Pergamon

Tetrahedron 58 (2002) 9137–9161

TETRAHEDRON

Tetrahedron report number 620

Construction of cyclopentyl units by ring contraction reactions

Luiz F. Silva, Jr.*

Instituto de Química, Universidade de São Paulo, CP 26077, CEP 05513-970, Sao Paulo, SP, Brazil

Received 20 May 2002

Contents

1. Introduction

There are several molecules—natural or non natural—with remarkable biological activity possessing in their structure a cyclopentyl unit. Such a moiety can be found in alkaloids, steroids, prostaglandins, triquinanes, indans, guaianes, etc.[1–6] Therefore, the development of expedient and efficient methods for the construction of this unit has been an important goal in organic synthesis. Probably, the most used strategies to prepare complex molecules possessing a functionalized cyclopentyl unit is by cyclization reaction or by direct transformation of commercially available substrates that already bear this moiety. Although less used, the ring contraction of a carbocyclic compound is also a good route to assemble cyclopentyl units, because, in several cases, the reorganization of the bonds occurs with a high level of selectivity, leading to compounds not easily accessed by other methodologies.

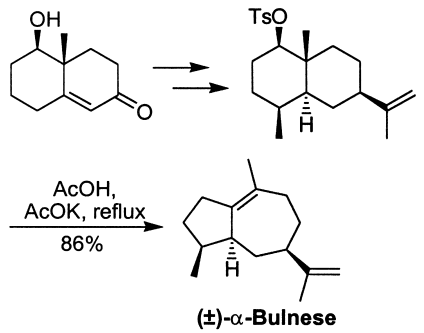
This article refers exclusively to the synthesis of cyclopentyl units from six-membered carbocyclic substrates. The definition of ring contraction through this article follows that previously mentioned by Redmore and Gutsche.[7,8]

This review is not intended to exhaustively cover the literature concerning the use of ring contraction reactions for the construction of cyclopentyl units. The intention is to present an overview of general and efficient methods, hoping that a panorama of the state-of-the-art of the subject can be given. Emphasis has been placed upon synthetic applications, particularly those involving the total synthesis of natural products. Thus, mechanisms are presented only in

Keywords: cyclopentyl unit; ring contraction; rearrangement; cyclopentanes.

* Tel.: +55-11-3091-3851; fax: +55-11-3815-5579;
e-mail: luizfsjr@iq.usp.br

PII: S0040-4020(02)00990-0

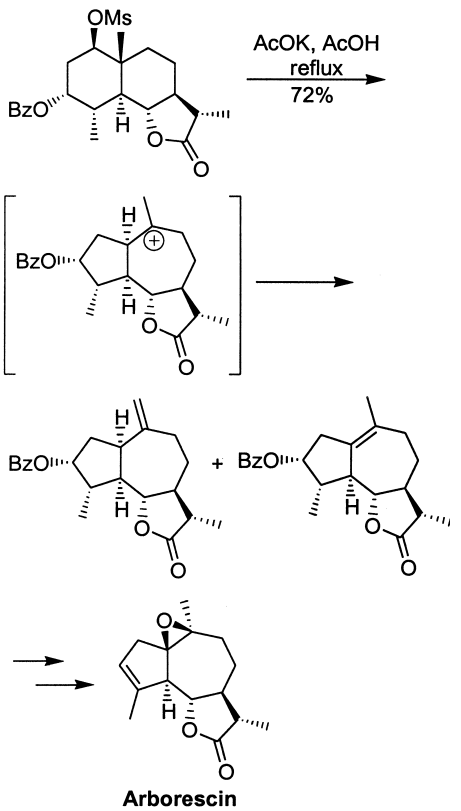


Heathcock and Ratcliffe, ref 12

Scheme 1.

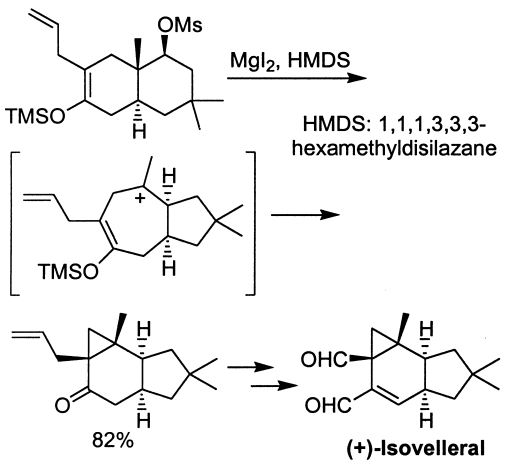
cases where recent advances were achieved and/or when they are crucial for understanding the formation of the products.

The ring contraction reactions were divided into five main groups: (i) acid-induced ring contractions; (ii) base-induced ring contractions; (iii) oxidative rearrangements; (iv) photochemical rearrangements; and (v) Wolff rearrangements. In the following items, a survey of each one of these groups is presented, by description of some selected examples.



Ando et al., ref 16

Scheme 2.



Wijnberg, de Groot and co-workers, ref 19

Scheme 3.

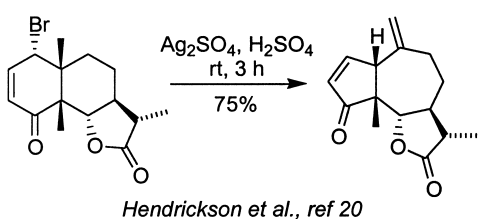
2. Acid-induced ring contractions

2.1. Wagner–Meerwein rearrangements

It is well documented that, under acidic conditions, an alcohol—or its derivatives—can generate a cationic intermediate, which is prone to a Wagner–Meerwein rearrangement.[9] Eventually, loss of a proton yields an olefin. When applied to cyclic compounds, this sequence may lead to a ring contraction product. Although in several cases this approach can give a mixture of isomeric olefins, a good level of selectivity has been obtained for a number of alicyclic molecules. Moreover, the isomeric olefins may be transformed into a single product later on in the synthetic sequence. Some selected examples are discussed below.

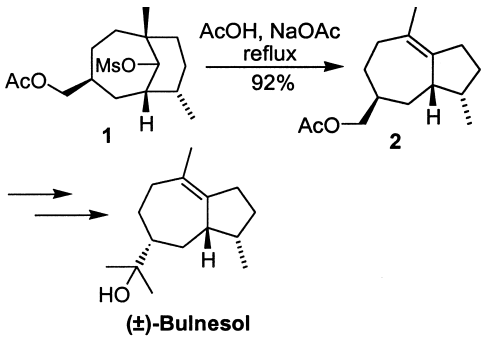
The solvolytic rearrangement of functionalized eudesmanolides has been used to construct the hydroazulene skeleton of guaianolides.[10] Such a reaction constituted the key step in the synthesis of several compounds,[11] including (±)-α-bulnese[12,13] (Scheme 1), (±)-bulnesol,[12,14] (±)-kessane,[15] arborescin[16] (Scheme 2), (+)-zaluzanin C,[17] and (−)-estafiantin.[18] In the recent total synthesis of (+)-isovelleral by De Groot and co-workers, an analogous rearrangement has been explored.[19] However, as shown in Scheme 3, in such a case a 5–7-fused system is not formed, because the cationic intermediate underwent a cyclization reaction leading to the tricyclic core of the target molecule.

Two other approaches have been described for the construction of 5–7-fused ring system utilizing a Wagner–Meerwein rearrangement. Treatment of halides with silver salts gives ring contraction products in good yield,[20,21] as exemplified for a santonin derivative in Scheme 4. In the synthesis of



Hendrickson et al., ref 20

Scheme 4.



Scheme 5.

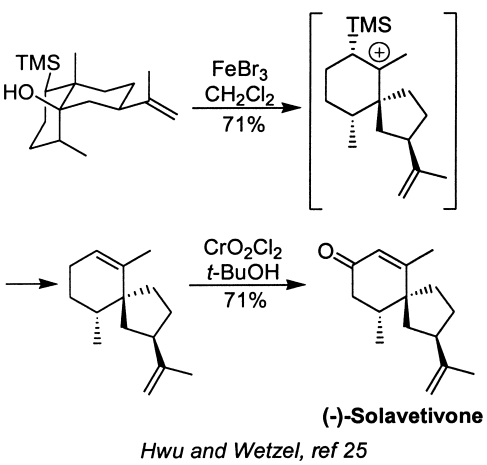
(±)-bulnesol, the bicyclic compound **1** was transformed into the hydroazulene compound **2**,[22] as shown in Scheme 5.

A silicon directed ring contraction reaction has been applied in the construction of carbocyclic spiro compounds.[23–25] This study culminated in the total synthesis of (−)-solavetivone,[25] as shown in Scheme 6. Finally, the preparation of spiro benzofuran derivatives[26] (Scheme 7) and the ring contraction of stannyl ketones toward the synthesis of (+)-β-cuparenone[27] (Scheme 8) have been described.

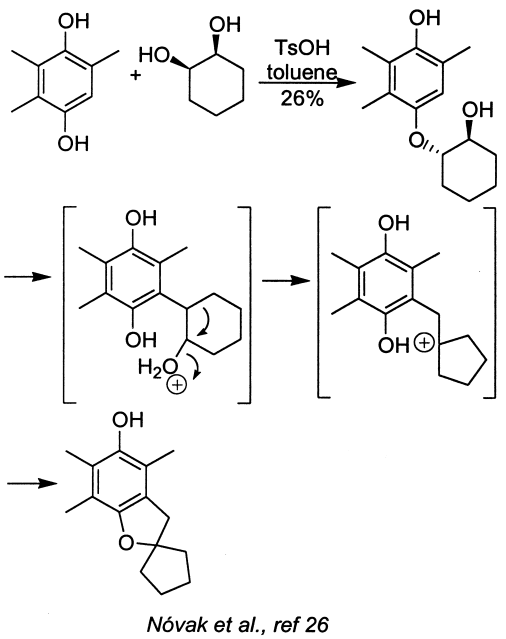
2.2. Pinacol rearrangements

Another strategy to generate a cationic intermediate that may undergo rearrangement is by the treatment of vicinal diols with an acid, yielding ketones or aldehydes, as the final product.[28] The earliest example of this transformation is the pinacol/pinacolone rearrangement, from which the name of the reaction was originated. Ring contraction products have been obtained with a good level of selectivity utilizing this approach, as shown in the following paragraphs.

