*Russian Journal of Organic Chemistry, Vol. 40, No. 9, 2004, pp. 1227–1257. Translated from Zhurnal Organicheskoi Khimii, Vol. 40, No. 9, 2004, pp. 1279–1432.*
*Original Russian Text Copyright © 2004 by L. Kas'yan, Tarabara, A. Kas'yan.*

**REVIEW**

# Transformation of Oxiranes into Other Oxygen-Containing Heterocyclic Systems

**L. I. Kas'yan[1], I. N. Tarabara[1], and A. O. Kas'yan[2]**

[1] *Dnepropetrovsk National University, per. Nauchnyi 13, Dnepropetrovsk, 49625 Ukraine*
[2] *Rheinisch–Westfälische technische Hochschule, Aachen, Germany*

Received December 2, 2003

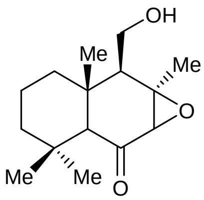
**Abstract**—The review analyzes published data on the transformations of epoxy derivatives into other oxygen-containing heterocyclic systems, such as cyclic ethers (including cage-like structures), dioxolanes, ortho esters, lactones, and cyclic carbonates, some of which occur in the nature and exhibit biological activity. Reaction mechanisms involving heterolytic, homolytic, enzymatic, and single-electron transfer processes, as well as [2+2]- and [3+3]-cycloadditions, are discussed.

## I. INTRODUCTION

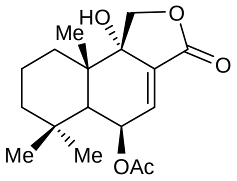
Processes involving opening of epoxy ring were extensively studied, and the results were discussed in a number of classical and recent reviews [1–10]; however, the formation of other oxygen-containing heterocycles from oxiranes was not the subject of a special study. Up to now, general relations holding in stereoelectronic control of the reaction with regard to orientation of unshared electron pair on the heteroatom have been studied (principle of least nuclear motion) [11], ring closure rules determining the reaction regioselectivity have been developed [12], and the possibility for controlling oxirane ring opening and closure via introduction of protecting groups has been established [13]. In the present review, specific attention is given to the results of studies published in the past decade.

## II. OCCURRENCE IN THE NATURE AND BIOLOGICAL ACTIVITY

Oxygen-containing cyclic systems having furan, di- and tetrahydrofuran, pyran, and oxetane rings are quite promising from the viewpoint of their high biological activity [14–16]; such systems are structural fragments of a number of natural compounds. Sesquiterpene keto epoxide uvidine (**1**) was used to obtain tricyclic sesquiterpene lactone cinnamosmolide (**2**), an analog of drimane derivatives which exhibit pronounced cytotoxic activity [17].



**1**

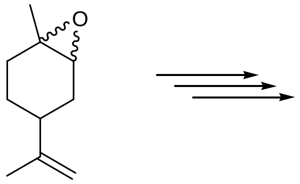


**2**

A quite illustrative example is the synthesis of optically active pheromone bicolorin (**3**) on the basis of epoxy derivative of limonene [18] (Scheme 1). Compounds exhibiting antitumor activity and containing furan and lactone fragments were synthesized from 16α,17α-epoxy steroids [19], as well as from euniolide analogs [20]. Al-Qawasmeh *et al.* [21] reported on

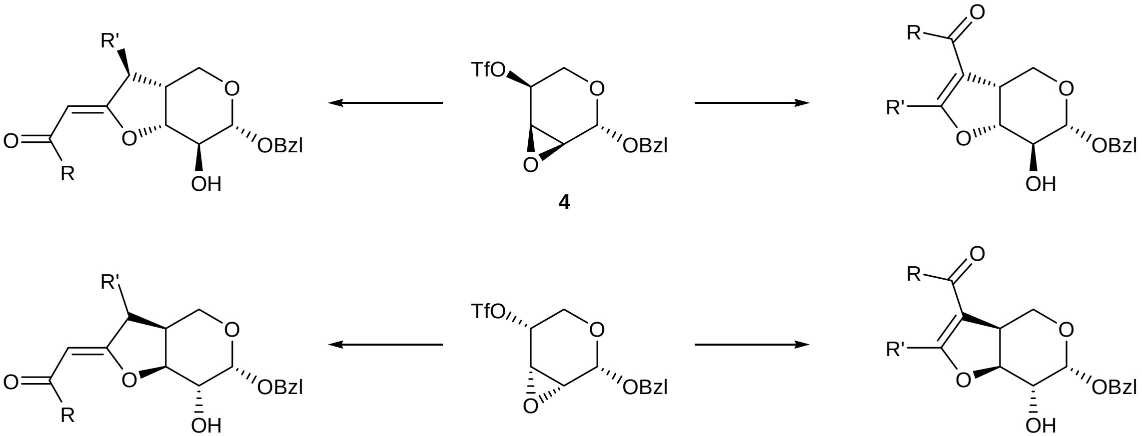
1070-4280/04/4009-1227 © 2004 MAIK "Nauka/Interperiodica"

**Scheme 1.**



**3**

**Scheme 2.**

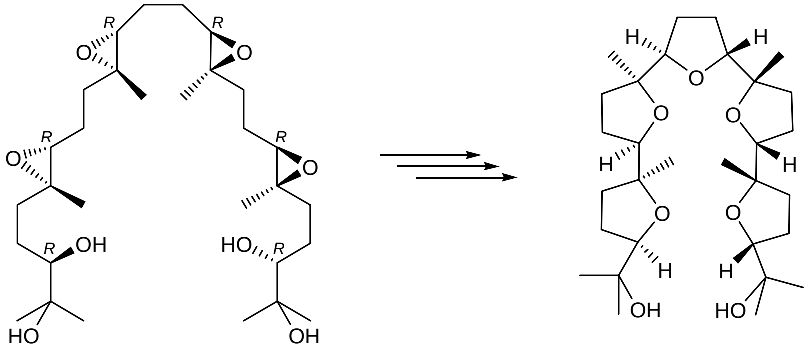


**4**

**5**

effective syntheses of polyfunctional dihydro- and tetrahydrofurans and γ-lactones with the use of anhydro sugars **4** and **5** as enantiomerically pure building blocks [21] (Scheme 2). Various cascade cyclizations of di- and polyepoxy derivatives were effected both by chemical methods and enzymatically, the latter processes involved biosynthesis of ionophoric antibiotics [22]. While searching for approaches to glabrescol which is the first pentacyclic representative of oxasqualenoids, Xiong and Corey [23] performed total enantioselective three-step synthesis of polytetrahydrofuran **7** from tetraepoxide **6** [23] (Scheme 3). Policyclic ethers of marine origin, such as brevetoxins, maitotoxins, etc., possess a high bio-

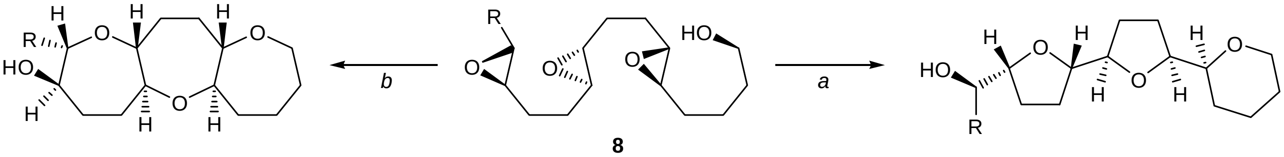
**Scheme 3.**



**6**

**7**

**Scheme 4.**



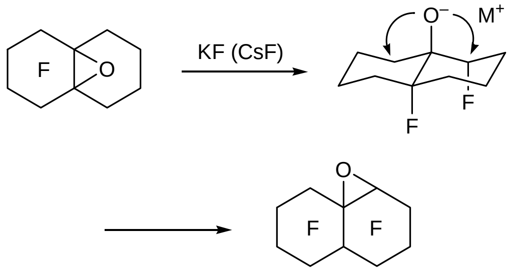
**8**

logical activity [24]. These compounds can be obtained from acyclic polyepoxy derivatives **8**. The transformations occur according to the Baldwin rule (path *a*) [12] or contrary to it (path *b*) (Scheme 4).

## III. SYNTHESIS OF HETEROCYCLES WITH ONE OXYGEN ATOM

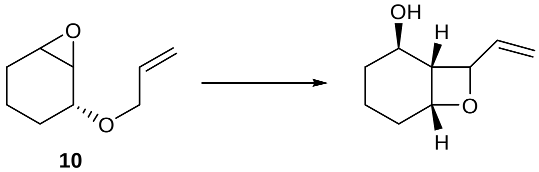
New three-membered oxygen-containing systems are formed, e.g., via isomerization of polyfluorinated epoxide **9** [25] (Scheme 5).

**Scheme 5.**



Analysis of published data indicates that, among cyclic ethers, tetrahydrofuran derivatives are the most accessible via transformations of oxiranes. Syntheses of oxetanes have been reported only in a few papers; an example is the isomerization of allyl 2,3-epoxycyclohexyl ether (**10**) [26] (Scheme 6).

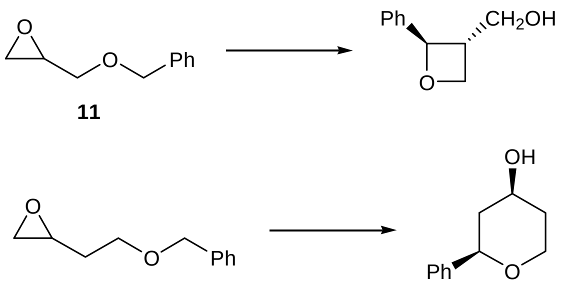
**Scheme 6.**



**10**

Transformations of benzyl ethers **11** and **12** into oxetanes and tetrahydropyrans were described by Cirelli *et al.* [27] (Scheme 7). The different regioselectivities in these reactions (which were performed in the presence of butyllithium) were interpreted in terms of structural specificity of the substrates, in particular in terms of mutual arrangement of the oxirane and nucleophilic center in the transition state.

**Scheme 7.**

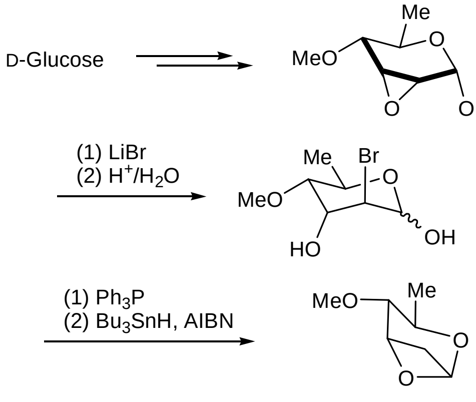


**11**

**12**

An unusual structure (**13**) having an oxetane fragment was obtained on the basis of D-glucose [28] (Scheme 8).

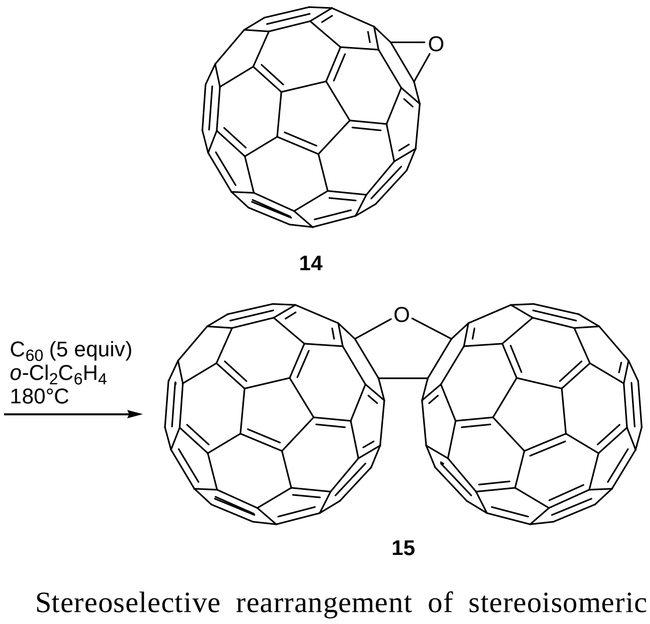
**Scheme 8.**



**13**

Smith *et al.* [29] reported on the synthesis of an unusual furan analog (**15**) including two fullerene molecules (Scheme 9) from epoxyfullerene **14** which was synthesized in 1992 [30].

**Scheme 9.**

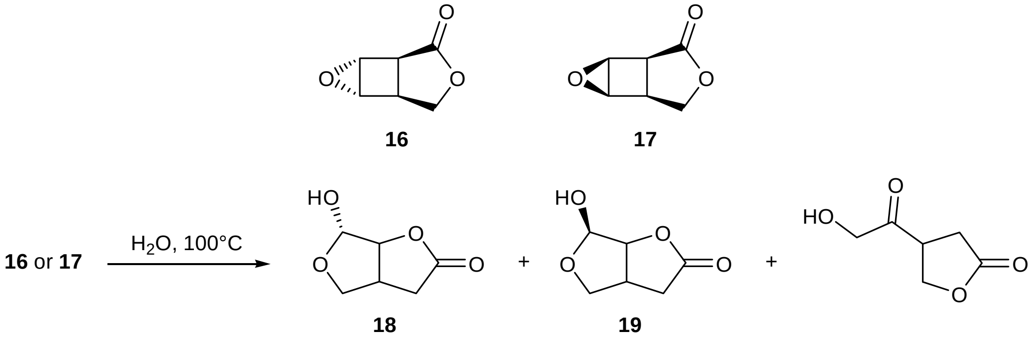


**14**

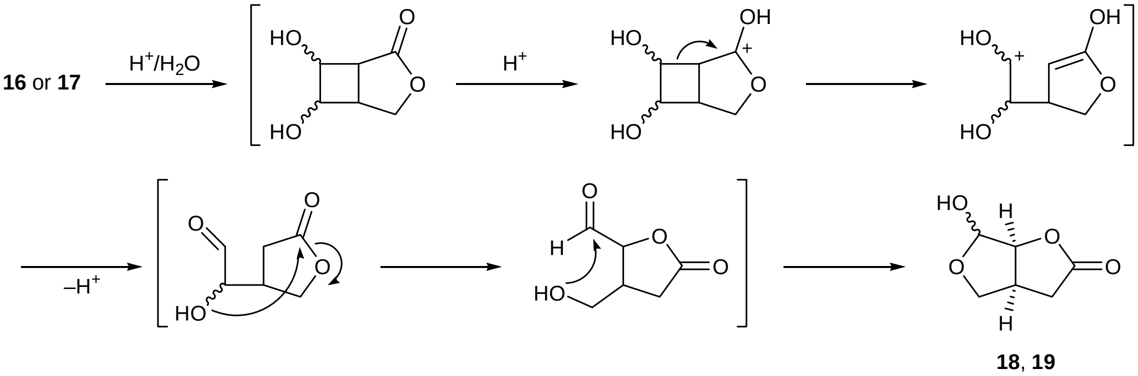
**15**

Stereoselective rearrangement of stereoisomeric 6,7-epoxy-3-oxabicyclo[3.2.0]heptan-2-ones **16** and **17** in water leads to bicyclic butyrolactones **18** and **19** (Scheme 10). The latter were used as initial compounds in the synthesis of new bicyclic nucleosides

**Scheme 10.**



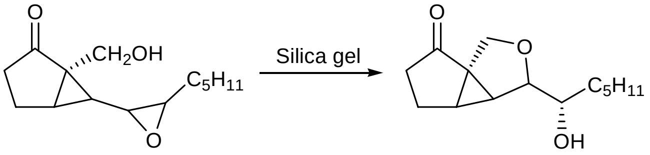
**Scheme 11.**



[31]. Stereoisomeric hydroxyperhydrofurofuranones **18** and **19** were obtained at a ratio of 9:1; the mechanism of their formation is shown in Scheme 11.

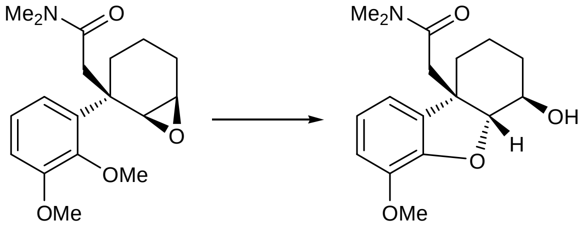
The ring closure can involve the side-chain epoxy fragment in **20**; this process is not hampered by cyclopentane–cyclopropane ring fusion [32] (Scheme 12). Some oxirane ring transformations, e.g., in compound **21**, are accompanied by elimination of methyl group from methoxy fragment, as shown in Scheme 13 [33, 34]. Tetrahydrofurans were obtained by chemo-, regio-, and stereoselective cyclization of 1,3-bis(trimethylsiloxy)-1,3-butadienes with epoxy derivatives (Scheme 14). An appropriate catalyst for such transformations is titanium tetrachloride; among others, zinc chloride, boron trifluoride–ether complex, etc., were used [35]. The reaction includes regioselective attack by the terminal carbon atom of the reagent at the epoxy ring. The configuration of the reaction center in intermediate **22** is inversed, and cyclization of **22** gives intermediate **23**. Dihydrofuran fragment was formed in the reaction of epoxy derivative **24** with telluride ion [36] (Scheme 15).

