

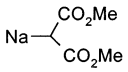
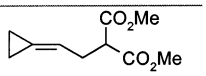
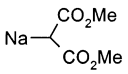
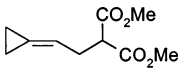
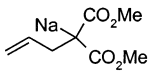
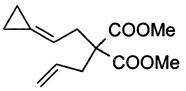
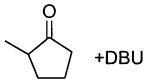
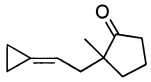
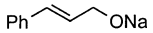
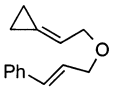
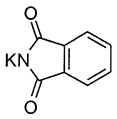
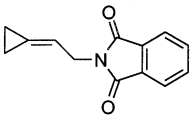
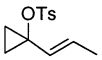
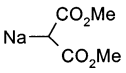
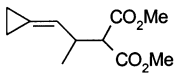
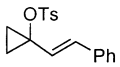
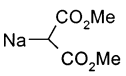
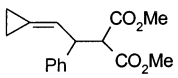
To activate the leaving group in 1-acetonylcyclopropanol **127** for substitution reactions by the elimination−addition mechanism, tosylation of the hydroxy group was undertaken. Treatment of the obtained tosylates with primary or secondary amines led to N-substituted 1-acetonylaminocyclopropanes (e.g., **128**) in quantitative yields (Scheme 59).[231]

B. Ring-Opening Reactions

The presence of an oxygen atom attached to a cyclopropane ring creates favorable possibilities for cyclopropanols in ring-opening or ring-expansion reactions. Such transformations are facilitated or initiated by (i) π-electron-donor effect of the oxygen due to stabilization of transition states in which

Table 3. Palladium-Catalyzed Reaction of 1-Alkenylcyclopropyl Esters with Stabilized Nucleophiles[166]



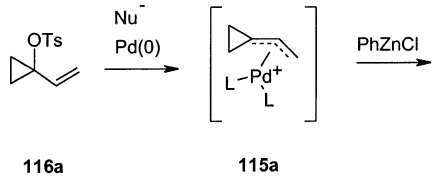
Entry	Cyclopropyl sulfonate	Catalyst	Nucleophile	Product (Yield, %)
1		$Pd(PPh_3)_4$		 (86%)
2		$Pd(dba)_2$, dppe (1:1)		 (84%)
3		$Pd(dba)_2$, dppe (1:1)		 (91%)
4		$Pd(dba)_2$, dppe (1:1)	 +DBU	 (72%)
5		$Pd(dba)_2$, dppe (1:1)		 (95%)
6		$Pd(PPh_3)_4$		 (65%)
7		$Pd(dba)_2$, (-)BINAP		 [86%(50% ee)]
8		$Pd(dba)_2$, (-)BINAP		 [92%(52% ee)]

electron deficiency is generated at the adjacent carbon atom, (ii) removal of one electron from the lone electron pair of oxygen with formation of an unstable oxycyclopropyl cation radical, or (iii) heterolytic cleavage of the carbon−oxygen covalent bond, which promotes cleavage of the opposite carbon−carbon bond of the cyclopropane ring. Such reactions often proceed with high selectivitiy; hence, numerous synthetically useful transformations of cyclopropanols involving ring opening have been studied.

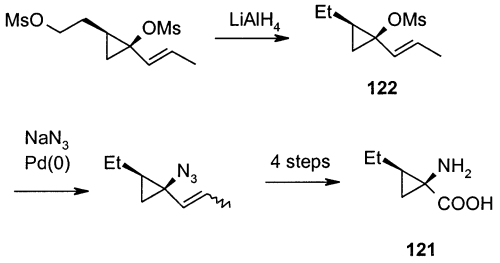
1. C^1–C^2 Ring-Opening Reactions

(a) Heterolytic Cleavage of Cyclopropane Ring. Cyclopropanol itself,[2] and a variety of substituted

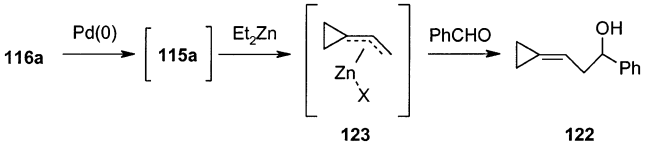
Scheme 55



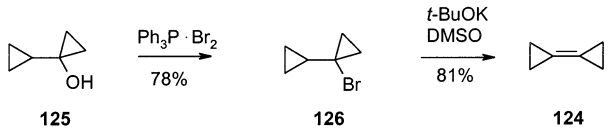
Scheme 56



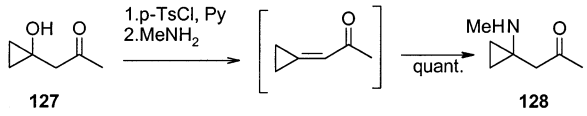
Scheme 57



Scheme 58



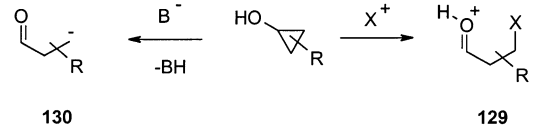
Scheme 59



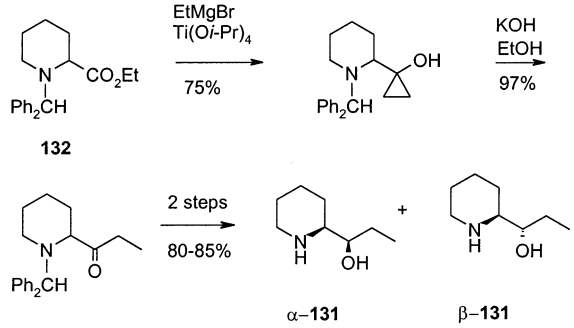
cyclopropanols, readily rearrange into the corresponding carbonyl compounds by C^1-C^2 ring-cleavage reactions, especially under basic or acidic solutions.[5] Early work on the regioselectivity and stereoselectivity of such transformations has been summarized.[3−5] The hydroxyl group strongly activates these reactions and directs the ring opening so that the electron-deficient center formed upon heterolytic C^1-C^2 ring cleavage is always attached to the π-electron-donor oxygen atom (as in the conjugate acid **129**), while the carbanion center is located at the β-position to the carbonyl group (as in the conjugate base **130**) (Scheme 60). These reactions, in which cyclopropanols act as homoenolate anion equivalents, play an important role in synthetic organic chemistry.[78,79,232,233]

A recent synthetic application of isomerization of cyclopropanols into the corresponding carbonyl compounds[100,102,135,136,138,183,234−243] is the straightforward preparation of α- and β-conhydrines **131** from pipecolic ester **132** (Scheme 61).[240]

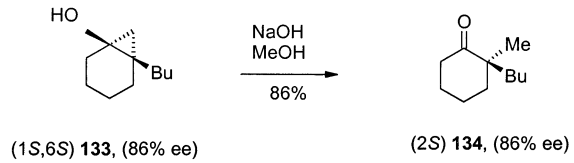
Scheme 60



Scheme 61



Scheme 62



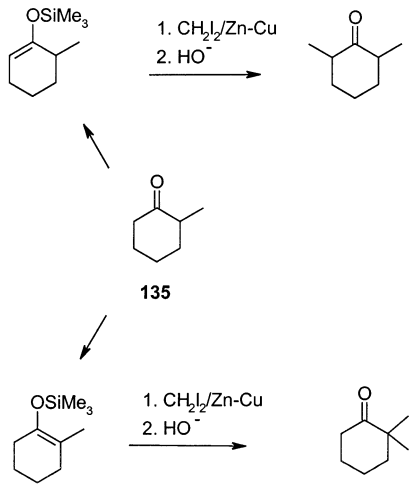
The base-induced heterolytic ring cleavage of unsymmetrically substituted cyclopropanols usually occurs regioselectively, so as to most effectively stabilize a negative charge.[5] For example, conversion of chiral bicyclopropanol **133** into the enantiomerically enriched 2-substituted 2-methylcyclohexanone **134** proceeded without any complications (Scheme 62).[135,136]

The Simmons−Smith reaction of appropriate enol derivatives, followed by regioselective isomerization of the cyclopropanol intermediates into the corresponding α-methyl ketones, is an effective method for α-methylation of carbonyl compounds without polymethylation.[6,132,133,244,245] Methylation can be directed to both α- and α′-positions of the starting ketone by using regioisomeric silyl ethers as substrates. Methylation of 2-methylcyclohexanone **135** by the Conia method is a classical example of such a transformation (Scheme 63).[132,244] This method of regioselective monomethylation of ketones via cyclopropanol intermediates has been successfully applied to natural product synthesis.[244,246]

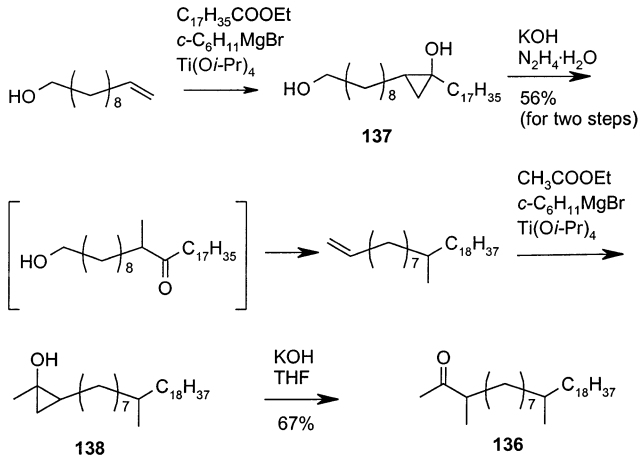
A convenient synthetic procedure for nonstereoselective preparation of 3,11-dimethylnonacosan-2-one (**136**), a component of the sex pheromone of the German cockroach *Blatella germanica*, from easily obtainable cyclopropanols **137** and **138**, involving two successive cyclopropane ring-opening steps, has been reported recently and represents an interesting application of isomerization of monocyclic 1,2-disubstituted cyclopropanols in the synthesis of natural products (Scheme 64).[237]

Compared with base-induced isomerization of cyclopropanols into carbonyl compounds, the corre-

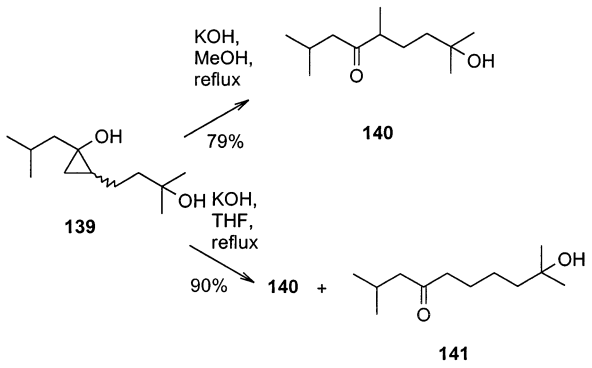
Scheme 63



Scheme 64



Scheme 65



sponding acid-induced processes are usually characterized by lower regioselectivity.[5] Furthermore, solvent can play an important role in determining the regioselectivity of ring opening. For example, cyclopropanol **139** could be selectively converted into stigmolone **140**, a pheromone of mixobacteria *Stigmatella aurantica*, only when protic solvent methanol was used, whereas the corresponding isomerization in THF led to an equimolar mixture of **140** and the isomeric ketone **141** (Scheme 65).[239]

Cyclopropanols bearing electon-withdrawing substituents at the cyclopropane ring in vicinal positions to the hydroxyl group undergo heterolytic ring cleavage under very mild conditions.[31,77,247] Several useful procedures for the preparation of 1,4-dicarbonyl compounds have been developed by employing carbonyl-substituted cyclopropanols or the respective alcoholates as key intermediates.[87,104,236,247−252] As a recent example, convenient experimental procedures were reported by Kel'in and Kulinkovich for the preparation of aryl-substituted 1,4-diketones **142**, starting with thermodynamically controlled cross-aldol condensation of methyl ketones **143** with α-bromo ketones **144** by means of *tert*-butoxymagnesium bromide etherate in benzene (method A) or diethylamidomagnesium bromide in toluene (method B) at room temperature. 1,3-Dehydrobromination of the aldol products **145** with triethylamine[251] led to unstable cyclopropanol intermediates **146**, which underwent rearrangement to 1,4-diketones **142** under the reaction conditions (Table 4). Method A failed to give satisfactory results when the α-bromoketones **144** contained secondary or tertiary α-carbon atoms or electron-donor substituents in the aromatic ring. In these cases, a more basic diethylamidomagnesium agent is required and leads to the formation of 1,4-diketones **142** in moderate to good yields.