The combination of a Lewis acid and a trialkyl orthoester is suitable to promote the rearrangement of a variety of 1,2-diols.[29,30] This protocol furnishes spirocyclic molecules in good yield, via a cyclic ortho ester intermediate, as exemplified in Scheme 9.

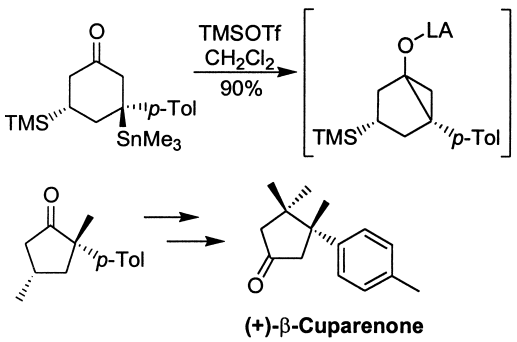


Scheme 6.

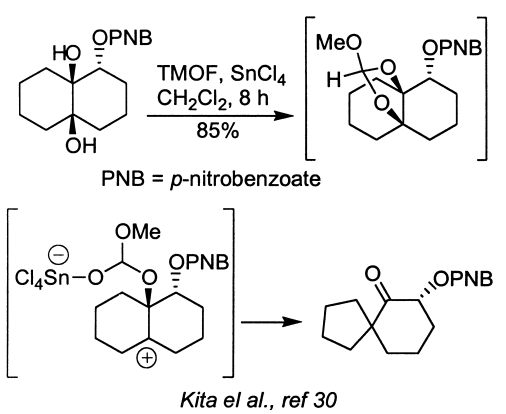


Scheme 7.

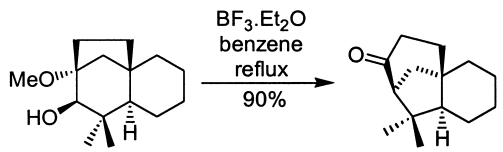
Cedrene and funebrene analogues were prepared by ring contraction of mono protected 1,2-diol substrates,[31] as exemplified in Scheme 10. Similarly, the same group accomplished the synthesis of (±)-hinesol.[32] The pinacol rearrangement was also employed in studies toward triterpenoids,[33] in the synthesis of (−)-aromadendrene[34,35] (Scheme 11), and in the construction of cyclopentane



Scheme 8.

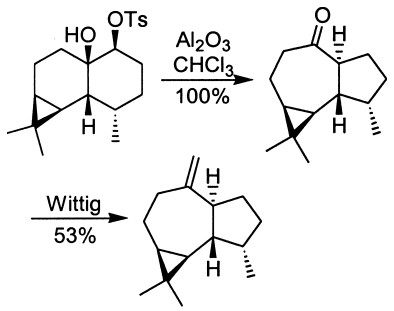


Scheme 9.



Hariprakasha and Subba Rao, ref 31

Scheme 10.



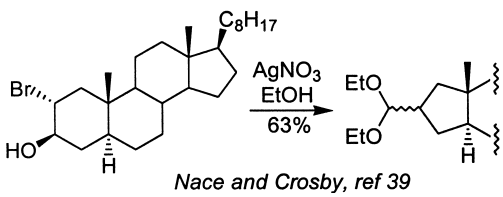
Büchi et al., ref 35

Scheme 11.

derivatives.[36] Semi-pinacol rearrangements are also an alternative for promoting the ring contraction,[37,38] as exemplified for the bromo-cholestanol shown in Scheme 12.[39]

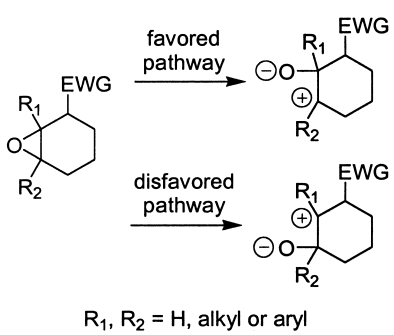
2.3. Rearrangement of epoxides

Epoxidation is one of the most important and general reactions in organic synthesis and can be performed with an outstanding level of enantioselectivity. In several instances, the acid-induced rearrangement of epoxides occurs in excellent yield and selectivity.[40–42] Therefore, this two-step sequence (epoxidation/rearrangement) constitutes a powerful method to a variety of complex ketones.[43] When the oxirane is within a six-membered ring, the rearrangement may lead to a ring contraction product in a highly efficient manner. Often, the presence of an electron withdrawing group in the substrate directs the oxirane opening, allowing a good level of regioselectivity in the reaction, as outlined in Scheme 13. Typically, the rearrangement is promoted by a Lewis acid in a non-nucleophilic solvent, and can be realized utilizing di-, tri- and tetrasubstituted epoxides as substrate.

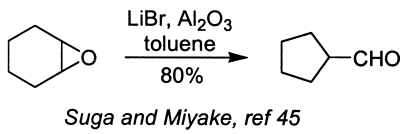


Nace and Crosby, ref 39

Scheme 12.

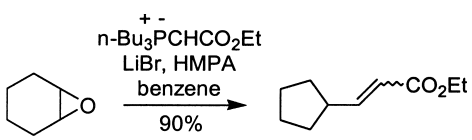


Scheme 13.



Suga and Miyake, ref 45

Scheme 14.

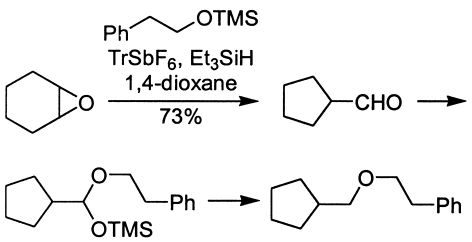


Gerkin and Rickborn, ref 46

Scheme 15.

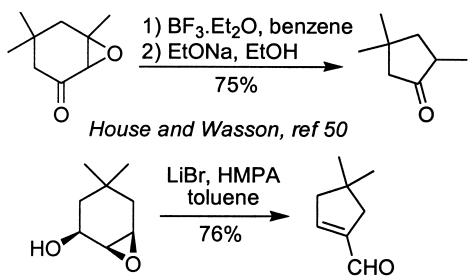
The ring contraction of the readily available cyclohexene oxide leads to cyclopentanecarboxaldehyde in good yield,[44,45] as exemplified in Scheme 14. This aldehyde can be further reacted in situ, giving more complex cyclopentyl units,[46–49] as shown in Schemes 15 and 16. Moreover, cyclopentyl units can also be obtained from other disubstituted epoxides,[50,51] as exemplified in Scheme 17. An unusual way to obtain ring contraction products from epoxides has been observed by treating a epoxy-cholestane with a Grignard reagent,[52] as shown in Scheme 18.

Treatment of trisubstituted epoxides with acids leads to ring opening in accordance to the Markovnikov rule, giving ring



Harada and Mukaiyama, ref 49

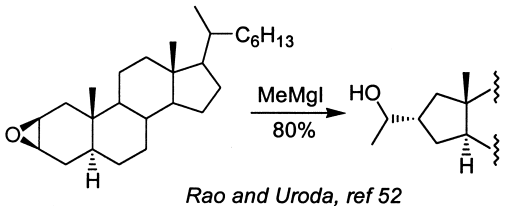
Scheme 16.



House and Wasson, ref 50

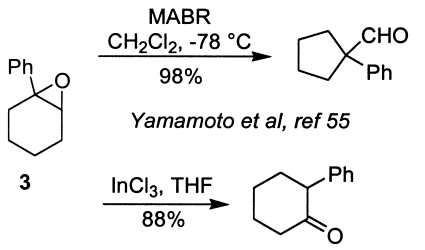
Magnuson and Thorén, ref 51

Scheme 17.



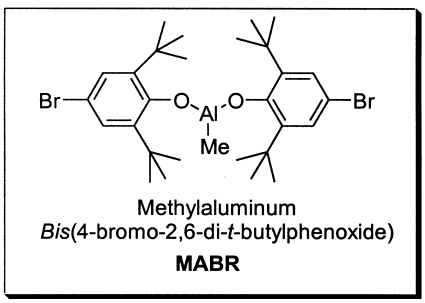
Rao and Uroda, ref 52

Scheme 18.



Yamamoto et al, ref 55

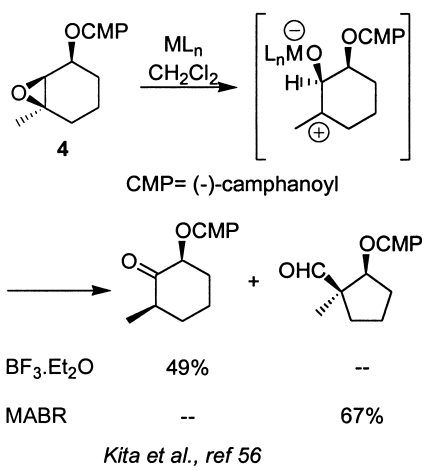
Ranu and Jana, ref 58



Scheme 19.