**Scheme 12.**



**20**

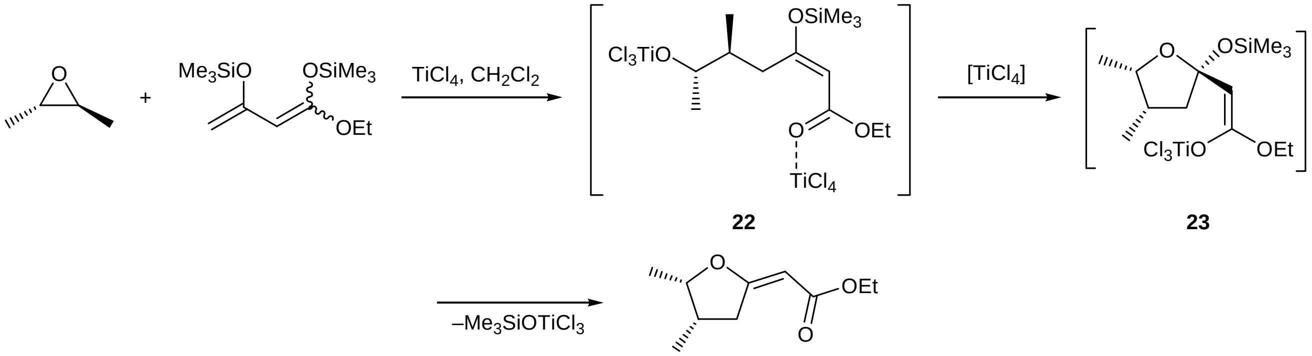
**Scheme 13.**



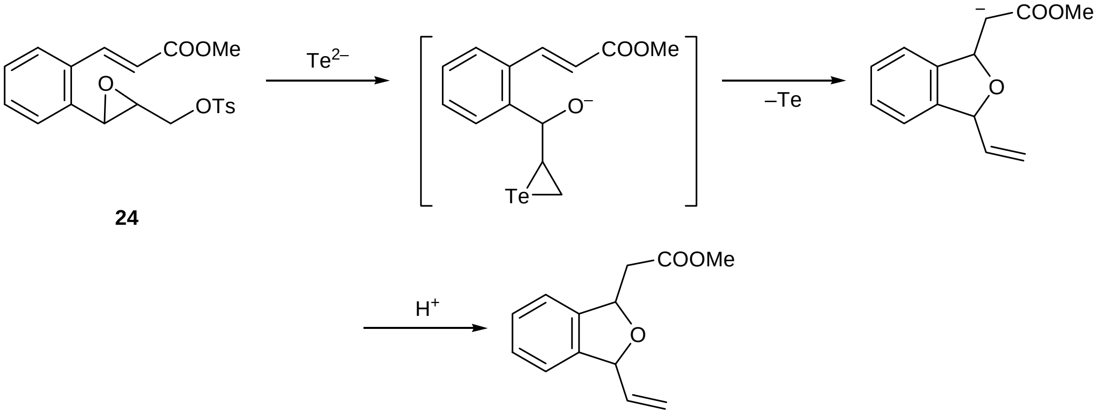
**21**

In the recent years, much attention was given to the synthesis of furans as structural fragments of natural compounds and those widely used in organic synthesis [37]. Epoxy derivatives with substituents containing double and triple bonds are suitable for the synthesis of unsaturated cyclic oxygen-containing systems. Disubstituted furans **25** were obtained on the basis of various epoxycycloalkanes (Scheme 16). It was presumed that the reaction involves formation of an intermediate which undergoes dehydration through the corresponding oxonium ion. For alicyclic epoxides, a different

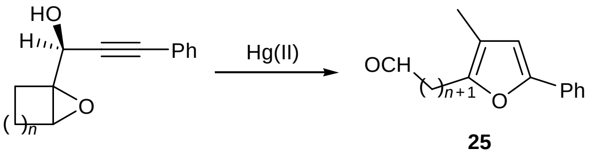
**Scheme 14.**



**Scheme 15.**

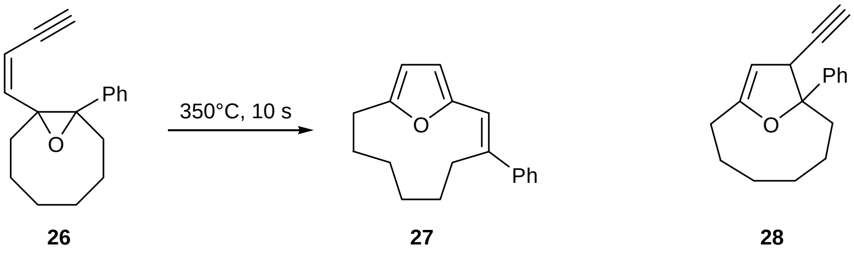


**Scheme 16.**

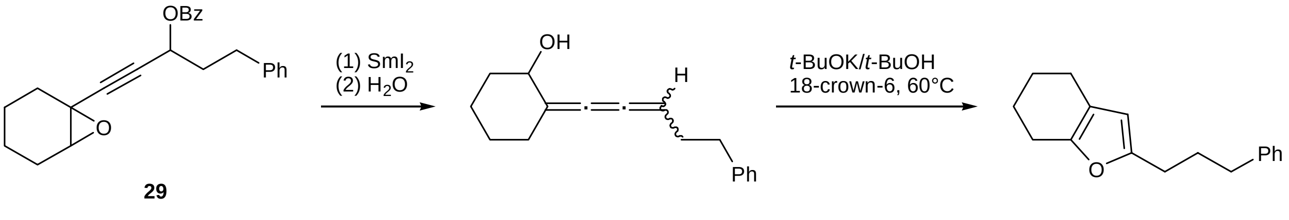


$n = 2–4$.

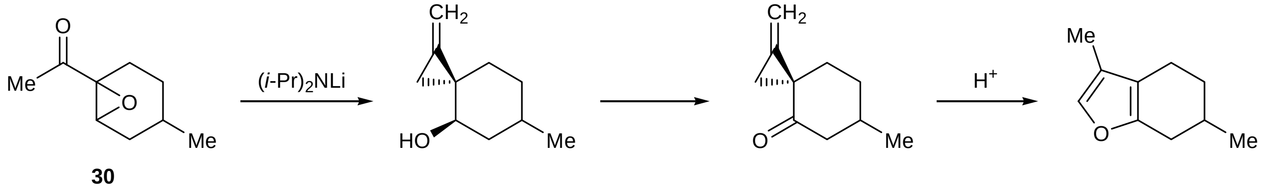
**Scheme 17.**



**Scheme 18.**



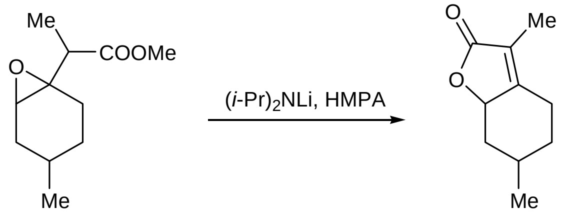
**Scheme 19.**



way of aromatization with formation of carbonyl group was reported [37]. Heterocyclization of 1-buten-3-ynyl-substituted epoxycyclooctane **26** can be effected under different conditions [38]. Apart from the major product containing a furan fragment (compound **27**, 70%), a mixture of stereoisomeric dihydrofurans **28** was obtained (Scheme 17).

Aurrecoechea *et al.* [39] described a two-step one-pot synthesis of 2,3,5-trisubstituted furans from 4,5-epoxy-2-alkynyl ethers **29** (Scheme 18). The process includes samarium iodide-promoted reduction and base-catalyzed cycloisomerization. Furan derivatives were also synthesized in a basic medium from 1-acetyl-1,2-epoxycycloalkanes **30** [26] (Scheme 19). Cyclization of epoxycyclohexane **31** also occurs by the action of a base [40] (Scheme 20).

**Scheme 20.**



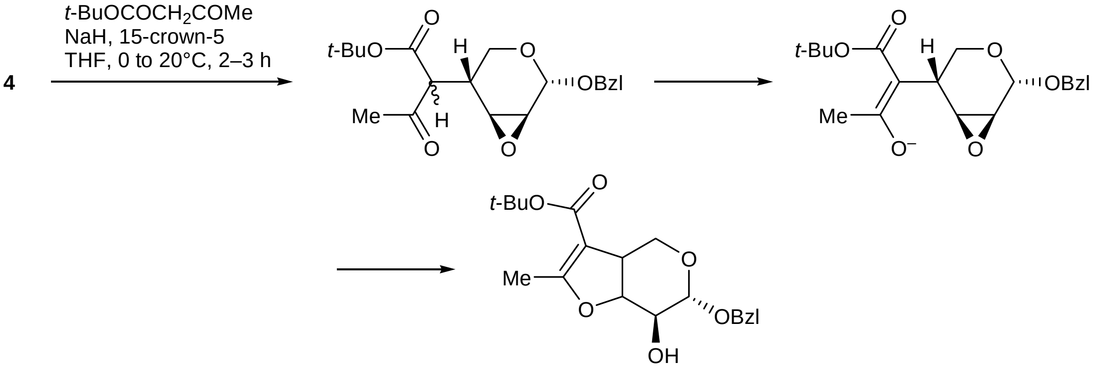
**31**

Quite successful attempts to obtain polysubstituted chiral dihydrofurans **32** on the basis of carbohydrate templates were reported in [41]. Compounds **32** were obtained in one step by reaction of epoxypyranose trifluoromethanesulfonates **4** with monoanions derived from 1,3-dicarbonyl compounds (Scheme 21). Spiro compound **35** was synthesized in 10% yield by isomerization of substituted 2,3-epoxypinane **33**; the major product was cyclopropane **34** [42] (Scheme 22).

In 1998, Marson *et al.* [37, 43] developed a simple procedure for the rearrangement of 2,3-epoxy alcohols, which leads to substituted furans **36** and 2,3-dihydropyran-4(4*H*)-ones **37** (Scheme 23). Here, the reaction direction is determined by the substrate structure, but in many cases five- and six-membered oxygen-containing rings are formed simultaneously [16, 44–46]. In particular, acid-catalyzed cyclization of optically active epoxy derivative **38** gives a mixture of five- and six-membered cyclic ethers [44] (Scheme 24). The ratio of ethers **39** and **40** obtained from 2-(3-hydroxypropyl)-2-methoxymethyloxiranes depends on the solvent and the presence (or absence) of molecular sieves [46] (Scheme 25). According to the data of [45], the ratio of isomeric products **42** and **43** (Scheme 26) ranges from 1.5:1 in acetonitrile to 17:1 in diethyl ether, i.e., the reaction selectivity is controlled by the solvent. Here, *endo* attack by the nucleophile ($H_2O$) on bridged oxonium intermediates **41** prevails.

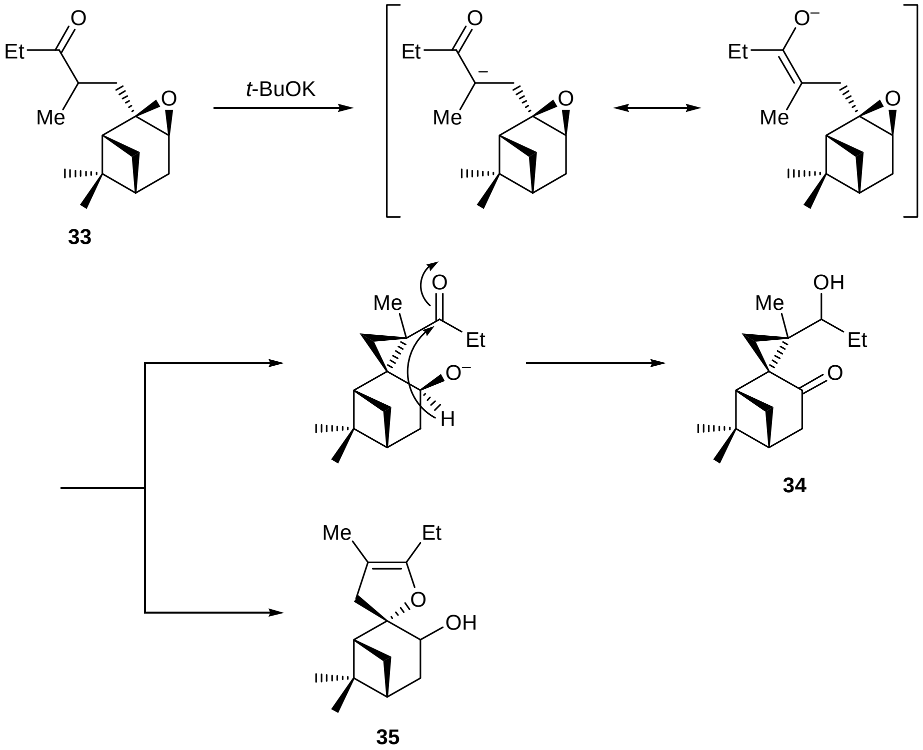
Taylor *et al.* [47, 48] studied concurrent intramolecular cyclization of epoxy derivatives with participation of an aromatic ring or double bond in

**Scheme 21.**



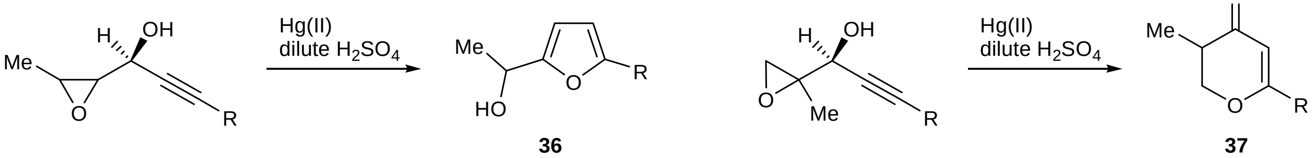
**32**

**Scheme 22.**



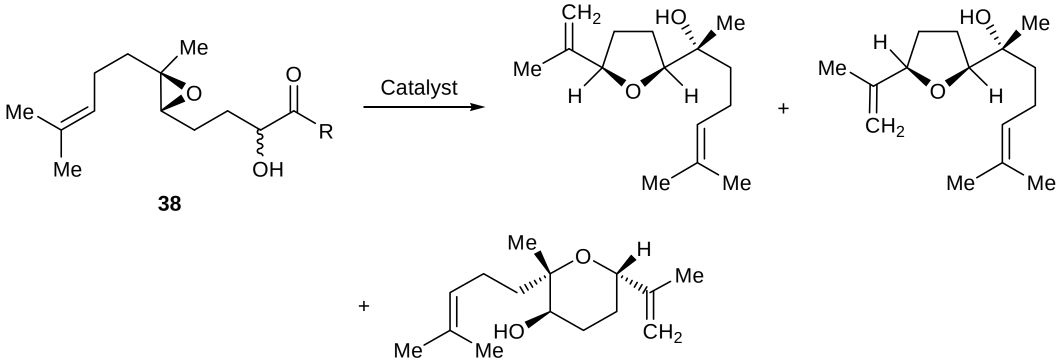
**33**, **34**, **35**

**Scheme 23.**



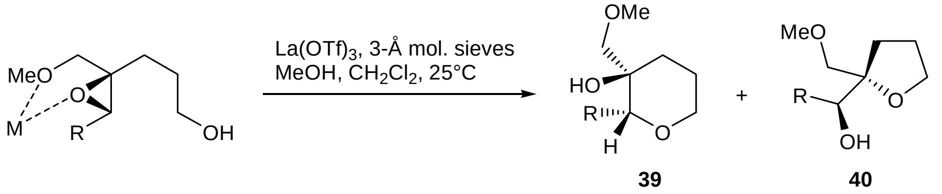
**36**, **37**

**Scheme 24.**



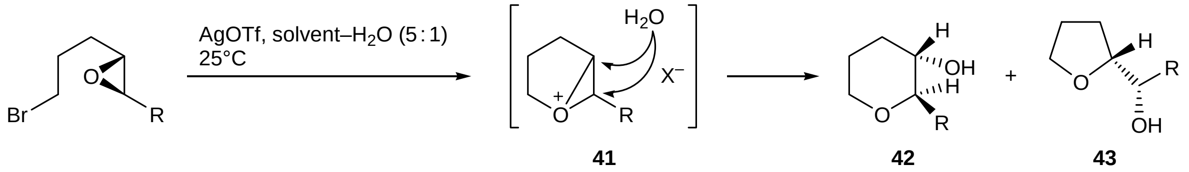
**38**

**Scheme 25.**

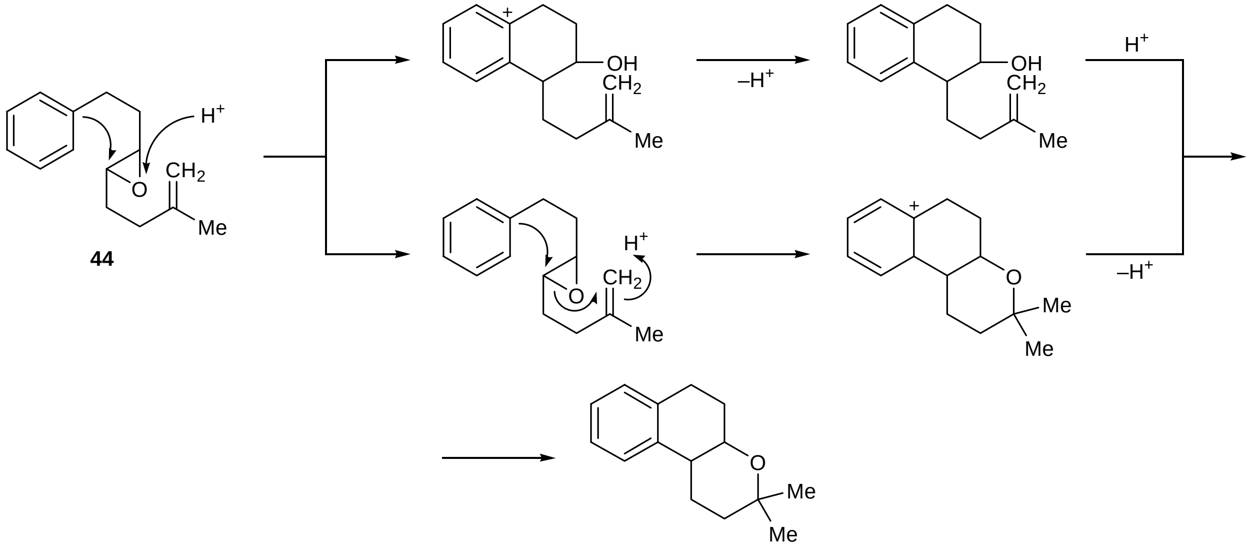


**39**, **40**

**Scheme 26.**

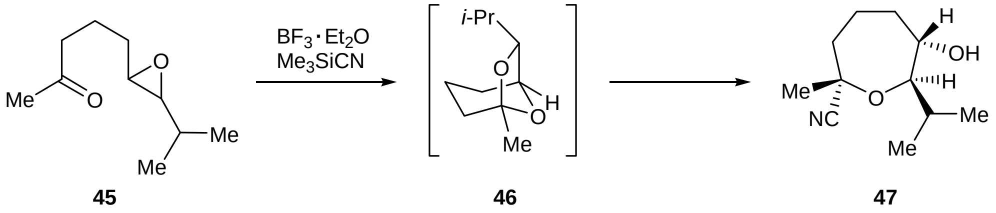


**Scheme 27.**

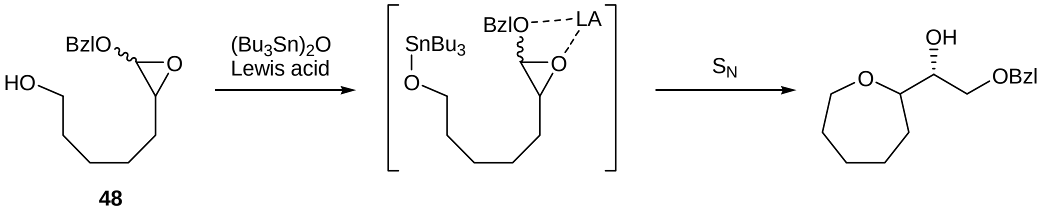


the substituent. The effect of substituents on the two cyclization pathways was determined. Scheme 27 illustrates possible ways of cyclization of compound **44**. The cyclization of epoxy ketone **45** in the presence of trimethylsilyl cyanide involves intermediate formation of bicyclic acetal **46**. Cleavage of one acetal bond in the latter yields oxepane **47** as a single stereoisomer [49] (Scheme 28). It should be noted that replacement of trimethylsilyl cyanide by other silicon-containing reagents ($Ph_3SiH$, $CH_2{=}CHCH_2SiMe_3$, $Me_3SiC{\equiv}CAlEt_2$) leads to formation of tetrahydropyran derivatives [49]. 2-(2-Benzyloxy-1-hydroxyethyl)oxepane was obtained by cyclization of 2-benzyloxy-3-(5-hydroxypentyl)oxirane (**48**) (Scheme 29). The cyclization occurred as a result of *exo* attack promoted by Lewis acids, such as zinc, tin, and lanthanide trifluoromethanesulfonates

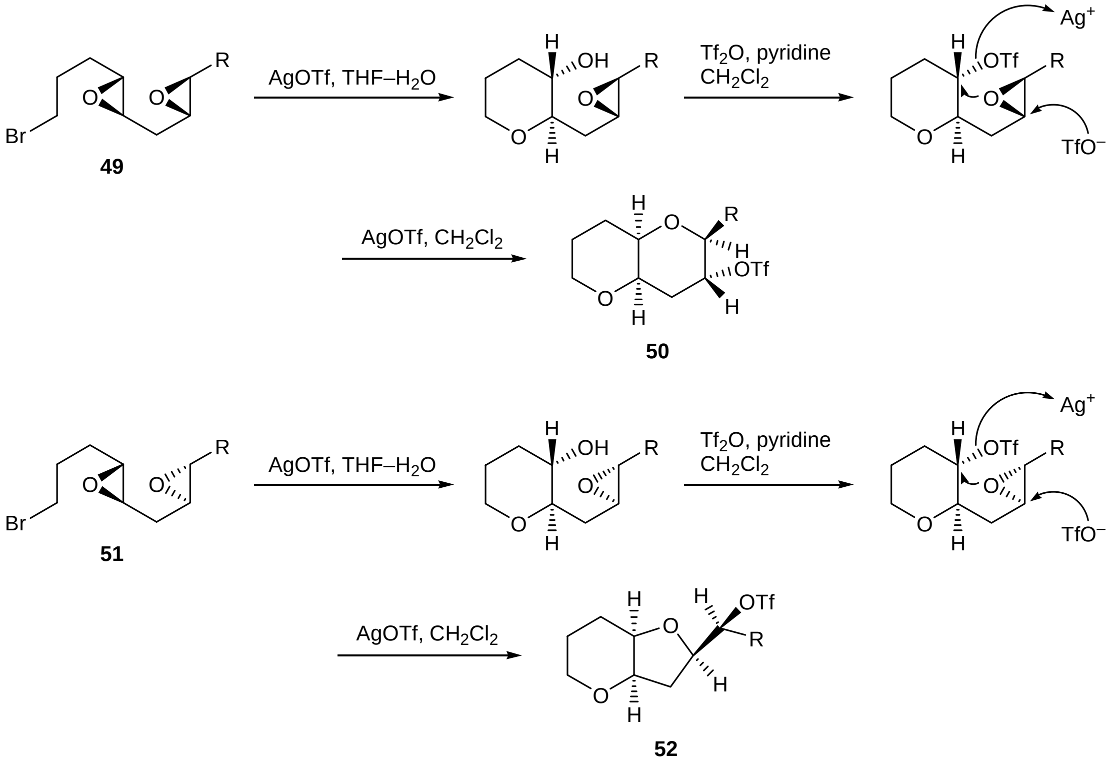
**Scheme 28.**



**Scheme 29.**



**Scheme 30.**



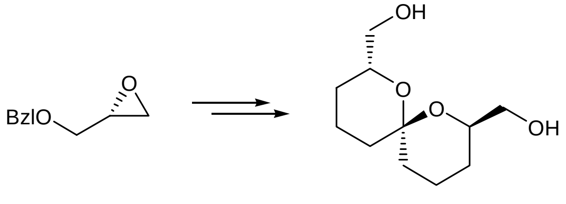
R = $t$-BuPh$_2$SiOCH$_2$.