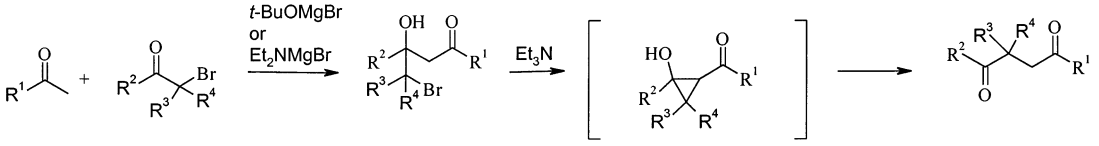
By using titanium(IV) isopropoxide as a condensing and dehydrohalogenating agent, this transformation may be performed in one step, as exemplified by the preparation of 1,2-dibenzoylethane from acetophenone and α-bromoacetophenone (Scheme 66).[250] Another one-pot preparation of 1,4-diketones from methyl ketones and α-bromo ketones via cyclopropanol intermediates involves the use of anhydrous zinc chloride in benzene in the presence of equimolar amounts of diethylamine or triethylamine and *tert*-butyl alcohol as the condensation agents.[252] This procedure gave better product yields in cases of compounds with electron-withdrawing functional groups.

Cyclopropylcarbinyl−homoallyl isomerization of 2-hydroxyalkyl-substituted cyclopropanols (e.g., **147)** proceeded with high regioselectivity and led to the formation of β,γ-unsaturated carbonyl compounds as a mixture of geometric isomers (e.g., **148)** (Scheme 67).[94,130]

Electrophilic bromination of cyclopropanols usually proceeds without complications to afford β-bromo ketones.[5] The proton-initiated carbon−carbon bond rupture in *cis*-2-phenyl-1-methylcyclopropanol was shown to proceed with *retention* of configuration,[253] whereas bromination of both *cis*,*trans*- and *trans*,*trans*-2,3-dimethyl-1-phenylcyclopropanols led stereospecifically to the corresponding bromo ketones with *inversion* of configuration.[254] A convenient and flexible method has been found for the preparation of α,β-unsaturated ketones from carboxylic esters, involving bromination of the corresponding 1-substituted or 1,2-disubstituted cyclopropanols as a key step (Table 5).[134,255−261] High regioselectivity of bromination of 1,2-disubstituted cyclopropanols was observed when aqueous methanol was used as solvent.[256]

The synthesis of the cyclopentenoid antibiotic methylenomicin B **149**, prepared in a reasonable yield through cyclopropanol **150** and α-methylene ketone **151** as key intermediates (Scheme 68),[261] is

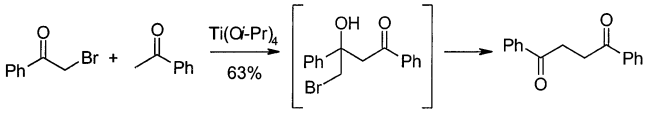
Table 4. 1,4-Diketones from Methyl Ketones and α-Bromomethyl Ketones



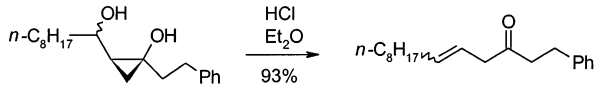
143 144 145 146 142

entry	R^1	R^2	R^3	R^4	method	yield (%)	ref
1	Ph	Ph	H	H	A	58	249
2	2-thienyl	2-thienyl	H	H	A	60	249
3	2-thienyl	2-(5-bromo)thienyl	H	H	A	56	249
4	4-$MeOC_6H_4$	Ph	H	H	A	61	249, 251
5	Me	Ph	H	H	A	46	249
6	Ph	Ph	Me	H	B	53	251
7	Ph	4-$MeOC_6H_4$	Me	H	B	54	251
8	Ph	Et	Me	H	B	44	251
9	Ph	Ph	Me	Me	B	63	251
10	2-thienyl	2-thienyl	n-$C_{16}H_{33}$	H	B	69	251
11	2-thienyl	2-thienyl	$(CH_2)_7CO_2Et$	H	B	63	251
12	n-C_6H_{13}	2-thienyl	Me	H	B	32	251

Scheme 66



Scheme 67



147 148

(E / Z = 89 / 11)

an example of the use of this pathway to α,β-unsaturated ketones for the synthesis of natural products.[257,259−261]

Another possibility for obtaining α,β-unsaturated carbonyl compounds is based on hypervalent iodine oxidation of cyclopropanol trimethylsilyl ethers, a reaction which is initiated as Si−O bond scission under the action of tetrabutylammonium fluoride.[262,263] Using this reaction, a methodology for the conversion of lactones into higher homologoues of α,β-unsaturated lactones via 1-trimethylsiloxy-2-oxa[*n*.1.0]-cycloalkanes has been developed. The latter were prepared by reaction of 1-trimethylsilyl ethers of the respective enols with CH_2I_2/Et_2Zn. Medium-ring-size lactone **152** was also successfully employed in this homologation reaction, to afford the α,β-unsaturated lactone **153**. It was suggested that the mechanism of the cyclopropanol ring opening may involve β-functionalized lactone intermediate **154** (Scheme 69). [262]

Cyclopropanols with nucleofugal substituents at a vicinal position to the hydroxyl group may be converted into α,β-unsaturated carbonyl compounds in good yields by simple treatment with base under mild conditions,[72,146] as exemplified by the transformation of sulfonyl-substituted cyclopropanol **155** into the aldehyde **156** (Scheme 70).[146]

Although base-induced ring opening of the cyclopropanols in aprotic solvents probably involves formation of the corresponding homoenolate anions as intermediates,[79,232,233] only a limited number of successful trappings of these species with carbon-centered electrophiles has been reported to date.[72,265−269] As an example, treatment of cyclopropanol **157** with sodium hydride led to ethyl ketone **158** when R = H, whereas a fused hydroxycyclopentanone **159** was obtained when R = alkyl (Scheme 71, Table 6). [264,266]

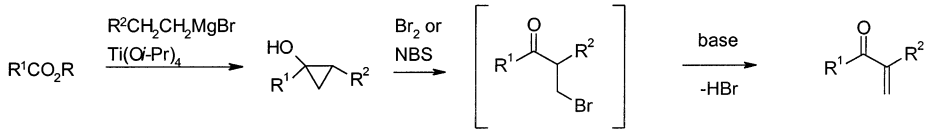
Intramolecular addition of such a homoenolate anion to a carbonyl group proceeds smoothly in cases of other 1-(3-oxoalkyl)cyclopropanols (Table 6, entries 1−4); however, no cyclopentanone product was obtained from the corresponding phenyl ketone due to a retro aldol ring scission process (Table 6, entry 5).[265] The starting 1-(2-oxoalkyl)cyclopropanols were prepared by alkylation of the respective ketones with cyclopropanone hemiacetals. The transformations described above, which were effectively used for the preparation of substituted hydrazulenones[267] as well as in short synthesis of estrone,[264,268,269] may be considered as cyclopentanone annelation reactions onto a pre-existing cyclic ketone framework.

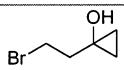
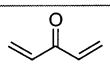
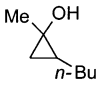
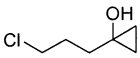
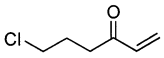
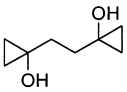
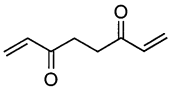
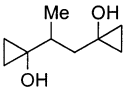
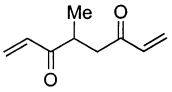
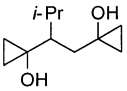
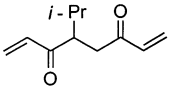
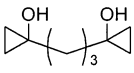
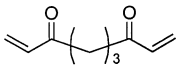
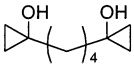
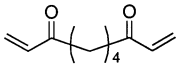
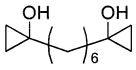
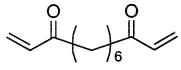
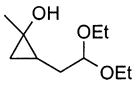
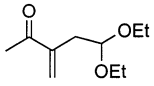
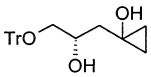
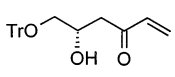
Treatment of cyclopropanediol derivative **160** with $NaN(SiMe_3)_2$ in the presence of benzaldehyde afforded aldol product **161** as a diastereoisomeric mixture. In this intermolecular trapping of a homoenolate anion, the corresponding β-siloxy ketone **162** was formed only as a byproduct (Scheme 72). However, hexanal did not undergo the same reaction with **160**, yielding mainly the ketone **162**.[78]

Cha and co-workers recently observed a similar transformation in the reaction of aldehyde **163** with Et_2AlCl.[270] The reaction proceeded smoothly to give, stereoselectively, the cyclopentanol derivative **164**, whose formation was attributed to the involvement of an aluminum homoenolate **165** (Scheme 73). In contrast, treatment of **163** with a protic acid (PPTS or *p*-TsOH) resulted in ring expansion to give the corresponding cyclobutanone (see below).