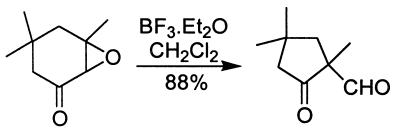
contraction products bearing a quaternary carbon stereocenter.[53–56] However, depending on the reaction conditions, cyclohexanones are formed exclusively,[57,58] because hydride migration occurs preferentially to the alkyl group. The behavior of the epoxides **3** and **4** toward different Lewis acids exemplifies well this dichotomy of the rearrangement, as shown in Schemes 19 and 20. Numerous cyclopentane derivatives have been prepared by acid-induced ring contraction of trisubstituted epoxides,[56,59–64] as shown in Scheme 21.

An useful application of the rearrangement of trisubstituted

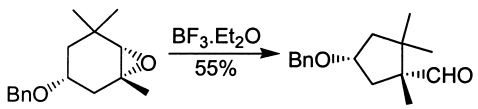


Kita et al., ref 56

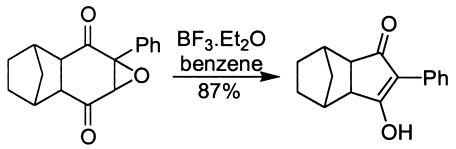
Scheme 20.



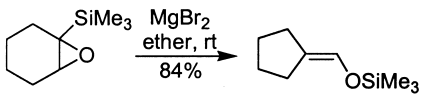
Bach and Klix, ref 60



Constantino et al., ref 62a



Wilgus, III et al., ref 63

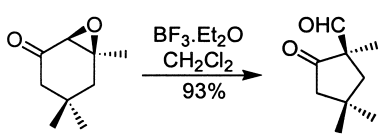


Hudrlik et al., ref 64

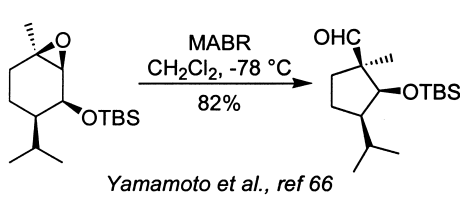
Scheme 21.

epoxides is the construction of functionalized enantiomerically pure cyclopentanes,[65–67] as exemplified in Scheme 22. Such a strategy has been used to accomplish the asymmetric total synthesis of (+)-β-cuparenone,[68] (−)-massoialactone,[68] (−)-frontalin,[69] and (−)-malyngolide,[69] as exemplified in Scheme 23.

The acid-mediated rearrangement of tetrasubstituted epoxides within a six-membered carbocyclic compound constitutes a powerful tool to the synthesis of cyclopentyl units bearing a quaternary carbon stereocenter. As should be expected, in non-symmetrical tetrasubstituted epoxides, the cleavage of the oxirane ring could occur in two possible ways, leading to a mixture of isomeric rearrangement products. Nevertheless, Kita and co-workers demonstrated that the regiochemistry of the cleavage of the oxirane could be easily predicted in epoxy acylates by analysis of the substituents, because the ionic intermediate bears the positive charge at the more stable position. Thus, the ring contraction of 2,3-dialkyl-epoxide[56] (such as **5**, in Scheme 24) and 2-alkyl-3-aryl-epoxide[70] (such as **6**, Scheme 25)

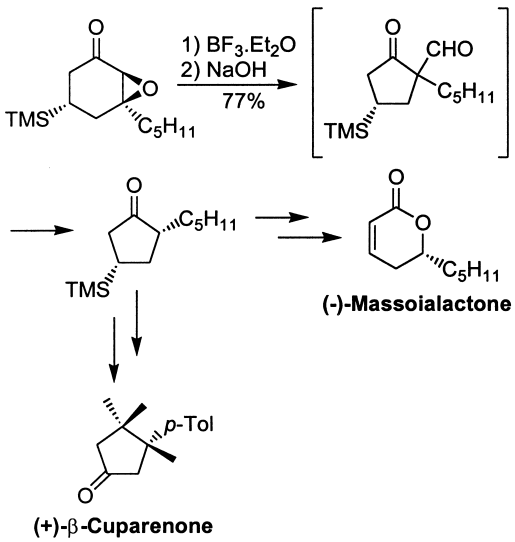


Wetzel et al., ref 65



Yamamoto et al., ref 66

Scheme 22.

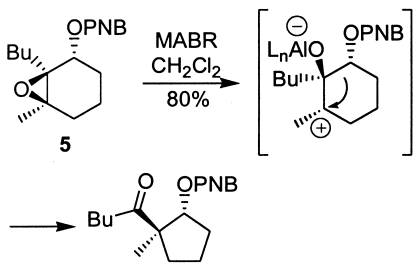


Asaoka et al., ref 68

Scheme 23.

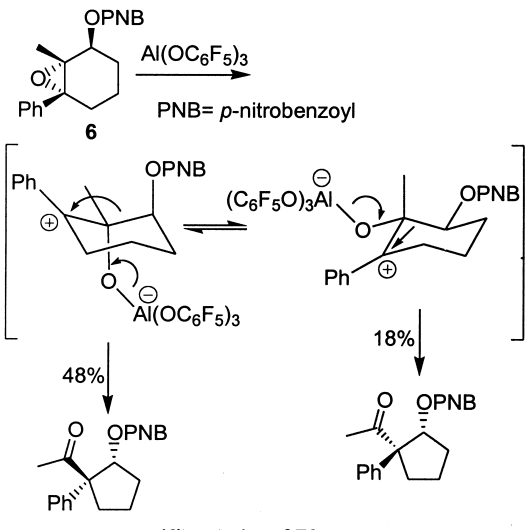
occurs by C-3 cleavage, whereas C-2 cleavage is observed in the rearrangement of 3-alkyl-2-aryl-epoxides,[71,72] as exemplified for **7** in Scheme 26.

The rearrangement of tetrasubstituted epoxides has been broadly applied in organic synthesis[73–79] and some representative examples are shown in Scheme 27.



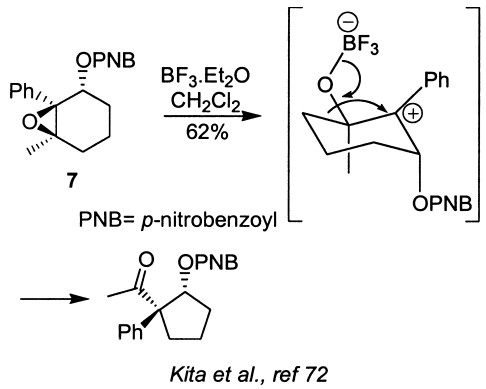
Kita et al., ref 56

Scheme 24.



Kita et al., ref 70

Scheme 25.



Kita et al., ref 72

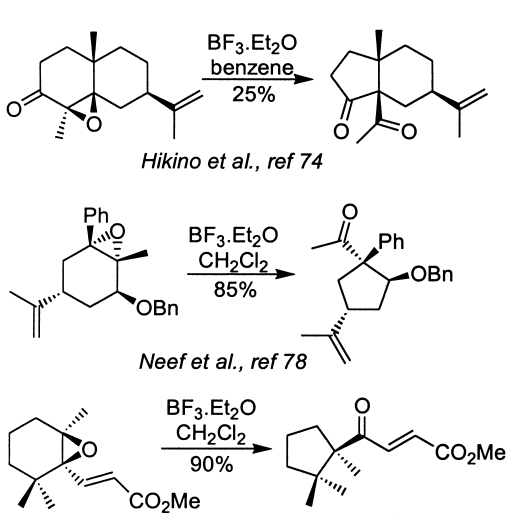
Scheme 26.

In addition to the construction of cyclopentanes in a highly selective manner, as above described, the rearrangement of tetrasubstituted epoxides has been used in the synthesis of numerous spiro cyclic compounds,[23,24,80–83] including optically active molecules.[82,84,85] Recently, this strategy has been used in the total synthesis of the potent antitumor antibiotic fredericamycin A.[85b,c] Representative examples are shown in Scheme 28. As already mentioned, the presence of an electron withdrawing group is crucial in the regioselectivity of the ring opening of the oxirane,[82] as shown in Scheme 29.

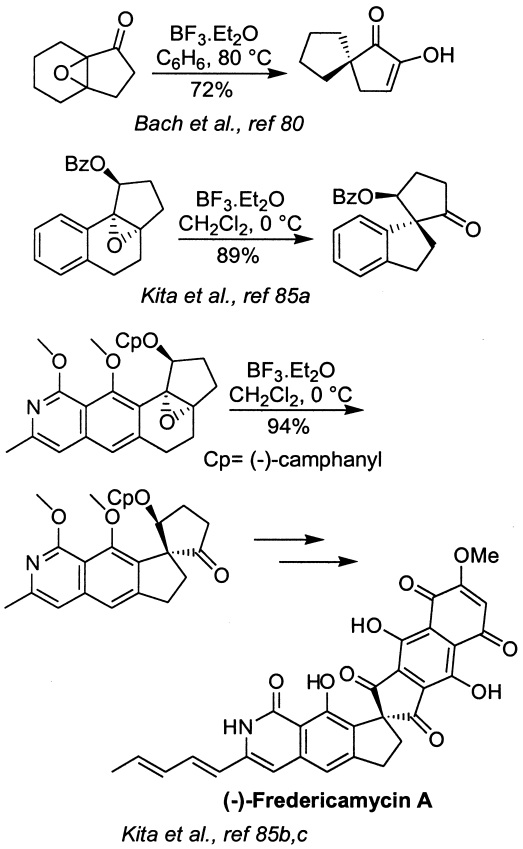
3. Base-induced ring contractions

3.1. Favorskii rearrangement

One of the most used methods to perform the ring contraction of a six-membered carbocyclic compound is the Favorskii rearrangement,[86–89] which is known for more than a hundred years.[90] This rearrangement occurs by treating α-halo-ketones with bases, such as alkoxides and amines. Due to its great versatility and broad application, this reaction has been intensively used in the last decades and some representative examples are discussed in the following paragraphs.