[50]. Following an analogous procedure, a series of disubstituted oxepanes was synthesized [51].

Fujiwara *et al*. obtained seven- and eight-membered cyclic ethers and their unsaturated analogs by cyclization of *trans*- and *cis*-5,6-epoxy-5-methoxymethylheptan-1-ols and *trans*- and *cis*-6,7-epoxy-6-methoxymethyl-3-octen-1-ols in the presence of Lewis acids [52]. Chelation of lanthanum trifluoromethanesulfonate at the oxygen atoms of the oxirane ring and methoxy groups favors predominant formation of the *endo* isomers [52].

Various cyclization products were obtained from 1-bromo-9-*tert*-butyldiphenylsiloxy-4,5:7,8-diepoxynonane having a bulky substituent [53]. Compound **49** with a *syn*,*trans* structure and its *anti*,*trans* isomer **51** were converted into oxygen-containing bicyclic systems **50** and **52** (Scheme 30).

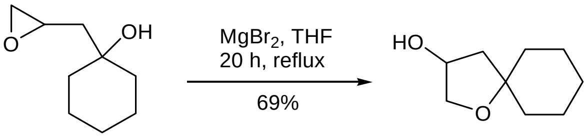
**Scheme 31.**



**53**

Uckun *et al*. [54] described a multistep procedure for the synthesis of a new 2,2'-spirobipyran, SPIKE-P (**53**), which was then used in the preparation of naturally occurring spongistatin I (Scheme 31). Spiro structure **55** was obtained by regio- and stereoselective cyclization of epoxy alcohol **54** [55] (Scheme 32).

**Scheme 32.**

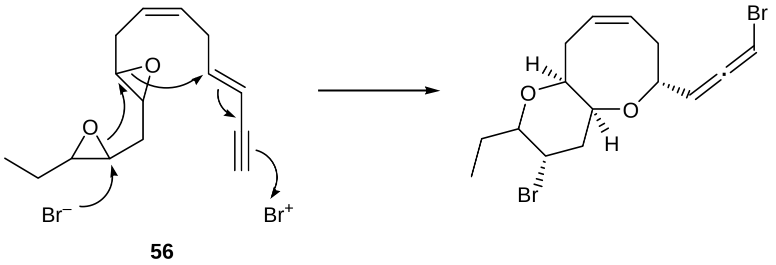


**54** **55**

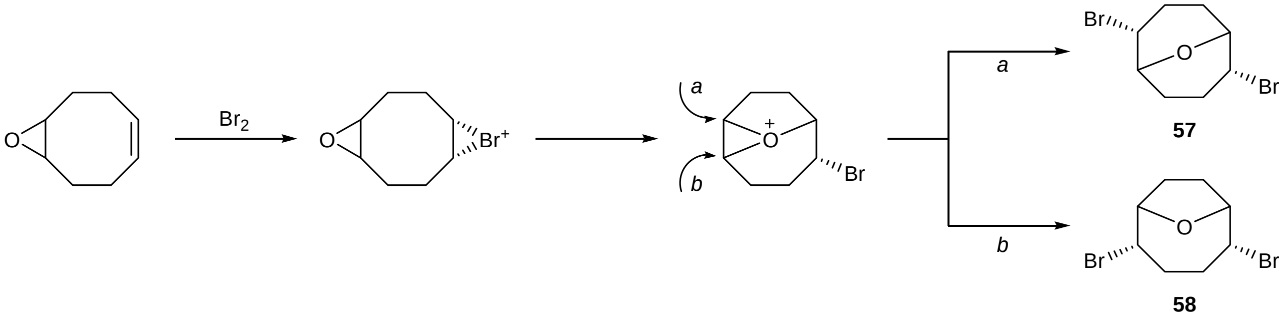
Natural bromine-containing sesquiterpenes with oxygen-containing heterorings were found. According to Davies *et al*. [56], such sesquiterpene systems are products of bromination of unsaturated epoxy derivatives, in particular, of compound **56** (Scheme 33) .

Cyclic ethers with medium-size rings are structural fragments of toxins and other bioactive compounds [57]. In this connection, studies on halogenation of

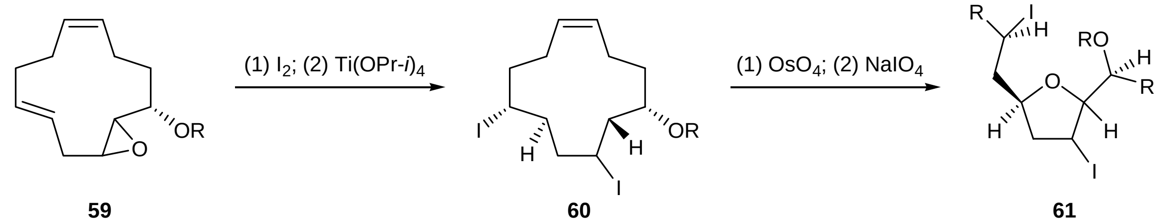
**Scheme 33.**



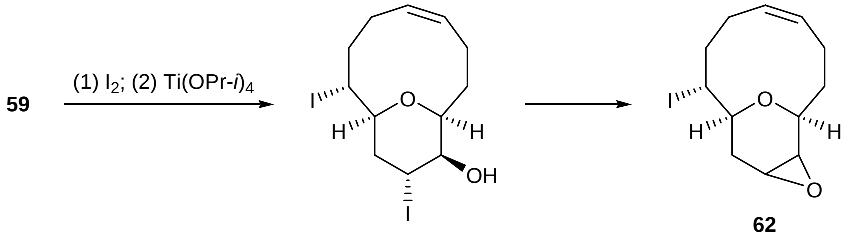
**Scheme 34.**



**Scheme 35.**



**Scheme 36.**

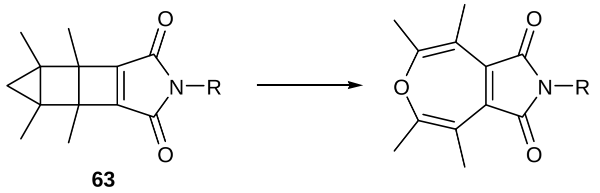


unsaturated epoxides with medium-size rings ($C_8$–$C_{10}$) have been initiated. Such substrates could give rise to transannular interactions leading to formation of smaller cyclic systems [56–60]. For example, the bromination of epoxycyclooctene gives a mixture of dibromo derivatives **57** and **58** at a ratio of 1.22:1 [56] (Scheme 34). The chlorination of unsaturated epoxides was described in [59], and halofluorination and hydrobromination, in [58].

Using 10-acetoxy-8,9-epoxy-1,5-cyclododecadiene (**59**, R = Ac), Zarraga *et al.* [61] developed a strategy for the regio- and stereoselective synthesis of substituted tetrahydrofurans and tetrahydropyrans via intramolecular heterocyclization of the substrate. Addition of iodine to acetate **59** (R = Ac) gave compound **60** in 66% yield. The subsequent hydrolysis, *cis*-hydroxylation, and oxidation of the resulting diol afforded dialdehyde **61** [R = $(CH_2)_2CHO$] (Scheme 35). The iodination of the corresponding alcohol (**59**, R = H) follows a different scheme due to participation of the hydroxy group and leads to formation of tricyclic diepoxy derivative **62** [61] (Scheme 36).

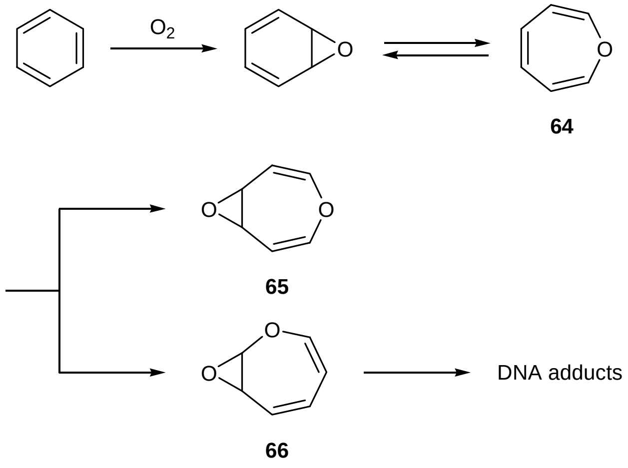
Polycyclic systems including unsaturated seven-membered ether fragments were obtained by nontrivial methods. Synthetic approaches to oxepines were developed on the basis of unstable strained epoxy derivatives **63** [62] (Scheme 37), as well as via Cope rearrangement of *cis*-2,3-divinyl epoxides [63].

**Scheme 37.**

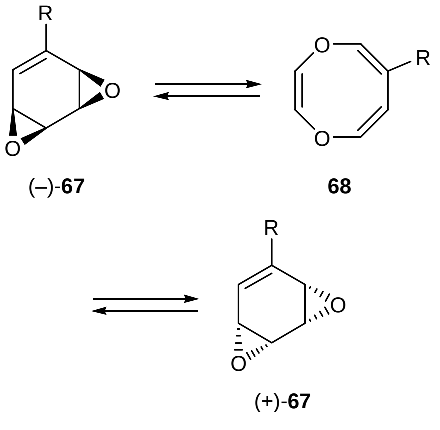


Oxepines were also obtained as components of tautomeric mixtures, which were formed by monooxygenase-catalyzed oxidation of aromatic systems [64] (Scheme 38). Ethers **64–66** and their analogs play an important role in the metabolism of carcinogenic aromatics. Enantiopure *syn*-diepoxycyclohexenes **67** were reported to undergo thermal racemization through 1,4-dioxocines **68** (R = Cl, Br, I) [64] (Scheme 39).

**Scheme 38.**



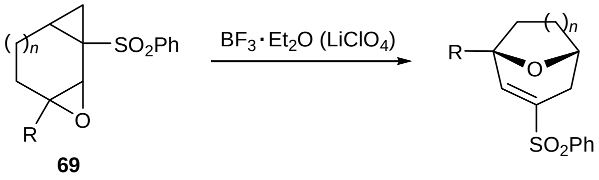
**Scheme 39.**



## IV. SYNTHESIS OF CYCLIC ETHERS WITH CAGE-LIKE FRAGMENTS

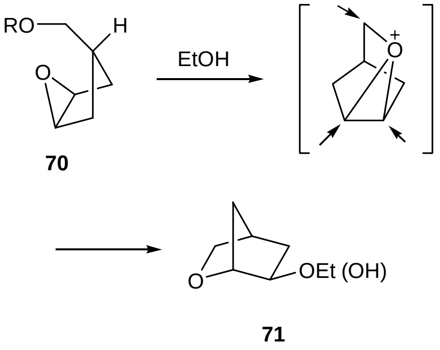
Compounds containing epoxy bridges constitute a specific group of oxirane transformation products. Lofstrom *et al.* [65] described rearrangement of epoxybicyclo[4.1.0]heptanes and epoxybicyclo[5.1.0]octanes **69** (*n* = 1, 2; Scheme 40).

**Scheme 40.**



Oxygen bridge is also formed in the solvolysis of *cis*-6-oxabicyclo[3.1.0]hexan-3-ylmethyl *p*-bromobenzenesulfonate (**70**, R = $SO_2C_6H_4Br$-*p*) [66]; an analogous process with the corresponding *trans* isomer is impossible. The reaction afforded alcohol (or ether) **71** (Scheme 41).

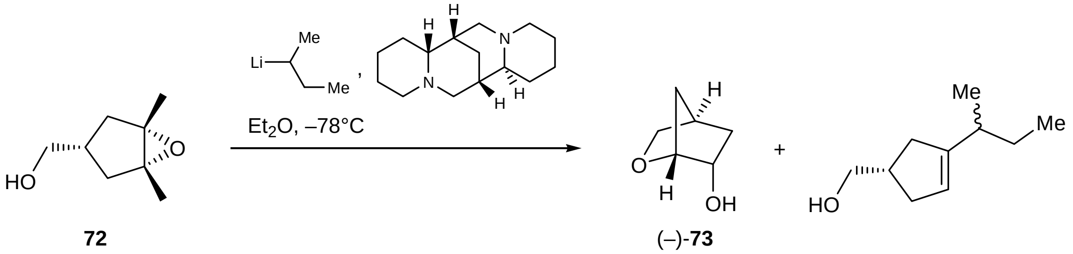
**Scheme 41.**



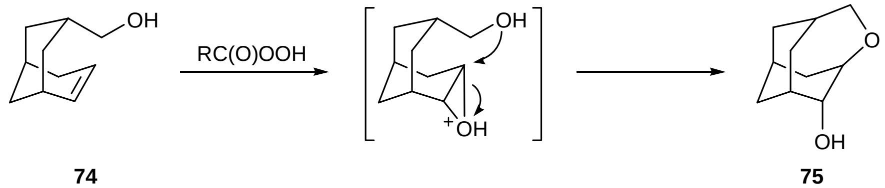
Structurally related compound **73** was recently obtained by enantioselective deprotonation of 1,2-epoxy-4-hydroxymethylcyclopentane **72** using (–)-sparteine as asymmetric catalyst [67] (Scheme 42).

Cage-like ether **75** was synthesized by rearrangement of 2,3-epoxy-7-hydroxymethylbicyclo[3.3.1]-nonane which was formed *in situ* by epoxidation of olefin **74** [68] (Scheme 43). The hydrolysis of epoxy derivative **76** was also accompanied by heterocyclization [69] (Scheme 44). Quite demonstrative examples were reported for formation of oxygen-containing systems on the basis of sterically strained molecules. Oxetanes **77** (R = H, OBzl) were obtained by rearrangement in the presence of *tert*-butoxide ion [70–73] (Scheme 45).

**Scheme 42.**

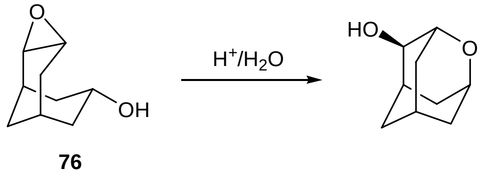


**Scheme 43.**

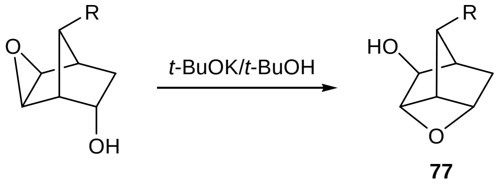


Le Drian and Vogel developed procedures for the synthesis of 4,7-dioxatricyclo[3.2.1.0$^{3,6}$]octan-*exo*-2-ol (**79**) which is an efficient herbicide and plant growth regulator [74]. Optically active compound **79** with an enantiomeric purity of 99% was obtained by treatment of alcohol (+)-**78** with potassium hydride in the system dimethoxyethane–HMPA. Later on, a direct procedure was proposed for the transformation of 2,5:3,4-diepoxycyclohexanone (**80**) into oxetane **79** by the action of lithium dihydrido(diisobutyl)aluminate [70, 75] (Scheme 46). An analogous reaction with epoxy derivative **81** became an important step in the synthesis of tropane alkaloids [76] (Scheme 47).

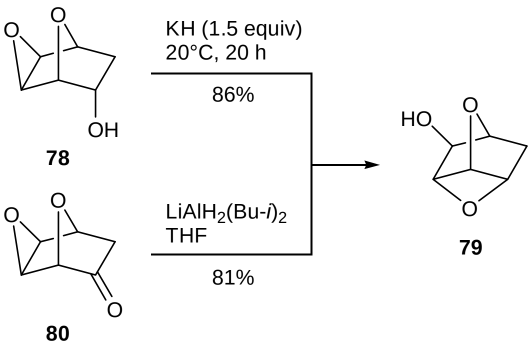
**Scheme 44.**



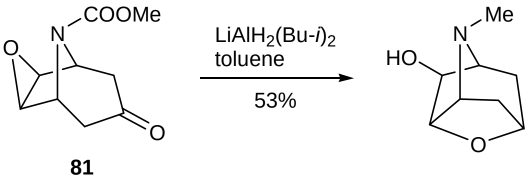
**Scheme 45.**



**Scheme 46.**



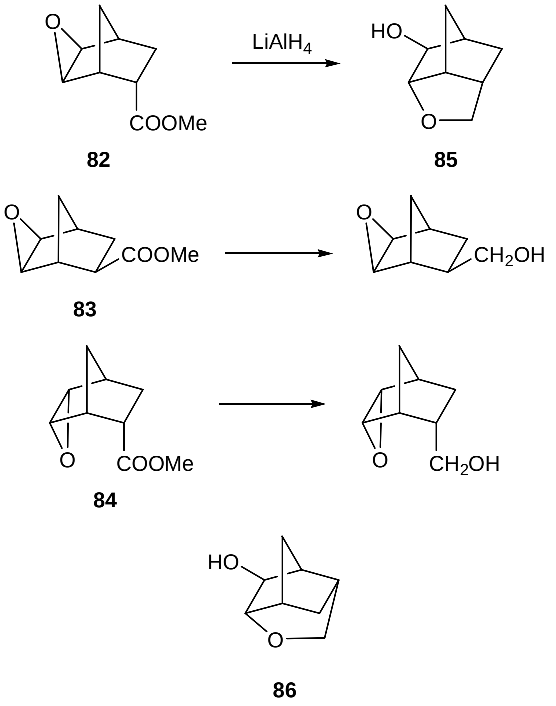
**Scheme 47.**



In the reduction of functionally substituted epoxynorbornanes, the determining factor is mutual orientation of the substituents [77]. Steric structure of the alcohol formed from epoxynorbornane **82** favors intramolecular attack on the *exo*-epoxy fragment. Isomeric epoxy esters **83** and **84** react in a chemoselective fashion with conservation of the epoxy fragment (Scheme 48). The structure of compound **85** was confirmed by calculation of vicinal coupling constants in esters **85** and **86** and comparison of the calculated and experimental data [78].