Mercuric acetate was the first metal salt used as an electrophilic agent for inducing ring-opening reactions in cyclopropanols.[5,271] As in the case of electrophilic halogenation and protolytic cleavage of cyclopropanols, the course of the mercury-induced reaction

Table 5. Preparation of α,β-Unsaturated Ketones from Esters via 1-Substituted and 1,2-Disubstituted Cyclopropanols

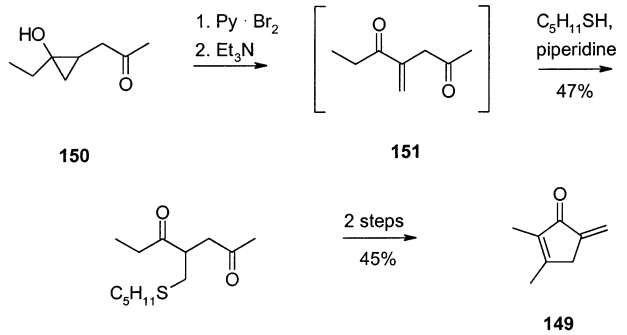


Entry	Cyclopropanol Intermediate	Brominating agent	Dehydrobrominating Agent	Product	Yield, %	Ref.
1		NBS	Na_2CO_3		78	255
2		NBS	Et_3N		73	294
3		Br_2	Al_2O_3		70	256
4		Br_2	Et_3N		>38	259
5		Br_2	Et_3N		67	258
6		$Br_2 \cdot Py$	Et_3N		61	258
7		$Br_2 \cdot Py$	Et_3N		84	258
8		Br_2	Et_3N		85	258
9		Br_2	Et_3N		74	258
10		Br_2	Et_3N		71	258
11		$Br_2 \cdot Py$	Al_2O_3		91	257
12		NBS	-		81	260

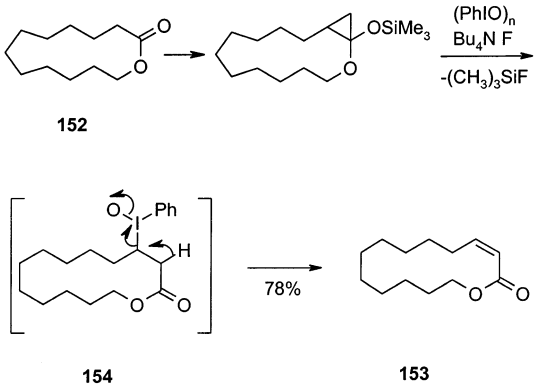
was sensitive to ring substituents. The attack of the metal proceeded preferably on the least substituted carbon of the cyclopropane ring. Products with retention or inversion of configuration at the carbon atom attached were observed, depending on steric effects.[5] β-Mercuro ketones are stable organometallic products of these reactions and are widely used as sources of β-oxocarbonyl radicals, generated under reductive demercuration with sodium borohydride.[272−274] Reductive demercuration of β-mercuroaldehyde, formed from an optically active cyclopropanol, was used to establish the absolute configuration of cyclopropanol **166** by chemical correlation (Scheme 74).[177,187]

Direct transformation of cyclopropanols into α,β-unsaturated ketones in the presence of palladium catalysts has been recently described by the Cha[275]

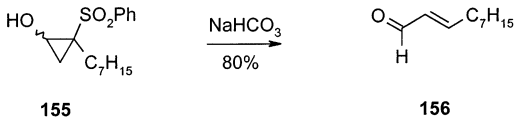
Scheme 68



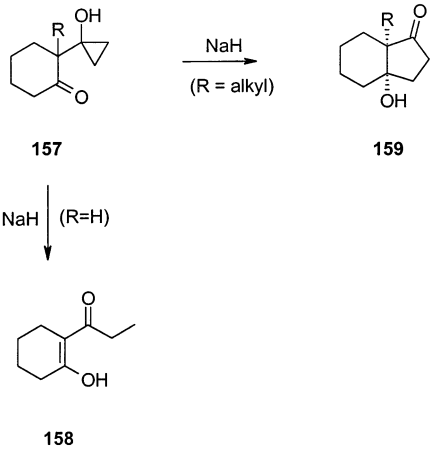
Scheme 69



Scheme 70



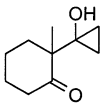
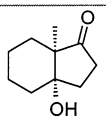
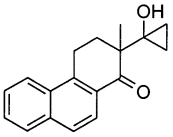
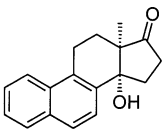
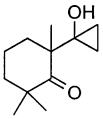
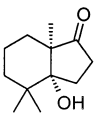
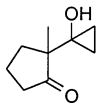
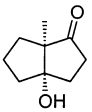
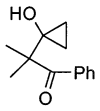
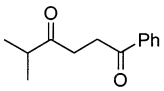
Scheme 71



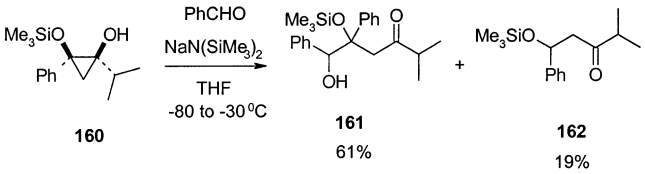
and Suzuki[276] research groups. Treatment of 1-substituted cyclopropanols **167** with various palladium catalysts in MeCN, or with $Pd(OAc)_2$, at elevated temperatures in the presence of pyridine in toluene gave vinyl ketones **168** in moderate to good yields, together with the corresponding saturated ketones **169** as side products (Table 7).[275,276]

The assumed pathway for this reaction includes transformation of cyclopropanols **167** into the corresponding palladium(II) cyclopropyloxides, followed by cyclopropane ring opening, with the formation of β-pallado ketones **170** as the key intermediates. The

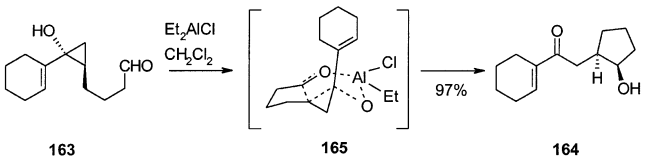
Table 6. Transformation of 1-(2-Oxoalkyl)cyclopropanols into Cyclopentanones[265]

Entry	Cyclopropanol	Product	Yield (%)
1			71
2			78
3			75
4			68
5			93

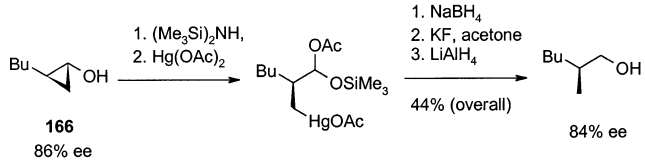
Scheme 72



Scheme 73



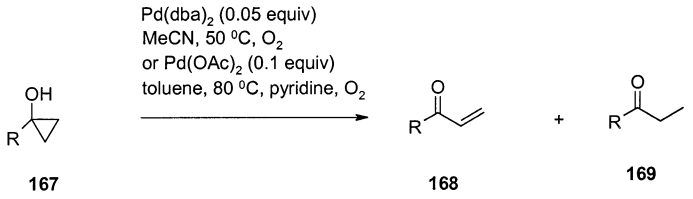
Scheme 74



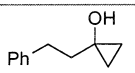
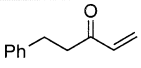
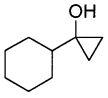
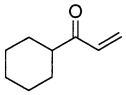
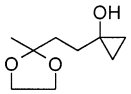
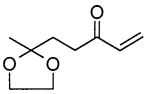
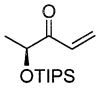
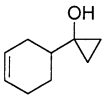
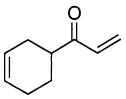
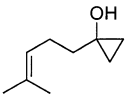
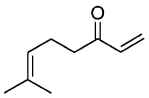
latter are transformed into enones **168** by β-elimination of palladium−hydride complex or into the corresponding saturated ketones by reductive elimination, depending on the reaction conditions (Scheme 75).[275,276]

Ring opening in 1,2-disubstituted cyclopropanols under Pd catalysis takes place predominantly via cleavage of the least substituted C−C bond.[275,276] Thus, cyclopropanol **30** gave a 3.9:1 mixture of the

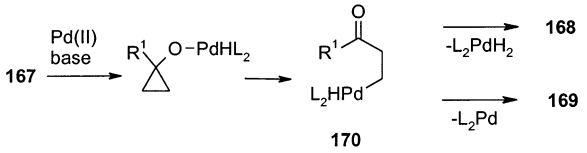
Table 7. Ring Opening of Cyclopropanols in the Presence of Pd Catalysts



167 168 169

Entry	Cyclopropanol	Catalyst	Enone	Ratio 168:169	Yield, (%) 168+169	Ref
1		$Pd(dba)_2$		20:1	99	276
2		$Pd(OAc)_2$		-	55	275
3		$Pd(dba)_2$		-	77	276
4		$Pd(OAc)_2$		-	88	275
5		$Pd(dba)_2$		20:1	48	276
6		$Pd(dba)_2$		25:7	75	276

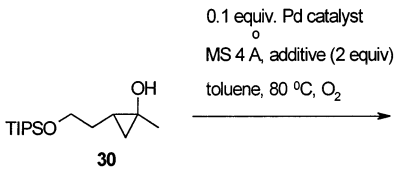
Scheme 75



two regioisomers **171** and **172** in high yields. As a result of testing various reaction conditions, exclusive formation of **171** was achieved by employing $Pd_2(dba)_3$ in the presence of benzoquinone as reoxidant (Scheme 76). Nevertheless, in the case of some other monocyclic 1,2-disubstituted cyclopropanols, and especially for bicyclic or tricyclic cyclopropanols, this reaction proceeded with poor regioselectivity.[275]

A convenient method for the generation of metal homoenolates is the ring-opening reaction of siloxycyclopropanes with suitable metal halides.[277] 1-Alkoxy-substituted siloxycyclopropanes react particularly smoothly, making it possible to prepare a variety of homoenolates of esters, which are widely used as useful synthetic intermediates (Scheme 77).[10,29,32,232,278,279] As indicated by some experimental data, these reactions may proceed via initial interaction of the metal and the cyclopropane ring to form

Scheme 76

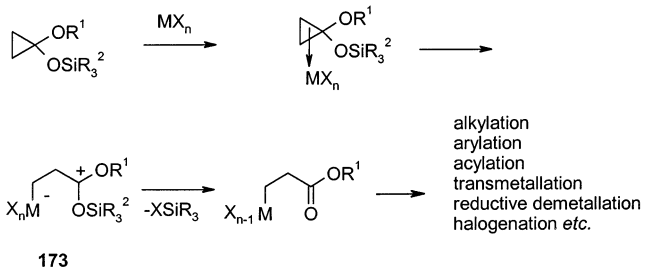


Catalyst	Additive	Ratio 171:172	Yield, (%)
$Pd(OAc)_2$	pyridine	3.9:1	87
$Pd(OAc)_2$	DMSO	4.2:1	93
$Pd_2(dba)_3$	DMSO	3.5:1	77
$Pd_2(dba)_3$	p-benzoquinone	1:0	79

an intermediate **173** with an oxygen-stabilized carbocationic center.[32]

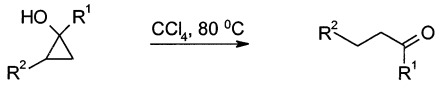
(b) Homolytic Cleavage of the Cyclopropane Ring. In early 1960s, De Puy and co-workers re-

Scheme 77

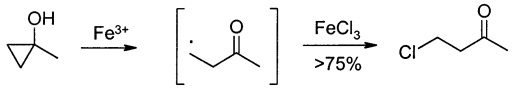


173

Scheme 78



Scheme 79



ported that parent cyclopropanol 1-methyl- and 2-phenyl-substituted cyclopropanols underwent rapid ring opening into propionaldehyde, 2-butanone, and β-phenylpropionaldehyde, respectively (Scheme 78), in hot chloroform or carbon tetrachloride solutions.[280]

These workers proposed a radical mechanism involving hydrogen abstraction from the hydroxyl group of the cyclopropanol, accompanied by opening of the three-membered ring. The suggestion that the ring opening and bond rupture between carbon atom and leaving group is a concerted process is consistent with a remarkable sensitivity of the reaction rates to the nature of the C^2 substituent of the cyclopropane ring observed for thermal homolysis of cyclopropyl nitrites,[281,282] as well as with some other experimental[5] and theoretical data.[283,284] Oxidation of cyclopropanols with Fe(III),[285−290] Cr(VI),[291,292] Mn(III),[293−297] Pb(III),[298,299] V(V),[300,301] Mn(II),[301] and Cu(II)[290] salts, as well as with non-metal-based oxidants,[5,302−304] is also likely to proceed by radical mechanisms. Most of the above-mentioned oxidants also successfully initiate homolytic ring opening in siloxycyclopropanes.[286,287,289,300,302,304−322]