Scheme 27.



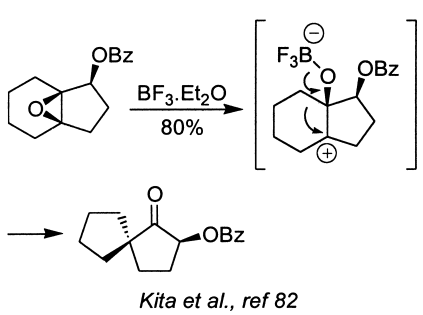
Scheme 28.

3.1.1. Favorskii rearrangements promoted by alkoxides.

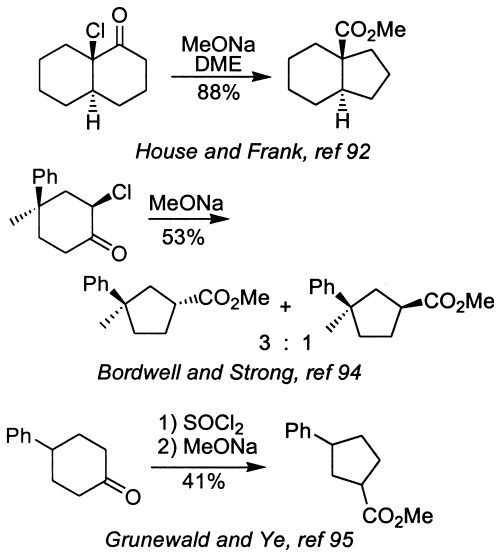
A classic protocol to assemble functionalized cyclopentanes is by the action of sodium methoxide on α-halo-cyclohexanones,[91–95] as exemplified in Scheme 30.

A well-established strategy for the preparation of optically active complex molecules is the selection of a readily available monoterpenic compound as starting material. An example of such a case in the context of ring contraction reactions is the cyclopentane **8**, which can be prepared in two steps from the monoterpene (+)-pulegone,[96–102] and has been used as a chiral non-racemic starting material in the synthesis of several natural products,[103–108] as outlined in Scheme 31. The skeletal rearrangement of carvone derivatives can also be utilized to obtain useful building blocks,[109,110] as exemplified in Scheme 32.

In addition to the typical examples above described, the Favorskii reaction has been applied in some less obvious



Scheme 29.



Scheme 30.

substrates. Fraga et al.,[111,112] in the synthesis of a gibberellin A12 isomer,[113] have utilized a chloro-enol lactone as substrate, as shown in Scheme 33. Another unusual type of Favorskii ring contraction is the Michael addition of the malonate anion to the cyclohexenone **9**, leading to the enolate **10**, which then rearranges to the isomeric cyclopentanes **12** and **13**,[114] as shown in Scheme 34. An analogous reaction is observed treating 6-chloro-2-vinylidenecyclohexanones with sodium methoxide.[115] Moreover, 2-chlorocyclohexanone yields ring contraction products when treated with the malonate anion.[116]

3.1.2. Favorskii rearrangements promoted by amines.

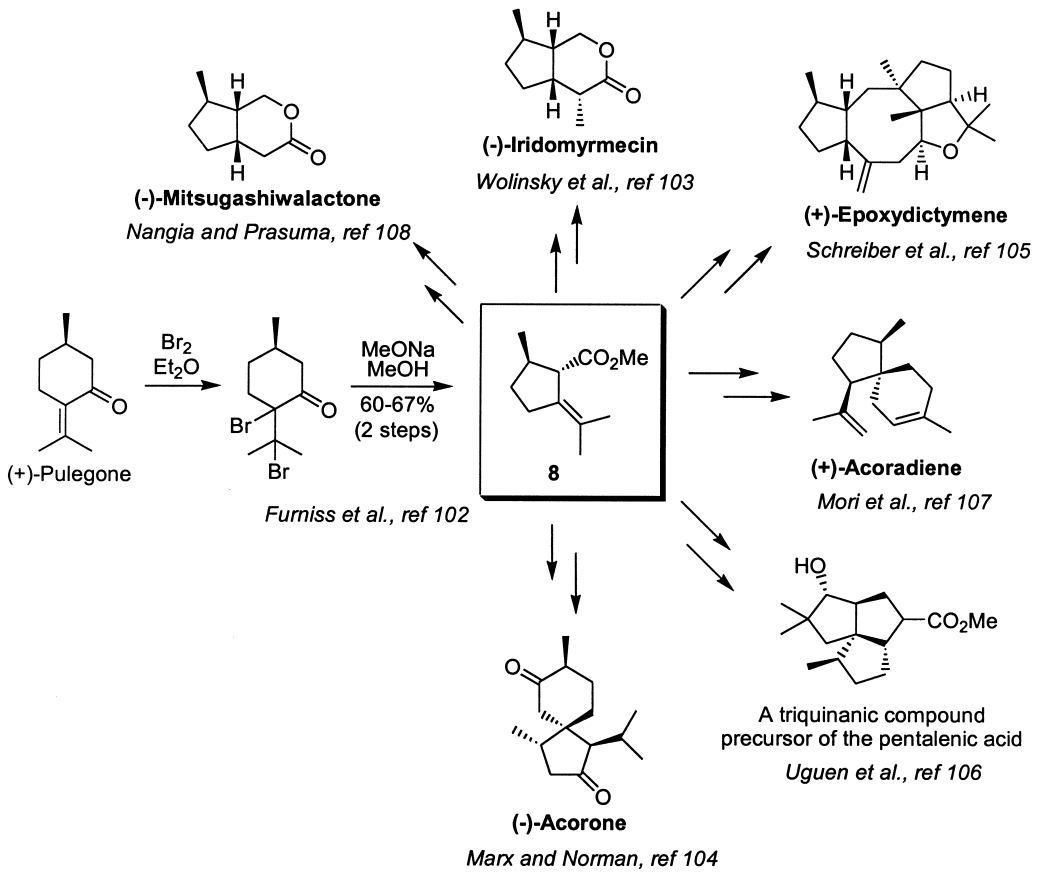
Amines are suitable bases to mediate the Favorskii rearrangement, as exemplified for the 2,6-dibromocyclohexanones[117–121] shown in Scheme 35. Indeed, this kind of base may lead to better results than alkoxides and hydroxides.[122,123] The behavior of 2-chloro-6-phenylcyclohexanone toward two different bases exemplifies well this statement,[122] as shown in Scheme 36. 2-Chlorocyclohexanone can also be transformed into an amide by an electrochemically induced Favorskii reaction.[124]

Another entry to α,β-unsaturated amides is the Favorskii rearrangement of α-chloro β-keto sulfones, followed by a reductive desulfonylation and β-elimination of the sulfonyl group formed,[125,126] as exemplified in Scheme 37.

3.2. Other base-induced ring contractions

Searching for other potent anticancer agents, some groups investigated the skeletal rearrangement of taxol® derivatives. As shown in Scheme 38, the ring contraction can be performed in either the A ring (compounds **14** and **15**)[127,128] or the B ring (compound **16**).[129] Although obtained in low yield, the compound **14** has an activity comparable to taxol® in the tubulin depolymerization assay.[127] The rearrangement of taxol® and its derivatives has also been performed by using Lewis acids,[130,131] by biotransformation,[132] and by photochemical rearrangement.[133]

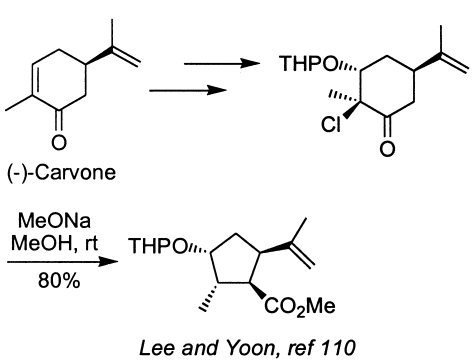
The negative-ion pinacol rearrangement allows the



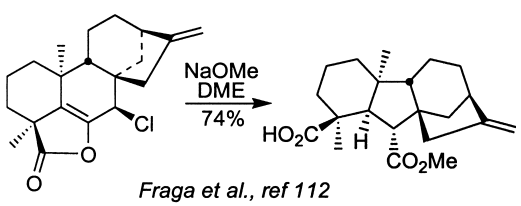
Scheme 31.

construction of cyclopentyl units,[134] as exemplified in Scheme 39. This ring contraction was used in the rearrangement of steroid derivatives.[135,136] The base catalyzed rearrangement of 1,3-diols also furnishes ring contraction products. Marshall and Brady,[137] for example, achieved the synthesis of (±)-hinesol by this rearrangement, as shown in Scheme 40.

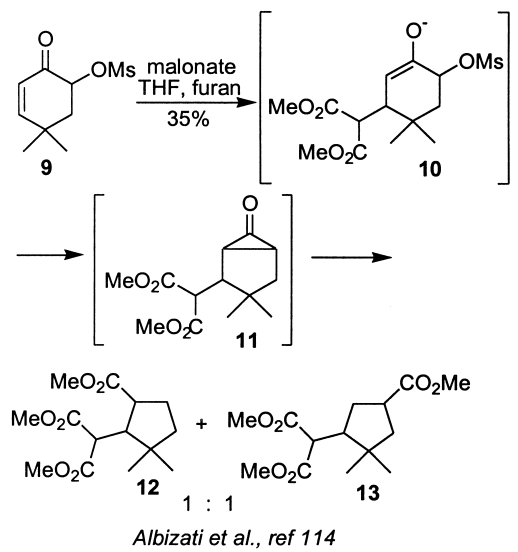
The guaiane skeleton has been obtained by a base-induced rearrangement of a 1,4-diol moiety,[138,139] which occurs by the mechanism shown in Scheme 41, as proposed by Wijnberg and co-workers.[140] Such a ring contraction/ring expansion strategy has been used to accomplish the total synthesis of (±)-5-*epi*-nardol,[140] of (±)-alloaromadendranediol,[141] of (±)-furanether B[142] and of an isomer of (±)-dictamnol,[143,144] whose structures are shown in Scheme 42.