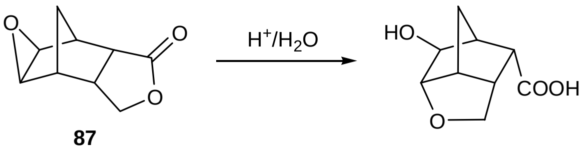
Tetrahydrofuran derivatives structurally related to compound **85** were obtained by epoxidation of substituted norbornenes [70]. The heterocyclization is favored by arrangement of the nucleophilic moiety in the area corresponding to antibonding molecular π* orbital of the emerging epoxy ring. In keeping with the Curtin–Hammett principle, the possibility for molecules to adopt a conformation favorable for formation

**Scheme 48.**



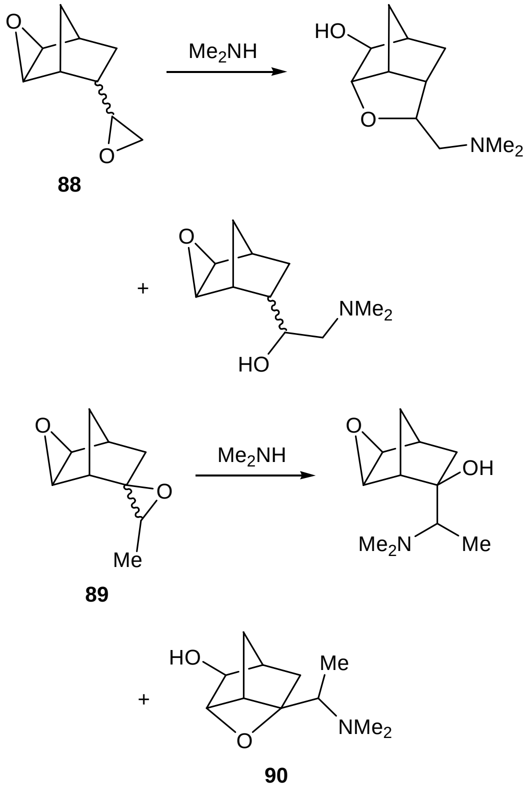
of activated complexes is especially important in these reactions [70]. The different reactivities of the hydroxy and carboxy groups in oxirane ring opening are reflected in the hydrolysis of epoxy lactone **87** [79] (Scheme 49).

**Scheme 49.**

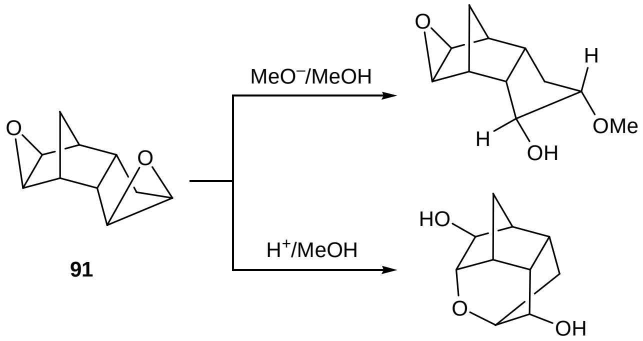


A reactive nucleophilic center can appear as a result of transformation of one epoxy ring in reactions of diepoxy derivatives of vinyl- and ethylidenenorbornenes (compounds **88** and **89**) with dimethylamine [80], which occur chemoselectively with participation of the outer epoxy fragment. Cleavage of the oxirane ring is generally regioselective (according to the Krasuskii rule), and generation of a nucleophilic hydroxy group at the rear *endo* side of epoxynorbornane in the initial step is accompanied by stereo- and regioselective attack by the nucleophile at the electrophilic carbon atom of the epoxynorbornane fragment. The cyclization is not hampered by steric strains in oxetane structure **90** [80] (Scheme 50). Methanolysis of epoxy derivatives **88** and **89** in alkaline medium [81, 82] occurs in a similar way, while the reaction with methanol in acid medium is accompanied by demethylation during heterocyclization, as in the methanolysis of compound **91** [83, 84] (Scheme 51).

**Scheme 50.**



**Scheme 51.**

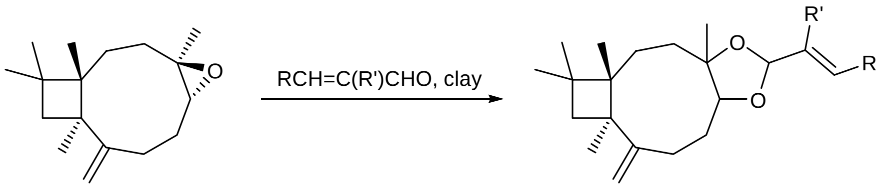


The structures of the transition states and products of acid-catalyzed methanolysis of **91** and the corresponding activation barriers were calculated in [85].

## V. TRANSFORMATIONS OF OXIRANES INTO DIOXOLANES, ORTHO ESTERS, AND TRIOXANES

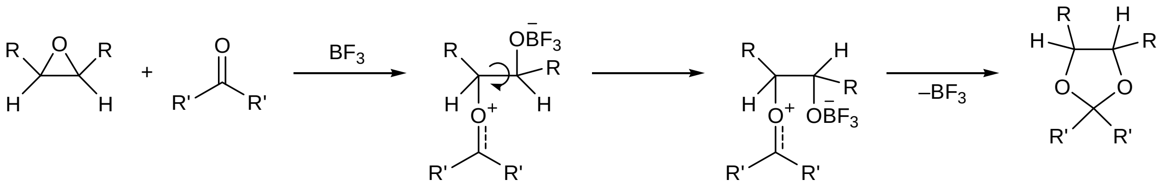
1,3-Dioxolanes are known transformation products of epoxy compounds, which are formed in the presence of Lewis acids [86, 87]. In the recent years, ruthenium [88] and titanium compounds [89] were successfully used as catalysts. Dioxolanes were obtained from epoxy derivatives of acyclic [4] and alicyclic alkenes [90], spiro compounds [91], etc. Barkhash and co-workers performed reactions of 4β,5α-epoxy derivative of cariophyllene (**92**) with carbonyl compounds, such as acrolein, crotonaldehyde, α-methylacrolein, and acetone, over clay; the authors also isolated related diols which were formed from compound **92** in the absence of aldehydes over the same catalyst [90] (Scheme 52). An example of formation of diol as the only product of the reaction of substituted epoxynorbornane with acetone was reported in [92]. This results was interpreted in terms of conformational rigidity of the substrate and difficulties in the formation of transition state leading to dioxolane: attack by the ketone from the *endo*-side of *exo*-epoxynorbornane is hindered for steric reasons (Scheme 53). Using compounds **93** and **94** as model structures, Yarovaya *et al.* [91] performed semiempirical (AM1, for cations) and molecular-mechanics calculations (MMX, for neutral molecules) and revealed the most thermodynamically stable reaction products. Barrierless protonation of stereoisomeric epoxy derivatives of camphene (compounds **93** and **94**) and α-fenchene gives common carbocation **95** which then either reacts at the aldehyde oxygen atom to afford cation **96** or undergoes 1,2-hydride shift [91] (Scheme 54). Zaitseva *et al.* [93]

**Scheme 52.**

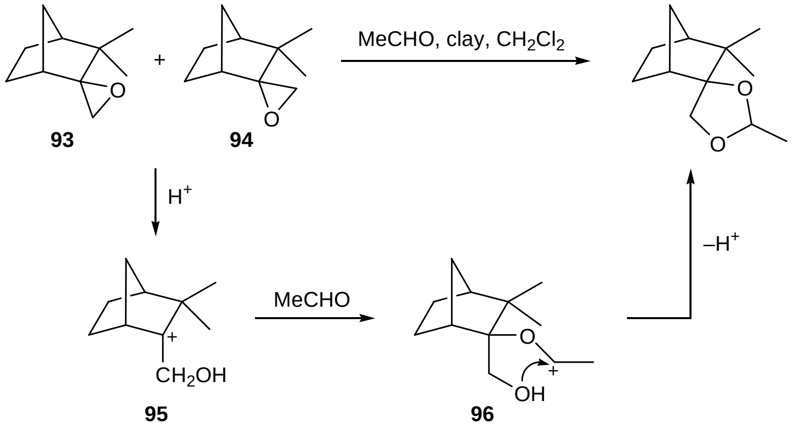


**92**

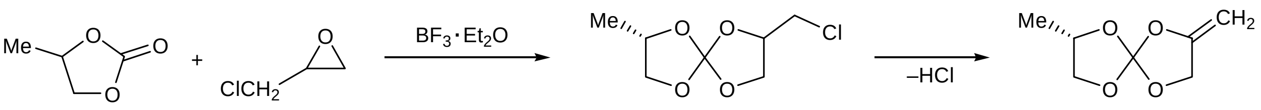
**Scheme 53.**



**Scheme 54.**

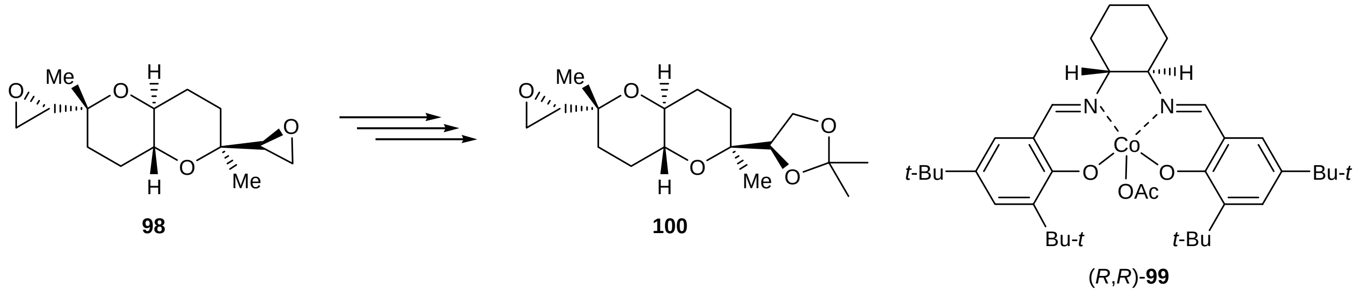


**Scheme 55.**

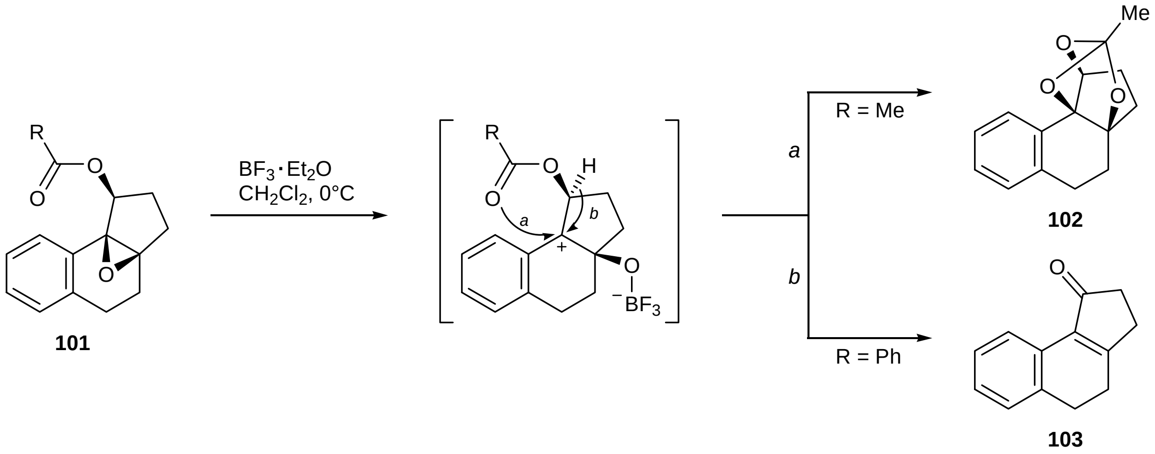


**97**

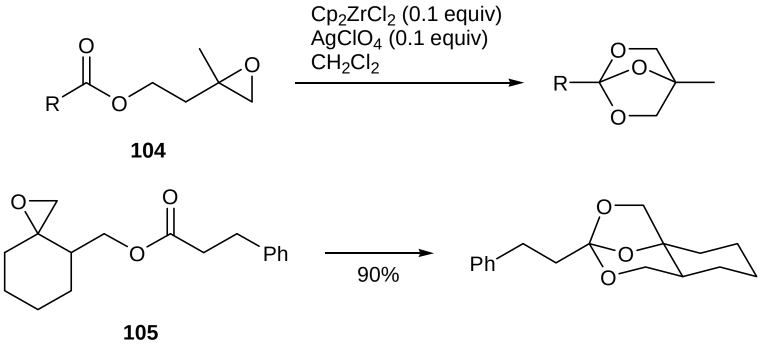
**Scheme 56.**



**Scheme 57.**



**Scheme 58.**

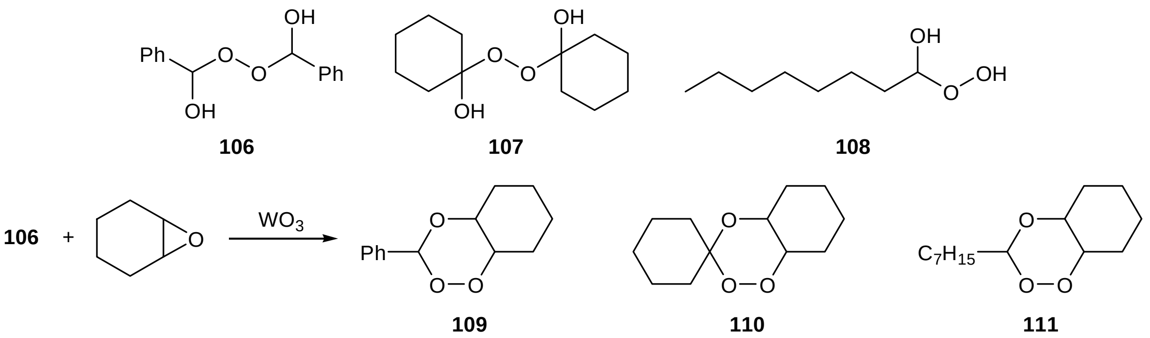


described the synthesis of spirodioxolane **97** by reaction of 2-chloromethyloxirane with propylene carbonate (Scheme 55).

Desymmetrization of centrosymmetric diepoxy derivative **98** was achieved using optically active cobalt catalyst **99** (Scheme 56). Dioxolane **100** was obtained as the final product and as stable intermediate in the synthesis of hemibrevetoxin B [94]. While developing procedures for the preparation of optically active anticarcinogenic antibiotic fredericamycin, ortho ester **102** was obtained from epoxy derivative **101** (R = $CH_3$). Under analogous conditions, epoxy compound **101** (R = Ph) was converted into ketone **103** [95] (Scheme 57).

A different approach to the synthesis of ortho esters was proposed by Wipf *et al*. [96–98]. The authors obtained 2,7,8-trioxabicyclo[3.2.1]octane via zirconocene-catalyzed rearrangement of epoxy esters **104** and **105** (Scheme 58). 1,2,4-Trioxanes were synthesized from epoxycyclohexane in methylene chloride in the presence of tungsten(VI) oxide and a catalytic amount of chlorosulfonic acid [98]; peroxides **106–108** were used as oxidants. The mechanism of formation of compounds **109–111** includes electrophilic activation

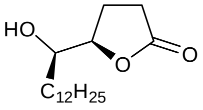
**Scheme 59.**



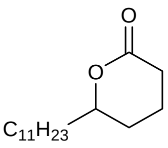
of the initial epoxy compound with $WO_3$, followed by attack on the resulting carbocation by the oxygen nucleophilic center of peroxide [99] (Scheme 59).

## VI. TRANSFORMATIONS OF OXIRANES INTO LACTONES AND ALKYLENE CARBONATES

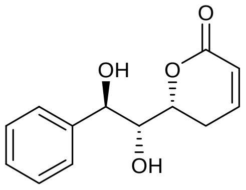
A considerable number of cyclization products obtained from epoxy compounds have a lactone structure. Some works in this field are concerned with total syntheses of biologically active natural compounds, e.g., natural acetogenin (–)-muricatacin (**112**) [100], pheromone **113** [101], cytotoxic lactone (+)-goniodiol (**114**) [102], and (–)-osmundalactone (**115**) [103].



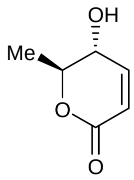
**112**



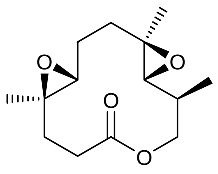
**113**



**114**



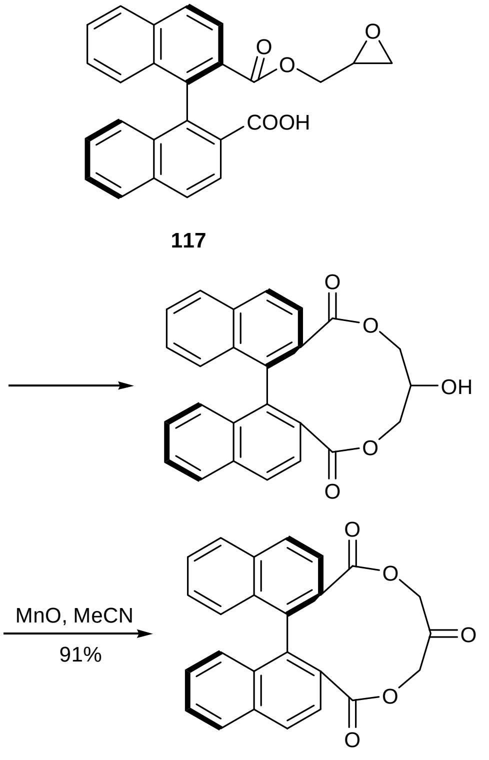
**115**



**116**

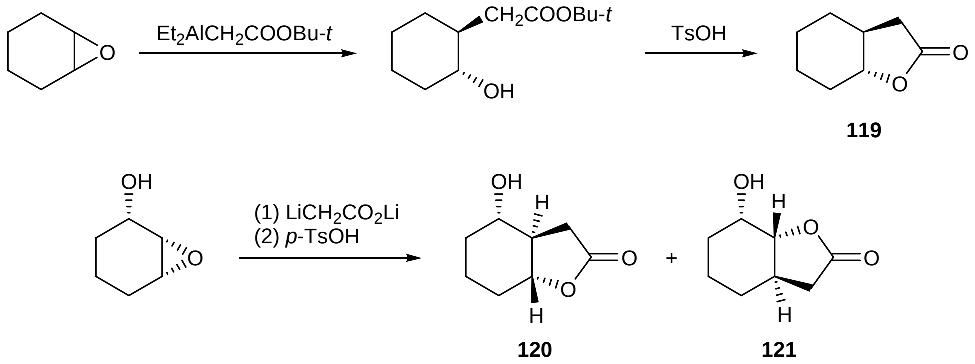
Macrocyclic epoxy lactone **116** and its analogs are transformed fairly readily into acyclic epoxycarboxylic acids which undergo cascade cyclization to afford systems containing tetrahydrofuran fragments [16, 104]. Lactones were obtained while searching for synthetic approaches to 11α,12α-epoxyprostanoids [105] and other complex products [106]. Kuroda *et al.* [107] succeeded in closing 11-membered ring in the synthesis of $C_2$-symmetric chiral ketone **118** which is an effective catalyst for asymmetric epoxidation of olefins with dioxirane. Lactonization of compound **117** was performed with the use of a cobalt catalyst (Scheme 60).