An important application of the β-oxocarbonyl radicals, formed as intermediates by oxidation of cyclopropanols, is their reactions with different radical-trapping species. In their pioneering work on cyclopropanol oxidation,[285,323] De Boer and co-workers found that reactions of cyclopropanols with ferric chloride led to β-chloro ketones in good yields (Scheme 79).[285] These results support the free radical oxidation mechanism of cyclopropanols, as well as their silyl ethers, in their reaction with $FeCl_3$.[285,306,307,310]

Cha and co-workers reported the tandem intramolecular cyclopropanation of ω-vinyl esters **174** and oxidation of the resulting cyclopropanols **175** with $FeCl_3$, followed by dehydrochlorination of the β-chloroketone intermediates with NaOAc. This represents a facile method for the construction of seven- and eight-membered carbocyclic ketones **176** (Table 8).[59] Whereas no diastereoselectivity was observed for intramolecular cyclopropanation of ω-vinyl esters **174**, both diastereomers cleanly underwent $FeCl_3$ oxidation to afford the same cycloalkenones **176** in good yields (Table 8, entries 4−8).[59] Sato and co-workers also used this methodology to prepare N-heterocyclic carbonyl compounds.[288]

Kinetic studies have revealed that chromic acid oxidation of secondary cyclopropanols proceeds 10^3−10^6 times faster than that of other secondary alcohols, and that tertiary cyclopropanols are even more reactive in these reactions.[291,292] Under these conditions, the corresponding β-hydroxycarbonyl compounds were formed in moderate to good yields; evidence for the formation of free radical intermediates was also obtained.[291]

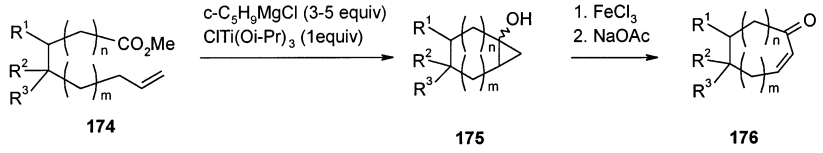
Catalytic,[289,300,301] noncatalytic,[289,324] and photoinduced[302,325] oxidation of cyclopropanols with oxygen led to β-oxy-functionalized carbonyl compounds. Recently, Kirihara and co-workers[300] found that bicyclo[*n*.1.0]alkan-1-ols underwent reaction with a catalytic amount of vanadyl(V) acetylacetonate under oxygen atmosphere to afford a mixture of β-hydroxy ketones and β-diketones. Copper- and iron-catalyzed oxidation of bicyclo[*n*.1.0]alkan-1-ols **177** with oxygen led to 3-hydroperoxycycloalkanones **178** and/or their bicyclic peroxyhemiketals **179**. The latter were easily transformed into α,β-epoxycycloalkanones **180** by treatment with base (Scheme 80).[290]

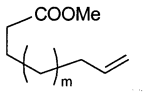
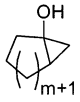
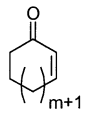
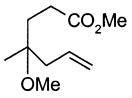
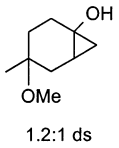
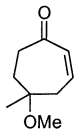
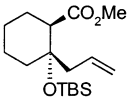
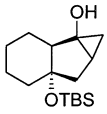
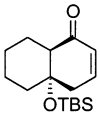
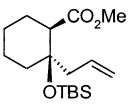
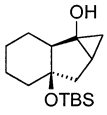
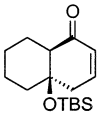
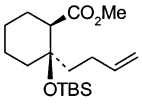
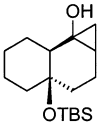
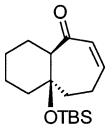
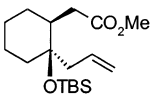
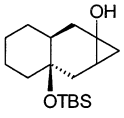
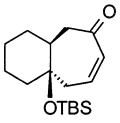
Attempts to involve monocyclic cyclopropanols in reaction with O_2 under the same conditions as applied to the oxidation of bicyclo[*n*.1.0]alkan-1-ols[289,290] failed.[301] Nevertheless, oxidation of monocyclic cyclopropanols **181** by molecular oxygen was effectively realized in the presence of Mn(II) abietate or tri-*n*-butylvanadate(V) to give the cyclic peroxy compounds **182** as major products (Scheme 81).[301] In the case of 1,2-disubstituted cyclopropanols, the cleavage of the most substituted carbon−carbon bond in a highly regioselective manner was observed. By treatment with alkali peroxide, compounds **182** were smoothly converted into α,β-epoxy ketones **183** in good yields.

Special attention has been given to oxidative reactions of cyclopropanols[144,285,293−296,303,319,326] and the respective silyl ethers,[287,300,308−312,316−319,321,327,328] in which trapping of the β-oxocarbonyl intermediates was accompanied by the formation of a new carbon−carbon bond. Narasaka and co-workers have shown that a wide variety of cyclopropanols smoothly underwent reaction with silyl enol ethers under the action of manganese(III) 2-pyridinecarboxylate to afford the corresponding 1,5-diketones,[293,295] as exemplified by addition of 1-phenylcyclopropanol to *tert*-butyldimethylsilyl ether **184**.[295] The authors suggest that the oxidatively generated β-keto radical **185** undergoes reaction with silyl ether **184** to give a radical intermediate **186**, which is further oxidized with $Mn(pic)_3$ into cation **187**, to afford the 1,5-diketone **188** (Scheme 82).

The combined use of $Mn(pic)_3$ and tributyltin hydride allowed 1:1 addition reactions of 1-substituted cyclopropanols with electron-deficient olefins **189** such as acrylonitrile, acrolein, methyl acrylate, methyl vinyl ketone, and *N*,*N*-dimethylacrylamide (Table 9).[295] In the absence of tributyltin hydride, polymeric mixtures were formed. In contrast to

Table 8. Intramolecular Cyclopropanation of ω-Vinyl Esters and Oxidative Ring Opening of Bicyclic Cyclopropanols[59]



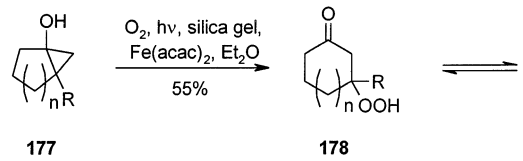
Entry	ω-Vinyl ester 174	Cyclopropanol 175	Yield, (%)	Cycloalkenone 176	Yield, (%)
					
1	m=0		55		98
2	m=1		62		80
3	m=2		11		82
4		 1.2:1 ds	85		60
5		 2:1 ds	79		76
6		 3:2 ds	42		70
7		 9:1 ds	86		75
8		 1.3:1 ds	78		72

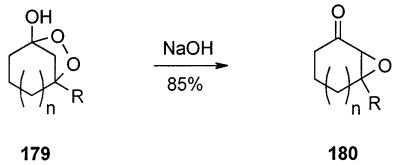
reactions involving electron-rich olefins, the electron-deficient olefins **189** were employed in excess in order to prevent formation of the respective ethyl ketones by hydrogen abstraction from the intermediate β-oxo radicals.

Bicyclic cyclopropanols with an olefinic side chain undergo oxidation with $Mn(pic)_3$ to generate cyclic β-oxocarbonyl radicals, which fragment to medium-sized bicyclic compounds.[296] This approach has been applied to fused carbocycles in a stereoselective total synthesis of natural isothiocyanato sesquiterpene **190**, using readily available bicyclic cyclopropanol **191** as the precursor of bicyclic key intermediate **192** via a 5-exo-trig ring-closure process (Scheme 83).[296] A similar type of radical cyclization of bicyclic cyclopropanol silyl ethers was performed earlier by Booker-Milburn and co-workers, using $FeCl_3$ as the oxidant.[287,308−313,329]

Ring cleavage in cyclopropyloxy radical to form a β-oxopropyl radical, followed by covalent addition to flavin cofactors, is probably responsible for the irreversible inactivation of methanol oxidase by cyclo-

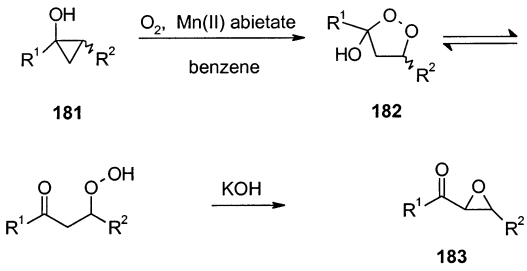
Scheme 80





n	R	Yield (%) 178, 179	Yield (%) 180 [289]
1	CH_3	35	77
1	C_4H_9	55	85
1	C_6H_{13}	68	82
1	$C_6H_5CH_2$	50	78
2	CH_3	54	78

Scheme 81



R^1	R^2	Yield, (%)
Me	n-C_6H_{13}	85
Me	Ph	73
Et	Ph	74
Et	Et	61
Pr	Me	70
n-C_6H_{13}	Me	75
n-C_7H_{15}	H	65

propanol.[13,15,16,326,330] Structural studies performed with adducts isolated from this reaction have shown that a covalent bond is formed between the methylene carbon of cyclopropanol and N^5 of flavin.[326]

2. C^2–C^3 Ring-Opening Reactions

Heterolytic dissociation of the C−X bond in cyclopropane derivatives **193** with nucleofugal substituents X is usually accompanied by disrotatory ring cleavage of the cyclopropane C^2−C^3 bond, leading to reaction products via allylic cation intermediates **194** (Scheme 84). The cyclopropyl-to-allyl rearrangement is one of the most well-known transformations of cyclopropane derivatives[4,5,8,331−337] and is widely used

Scheme 82

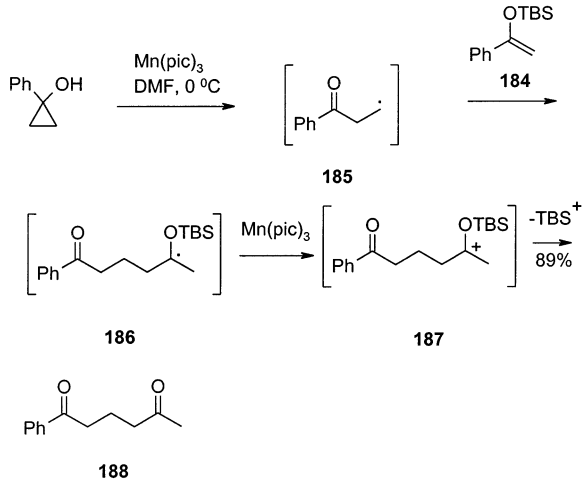
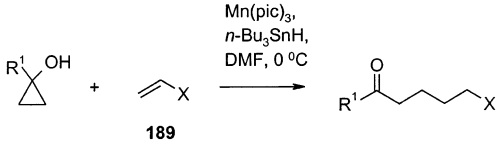
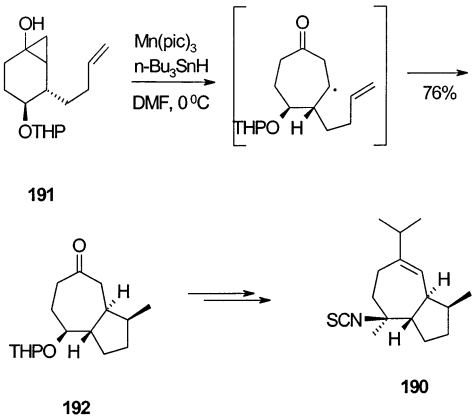


Table 9. Addition of Cyclopropanols to Electron-Deficient Olefins[295]



entry	R^1	X	olefin:cyclopropanol ratio	yield (%)
1	Ph	CN	5.7	47
2	Ph	COOMe	10.2	57
3	$PhCH_2CH_2$	CHO	13.0	46
4	$PhCH_2CH_2$	COMe	4.8	43
5	$PhCH_2CH_2$	$CONMe_2$	5.9	27
6	EtO	CN	6.1	72
7	EtO	COMe	2.8	51
8	$(CH_2)_5N$	CHO	6.7	48
9	$(CH_2)_5N$	COOMe	3.8	49

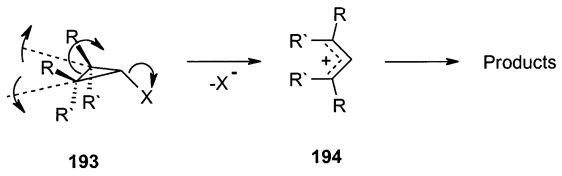
Scheme 83



for the preparation of allylic compounds from halogenocyclopropanes.[333,334]

Although direct use of cyclopropanols in cyclopropyl−allyl isomerization is rare, some exceptions exist. These are solvolysis of 2,2-bis(alkylthio)cyclopropanols promoted by internal alkylthio groups,[338] and acid-catalyzed [4 + 3] cycloaddition of cyclopropanone hemiacetals to substituted furans.[339] For successful realization of the latter transformation, the use of non-nucleophilic and highly ionizing solvents, such as perfluorinated alcohols, is of critical importance.