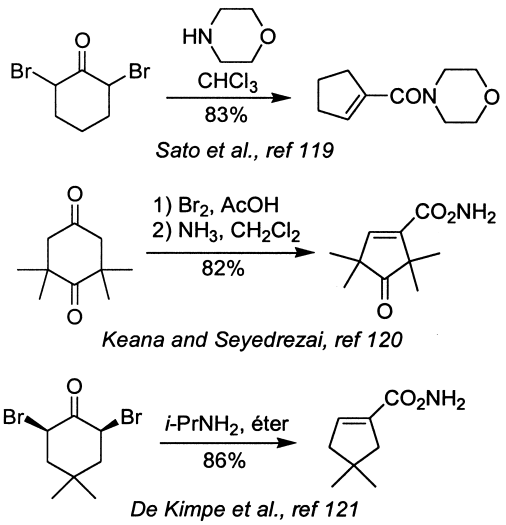
Scheme 32.



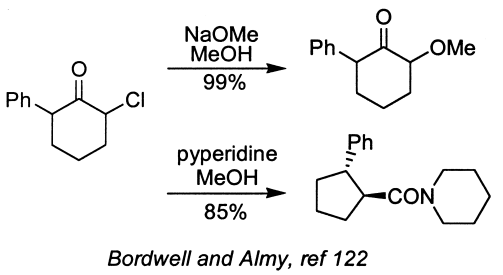
Scheme 33.



Scheme 34.



Scheme 35.



Scheme 36.

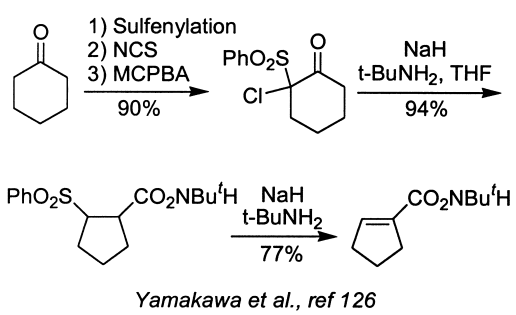
The reaction pathway is clearly dependent on the structure of the 1,4-diol,[19] as shown in Scheme 43.

Epoxy-ketones can be converted into cyclopentenols by treatment with H_2O_2 and NaOH,[145a] as shown in Scheme 44. During this reaction, a decarboxylation reaction also occurs. The rearrangement of epoxy-ketones has also been used to prepare chiral building blocks bearing a cyclopentyl unit.[145b]

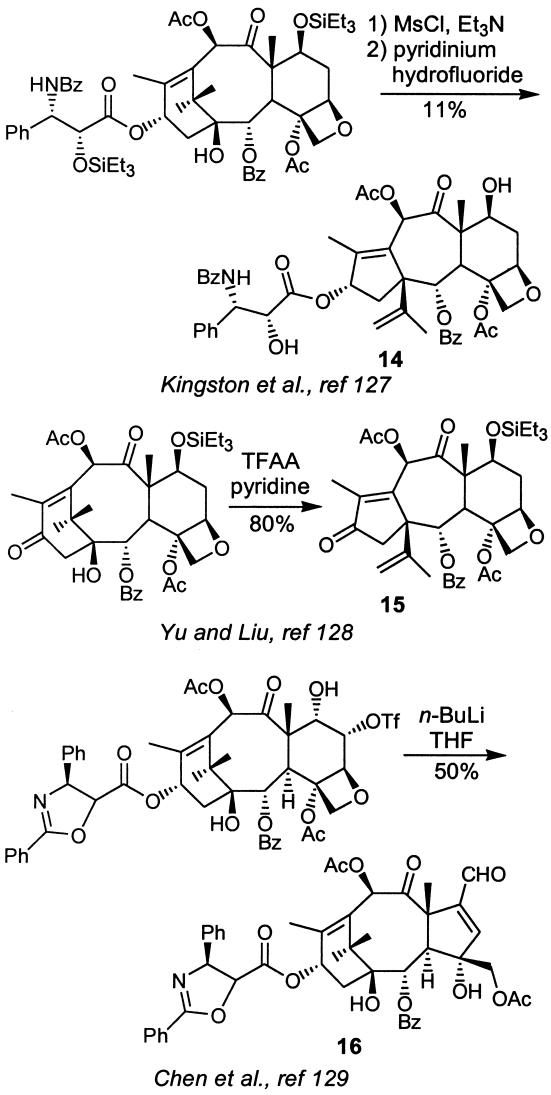
The oxidation of phenanthrols, followed by ring contraction, established a new route to the synthesis of fluorenones such as **17**,[146,147] as exemplified in Scheme 45.

4. Oxidative rearrangements

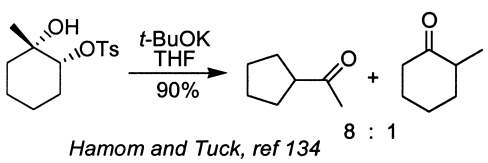
Although there is a plethora of oxidizers available in organic



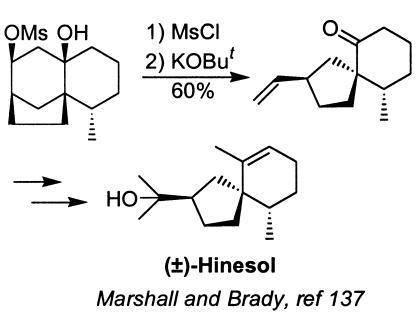
Scheme 37.



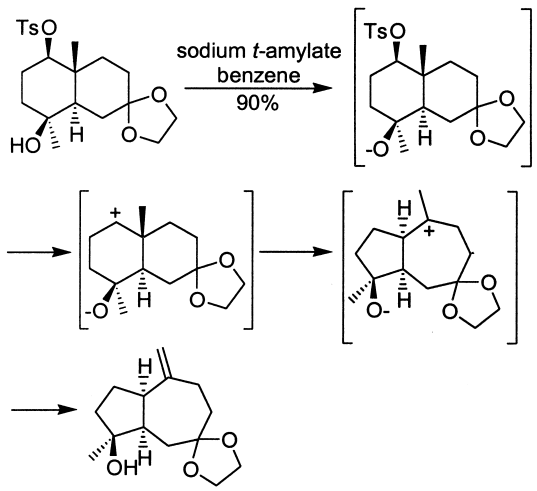
Scheme 38.



Scheme 39.



Scheme 40.



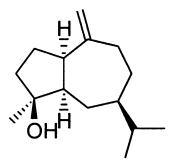
Wijnberg, De Groot, and co-workers, ref 140

Scheme 41.

synthesis, only a few are effective to promote oxidative rearrangements that lead to ring contraction products, as discussed in the following paragraphs.

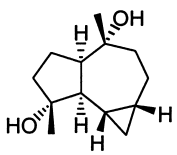
4.1. Thallium(III)-promoted ring contraction

Thallium(III) salts can mediated the rearrangement of



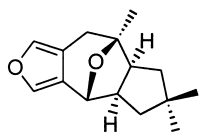
(±)-5-*epi*-Nardol

Wijnberg, De Groot, and co-workers, ref 140



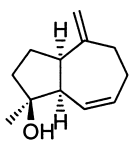
(±)-Alloaromadendranediol

Wijnberg, De Groot, and co-workers, ref 141



(±)-Furanether B

Wijnberg, De Groot, and co-workers, ref 142

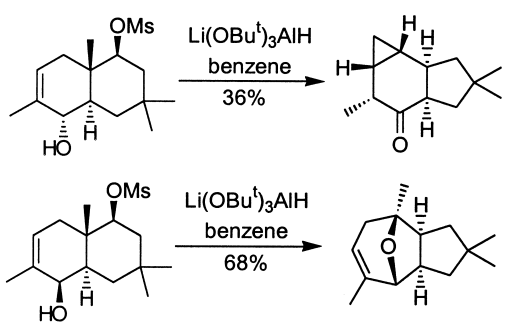


A Dictamnol isomer

Koike et al., ref 143

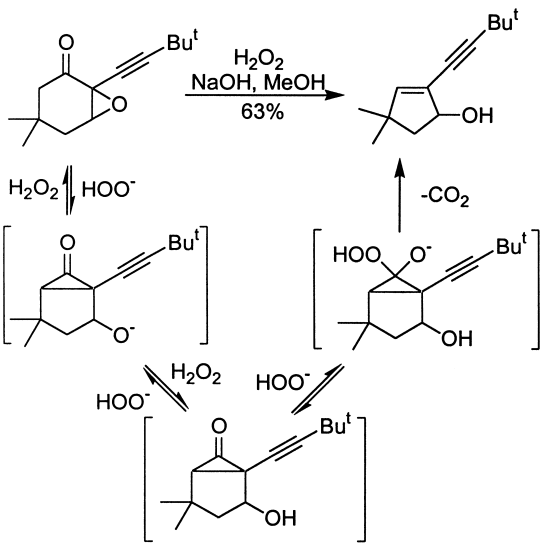
Wijnberg, De Groot, and co-workers, ref 144

Scheme 42.