**Scheme 60.**

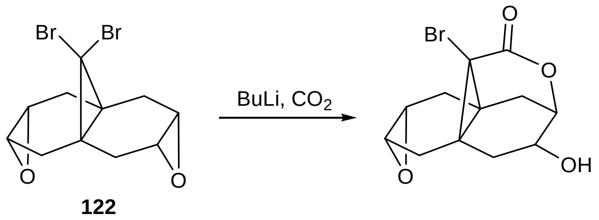


Numerous examples of the synthesis of lactones **119–121** and other related structures from epoxy derivatives by the action of metalated esters were reviewed in [108] (Scheme 61). The formation

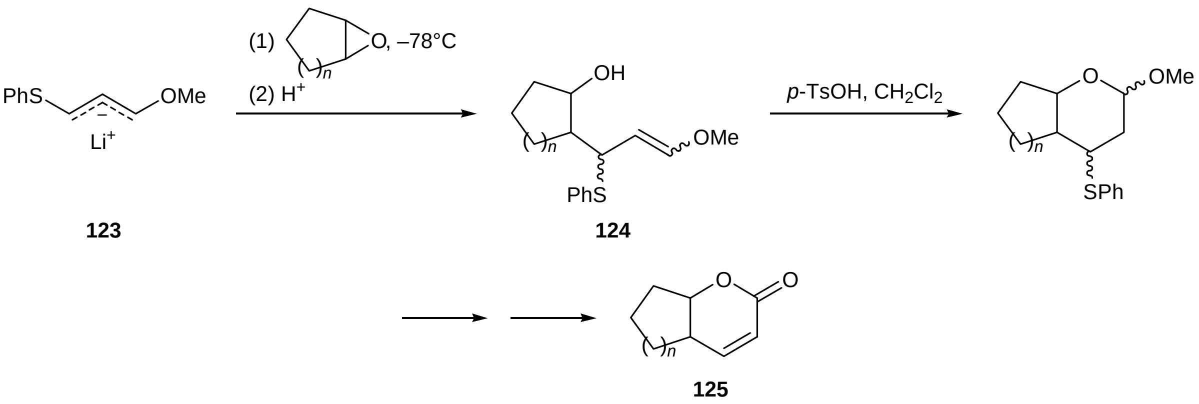
**Scheme 61.**



**Scheme 62.**



**Scheme 63.**



*n* = 1, 2.

of lactone from diepoxide **122** is favored by high nucleophilicity of carboxylate ion. The process is accompanied by debromination of the substrate [109] (Scheme 62). Stable anion **123** as nucleophile is capable of reacting at the electrophilic centers of epoxycyclohexane and epoxycyclopentane; acid-catalyzed cyclization of alcohols **124** yields lactones **125** [110] (Scheme 63).

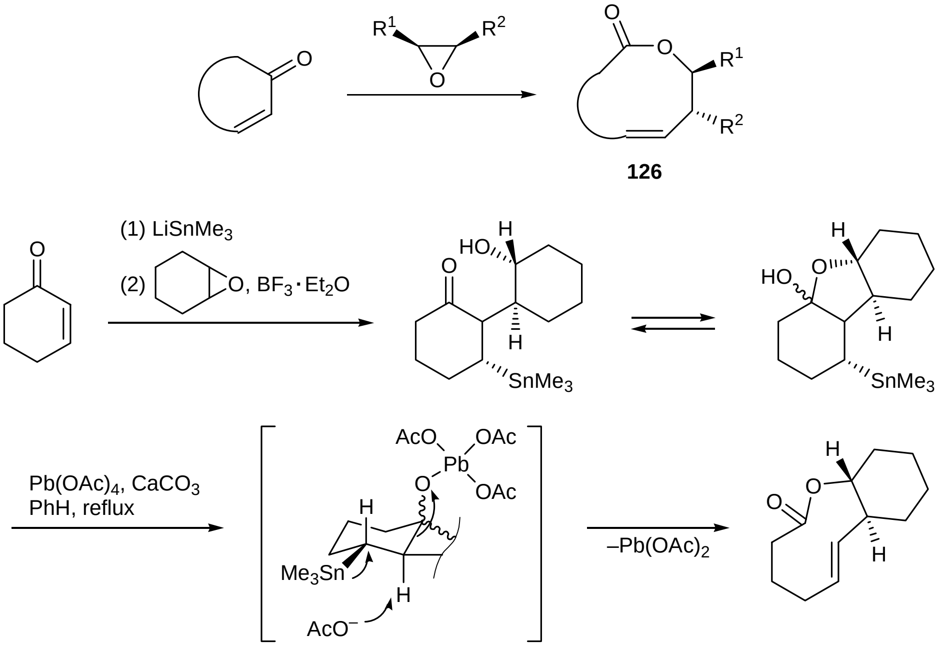
In 2000, a large series of unsaturated lactones **126** was synthesized on the basis of oxiranes and unsaturated ketones in the presence of boron trifluoride–ether complex. Multicomponent syntheses initiated by reaction of oxiranes with enolates are especially valuable due to the possibility for their implementation in a one-pot process. Scheme 64 shows the mechanism of this complex reaction.

Since 1970s, ynolates were used as nucleophiles in reactions with epoxy derivatives. An example is lithium trimethylsilylethynolate (**127**) (Scheme 65). The reaction is characterized by *trans*-stereoselectivity, and it involves intermediate formation of trimethylsilylketene **128** which undergoes intramolecular cyclization [112]. 1,2-Epoxy-4-cyclohexene and 1,2-epoxy-1-methylcyclohexane react in a similar way; in the latter case, nucleophilic attack at C$^2$ is controlled by steric factor [112].

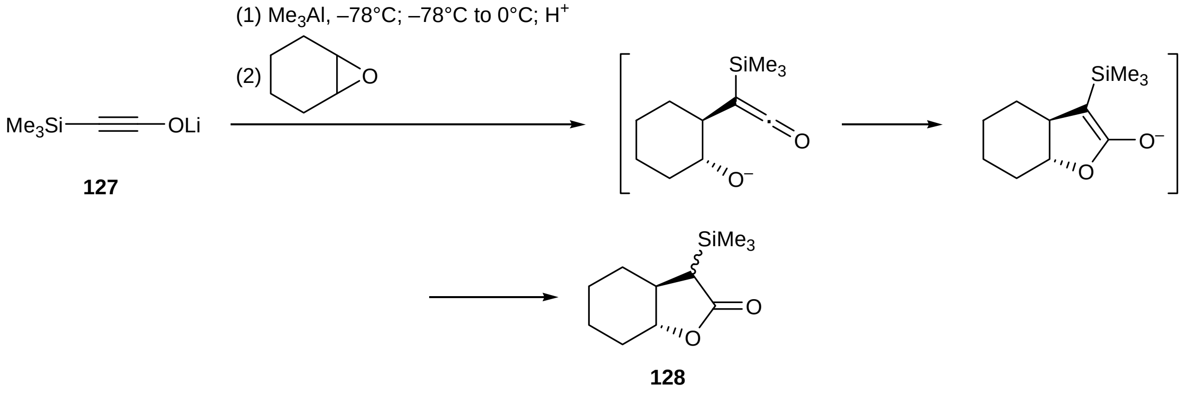
The reaction of 1-diethylaminopropyne with epoxy ketone **129** at the carbonyl group gives rise to a fragment suitable for subsequent cyclization which is favored by activation of the oxirane oxygen atom in acid medium [113] (Scheme 66). (*R*)-2-Chloromethyloxirane (**130**) reacted with phenylacetonitrile to give product **131** which was isolated as lactone **132** [114] (Scheme 67). The latter was converted into (+)-milnacipran which is known as antidepressant and a representative of a new class of NMDA receptor antagonists.

The crucial role of stereochemical factor in the formation of lactones is illustrated by ready enzymatic hydrolysis of one of the two stereoisomeric esters **133** and **134**, which leads to lactone **135** [115] (Scheme 68). Mixtures of δ-hydroxy-γ-lactones and

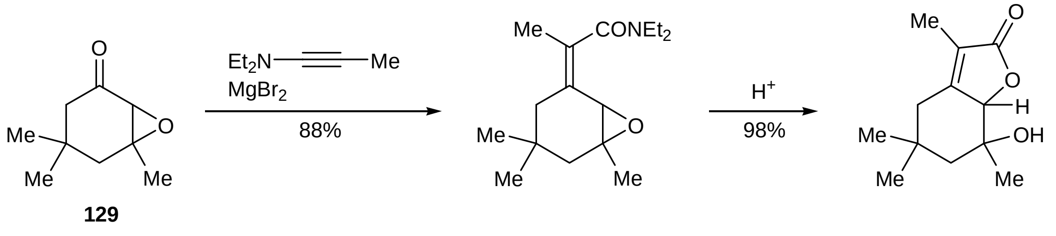
**Scheme 64.**



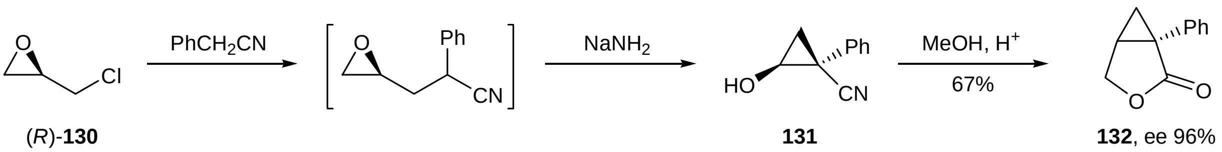
**Scheme 65.**



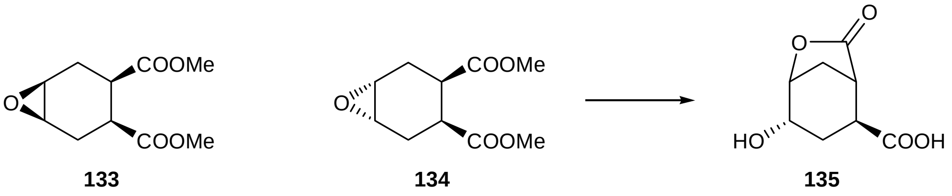
**Scheme 66.**



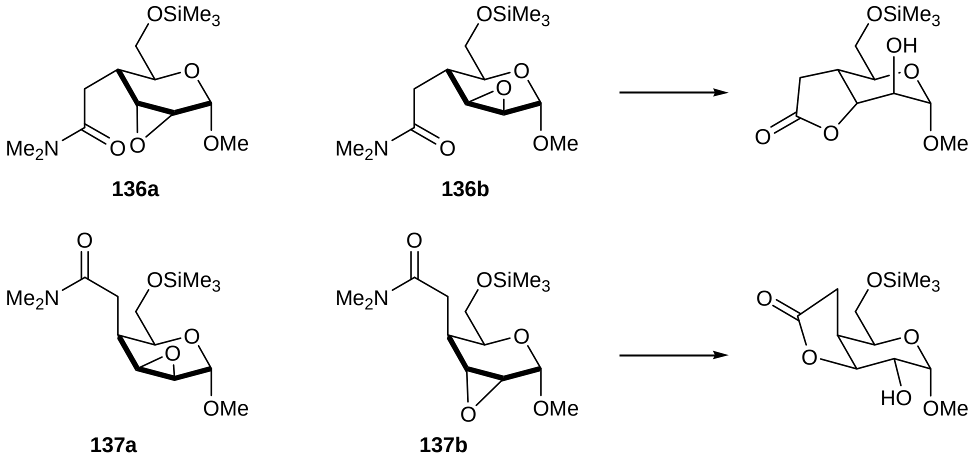
**Scheme 67.**



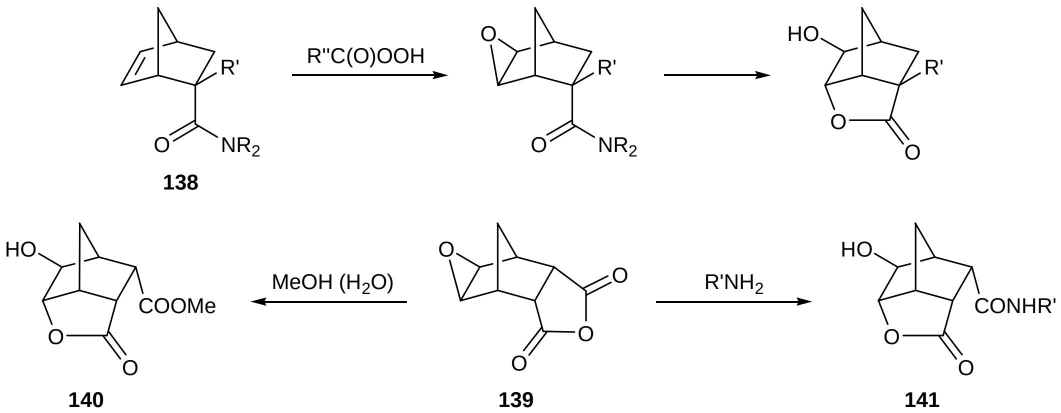
**Scheme 68.**



**Scheme 69.**

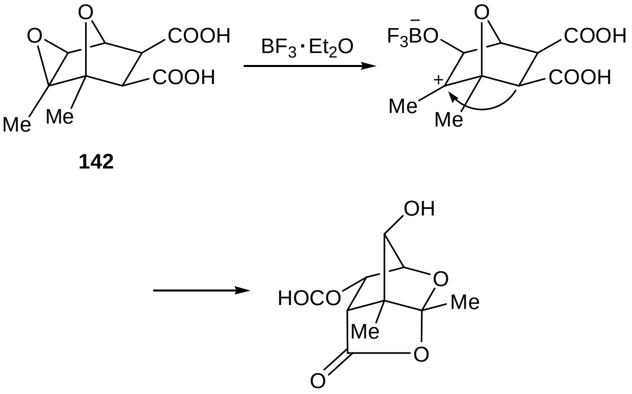


**Scheme 70.**



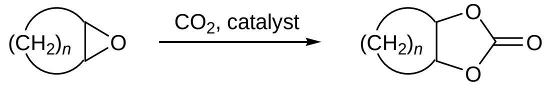
γ-hydroxy-δ-lactones Lactones were also obtained by transformation of γ,δ-epoxy esters in acid medium [116]. Among the stereoisomeric pairs of epoxides given in Scheme 69, only one (**136b** and **137b**) undergoes lactonization during epoxidation of olefins by the action of *m*-chloroperoxybenzoic acid [28]. In each case, the cyclization is favored by stereochemical factor, i.e., by the possibility for rear attack by nucleophile at the oxirane carbon atom. Participation of amide groups in the formation of lactone rings was reported for bicyclic systems **138** (R = H, Me) in reactions with peroxy acids [2, 10, 117–119]. Heating of epoxy derivative **139** with anhydrous methanol or water afforded hydroxy lactone **140** [120, 121], and reactions with amines gave amidolactones **141** (R' = H, $CH_2Ph$, Ph) [122] (Scheme 70). 1- and 7-Alkyl-substituted anhydrides **139** are converted into analogous lactones **140** at room temperature in the presence of hydrochloric acid [123, 124]. Fray and Hilton [125] described the corresponding hydrazide obtained by heating anhydride **139** with hydrazine in boiling acetonitrile. Lactonization of compound **142** with *exo*-oriented carboxy groups was possible due to readily occurring Wagner–Meerwein rearrangement [126] (Scheme 71).

**Scheme 71.**



Reactions leading to formation of heterorings with two and more oxygen atoms include widely known synthesis of alkylene carbonates which have found extensive application in chemical and pharmaceutical industry and in the manufacture of chemical means for plant protection [127] (Scheme 72).

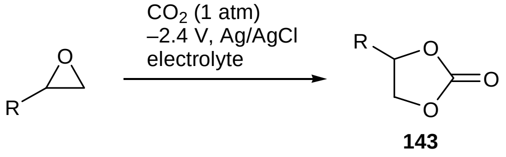
**Scheme 72.**



Developments in this line of epoxide transformations involve design of new catalytic systems and search for optimal reaction conditions; the effects of carbon dioxide pressure, ultrasound, and reaction time on the yield of cyclic carbonate were studied [128]. As catalysts for reactions in DMF, metal halides [127, 129], organotin and organoantimony halides [128], bismuth bromide [130], mixed magnesium–aluminum oxides (which exhibit both acidic and basic properties) [131], and lanthanide diphthalocyanines (para- and diamagnetic forms) [132] were proposed. Difunctional catalysis by $ZnCl_2/(C_4H_9)_4NI$ [133] and catalysis by tin halide complexes with tetraalkylphosphonium halides [134] were also successful in the above reaction. The use of $Bu_3SnI/Bu_4PI$ ensured quantitative yield of the cycloaddition products even under atmospheric pressure.

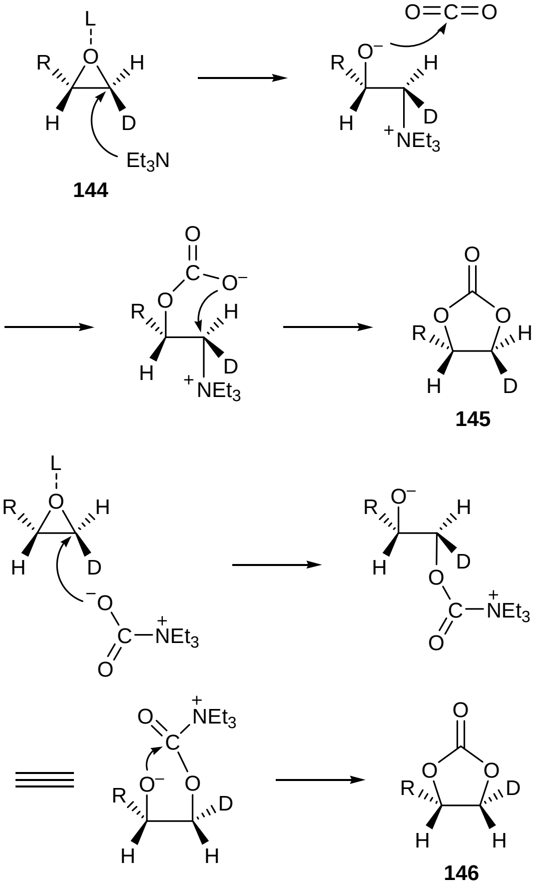
Reactions in ionic liquids were recently proposed for the synthesis of cyclic carbonates [135–137]. Successful application of *N*-alkylpyridinium and *N*,*N'*-dialkylimidazolium salts was noted in review [136]. Electrochemical activation of carbon dioxide was found to be important in the synthesis of cyclic carbonates **143** under mild conditions [137] (Scheme 73).