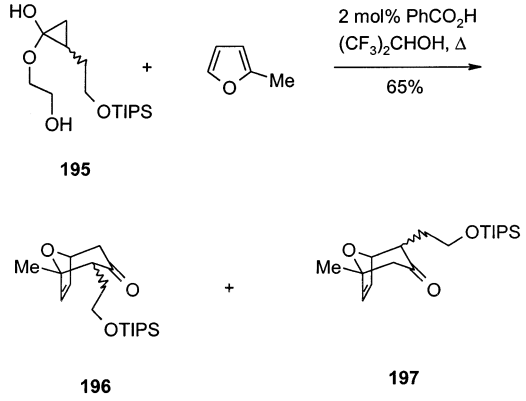
Scheme 84[a]



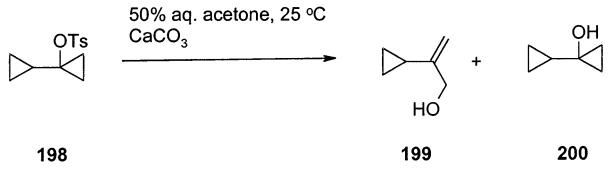
193 194

[a] X = heteroatomic nucleofugal group (e.g., Hal, OTs, N_2^+, etc.).

Scheme 85



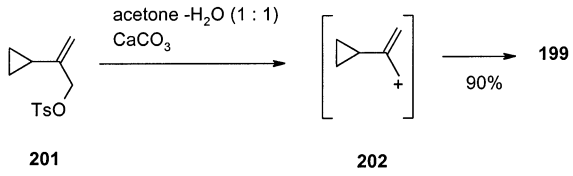
Scheme 86



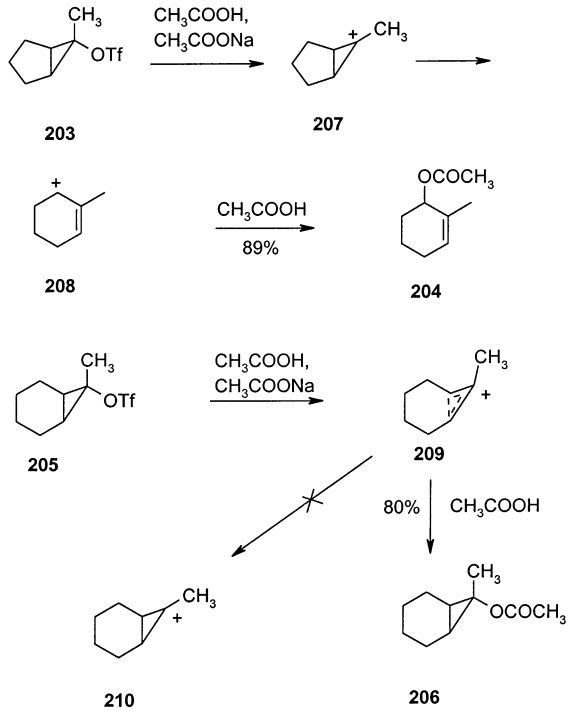
Regioselectivity in the cycloaddition of acetal **195** to 2-methylfuran was low, and all of four possible isomers of **196** and **197** were obtained in a ratio of 1:0.9:0.6:0.6 (Scheme 85). The lack of diastereoselectivity in cycloadditions of cyclopropanone hemiacetals was also observed for intramolecular [4 + 3] cycloadditions of furan-tethered cyclopropanone hemiacetals, and this was attributed to the high-temperature conditions (e.g., refluxing 1,1,1,3,3,3-hexafluoro-2-propanol or 2,2,2-trifluoroethanol).

Conversion of the hydroxy group into a better leaving group, such as a tosylate, triflate, or other esters, facilitates this ring-opening reaction.[5,8,340−355] At 175 °C, cyclopropyl tosylate undergoes slow acetolysis to give allyl acetate.[356] Cyclopropyl tosylates,[5] triflates,[347,349] and 3,5-dinitrobenzoates[351] bearing carbocation-stabilizing substituents are solvolyzed more rapidly than the parent cyclopropyl esters. No ring-opening products were formed in solvolysis of cyclopropyl esters containing a strong electron-donor group on the same ring carbon atom as the leaving group. Thus, solvolysis of 1-cyclopropylcyclopropyl tosylate **198** in aqueous acetone in the presence of calcium carbonate led to the formation of 2-cyclopropyl allyl alcohol **199** in modest yield, while the main component of the resulting product mixture was unrearranged 1-cyclopropylcyclopropanol (**200**), and the product ratio for **199** and **200** was 49:51 (Scheme 86).[340] The use of dimethylformamide as solvent for performing cyclopropyl−allyl rearrangement of cyclopropyl tosylate **198** led, after hydrolysis of the reaction mixture, to 2-cyclopropyl allyl formate in 60% yield.[354]

Scheme 87



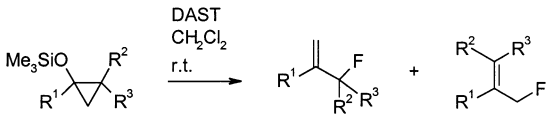
Scheme 88

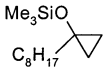
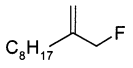
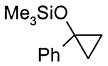
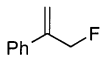
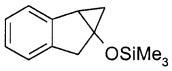
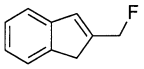
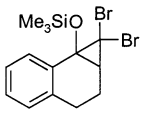
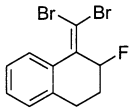
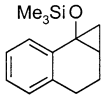
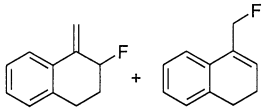
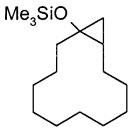
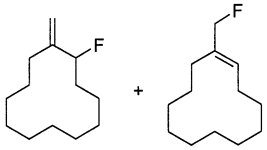
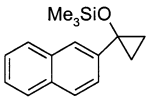
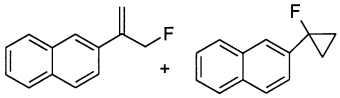
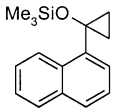
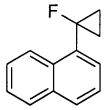


Taking into account the ability of a cyclopropane ring to strongly stabilize an adjacent carbocation center, Salaün[357] studied the solvolysis of allyl tosylate **201** in order to determine the propensity of the allylic cation **202** to undergo ring closure into the 1-cyclopropylcyclopropyl cation.[343] No detectable amount of the expected product from, e.g., 1-cyclopropylcyclopropanol (**200**) was formed, and only 2-cyclopropylallyl alcohol **199** was identified as the main solvolysis product (Scheme 87).

Solvolysis of bicyclic and tricyclic cyclopropanol triflates leads to the formation of solvolyzed products with expanded ring structures or with intact three-membered rings, depending on the fused-ring size, substituents, and position of the leaving group. The same factors determined also the reaction pathway, i.e., whether the ring-opening reaction proceeds via concerted ionization−ring opening, stepwise ionization−ring opening, or unopened cyclopropyl cation intermediates.[346,347,349,350,352] For example, acetolysis of *endo*-6-methyl-*exo*-bicyclo[3.1.0]hexen-6-yl triflate **203** at room temperature gave 2-methylcyclohex-2-enyl acetate **204** as the only product. Solvolysis of *endo*-7-methyl-*exo*-bicyclo[4.1.0]hepten-7-yl triflate **205** proceeded slightly faster (8.8 times) than that of **203** and resulted in the formation of bicyclic cyclopropanol acetate **206**. The authors rationalized these results by assuming that solvolysis of **203**

Table 10. Preparation of Allyl Fluorides via Cleavage of Tertiary Cyclopropanol Silyl Ethers with Diethylaminosulfur Trifluoride[358]



Entry	Silyl ether	Allylic fluorides	Yield (%)
1			96
2			45
3			95
4			73
5			85 (6:1)
6			85 (3.5:1)
7			55 (4.5:1)
8			63

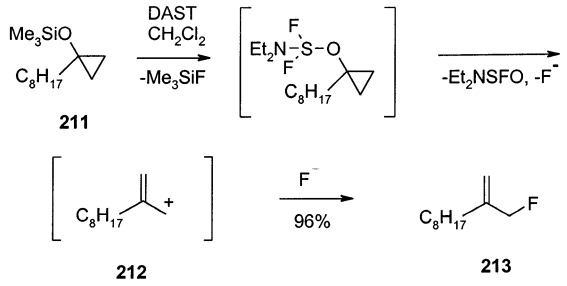
involved formation of unopened tertiary cyclopropyl cation **207** as the initial intermediate, which underwent rearrangement into allylic cation **208**. In contrast, solvolysis of triflate **205** proceeded through a partially opened allylic cation **209** without the involvement of the corresponding unopened tertiary cyclopropyl cation **210** (Scheme 88).[47]

Although both stereochemistry and kinetics of the solvolysis reactions of the cyclopropanol derivatives were extensively studied owing to the mechanistic interest in the cationic cyclopropyl−allyl rearrangement,[340−342] their preparative value has not been demonstrated until recently. The first remarkable study was done by Momose and co-workers, who found that reaction of tertiary cyclopropyl silyl ethers with diethylaminosulfur trifluoride (DAST) provides a convenient method for preparation of allyl fluorides in moderate to high yields (Table 10).[358] Allyl fluorides were the sole products in most cases, and secondary fluorides predominated over primary fluorides (Table 10, entries 6 and 7). Cyclopropanol silyl ethers bearing a stronger electron-donating naphthyl substituent afforded the corresponding fluorocyclopropanes (Table 10, entries 8 and 9).