Wijnberg, De Groot, and co-workers, ref 19

Scheme 43.



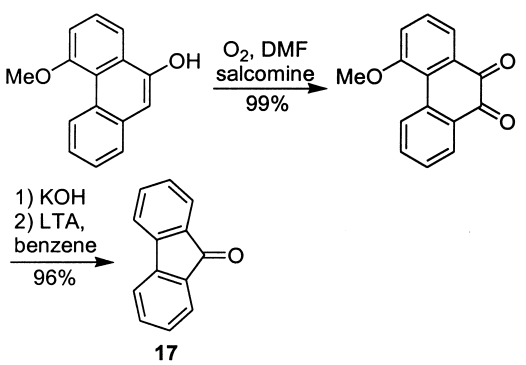
Margaretha et al., ref 145

Scheme 44.

several olefins and ketones.[148–150] The most efficient salt in ring contraction reactions is thallium trinitrate (TTN), which was used to promote the ring contraction in more than 60% of the papers concerning this transformation.[151] In the last years, only TTN has been used to construct cyclopentyl units from carbocyclic six-membered rings.

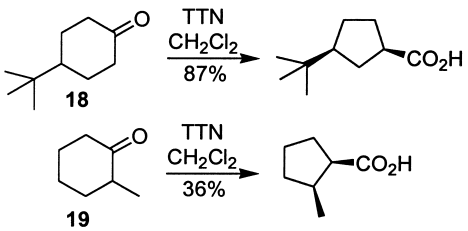
Using TTN-promoted rearrangements, cyclopentanes, hydrindanes and indans have been obtained. The preparation of cyclopentanecarboxylic acids by the oxidative rearrangement of alkylcyclohexanones can be performed using TTN,[152] as exemplified in Scheme 46. Under similar conditions, *trans*-hydrindanes are obtained in excellent yield and diastereoselectivity from readily available *trans*-2-decalones,[153] as illustrated for **20** in Scheme 47. However, the ring contraction of alkylcyclohexanones and *trans*-2-decalones do not occur efficiently using ketones with alkyl groups closer to the carbonyl group, as shown for **19** (Scheme 46) and for **21** (Scheme 47). In contrast to the oxidation of *trans*-2-decalones, the reaction of the corresponding *cis*-2-decalones led to the *cis*-hydrindanes with low regio and/or diastereoselectivity, as exemplified in Scheme 48.[154]

The diastereoselectivity of the ring contraction of ketones



Fu and Snieckus, ref 146

Scheme 45.

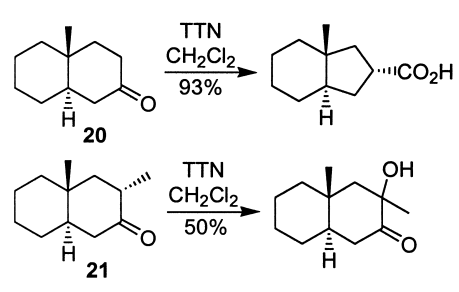


Ferraz and Silva, Jr, ref 152

Scheme 46.

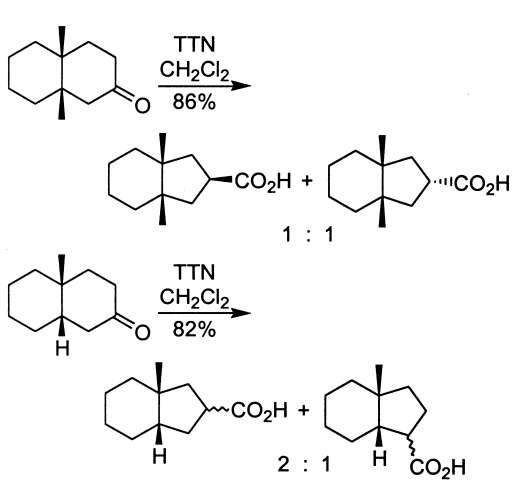
was explained invoking the mechanism proposed by McKillop and Taylor,[152,153,155] as exemplified in Scheme 49 for a *trans*-2-decalone.

Three approaches for the construction of indans were investigated using TTN-promoted ring contraction. The first was by the oxidation of 1-tetralones using TTN supported on K-10,[156] which led to ring contraction products in moderated yield. The second approach was by the reaction of 1,2-dihydronaphthalenes with TTN in MeOH or in TMOF, which furnished indans in good yield,[157] as shown for **22** and for **23** in Scheme 50. It is worth noting that only the *trans*-1,3-disubstituted indan, which is present in natural products such as mutisianthol[158,159] and *trans*-trikentrins,[160] was obtained in the reaction of 4-methyl-1,2-dihydronaphthalene (**22**). The diastereoselectivity can be explained by the mechanism shown in Scheme 51. The ring contraction of 1,2-dihydronaphthalenes does not take place applied for olefins bearing an alkyl group at the



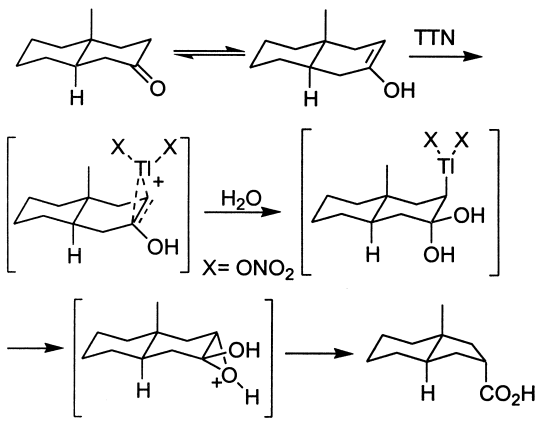
Ferraz and Silva, Jr, ref 153

Scheme 47.



Ferraz and Silva, Jr, ref 154

Scheme 48.

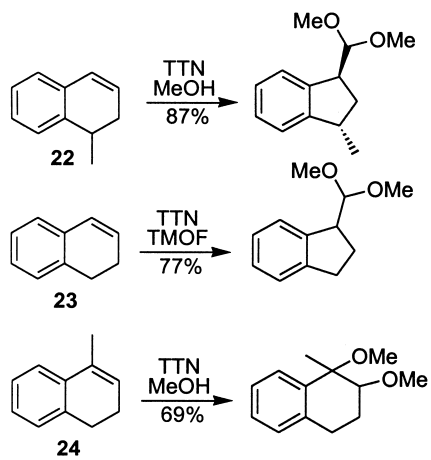


Ferraz and Silva, Jr, ref 153

Scheme 49.

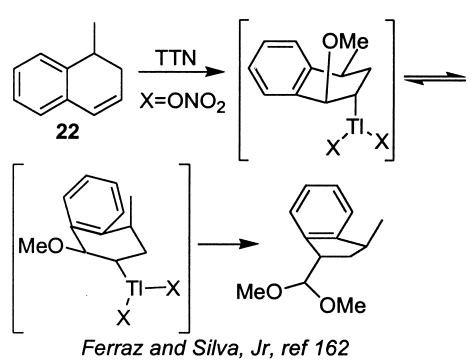
double bond, such as **24** (Scheme 50). However, this drawback could be overcome by using 3-alkenols as substrate.[161,162] When treated with TTN in a mixture of AcOH and H_2O, these substrates furnished functionalized indans, as a single diastereomer (Scheme 52). The diastereoselectivity can be explained by coordination of the thallium(III) and the oxygen during the rearrangement step. Similar behavior was observed for the corresponding alkyl ethers of the alkenols.[163]

The oxidation of 3-alkenols by TTN is also useful to obtain cyclopentanes,[161,164] as exemplified in Scheme 53.



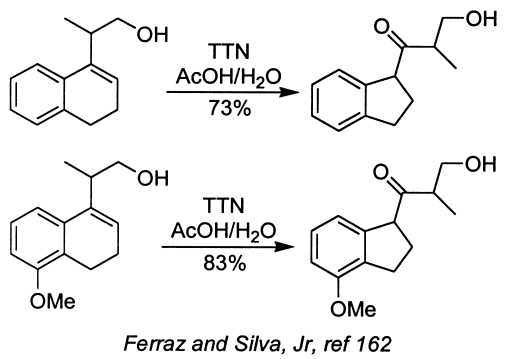
Ferraz et al., ref 157

Scheme 50.



Ferraz and Silva, Jr, ref 162

Scheme 51.



Ferraz and Silva, Jr, ref 162

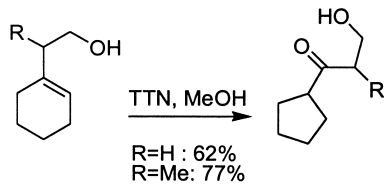
Scheme 52.

4.2. Lead(IV)-promoted ring contraction

Lead(IV), which is isoeletronic to thallium(III),[165] is a suitable oxidant to perform ring contraction reactions of cyclic ketones, although α-acetoxyketones are the main (or exclusive) product in several cases.[166] The rearrangements are usually performed using lead tetraacetate (LTA) in the presence of acids, such as BF_3 or $HClO_4$. In the following paragraphs examples of ring contraction reactions utilizing LTA as oxidant are presented.

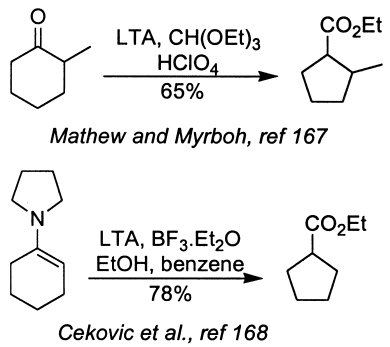
Cyclopentane units are obtained treating cyclohexanones[167] or their corresponding enamines[168] with lead tetraacetate, as exemplified in Scheme 54. The stereochemical aspects of the rearrangement of alkylcyclohexanones were not investigated by the authors. However, from our point of view, a diastereoselectivity similar to that observed in TTN promoted ring contraction of alkylcyclohexanones (cf. Scheme 46) can be expected.[169]

The synthesis of bioactive 1,1,6-trisubstituted indans was achieved from 1-tetralones.[170,171] The first step in this sequence was a LTA promoted ring contraction of 1-tetralone,[172] as exemplified in Scheme 55.