**Scheme 73.**

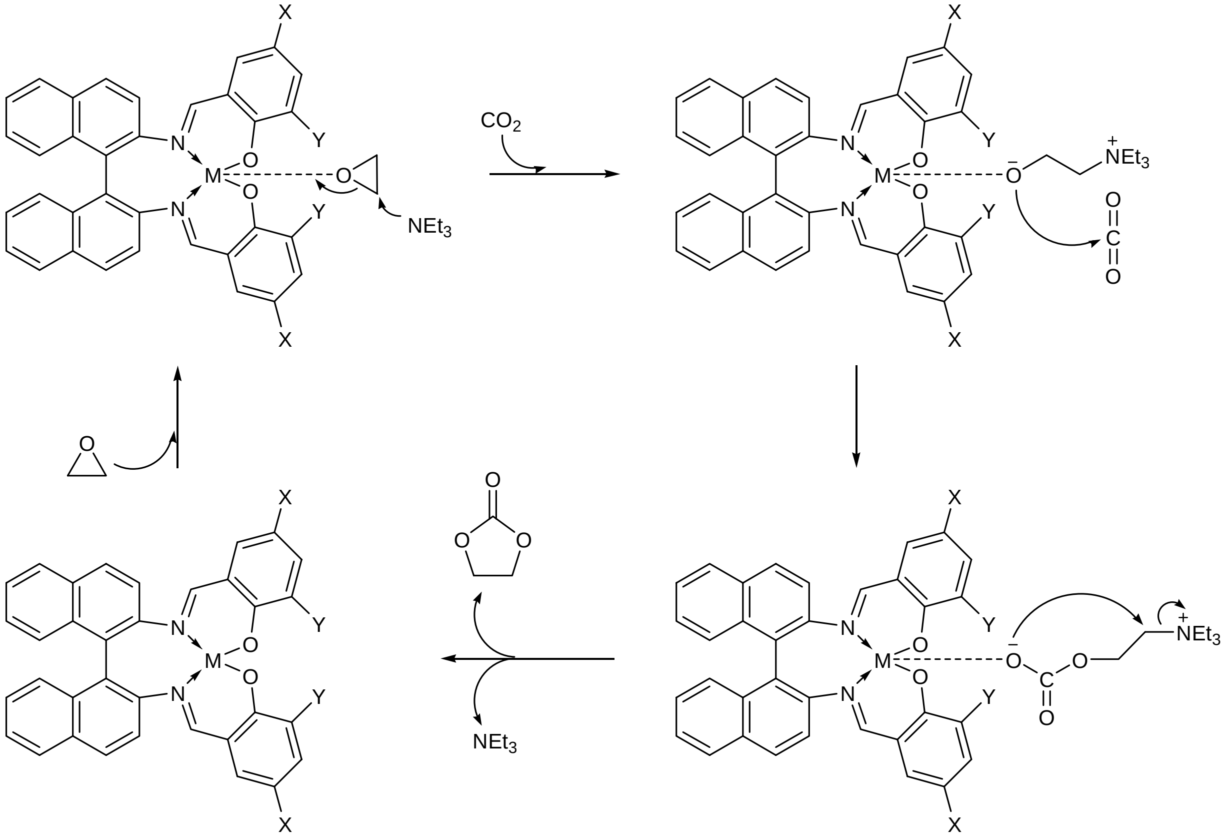


Chromium-containing porphyrin complexes [138, 139], as well as binaphthyldiamine complexes of zinc, copper, and cobalt in the presence of organic bases, were used as catalysts. Using deuterated epoxy derivatives **144**, Shen *et al.* [79] proposed a mechanism

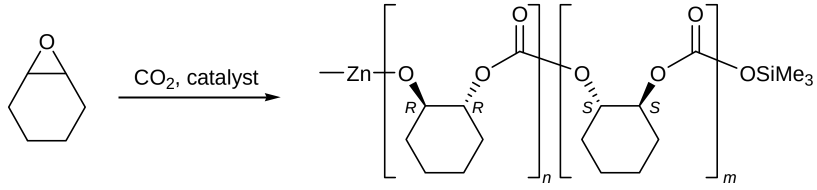
**Scheme 74.**



**Scheme 75.**



**Scheme 76.**



**147**

involving Lewis acids and bases (Scheme 74). The proposed mechanism is confirmed by the formation of carbonate **145** as the only product; alternative preliminary reaction of carbon dioxide with triethylamine would give rise to stereoisomeric product **146**. On the basis of these data, a mechanism was proposed for chemical trapping of carbon dioxide with epoxy compounds [79] (Scheme 75). By the reaction with 2-phenyloxirane Brunner *et al.* [140] succeeded in obtaining the corresponding carbonate in up to 40% ee using chiral Lewis acids as catalysts. Enantiomerically pure zinc complexes successfully catalyzed enantioselective copolymerization of epoxycycloalkanes with carbon dioxide [141]; from epoxycyclohexane, copolymer **147** was obtained (Scheme 76).

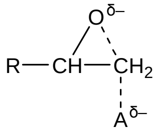
## VII. MECHANISMS OF TRANSFORMATION OF EPOXY DERIVATIVES INTO HETEROCYCLIC SYSTEMS

The formation of heterocyclic systems on the basis of oxiranes is generally preceded by opening of the three-membered ring, which follows either bimolecular nucleophilic substitution mechanism [142, 143] or single-electron reduction through a radical intermediate.

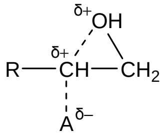
### *VII.1. Heterolytic Processes*

In most cases, opening of the oxirane ring occurs as nucleophilic substitution at the ring carbon atom, where the leaving group is the oxygen atom [142].

These reactions are generally *trans*-stereoselective and regioselective (according to the Krasuskii rule [144]), and they involve formation of transition states **148** and **149** in neutral and acid media, respectively ($S_N2$, $S_N2'$) [142].



**148**

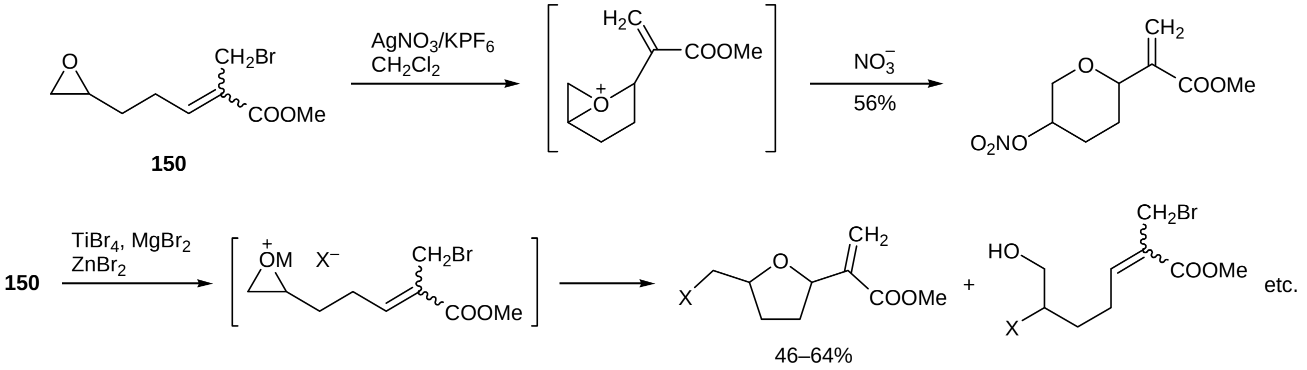


**149**

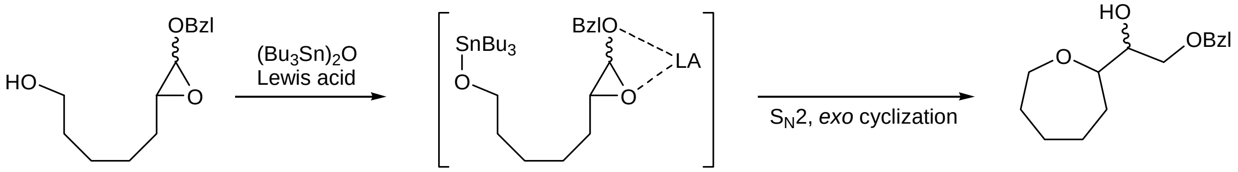
Using unsaturated epoxy ester **150** as an example, Tokumasu *et al.* [145] demonstrated how Lewis acids affect the character of the resulting ring (tetrahydrofuran or tetrahydropyran; Scheme 77). Scheme 78 shows the mechanism of recyclization of epoxy alcohol **151** in the presence of bis(tributylstannyl) ether. An activating effect of silica gel (and irradiation) on the heterocyclization of epoxy derivative **152** was revealed (Scheme 79). Vacuum thermolysis of epoxytricyclodecenone **153** (R = COOEt) afforded unusual rearrangement product **154** whose structure was proved by X-ray analysis [146]. The reaction mechanism is shown in Scheme 80.

Alkylation with ketones of optically active (*R*)- and (*S*)-1,2-epoxypropanes as the key stage and the subsequent acid-catalyzed cyclization gave naturally occurring (±)-nocardione, (*S*)-(–)-nocardione (**155**), and (*R*)-(+)-nocardione B [147] (Scheme 81). Barkhash and co-workers studied reactions of epoxy derivatives of terpenes in acid media. Heterocyclization products **157** and **158** were obtained by reaction of α-(*trans*)-3,4-epoxycarane (**156**) with superacids [114] (Scheme 82). Reactions of epoxygeraniol and epoxy derivatives of linalool and nerolidyl acetate [148] in

**Scheme 77.**

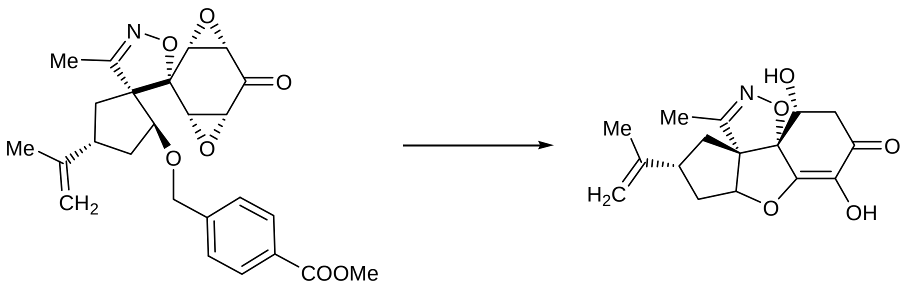


**Scheme 78.**



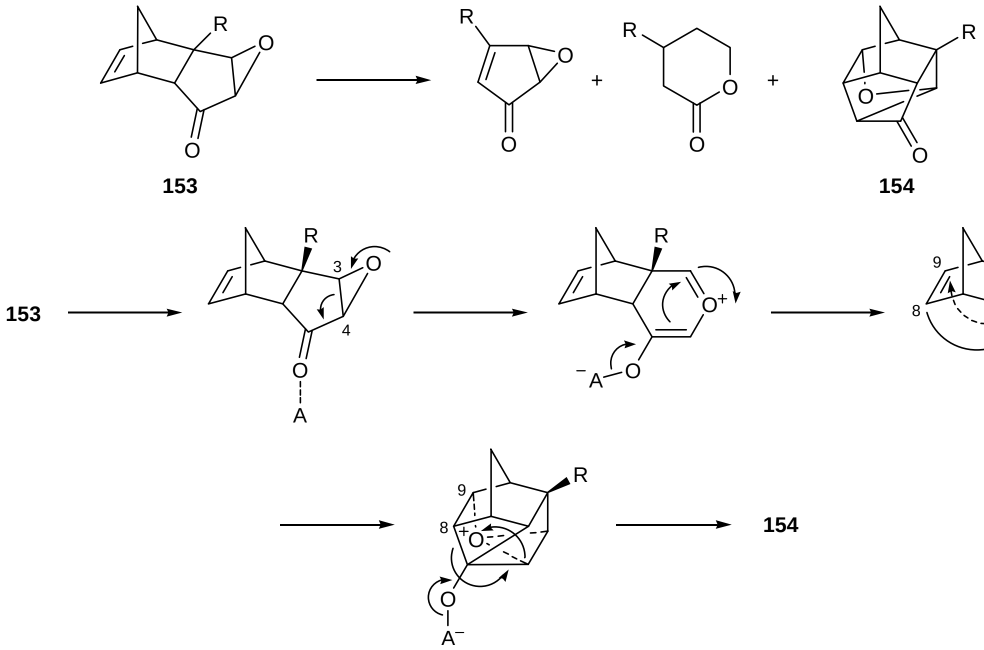
**151**

**Scheme 79.**

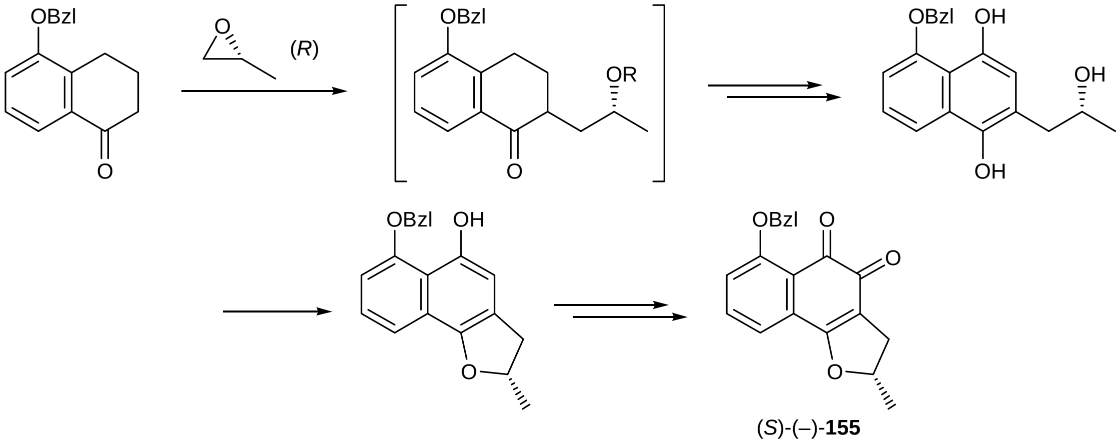


**152**

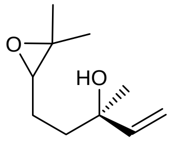
**Scheme 80.**



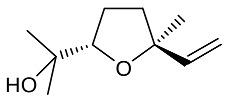
**Scheme 81.**



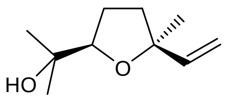
various acid media were also examined. Scheme 83 illustrates the formation of products **160** and **161** obtained from 1,2-epoxylinalool (**159**) over β-zeolite at 20°C. The major products of rearrangements of 6,7-epoxylinalool (**162**) under different conditions (in the system $HSO_3F–SO_2FCl$, –100°C, followed by quenching with a mixture of methanol with ether; $ZrO_2/SO_4^{2-}$) were cyclic ethers **163–165**. An unusual scheme was developed on the basis of reactions of epoxy derivatives of α- and β-pinene with aldehydes over askanite–bentonite clay. Presumably, it originates from the high rate of rearrangement into carbocation **166** where the hydroxy group is remote from the cationic center; this prevents formation of the expected acetal and favors heterocyclization to oxabicyclononanes **167** [149] (Scheme 84). Analogous reaction



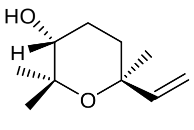
**162**



**163**

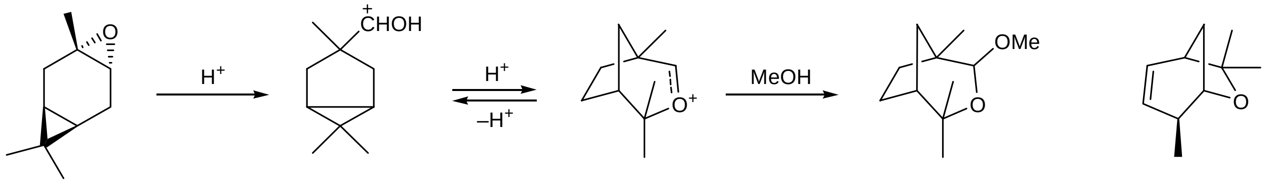


**164**



**165**

**Scheme 82.**

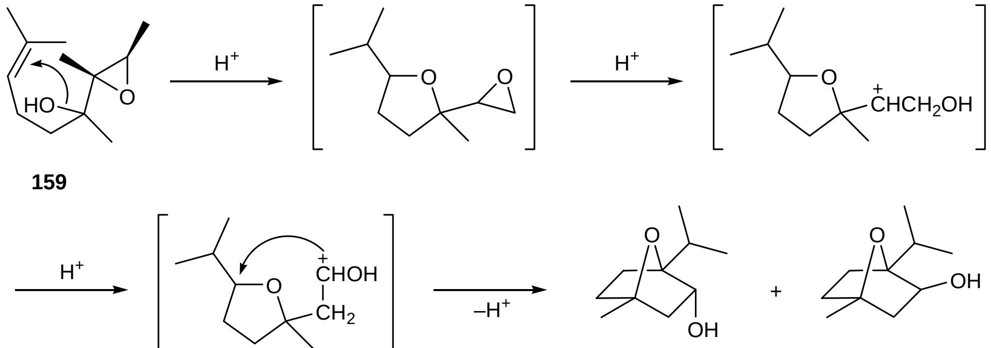


**156**

**157**, 26–34%

**158**, 2.5–10%

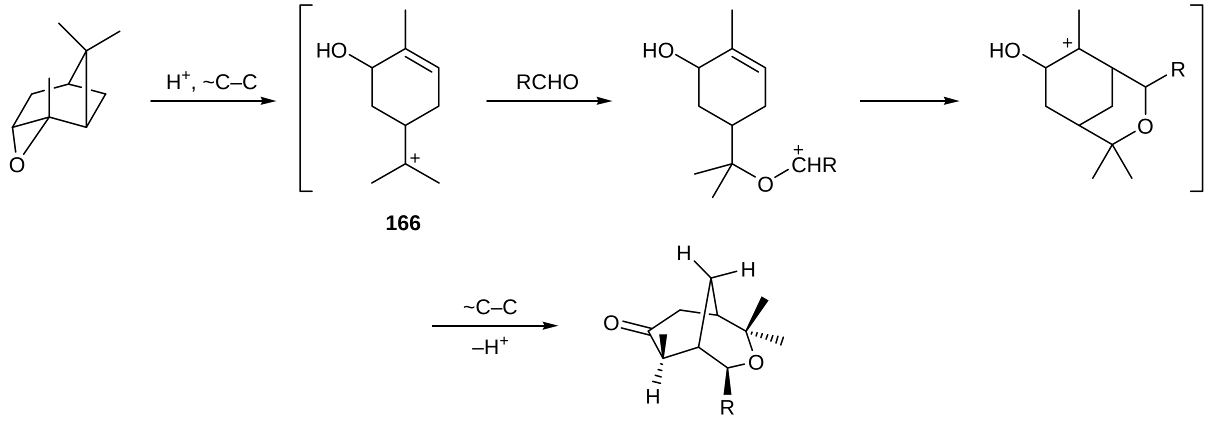
**Scheme 83.**



**160**, 56%

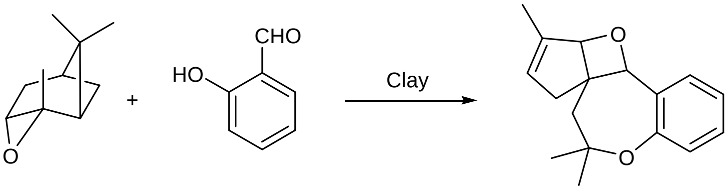
**161**, 28%

**Scheme 84.**



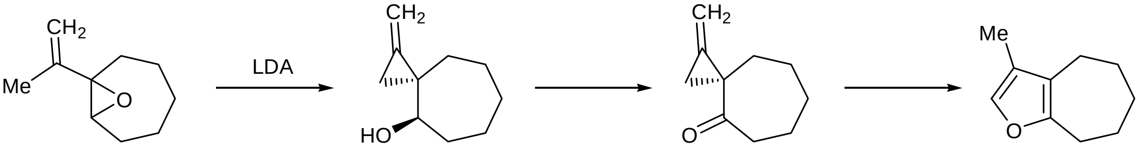
**167**

**Scheme 85.**



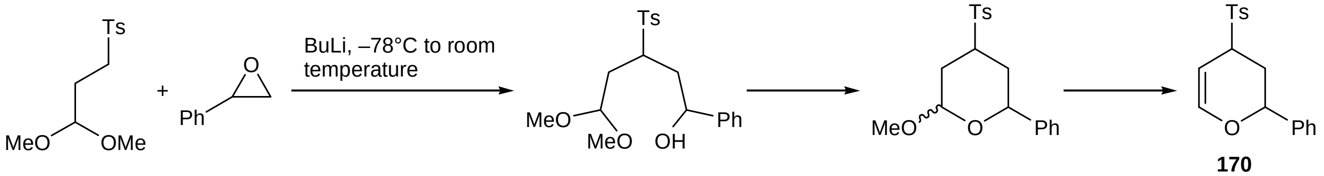
**168**

**Scheme 86.**



**169**

**Scheme 87.**



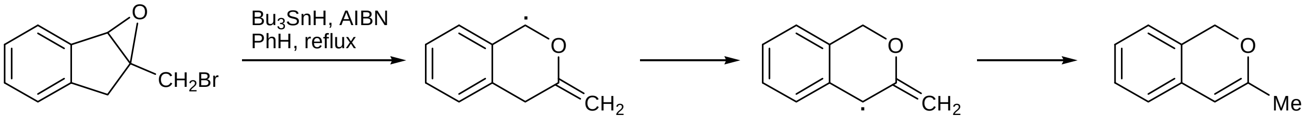
with aromatic salicylaldehyde afforded a new heterocyclic system, 5,6-benzo-3,3,10-trimethyl-4,8-dioxatricyclo[5.5.0.0$^{1,9}$]dodeca-5,10-diene (**168**) (Scheme 85). Sato *et al*. [150] developed a novel procedure for the synthesis of 3-methylfurans by reaction of epoxycycloalkanes **169** with bases (lithium diisopropylamide) (Scheme 86). Opening of oxiranes with bases underlies the synthesis of dihydropyran **170** (Scheme 87).