It was suggested that the first step of this transformation is a nucleophilic displacement of the fluorine atom in DAST by the oxygen of the substrate (e.g., **211**), with elimination of trimethylsilyl fluoride. Subsequent elimination of diethylaminosulfino fluoride affords allylic cation **212** (or cyclopropyl cation, for cyclopropanol substrates with electron-donating substituents), which undergoes reaction with fluoride to give product **213** (Scheme 89).[358]

Recently, Kozyr'kov and Kulinkovich disclosed a simple and useful procedure for converting cyclopropyl sulfonates into 2-substituted allyl halides.[355]

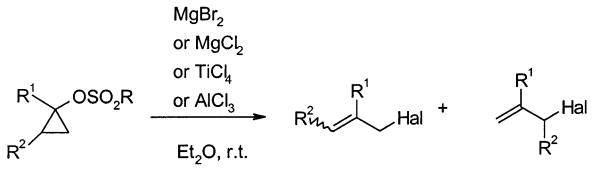
Scheme 89



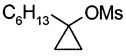
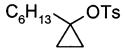
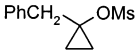
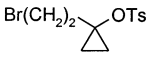
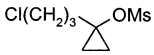
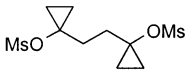
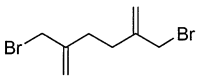
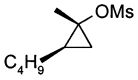
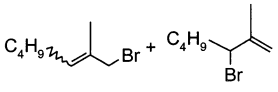
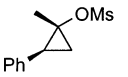
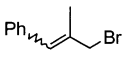
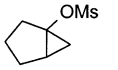
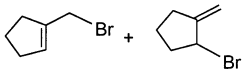
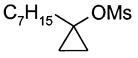
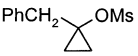
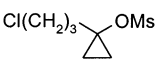
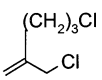
211 212 213

Readily available sulfonates of tertiary cyclopropanols **214** were converted into 2-substituted allyl bromides **215** in high yields under the action of magnesium bromide in diethyl ether (Table 11, entries 1−9). Magnesium chloride, aluminum chloride, and titanium tetrachloride also effectively induced this transformation (Table 11, entries 10−12). Monocyclic and bicyclic 1,2-disubstituted cyclopropyl sulfonates gave allyl halides **215** and **216** as a mixture of stereo- and regioisomers, with preference for the formation of **215** with the most substituted double bond (Table 11, entries 7−9). The development of this simple and efficient procedure will help reduce the current imbalance in synthetic applications of C^1-C^2 versus C^2-C^3 modes of the cyclopro-

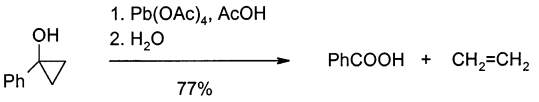
Table 11. Reaction of Cyclopropyl Sulfonates with Metal Halides in Diethyl Ether[355]



214 215 216

Entry	Cyclopropyl sulfonate	Metal halide	Product	Yield (%)
1		$MgBr_2$		95
2		$MgBr_2$		80
3		$MgBr_2$		68
4		$MgBr_2$		81
5		$MgBr_2$		71
6		$MgBr_2$		88
7		$MgBr_2$	 75% (E/Z=85:15) 27%	75
8		$MgBr_2$	 (E/Z=85:15)[e]	74
9		$MgBr_2$	 90% 10%	80
10		$AlCl_3$		80
11		$MgCl_2$[d]		72
12		$TiCl_4$		79

Scheme 90



panol ring-opening reactions. In view of this finding, the opinion that cyclopropyl sulfonates "have no advantage in synthetic applications as compared to silver(I)-assisted halocyclopropane rearrangement" [332] would seen outdated.

3. Transformations Involving Both C^1–C^2 and C^1–C^3 Scission Reactions

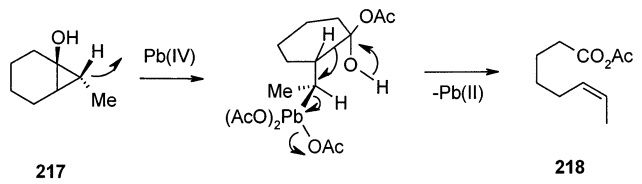
Rubottom and co-workers discovered the oxidation of cyclopropanol trimethylsilyl ethers with lead(IV) acetate in acetic acid to give the corresponding alkenoic acids. In this degradation reaction, both C^1–C^2 and C^1–C^3 scission occurs, and strong evidence was obtained that the fragmentation process was actually an oxidation reaction of cyclopropanols formed after desilylation of the starting silyl ethers.[298,299] For example, oxidation of phenylcyclopropanol with lead tetraacetate led to benzoic acid in high yield (Scheme 90).[298]

Formation of alkenes in this remarkable reaction proceeds in a highly stereoselective manner, the mechanism for which was interpreted by assuming electrophilic opening of the cyclopropane ring, with inversion of configuration at the carbon atom, followed by a Grob-type fragmentation with lead(II) acetate as the leaving group.[299] For example, bicyclic cyclopropanol **217** was stereoselectively transformed into the *cis*-alkenoic ester **218** (Scheme 91).

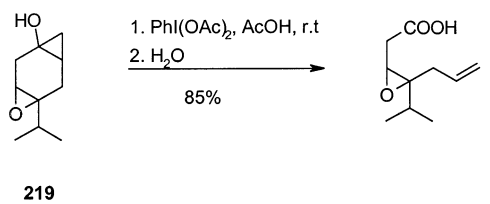
The same reaction may be performed by using less toxic phenyliodine(III) diacetate as oxidant.[263,359] Treatment of 1-hydroxybicyclo[*n*.1.0]alkanes and their trimethylsilyl ethers with this oxidant, or with other hypervalent iodanes (phenyliodine bisfluoroacetate, iodosobenzene, iodoxybenzene) in acetic acid, caused fragmentation to give alkenoic acids in high yields.[359] The reaction proceeded smoothly also with substrates containing labile functional groups (e.g., **219**) (Scheme 92).

Using this oxidative approach, the asymmetric synthesis of (−)-pinidine **220** and its enantiomer was achieved via asymmetric enolization of *N*-tosylated

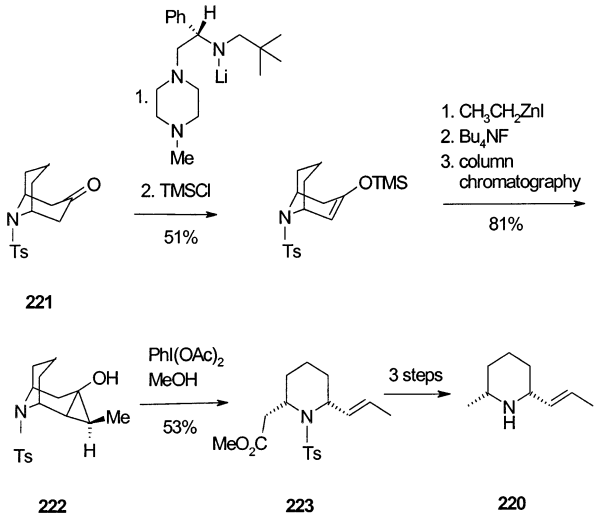
Scheme 91



Scheme 92



Scheme 93



norgranatanone **221**, stereoselective cyclopropanation, and oxidative ring cleavage of the resulting cyclopropanol **222** with hypervalent iodane as key steps.[360] The desired *trans*-alkene **223**, obtained in >96% ee, was transformed into (−)-pinidine **220** in three steps in good overall yield (Scheme 93).

C. Ring-Expansion Reactions

1. C^3–C^4 Ring-Expansion Reactions

Cyclopropanols readily undergo a cationic cyclopropylcarbinyl−cyclobutyl rearrangement, in which a carbocationic center is generated adjacent to the hydroxyl group, to form cyclobutanones.[6,7,27,361] In the absence of electron-stabilizing substituents in the α-position of the cyclopropane ring, a cyclopropylmethyl−homoallyl rearrangement is usually observed.[361,362] In their pioneering work, Wasserman and Clagett found that unstable cyclopentadienylcyclopropanol **224** was isomerized into spirocyclic cyclobutanone **225** when shaken briefly with 10% aqueous H_2SO_4 (Scheme 94).[363]

A wide variety of alkenyl-, alkynyl-, and carbonyl-substituted cyclopropanols successfully particpate in this synthetically useful rearrangement.[7,364−366] For example, parent vinylcyclopropanol readily underwent ring-expansion reactions with a variety of electrophilic reagents, such as protic acids, oxygenating agents, halogens, and iminium ions, to form the corresponding 2-substituted cyclobutanones **226** (Table 12).[365] Silyl ethers of vinylcyclopropanols were also easily utilized in this ring-expansion reaction.[367,368]

Scheme 94

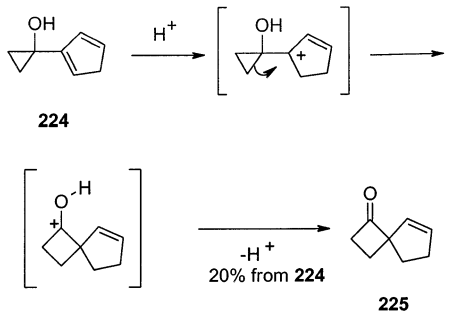
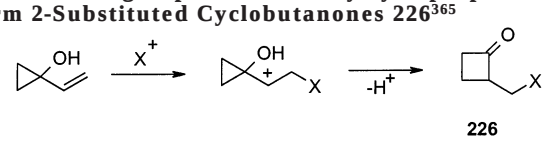


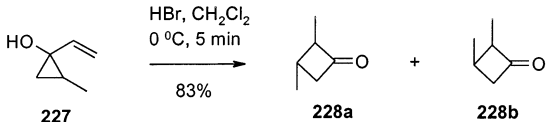
Table 12. Ring Expansion of Vinylcyclopropanol To Form 2-Substituted Cyclobutanones 226[365]



226

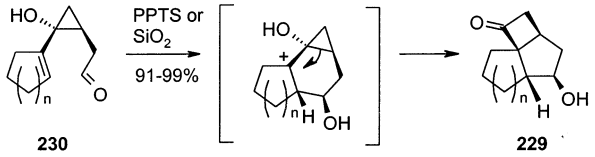
entry	reagent	X	yield (%)
1	dry HBr	H	83
2	concentrated H_2SO_4	H	42
3	$HClO_4$, aqueous acetone	H	20
4	t-BuOCl	Cl	81
5	Br_2	Br	45
6	PhCOOOH	OH	32
7	$(CH_2O)_3$, $NH(CH_2Ph)_2$	$CH_2N(CH_2Ph)_2$	60

Scheme 95



227 **228a** **228b**

Scheme 96[a]



230 **229**

[a] $n = 1$ or 2.

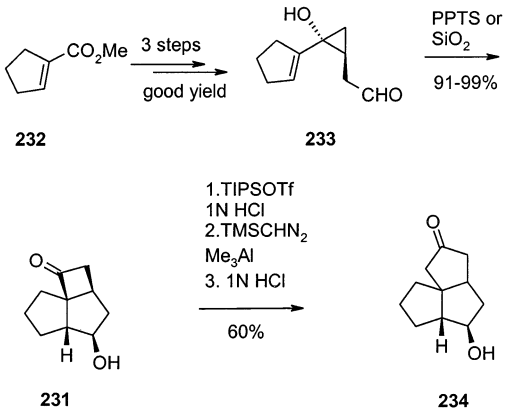
Ring expansion in 2-methyl-1-vinylcyclopropanol **227** by treatment with anhydrous HBr in methylene chloride led to 2,3-dimethylcyclobutanones **228** in a 3:1 trans/cis ratio (**228a**:**228b**) (Scheme 95). In concentrated sulfuric acid, a mixture of stereoisomeric 2,3- and 2,4-dimethylcyclobutanones was obtained.[365]

An efficient strategy for the diastereoselective construction of fused cyclobutanones **229** was developed by Cha and co-workers, based on sequential acid-catalyzed intramolecular electrophilic addition of carbonyl carbon to the double bond in 2-(ω-formyl)-alkyl-substituted 1-alkenylcyclopropanols **230** and cyclopropane ring expansion to provide **229** in high yield and diastereoselectivity (Scheme 96).[270]

A short and effective route to the triquinane skeleton was developed by use of cyclobutanone **231** as the key intermediate.[270] The latter was prepared by sequential application of titanium-mediated cyclopropanation of α,β-unsaturated ester **232** and electrophilic cyclization of the resulting aldehyde-tethered cyclopropanol **233** by treatment with PPTS or silica gel to give **231**. After hydroxyl group protection, treatment with $TMSCHN_2$ in the presence of Me_3Al led to ring expansion to give triquinane **234** (Scheme 97).