Ferraz et al., ref 164

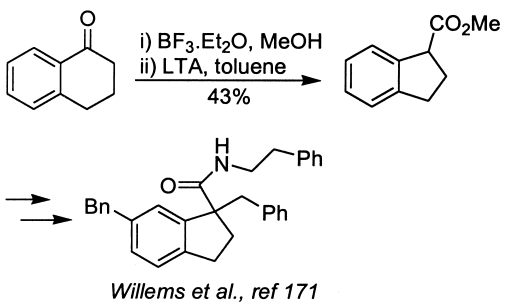
Scheme 53.



Mathew and Myrboh, ref 167

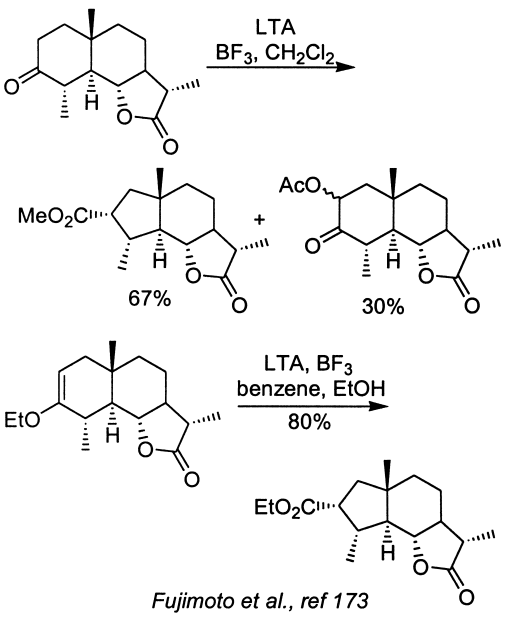
Cekovic et al., ref 168

Scheme 54.



Willems et al., ref 171

Scheme 55.

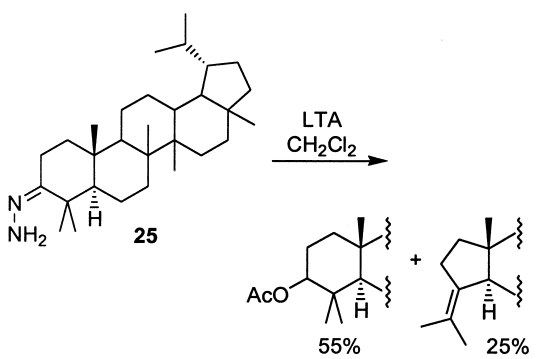


Fujimoto et al., ref 173

Scheme 56.

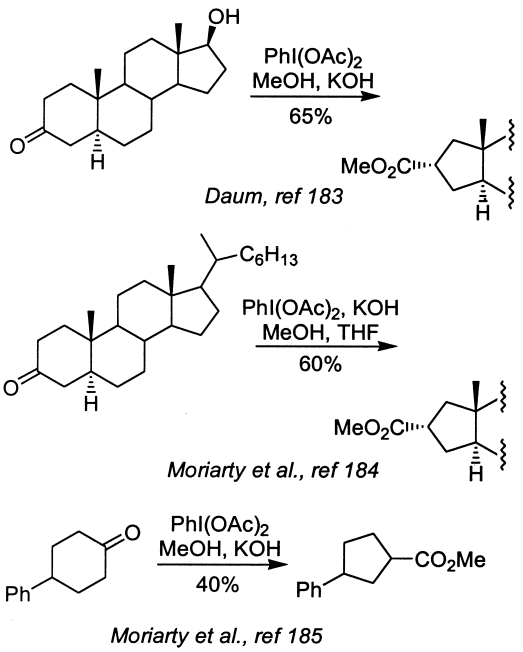
The reaction of a santonin derivative with LTA allowed the preparation of a highly functionalized hydrindane.[173] Better yields were observed with the corresponding enol ether, as shown in Scheme 56. However, other substrates, also possessing a *trans*-decalone unit, led to a mixture of α-acetoxyketones and the ring contraction products, where the latter was always the minor compound.[174–176]

Although formed as a minor constituent, the ring contraction product of the hydrazone **25** was isolated after treatment with LTA,[177] as shown in Scheme 57. However,

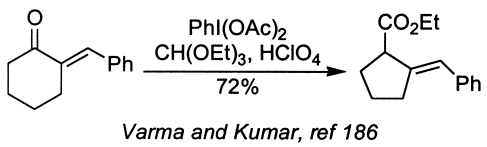


Nag and Bose, ref 177

Scheme 57.



Scheme 58.



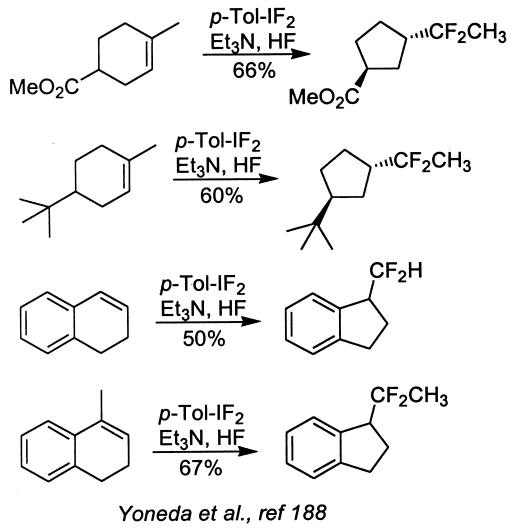
Scheme 59.

this behavior does not appear to be general to this class of compound.[178,179]

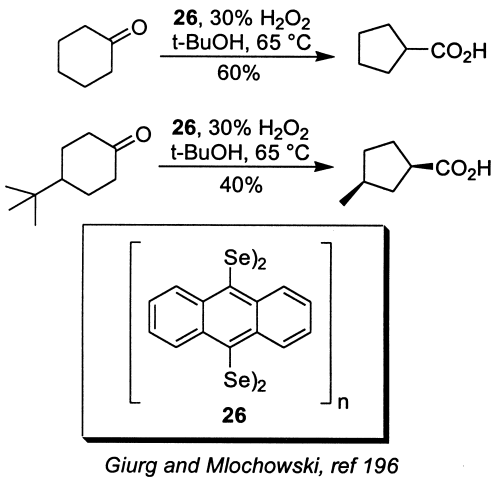
4.3. Hypervalent iodine-promoted ring contraction

Similarly to thallium(III) salts, hypervalent iodine reagents can react as electrophile with ketones and olefins, giving an adduct possessing a good leaving group.[180–182] Therefore, this class of compounds is also a good rearrangement promoter.

Typically, the ring contractions can be performed using iodobenzene diacetate under basic conditions,[183–185] as shown in Scheme 58. However, α,β-unsaturated ketones led to functionalized cyclopentanes under acidic condition,[186a] as exemplified in Scheme 59. The isolation of the iodonium intermediate, followed by thermal rearrangement has also been reported.[186b]



Scheme 60.

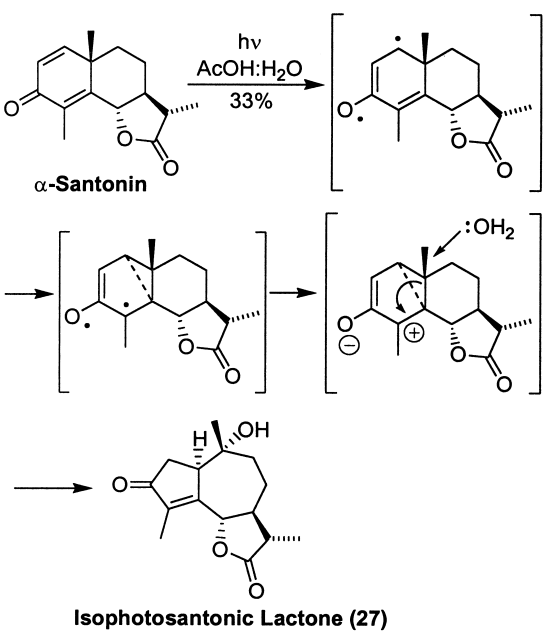


Scheme 61.

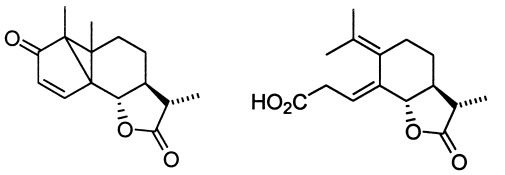
Other hypervalent iodine compounds were also used in ring contraction reactions. Utilizing *p*-iodotoluene difluoride as oxidant, the construction of cyclopentanes and of indans has been described by Yoneda et al.,[187,188] as exemplified in Scheme 60. Fluorinated indans can also be obtained by reaction of fluorinated tetralins with antimony pentafluoride.[189] Finally, the ring contraction of cyclohexene yielded cyclopentanecarboxaldehyde when treated with $PHI^{+}OBF_3^{-}$ in CH_2Cl_2.[190]

4.4. Selenium(IV)-promoted ring contraction

The oxidation of cyclohexanones by selenium dioxide is known for some decades.[191–195] The use of catalytic



Scheme 62.