### *VII.2. Homolytic and Other Mechanisms*

Although most transformations of oxiranes into ethers follow heterolytic mechanism of cleavage of the carbon–oxygen bond, some examples of radical-induced opening of epoxy ring have been reported [151–153]. Hydroxycarbinyl radicals were formed as intermediates in the synthesis of oxepanes and other medium-size oxygen-containing heterocycles [154]. Examples are reactions of compound **171** and others in the presence of tributylstannane and AIBN [151, 154] (Scheme 88). The reductive cyclization of epoxide **172** is accompanied by radical carbonylation of the precursor [155] (Scheme 89).

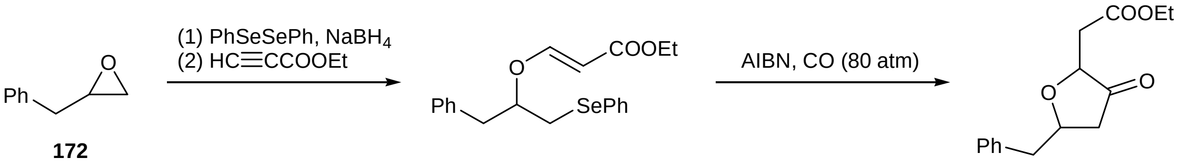
In the recent years, various reactions of epoxy derivatives in the presence of transition metal-containing radical species have attracted specific interest; in particular, such transition metal reagent is bis(cyclopentadienyl)titanium(III) chloride which was synthesized for the first time in 1972 [156, 157]. At present, $Cp_2TiCl$ is one of the most promising in the chemistry of oxiranes [158, 159]; it is used as catalyst for deoxygenation and cyclization [156, 157]. Scheme 90 shows the mechanism of action of $Cp_2TiCl$ in the reaction with epoxy derivative **173**.

**Scheme 88.**



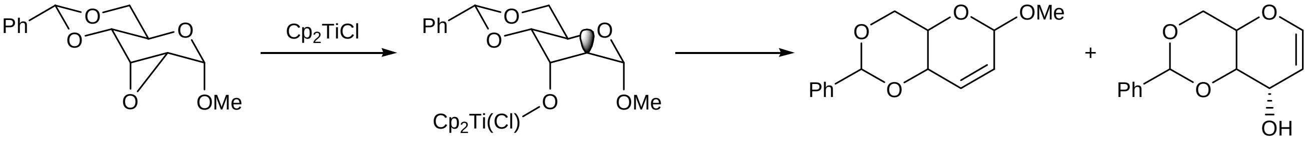
**171**

**Scheme 89.**



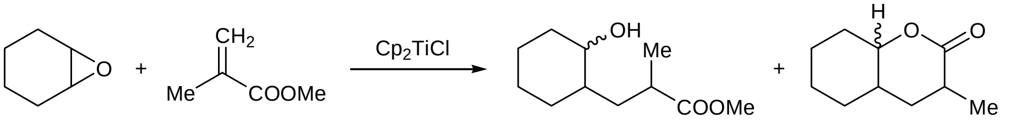
**172**

**Scheme 90.**



**173** 78% 16%

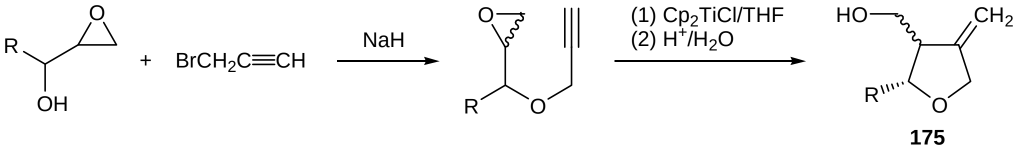
**Scheme 91.**



**174** 33% 66%

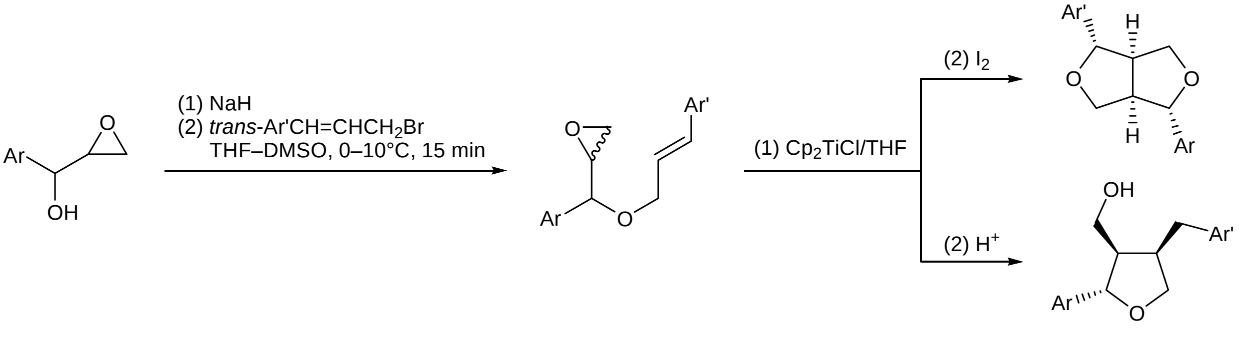
New heterocyclic systems are formed by the action of $Cp_2TiCl$ in reactions of epoxycyclohexane (**174**) with electron-deficient olefins such as methyl methacrylate and ethyl acrylate [156, 160] (Scheme 91). A procedure for the synthesis of polysubstituted tetrahydrofurans **175** was developed on the basis of the simplest oxiranes [152] (Scheme 92). Likewise, a furofuran lignan, (±)-sesamine (**176**), was synthesized [161, 162] (Scheme 93). Kumar *et al.* [163] demonstrated the determining role of single-electron

**Scheme 92.**



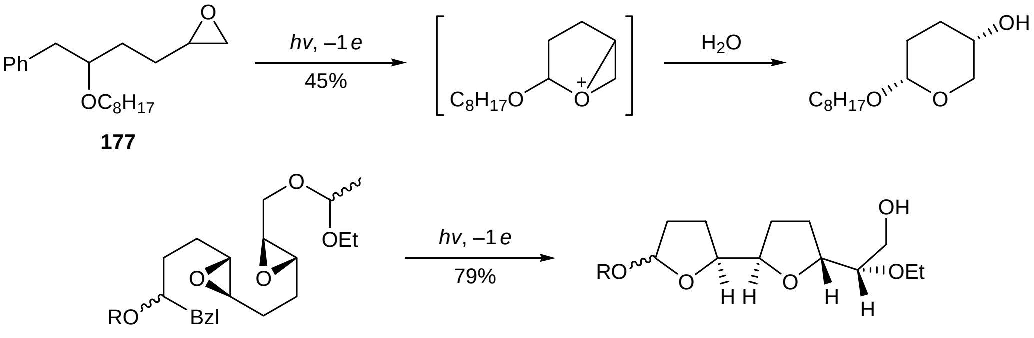
**175**

**Scheme 93.**



**176**

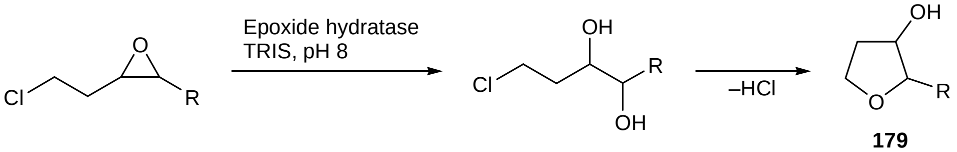
**Scheme 94.**



**177**

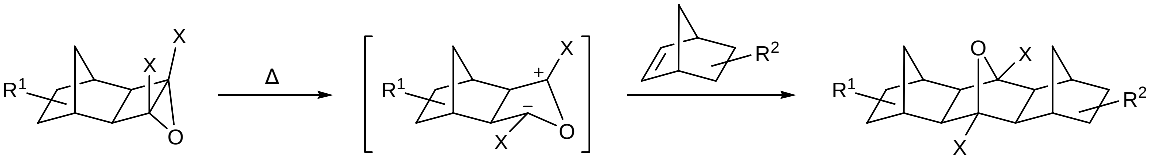
**178**

**Scheme 95.**



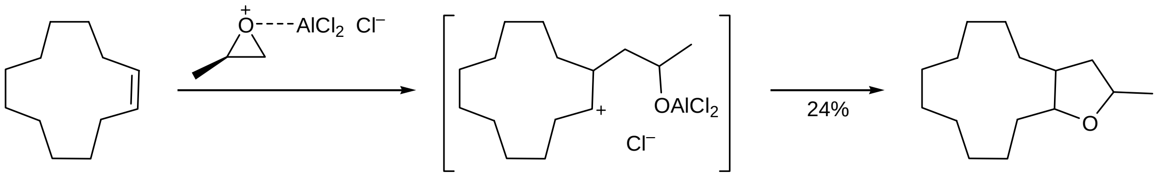
**179**

**Scheme 96.**



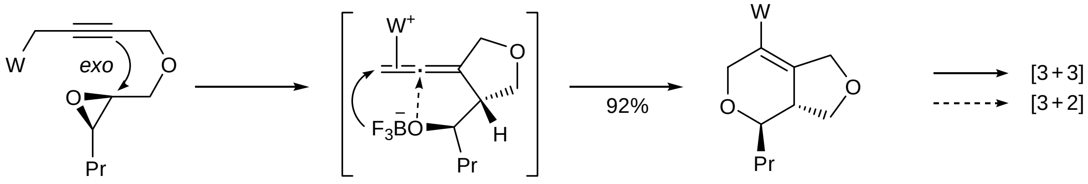
**180**

**Scheme 97.**



**181** **182**

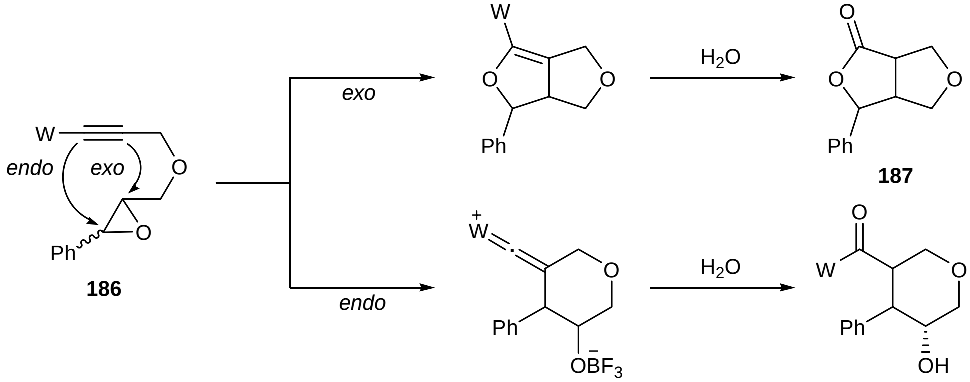
**Scheme 98.**



**183** **184** **185**

W = CpW(CO)$_3$.

**Scheme 99.**



**186** **187** **188**

oxidation in the initiation of cascade cyclization of epoxides **177** and **178** and other oxiranes in neutral medium, which leads to cyclic ethers and polyethers (Scheme 94); this process is likely to be important in the synthesis of natural compounds.

Apart from the above mechanisms, biocatalytic hydrolysis of 2,3-substituted racemic epoxy derivatives was studied. The reaction is catalyzed by epoxide hydratase, and it involves intermediate formation of vicinal diols; spontaneous formation of cyclic ethers was also observed as a result of enzymatic cascade reactions [164]. Cyclic compound **179** was obtained with an enantioselective purity of 70–90% in the presence of some microorganisms [164] (Scheme 95).

In 2000–2003, a series of works were published, which described the synthesis of oxygen-containing heterocycles by reaction of epoxy derivatives with olefins. High reactivity of epoxycyclobutanes was utilized in the synthesis of hydrophilic ribbon molecules which were studied since 1997. Ribbon molecules were obtained from epoxycyclobutane blocks **180** (X = COOR, COCl, CONHR', etc.) and dipolarophiles of the norbornene series [165] (Scheme 96). Munro and Newman [166] isolated aldehydes and unsaturated alcohols together with tetrahydrofuran **182** in the acid-catalyzed reaction with cyclododecene (**181**) (Scheme 97). An alternative pathway includes transformation of tungsten-containing compounds derived from 2,3-epoxyhexyl 2-alkynyl ether **183** [106] (Scheme 98). The presence of boron trifluoride–ether complex favors [3+3]-cycloaddition of epoxide. The cyclization of intermediate **184** is highly diastereoselective: bicyclic compound **185** is formed as the only product, and functional groups present in the initial molecule are conserved. The cycloaddition begins with opening of the oxirane ring via *exo*-attack by the 2-propynyltungsten moiety. Enantioselective synthesis of bicyclic oxygen-containing compounds was effected with the use of chiral epoxides.

Alkenyltungsten substrate **186** undergoes intramolecular [3+2]-cycloaddition with participation of the oxirane fragment. Bicyclic lactone **187** is formed when the substrate has *cis* configuration, and the corresponding *trans*-epoxide gives rise to tetrahydropyran derivative **188** [167] (Scheme 99). The same authors reported on stereocontrolled synthesis of a large group of new bicyclic lactones containing nitrogen atoms as a result of cyclization via regioselective *exo*-attack on the oxirane ring [167].

## REFERENCES

1. Malinovskii, M.S., *Okisi olefinov i ikh proizvodnye* (Olefin Oxides and Their Derivatives), Moscow: Goskhimizdat, 1961.
2. Prilezhaeva, E.N., *Reaktsiya Prilezhaeva. Elektrofil'noe okislenie* (Prilezhaev Reaction. Electrophilic Oxidation), Moscow: Mir, 1974.
3. Rao, A.S., Paknicar, S.K., and Kirtane, J.C., *Tetrahedron*, 1983, vol. 39, p. 2323.
4. Yandovskii, V.N., Karavan, V.S., and Temnikova, T.I., *Usp. Khim.*, 1970, vol. 39, p. 571.
5. Gorzinsky, J., *Synthesis*, 1984, no. 8, p. 629.
6. Paquette, L.A. and Stirling, J.M., *Tetrahedron*, 1992, vol. 48, p. 7383.
7. Kas’yan, L.I., *Russ. J. Org. Chem.*, 1999, vol. 35, p. 635.
8. Kas’yan, L.I., Kas’yan, A.O., and Tarabara, I.N., *Russ. J. Org. Chem.*, 2001, vol. 37, p. 1361.
9. Seferova, M.F., Kas’yan, L.I., Dryuk, V.G., and Kartsev, V.G., Specific Features of the Formation and Opening of Epoxy Ring in the Series of Cyclo- and Bicycloalkanespirooxiranes, *Preprint*, Chernogolovka, 1991.
10. Kas’yan, L.I., *Usp. Khim.*, 1998, vol. 67, p. 299.
11. Linnott, M.L., *Adv. Phys. Org. Chem.*, 1988, vol. 24, p. 113; *Ref. Zh., Khim.*, 1989, no. 24B1165.
12. Baldwin, J.E., *J. Chem. Soc., Chem. Commun.*, 1976, p. 734.
13. Diez, D., Moro, R.F., Lumeras, W., Rodriguez, L., Marcos, I.S., Basabe, P., Escarcena, R., and Urones, J.G., *Synthesis*, 2002, p. 175.
14. Elliott, M.C., *J. Chem Soc., Perkin Trans. 1*, 1998, p. 4175.
15. Karikomi, M., Yamazaki, T., and Toba, T., *Chem. Lett.*, 1993, p. 1965.
16. Koert, U., *Synthesis*, 1995, p. 115.
17. Garlaschelli, L., de Tullio, P., and Vidari, G., *Tetrahedron*, 1991, vol. 47, p. 6769.
18. Takikawa, H., Sano, S., and Mori, K., *Leib. Ann., Recl.*, 1997, p. 231.
19. Morzycki, J.W., Gryszkiewicz, A., and Jastrzebska, I., *Tetrahedron Lett.*, 2000, vol. 41, p. 3751.
20. Rodriguez, A.D., Pina, I.C., Acosta, A.L., Ramirez, C., and Soto, J.J., *J. Org. Chem.*, 2001, vol. 66, p. 648.
21. Al-Qawasmeh, R.A., Al-Tel, T.H., Abdel-Jalil, R.J., Thurmer, R., and Voelter, W., *Pol. J. Chem.*, 1999, vol. 73, p. 71.
22. Russel, S.T., Robinson, J.A., and Williams, D.J., *J. Chem. Soc., Chem. Commun.*, 1987, p. 351.
23. Xiong, Z. and Corey, E.J., *J. Am. Chem. Soc.*, 2000, vol. 122, p. 9328.
24. Hayashi, N., Noguchi, H., and Tsuboi, S., *Tetrahedron*, 2000, vol. 56, p. 7123.
25. Zakharova, E.V., Pletnev, S.I., and Makarov, K.N., *J. Flourine Chem.*, 1989, vol. 45, p. 132.
26. Bird, C.W. and Hormozi, N., *Tetrahedron Lett.*, 1990, vol. 31, p. 3501.
27. Bird, C.W. and Hormozi, N., *Synth. Commun.*, 1990, vol. 20, p. 1777.
28. Cirelli, A.F., Moradei, O., and Thiem, J., *Lieb. Ann., Recl.*, 1997, p. 1983.
29. Smith, A.B., Tokuyama, H., Strongin, R.M., Furst, G.T., Romanow, W.J., Chait, B.T., Mirza, U.A., and Haller, I., *J. Am. Chem. Soc.*, 1995, vol. 117, p. 9359.
30. Creegan, K.M., Robbins, J.L., Robbins, W.K., Millar, J.M., Sherwood, R.D., Tindall, P.J., Cox, D.M., Smith, A.B., McCauley, J.P., Jones, D.R., and Gallagher, R.T., *J. Am. Chem. Soc.*, 1992, vol. 114, p. 1103.
31. Lescop, C., Nguyen-Kim, P.-P., and Huet, F., *Tetrahedron Lett.*, 2000, vol. 41, p. 3057.
32. Ziegler, F.E. and Petersen, A.K., *Tetrahedron Lett.*, 1996, vol. 37, p. 809.
33. Burourt, R., Clapier, P., Guenard, D., and Thal, C., *Tetrahedron Lett.*, 1989, vol. 30, p. 3973.
34. Labidalle, S., Min, Z.Y., Reynet, A., Moskowitz, H., Vierfond, J.M., Miocque, M., and Bucourt, R., *Tetrahedron*, 1988, vol. 44, p. 1159.
35. Langer, P. and Eckardt, T., *Angew. Chem., Int. Ed. Engl.*, 2000, vol. 39, p. 4343.
36. Chao, B. and Dittmer, D.C., *Tetrahedron Lett.*, 2000, vol. 41, p. 6001.
37. Marson, C.M., Harper, S., and Wrigglesworth, R., *J. Chem. Soc., Chem. Commun.*, 1994, p. 1879.
38. Eberbach, W. and Laber, N., *Tetrahedron Lett.*, 1992, vol. 33, p. 57.
39. Aurrecoechea, J.M., Perez, E., and Solay, M., *J. Org. Chem.*, 2001, vol. 66, p. 564.
40. Brooks, P.B. and Marson, C.M., *Tetrahedron*, 1998, vol. 54, p. 9613.