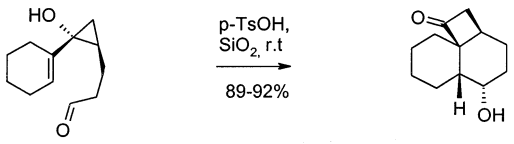
Similar cyclization reactions of the homologous aldehyde **235** gave cyclobutanone **236** in high yield and with good diastereoselectivity (Scheme 98). It is noteworthy that the stereochemistry of the hydroxyl group in **236** was found to be opposite to that of **229**. Inspection of molecular models led the authors to conclude that the divergence in the stereochemistry of the five-membered and six-membered ring-closure reactions is associated with nonbonding interactions in the respective transition states between one of the

Scheme 97



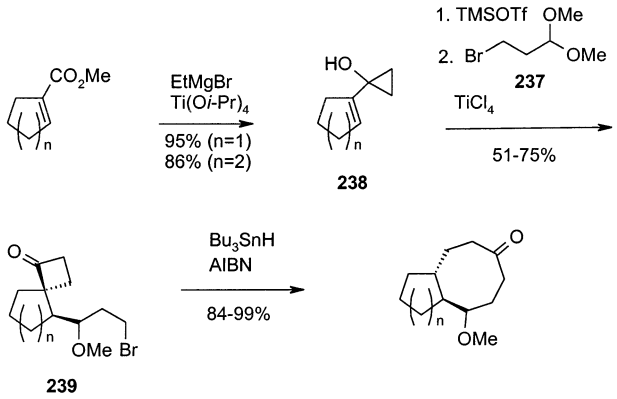
232 **233** **231** **234**

Scheme 98



235 **236**

Scheme 99[a]



238 **239**

[a] $n = 1$ or 2.

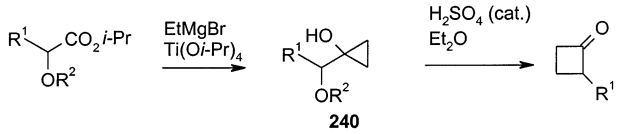
hydrogens of the cyclopropane ring and the carbonyl oxygen.[270]

Cha and co-workers used this approach as a convenient method of annelation of cycloalkene carboxylates to construct an eight-membered ring. This involved an intermolecular addition of 3-bromoalkylacetal **237** to readily available alkenyl cyclopropanols **238**, followed by radical cyclization−fragmentation of spirocyclobutanones **239**, to give the products (Scheme 99).[370]

A simple method has been developed for the preparation of 2-substituted cyclobutanones by ring-enlargement reaction of 1-(1-alkoxy)alkylcyclopropanols **240**, compounds which are easily obtained by cyclopropanation of the corresponding 2-alkoxyalkanoic esters (Scheme 100).[371] However, the use of the respective 1,2-disubstituted (1-alkoxyalkyl)cyclopropanols for this rearrangement led to the formation of stereoisomeric mixtures of 2,3- and 2,4-disubstituted cyclobutanones.

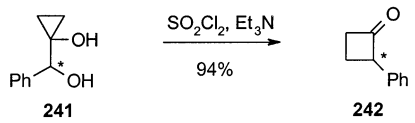
Rearrangement of chiral 1-(1-hydroxyalkyl)cyclopropanols and related compounds resulted in the formation of optically active cyclobuta-

Scheme 100

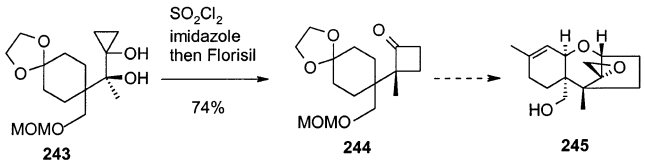


R^1	R^2	Yield (%)	Yield (%)
Ph	CH_3	55	71
C_2H_5	i-C_3H_7	55	49
C_3H_7	i-C_3H_7	67	51
$C_{12}H_{25}$	i-C_3H_7	69	84
$C_{14}H_{29}$	i-C_3H_7	70	87

Scheme 101



Scheme 102



nones.[119,172−174,368,372−376] When diol **241**, obtained by Sharpless asymmetric dihydroxylation,[172,174,373,374] was exposed to thionyl chloride and triethylamine, formation of 2-phenylcyclobutanone (**242**) as a ring-enlargement product was observed in good yield (Scheme 101),[172] but with a considerable loss in enantiomeric purity.[174]

Ring-enlargement reaction of cyclopropanol **243**, proceeding via a cyclic sulfate intermediate to afford enantiomerically enriched cyclobutanone **244**, was used as a key step in the synthesis of (−) 4-deoxyverucarrol **245** (Scheme 102). [375]

Application of the titanium-mediated cyclopropanation of readily available, optically active α-hydroxy esters in tandem with the ring enlargement of the resulting 1-(1-hydroxyalkyl)cyclopropanols **246** constitutes a convenient route to chiral 2-substituted cyclobutanones **247** (Table 13).[376] The stereochemical outcome observed in the rearrangement of (1-hydroxyalkyl)cyclopropanols to 2-substituted cyclobutanones was consistent with a concerted rearrangement ring-expansion mechanism involving a reactive conformation **A** and excluded the intermediacy of the respective oxaspiropentanes.[376]

Oxidation of 1-(1-phenylselenoalkyl)cyclopropanols with *m*-chloroperbenzoic acid in the presence of tertiary amines at low temperature also leads to cyclobutanones.[160,377−380] In several cases, high stereoselectivity was observed for this transformation, and the stereochemistry of the obtained cyclobutanones was opposite to that normally resulting from direct acid-catalyzed rearrangement of oxaspiropentanes.[141] The latter were also used as starting compounds for the preparation of 1-(1-phenylselenoalkyl)cyclopropanols. Thus, from a common oxaspiropentane, either stereoisomeric cyclobutanone may be produced, as exemplified by the preparation of **248** and **249** from oxaspiropentane **250** (Scheme 103).[160]

Cyclopropane and cyclobutane acyloins are easily equilibrated by means of the respective ring-expansion and ring-contraction reactions.[6] This rearrangement was recently used for the preparation of fused vinylcyclobutanediol **251** by addition of excess vinyllithium to the rapidly equilibrating cyclopropanol **252**.[381] The resulting diol **251** was easily converted into diketone **253** via an oxy retro-ene rearrangement (Scheme 104). Although the fused-ring diol **251** was obtained in very low yield, this method for the preparation of this compound was reported to be the best among several other approaches studied.[381]

2. $C^3 \rightarrow C^5$–C^7 Ring-Expansion Reactions

The vinylcyclopropane−cyclopentene rearrangement[382,383] has found numerous synthetic applications,[77,336,382−385] and vinylcyclopropanol derivatives are particularly conducive to this transformation.[155,162,386−388] The rate-accelerating effect of electron-donor substituents in position 2 of vinylcyclopropanes facilitates the ring-expansion reaction of these compounds to a greater extent than does the effect of these substituents in position 1.[182,389−391] The rearrangement of 2-alkenyl-substituted lithium cyclopropanolates proceeded even at room temperature or below.[182] Magnesium cyclopropanolate **254** is thermally unstable and undergoes ring expansion upon heating to give the fused carbocyclic product **255** (Scheme 105).[70,71]

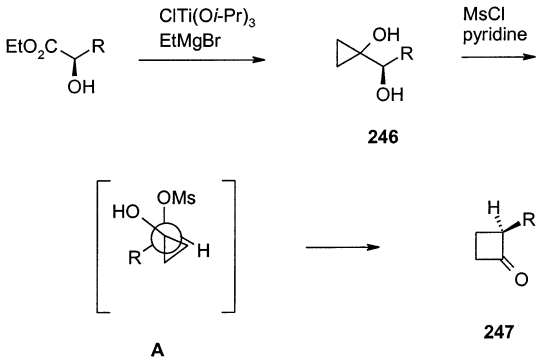
Iwasawa discovered that various 1-alkynylcyclopropanols **256** are converted into 3-substituted 2-cyclopenten-1-ones **257** under mild conditions and in good yields by heating the respective dicobalthexacarbonyl complexes in dimethoxyethane or tetrahydrofuran (Scheme 106).[392−395]

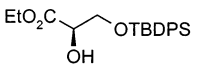
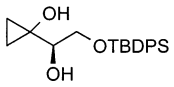
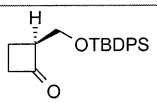
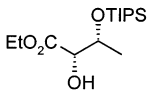
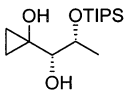
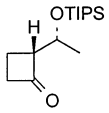
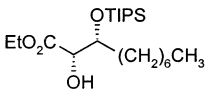
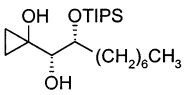
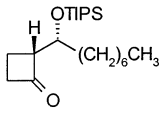
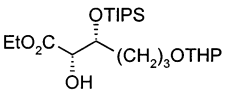
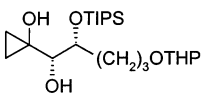
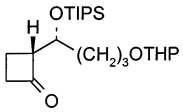
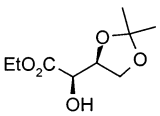
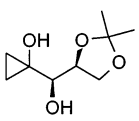
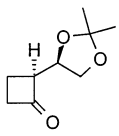
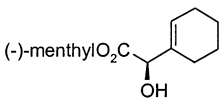
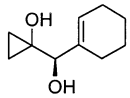
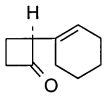
The reaction of (1*R**,2*S**)-2-methyl-1-phenylethynylcyclopropanol led to the formation of an equimolecular mixture of 4-methyl-3-phenyl-1-cyclopenten-1-one and 5-methyl-3-phenyl-1-cyclopenten-1-one.[394,396] In contrast, in the case of 2-alkyl-substituted cyclopropanols **258** containing an alkyl substituent in the trans-position to the hydroxyl group, 5-substituted 2-cyclopenten-1-ones **259** were formed regioselectively (Scheme 107).[393,396]

This rearrangement may be performed catalytically in the presence of triaryl phosphite as ligand.[393,397] Thus, octynylcyclopropanol **260** gave hexylcyclopentenone **261** in good yield when bulky tri(*o*-isopropylphenyl)phosphite was used as ligand (Scheme 108).

Mechanistic studies have revealed that this rearrangement has a close similarity to the Pauson−Khand reaction.[393] The rate-determining step is dissociation of a carbonyl ligand from the alkyne−$Co_2(CO)_6$ complex **262** to generate the alkyne−$Co_2(CO)_5$ complex **A**. The coordinatively unsaturated cobalt species thus generated undergoes insertion into the carbon−carbon bond of the cyclopropanol to give a four-membered metallacyclic intermediate **B**, which undergoes rearrangement into a metallacyclo-

Table 13. Enantioselective Synthesis of 2-Substituted Cyclobutanones[376]



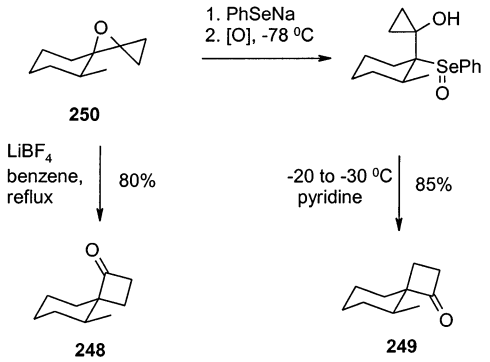
Entry	Starting Ester	Hydroxyalkylcyclopropanol Yield (%)	Cyclobutanone Yield (%)
1		 (62%)	 (98%)
2		 (56%)	 (57%)
3		 (43%)	 (67%)
4		 (49%)	 (57%)
5		 (41%)	 (71%)
6		 (43%)	 (72%)

[a] $n = 1$ or 2.

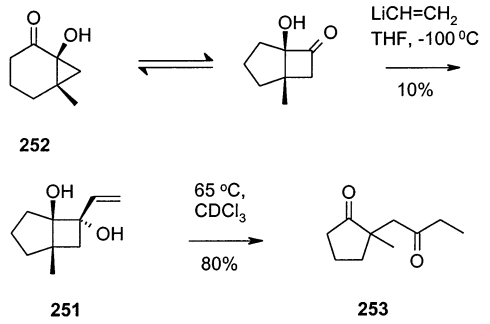
hexanone intermediate **C** by C−Co bond cleavage with proton transfer. Reductive elimination gives cyclopentenone−cobaltcarbonyl complex **D** which, after elimination of $Co_2(CO)_5L$, leads to free cyclopentenone **263** (Scheme 109).

1-[*o*-(1-Alkynyl)phenyl]cyclopropanols and the corresponding naphthyl derivatives (e.g., **263**) may be converted into 2,3-dihydro-1-naphthalenone and the corresponding phenanthrene derivatives (e.g., **264**) in high yields by heating their hexacarbonyldicobalt

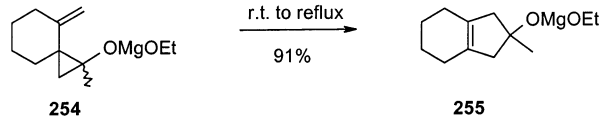
Scheme 103



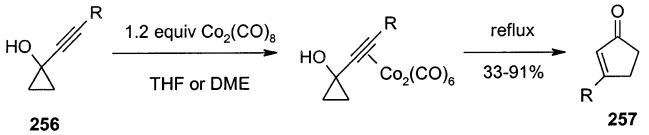
Scheme 104



Scheme 105



Scheme 106[a]

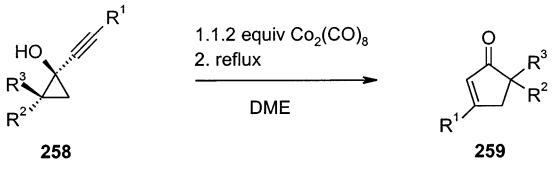


[a] R = C_6H_{13}, *t*-Bu, Ph, *t*-$BuOCH_2$, CH_2CH_2OH, CH_2CH_2OTBS, COOEt, *t*-$BuSCH_2$, Me_3Si, *i*-Pr_3Si, Ph_3Si, *n*-BuS.

complexes in 2-propanol (Scheme 110).[398] This reaction was believed to proceed via intermediate cyclopentenone formation from alkynylcyclopropanols (Scheme 109). The success of this reaction indicates that the presence of an aromatic ring between the alkynyl group and the cyclopropane ring does not prevent oxidative addition of a coordinatively unsaturated cobalt species to the carbon−carbon bond of the cyclopropanol moiety.[398]

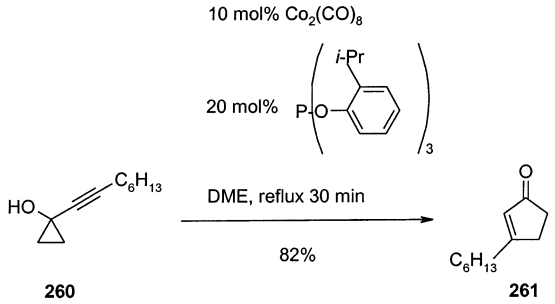
C^3-C^6 ring expansion was also observed in the reaction of 1-(1,2-propadienyl)cyclopropanol **265** with octacarbonyldicobalt ($Co_2(CO)_8$), resulting in the formation of the acetylated hydroquinone **266** after the reaction mixture was treated with acetic anhydride in order to avoid oxidation of the 1,4-hydroquinone intermediate **267** (Scheme 111).[399,400] It was assumed that the mechanism of the reaction included the formation of a carbonyl-inserted intermediate **A**, which underwent ring expansion to give metallacyclic intermediate **B**, and the latter finally gave the

Scheme 107

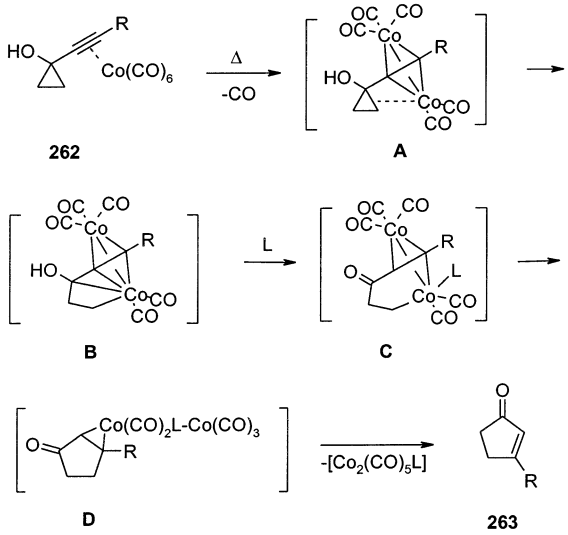


R^1	R^2	R^3	Yield (%)
Ph	*i*-Pr	H	86
n-Hex	Me	H	83
n-Hex	*i*-Pr	H	88
Ph	Me	Me	80
Ph	-$(CH_2)_5$-		83
n-Hex	Me	Me	81

Scheme 108



Scheme 109[a]



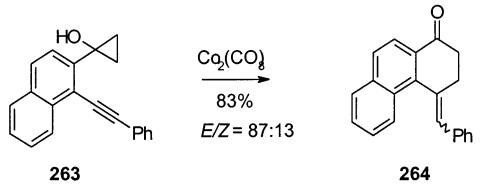
[a] L = CO or solvent.

cyclohexadienone derivative **267** by reductive elimination.

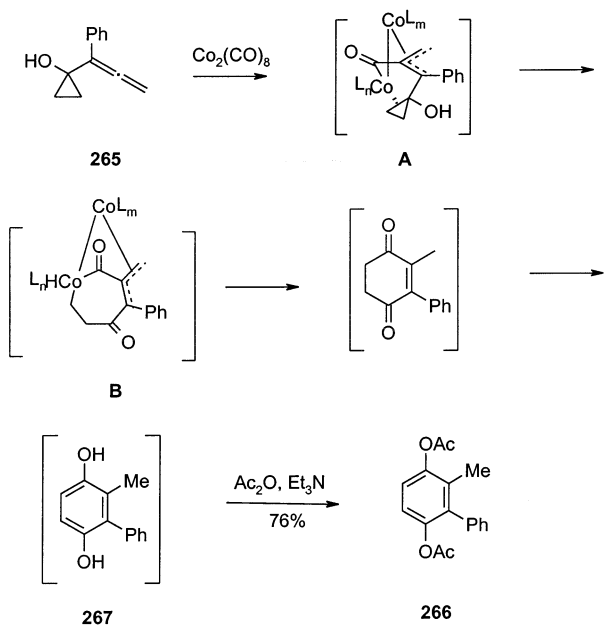
This reaction was applied to the syntheses of vitamin E and vitamin K analogues.[400] To prepare benzene analogues of vitamin K **268**, treatment of 1-substituted 1,2-propadienylcyclopropanols **269** with $Co_2(CO)_8$ was followed by oxidative quenching using iron(III) chloride solution (Scheme 112).

Although the Cope rearrangement of *cis*-divinylcyclopropanes is one of the most efficient methods to construct seven-membered carbocycles,[401,402] only a

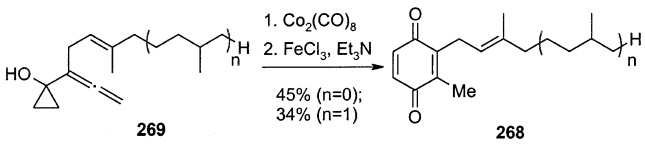
Scheme 110



Scheme 111



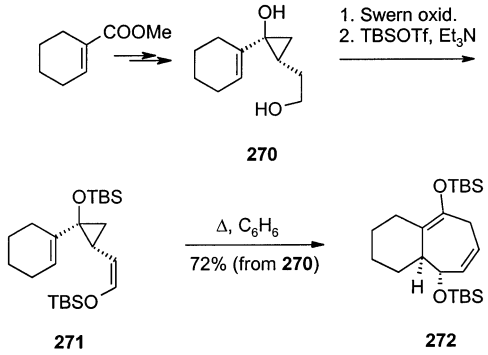
Scheme 112



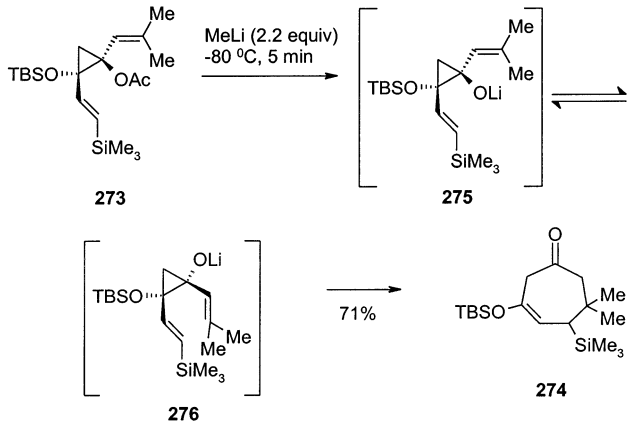
few results on cyclopropanol derivatives being involved in this reaction have appeared.[74,403] Cha and co-workers developed a stereoselective synthesis of bicyclic compounds with fused seven-membered rings based on tandem application of cyclopropanation of 1-cycloalkene-1-carboxylate and the oxy-Cope rearrangement.[403] For example, chemoselective Swern oxidation of diol **270**, followed by treatment with TBSOTf and triethylamine, led to the *cis*-divinylcyclopropanol derivative **271**, which underwent the oxy-Cope rearrangement when heated at reflux in benzene to give the bicyclic cycloheptadiene **272** in good yield (Scheme 113).

The anionic oxy-Cope rearrangement of *cis*-divinylcyclopropanolates proceeds at low temperatures very rapidly and stereospecifically. When the *trans*-divinylcyclopropanol derivative **273** (the corresponding cis-isomer could not be obtained due to its instability) was treated with an excess of MeLi at −80 °C for 5 min and then quenched with acetic acid, cycloheptenone **274** was obtained in good yield. All steps, including isomerization of the *trans*-divinylcyclopropanol derivative **275** into the cis-isomer **276**, are thought to be rapid, even at −80 °C.[74]

Scheme 113



Scheme 114



IV. Acknowledgments

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