41. Al-Tel, T.H., Al-Abed, Y., and Voelter, W., *J. Chem. Soc., Chem. Commun.*, 1994, p. 1735.
42. Vialemaringe, M., Bourgeois, M.-J., Campagnole, M., and Montaudon, E., *Tetrahedron Lett.*, 2000, vol. 41, p. 4901.
43. Marson, C.M., Harper, S., and Oare, C.A., *J. Org. Chem.*, 1998, vol. 63, p. 3798.
44. Gonzalez, I.C. and Forsyth, C.J., *Tetrahedron Lett.*, 2000, vol. 41, p. 3805.
45. Hayashi, N., Fujiwara, K., and Murai, A., *Chem. Lett.*, 1996, p. 341.
46. Tokiwano, T., Fujiwara, K., and Murai, A., *Chem. Lett.*, 2000, p. 272.
47. Taylor, S.K., Bischoff, D.S., Blankespoor, C.L., Curtis, L., and Deck, P.A., *J. Org. Chem.*, 1990, vol. 55, p. 4202.
48. Taylor, S.K., May, S.A., and Stansby, E.S., *J. Org. Chem.*, 1996, vol. 61, p. 2075.
49. Rychnovsky, S.D. and Dahanukar, V.H., *Tetrahedron Lett.*, 1996, vol. 37, p. 339.
50. Matsumura, R., Suzuki, T., Sato, K., Oku, K., Hagiwara, H., Hoshi, T., Ando, M., and Kamat, V.P., *Tetrahedron Lett.*, 2000, vol. 41, p. 7701.
51. Matsumura, R., Suzuki, T., Sato, K., Inotsume, T., Hagiwara, H., Hoshi, T., Kamat, V.P., and Ando, M., *Tetrahedron Lett.*, 2000, vol. 41, p. 7697.
52. Fujiwara, K., Mishima, H., Amano, A., Tokiwano, T., and Murai, A., *Tetrahedron Lett.*, 1998, vol. 39, p. 393.
53. Hayashi, N., Fujiwara, K., and Murai, A., *Tetrahedron Lett.*, 1996, vol. 37, p. 6173.
54. Uckun, F.M., Mao, C., Vassilev, A.O., Huang, H., and Jan, S.-T., *Bioorg. Med. Chem. Lett.*, 2000, p. 541.
55. Karikomi, M., Watanabe, S., Kimura, Y., and Uyehara, T., *Tetrahedron Lett.*, 2002, vol. 43, p. 1495.
56. Davies, S.G., Polynka, M.E.C., and Thomas, S.E., *Tetrahedron Lett.*, 1985, vol. 26, p. 1461.
57. Alvarez, E., Manta, E., Martin, J.D., Rodrigues, M.L., and Ruiz-Perez, C., *Tetrahedron Lett.*, 1988, vol. 29, p. 2093.
58. Haufe, G., Alverine, G., and Laurent, A., *J. Flourine Chem.*, 1990, vol. 46, p. 83.
59. Richardson, P.F. and Marko, I.E., *Synlett*, 1991, p. 733.
60. Alvarez, E., Manta, E., Martin, J.D., Rodrigues, M.L., Ruiz-Perez, C., and Zurita, D., *Tetrahedron Lett.*, 1988, vol. 29, p. 2097.
61. Zarraga, M., Rodrigues, M.L., Ruiz-Perez, C., and Martin, J.D., *Tetrahedron Lett.*, 1989, vol. 30, p. 3725.
62. Warrener, R.N., Pitt, J.G., Weerasuria, K.D.V., and Russell, R.A., *Aust. J. Chem.*, 1992, vol. 45, p. 155.
63. Clark, D.L., Chou, W.-N., and White, J.B., *J. Org. Chem.*, 1990, vol. 55, p. 3975.
64. Boyd, D.R., Sharma, N.D., O'Dowd, C.R., and Hempenstall, F., *J. Chem. Soc., Chem. Commun.*, 2000, p. 2151.
65. Lofstrom, C.M.G., Ericsson, A.M., Bourrinet, L., Juntunen, S.K., and Backvall, J.-E., *J. Org. Chem.*, 1995, vol. 60, p. 3586.
66. David, F., *J. Chem. Soc., Chem. Commun.*, 1979, p. 553.
67. Hodgson, D.M., Lee, G.P., Marriott, R.E., Thompson, A.J., Wisedale, R., and Witherington, J., *J. Chem. Soc., Perkin Trans. 1*, 1998, p. 2151.
68. Krasutsky, P.A., Kolomitsyn, I.V., Sidorenko, N.A., and Carlson, B.M., Abstracts of Papers, *Conf. "Alkane Activation and Cage Compounds Chemistry,"* Kyiv, 1998, p. 33.
69. Subramanian, R. and Fort, R.C., *J. Org. Chem.*, 1984, vol. 16, p. 2891.
70. Le Drian, C. and Vogel, P., *Helv. Chim. Acta*, 1988, vol. 71, p. 1399.
71. Henbest, H.B. and Nicholls, B., *J. Chem. Soc.*, 1959, p. 221.
72. Shibasaki, M., Nishida, A., and Ikegami, S., *Tetrahedron Lett.*, 1980, vol. 21, p. 3061.
73. Meinwald, J., Crandall, J., and Gassman, P., *Tetrahedron*, 1962, vol. 18, p. 815.
74. Le Drian, C. and Vogel, P., *Tetrahedron Lett.*, 1987, vol. 28, p. 1523.
75. Le Drian, C. and Vogel, P., *J. Org. Chem.*, 1993, vol. 58, p. 2328.
76. Mann, J. and de Almeida Barbosa, L.-C., *J. Chem. Soc., Perkin Trans. 1*, 1992, p. 783.
77. Kas'yan, L.I., Zefirov, N.S., Gnedenkov, L.Yu., Stepanova, N.V., Shashkov, A.S., and Cherepanova, E.G., *Zh. Org. Khim.*, 1982, vol. 18, p. 1212.
78. Kasyan, L.I., Okovity, S.I., and Kasyan, A.O., *Heteroatom Chem.*, 1997, vol. 8, p. 185.
79. Shen, Y.-M., Duan, W.-L., and Shi, M., *J. Org. Chem.*, 2003, vol. 68, p. 1559.
80. Kas'yan, L.I., Zefirov, N.S., Stepanova, N.V., Saltykova, L.E., and Ryzhik, O.L., *Zh. Org. Khim.*, 1984, vol. 20, p. 2136.
81. Kas'yan, L.I., Stepanova, N.V., Belyakova, T.A., Kunanets, V.K., Lutsenko, A.I., and Zefirov, N.S., *Zh. Org. Khim.*, 1984, vol. 20, p. 2295.
82. Kas'yan, L.I., Galafeeva, M.F., Zhilina, N.I., Lutsenko, A.I., Trachevskii, V.V., and Zefirov, N.S., *Zh. Org. Khim.*, 1987, vol. 23, p. 117.
83. Kas'yan, L.I., Seferova, M.F., Martynova, V.V., Iksanova, S.V., Boldeskul, I.E., and Dryuk, V.G., *Zh. Org. Khim.*, 1992, vol. 28, p. 292.
84. Kas'yan, L.I., Gaponova, R.G., and Okovityi, S.I., *Zh. Org. Khim.*, 1994, vol. 30, p. 692.

85. Okovityi, S.I., Gouvar, Yu.A., Platitsina, E.L., and Kas'yan, L.I., *Visn. Dnipropetr. Nats. Univ., Khim*, 2000, no. 4, p. 43.
86. Dryuk, V.G., Avramenko, V.I., and Yandovsky, V.N., *J. Chem. Soc., Perkin Trans. 2*, 1977, p. 1526.
87. Blackett, B., Coxon, J., and Hartshorn, M.P., *Tetrahedron*, 1970, vol. 26, p. 1311.
88. Iranpoor, N. and Kazemi, F., *Synth. Commun.*, 1998, vol. 28, p. 3189.
89. Iranpoor, N. and Zeynizadeh, B., *J. Chem. Res., Synop.*, 1998, no. 8, p. 466.
90. Tatarova, L.E., Korchagina, D.V., and Barkhash, V.A., *Russ. J. Org. Chem.*, 2002, vol. 38, p. 519.
91. Yarovaya, O.I., Korchagina, D.V., Gatilov, Yu.V., and Barkhash, V.A., *Russ. J. Org. Chem.*, 2002, vol. 38, p. 810.
92. Malinovskii, M.S., Kas'yan, L.I., Ovsyanik, V.D., and Sil'chenko, L.A., *Zh. Org. Khim.*, 1973, vol. 9, p. 1306.
93. Zaitseva, V.V., Tyurina, T.G., Suikov, S.Yu., Bogza, S.L., and Kobzev, S.P., *Russ. J. Org. Chem.*, 2002, vol. 38, p. 588.
94. Holland, J.M., Lewis, M., and Nelson, A., *J. Org. Chem.*, 2003, vol. 68, p. 747.
95. Kita, Y., Kitagaki, S., Imai, R., Okamoto, S., Mihara, S., Yoshida, Y., Akai, S., and Fujioka, H., *Tetrahedron Lett.*, 1996, vol. 37, p. 1817.
96. Wipf, P., Xu, W., Kim, H., and Takahashi, H., *Tetrahedron*, 1997, vol. 53, p. 16575.
97. Wipf, P. and Aslan, D.C., *J. Org. Chem.*, 2001, vol. 66, p. 337.
98. Wipf, P. and Xu, W., *J. Org. Chem.*, 1993, vol. 58, p. 5880.
99. Fujisaka, T., Miura, M., Nojima, M., and Kusabayashi, S., *J. Chem. Soc., Perkin Trans. 1*, 1989, p. 1031.
100. Baylon, C., Prestat, G., Heck, M.-P., and Mioskowski, C., *Tetrahedron Lett.*, 2000, vol. 41, p. 3833.
101. Marion, F., Le Fol, R., Courillon, C., and Malacria, M., *Synlett*, 2001, p. 138.
102. Surivet, J.-P., Gore, J., and Vatele, J.-M., *Tetrahedron Lett.*, 1996, vol. 37, p. 371.
103. Ono, M., Saotome, C., and Akita, H., *Heterocycles*, 1999, vol. 51, p. 1503.
104. Evans, D.A., Ratz, A.M., Huff, B.E., and Sheppard, G.S., *J. Am. Chem. Soc.*, 1995, vol. 117, p. 3448.
105. Tolstikov, G.A., Miftakhov, M.S., Akhmetvaleev, R.R., Berg, A.A., Vasil'eva, E.V., Khalilov, L.M., and Valeev, F.A., *Zh. Org. Khim.*, 1991, vol. 27, p. 2341.
106. Shen, K.-H., Lush, S.-F., Chen, T.-L., and Liu, R.-S., *J. Org. Chem.*, 2001, vol. 66, p. 8106.
107. Kuroda, T., Imashiro, R., and Seki, M., *J. Org. Chem.*, 2000, vol. 65, p. 4213.
108. Taylor, S.K., *Tetrahedron*, 2000, vol. 56, p. 1149.
109. Hashem, M.A., Marschall-Weyerstahl, H., and Weyerstahl, P., *Chem. Ber.*, 1986, vol. 119, p. 464.
110. Tiedemann, R., Narjes, F., and Schaumann, E., *Synlett*, 1994, p. 494.
111. Posner, G.H., Wang, Q., Halford, B.A., Elias, J.S., and Maxwell, J.P., *Tetrahedron Lett.*, 2000, vol. 41, p. 9655.
112. Kai, H., Iwamoto, K., Chatani, N., and Murai, S., *J. Am. Chem. Soc.*, 1996, vol. 118, p. 7634.
113. Pennanen, S.I., *Tetrahedron Lett.*, 1977, vol. 30, p. 2631.
114. Polovinka, M.P., Vyglazov, O.G., Korchagina, D.V., and Barkhash, V.A., *Zh. Org. Khim.*, 1991, vol. 27, p. 2623.
115. Kuhn, T., Tamm, C., Riesen, A., and Zehnder, M., *Tetrahedron Lett.*, 1989, vol. 30, p. 693.
116. Olejniczak, T., Nawrot, J., Ciunik, Z., and Wawrzenczyk, C., *Pol. J. Chem.*, 2000, vol. 74, p. 673.
117. Kas'yan, L.I., Seferova, M.F., and Okovityi, S.I., *Alitsiklicheskie epoksidnye soedineniya. Metody sinteza* (Alicyclic Epoxy Compounds. Methods of Synthesis), Dnepropetrovsk: Dnepropetr. Gos. Univ., 1996.
118. Malinovskii, M.S., Kas'yan, L.I., and Ovsyanik, V.D., *Zh. Org. Khim.*, 1974, vol. 10, p. 1173.
119. Malinovskii, M.S., Kas'yan, L.I., and Ovsyanik, V.D., *Khim. Geterotsikl. Soedin.*, 1974, p. 29.
120. Nazarov, I.N., Kucherov, V.F., and Bukharov, V.G., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1958, p. 192.
121. Nazarov, I.N., Kucherov, V.F., and Bukharov, V.G., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1958, p. 328.
122. Kas'yan, A.O., Krishchik, O.V., Umrykhina, L.K., and Kas'yan, L.I., *Russ. J. Org. Chem.*, 1999, vol. 35, p. 630.
123. Giese, B., *Chem. Ber.*, 1974, vol. 107, p. 808.
124. Giese, B., *Chem. Ber.*, 1974, vol. 107, p. 819.
125. Fray, G.I. and Hilton, R.J., *J. Chem. Soc.*, 1966, vol. 11, p. 592.
126. Moss, G.P., Keat, O.C., and Bondar, G.V., *Tetrahedron Lett.*, 1996, vol. 37, p. 2877.
127. FRG Patent no. 4138438, 1994; *Ref. Zh., Khim.*, 1994, no. 7N83P.
128. Ninagawa, A., Suzuki, T., and Matsada, H., *Chem. Express*, 1986, p. 169.
129. Iwasaki, T., Kihara, N., and Endo, T., *Bull. Chem. Soc. Jpn.*, 2000, vol. 73, p. 713.
130. Le Boisselier, V., Postel, M., and Dunach, E., *J. Chem. Soc., Chem. Commun.*, 1997, p. 95.
131. Yamaguchi, K., Ebitani, K., Yoshida, T., Yoshida, H., and Kanedo, K., *J. Am. Chem. Soc.*, 1999, vol. 121, p. 4526.

132. Magdesijva, T.V., Zhukov, I.V., Chilov, G.G., Tomilova, L.G., and Butin, K.P., Abstracts of Papers, *XVIth Mendeleev Congress of General and Applied Chemistry*, St. Petersburg, 1998, vol. 4, p. 160.

133. Dumler, W. and Kisch, H., *Chem. Ber.*, 1990, vol. 123, p. 277.

134. Baba, A., Nozaki, T., and Matsuda, H., *Bull. Chem. Soc. Jpn.*, 1987, vol. 60, p. 1552.

135. Fuller, J., Carlin, R.T., De Lang, H.C., and Haworth, D., *J. Chem. Soc., Chem. Commun.*, 1994, p. 299.

136. Sheldon, R., *J. Chem. Soc., Chem. Commun.*, 2001, p. 2399.

137. Yang, H., Gu, Y., Deng, Y., and Shi, F., *J. Chem. Soc., Chem. Commun.*, 2002, p. 274.

138. Kruper, W.J. and Dellar, D.V., *J. Org. Chem.*, 1995, vol. 60, p. 725.

139. Paddock, R.L. and Nguyen, S.T., *J. Am. Chem. Soc.*, 2001, vol. 123, p. 11498.

140. Brunner, M., Mubmann, L., and Vogt, D., *Synlett*, 1994, p. 69.

141. Cheng, M., Darling, N.A., Lobkovsky, E.B., and Coates, G.W., *J. Chem. Soc., Chem. Commun.*, 2000, p. 2007.

142. Parker, R.E. and Isaacs, N.S., *Chem. Rev.*, 1959, vol. 59, p. 737.

143. Kirk, D.N., *Chem. Ind.*, 1973, p. 109.

144. Krasuskii, K.A., *Zh. Obshch. Khim.*, 1936, vol. 6, p. 460.

145. Tokumasu, M., Sasaoka, A., Takagi, R., Hiraga, Y., and Ohkata, K., *J. Chem. Soc., Chem. Commun.*, 1997, p. 875.

146. Derksen, A.J., van der Waals, A.C.L.M., van Ham, M.H.A., van Dongen, M., Borkent, J.H., de Gelder, R., Klunder, A.J.H., and Zwanenburg, B., *Tetrahedron Lett.*, 2000, vol. 41, p. 9189.

147. Tanada, Y. and Mori, K., *Eur. J. Org. Chem.*, 2001, no. 22, p. 4313.

148. Khomenko, T.M., Tatarova, L.E., Korchagina, D.V., and Barkhash, V.A., *Russ. J. Org. Chem.*, 2002, vol. 38, p. 498.

149. Il’ina, I.V., Korchagina, D.V., Salakhutdinov, N.F., and Barkhash, V.A., *Russ. J. Org. Chem.*, 2000, vol. 36, p. 1446.

150. Satoh, T., Kawase, Y., and Yamakawa, K., *Bull. Chem. Soc. Jpn.*, 1991, vol. 64, p. 1129.

151. Murfy, J.A. and Patterson, C.W., *J. Chem Soc., Perkin Trans. 1*, 1993, p. 405.

152. Mandal, P.K., Maiti, G., and Roy, S.C., *J. Org. Chem.*, 1998, vol. 63, p. 2829.

153. Dickinson, J.M., Murphy, J.A., Patterson, C.W., and Wooster, N.F., *J. Chem. Soc., Perkin Trans. 1*, 1990, p. 1179.

154. Corser, D.A., Marpless, B.A., and Dart, R.K., *Synlett*, 1992, p. 987.

155. Berlin, S., Ericsson, C., and Engman, L., *Org. Lett.*, 2002, vol. 4, p. 3.

156. Rajan Babu, T.V. and Nugent, W.A., *J. Am. Chem. Soc.*, 1994, vol. 116, p. 986.

157. Barrero, A.F., Cuerva, J.M., Herrador, M.M., and Valdivia, M.V., *J. Org. Chem.*, 2001, vol. 66, p. 4074.

158. Gansauer, A., *Synlett*, 1998, p. 801.

159. Gansauer, A., Pierobon, M., and Bluhm, H., *Synthesis*, 2001, vol. 16, p. 2500.

160. Rajan Babu, T.V. and Nugent, W.A., *J. Am. Chem. Soc.*, 1989, vol. 111, p. 4525.

161. Rana, K.K., Guin, C., and Roy, S.C., *Tetrahedron Lett.*, 2000, vol. 41, p. 9337.

162. Rana, K.K., Guin, C., and Roy, S.C., *Synlett*, 2001, p. 1249.

163. Kumar, V.S., Aubele, D.L., and Floreancig, P.E., *Org. Lett.*, 2002, vol. 4, p. 2489.

164. Mayer, S.F., Steinreiber, A., Orru, R.V.A., and Faber, K., *Eur. J. Org. Chem.*, 2001, no. 23, p. 4537.

165. Warrener, R.N., Butler, D.M., Margetic, D., Pfeffer, F.M., and Russell, R.A., *Tetrahedron Lett.*, 2000, vol. 41, p. 4671.

166. Munro, D. and Newman, Ch., *Tetrahedron Lett.*, 2000, vol. 41, p. 1483.

167. Madhushaw, R.J., Li, C.-L., Su, H.-L., Hu, C.-C., Lush, S.-F., and Liu, R.-S., *J. Org. Chem.*, 2003, vol. 68, p. 1872.