Scheme 63.

amounts of poly(bisanthracenyl)diselenide (**26**) to promote the ring contraction of ketones has been recently described,[196] as shown in Scheme 61. The oxidative rearrangement of ketones promoted either by thallium(III) or by selenium(IV) occurs with similar diastereoselectivity (compare, for example, Schemes 46 and 61), because both oxidants react through an electrophilic addition to the enol form of the ketones. These additions follow the Markovnikov rule and occur in a *trans*-diaxial fashion.

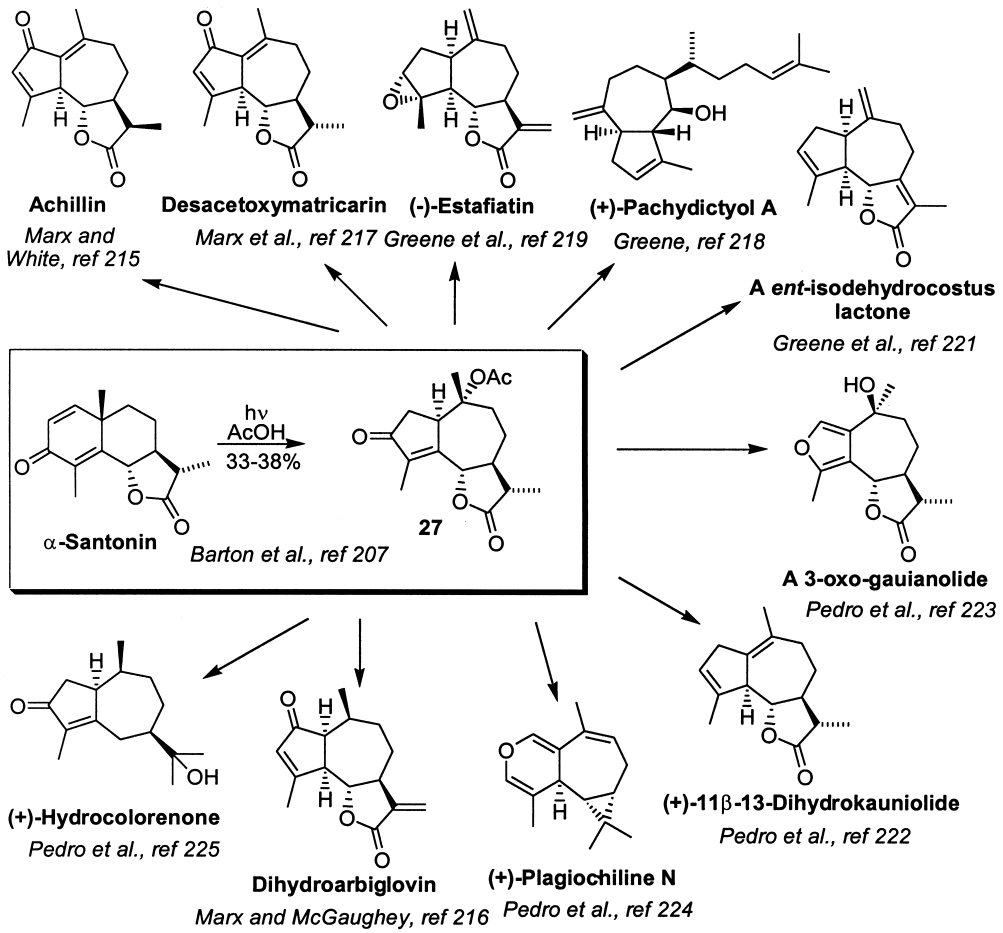
5. Photochemical rearrangements[197]

5.1. Ring contraction of cross-conjugated dienones

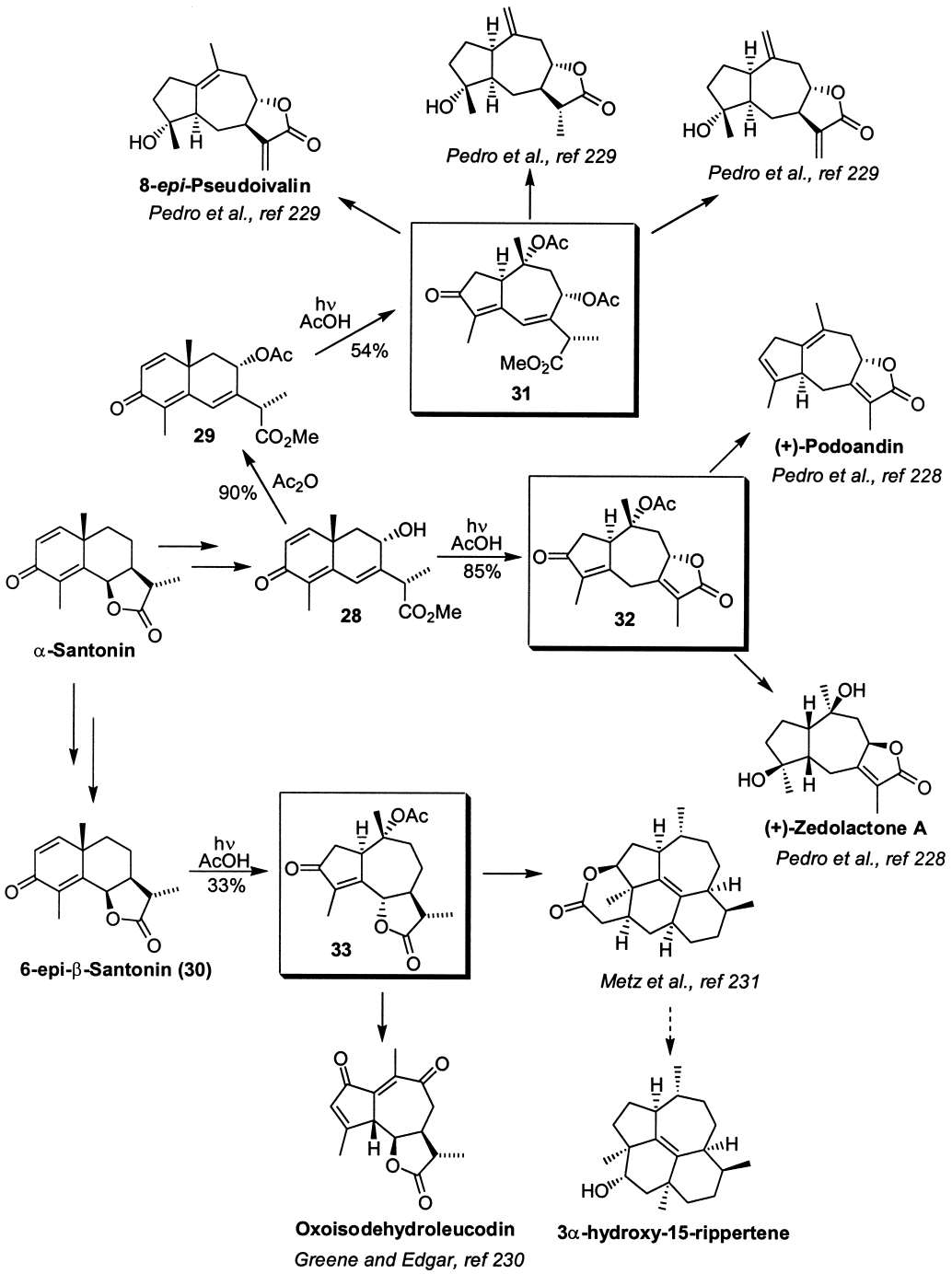
The photochemical rearrangement of cross-conjugated cyclohexadienones is a highly efficient method to obtain functionalized cyclopentyl units in either fused or spiro ring systems.[198–204] Since the late 1950s, this reaction has been involved in a number of total synthesis of natural products,[205,206] and some selected examples of this photochemical rearrangement are discussed below.

Barton and co-workers have performed a detailed study of the photo-induced rearrangement of α-santonin, a commercially available sesquiterpene lactone that bears a 2,5-cyclohexadienone unit in a 6–6-fused framework. When irradiated in acetic acid, this lactone can lead to the isophotosantonic lactone (**27**),[207] which has a 5,7-fused system. Thus, during this process a ring contraction occurs, as well as a ring expansion, by the sequence of steps shown in Scheme 62. Under other conditions, α-santonin yields lumisantonin[208] and/or photosantonic acid[209] (Scheme 63). Barton and his group have also applied this reaction toward other substrates[210,211] and toward the synthesis of natural products.[212] Other researchers have also contributed in the initial studies related to the photochemical mediated rearrangements of 2,5-cyclohexadienones.[213,214]

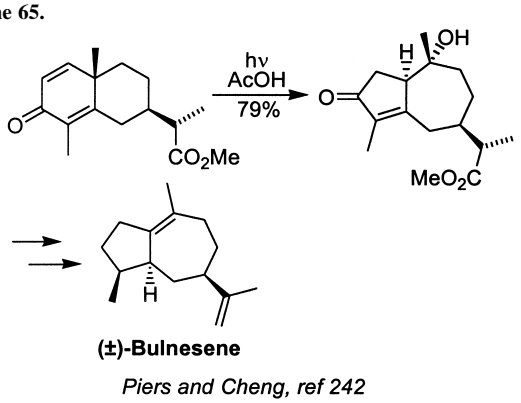
The rearrangement of santonin developed by Barton has been applied by a number of different groups in the synthesis of several natural products,[215–226] as exemplified in Scheme 64. Santonin derivatives such as **28**[227,228] and **29**,[229] as well as 6-*epi*-β-santonin (**30**)[226,230,231] have also been utilized as starting material in this photochemical rearrangement. Such a studies have culminated in a series of interesting applications toward the total synthesis of natural products, as summarized in Scheme 65. It is of note that the rearrangement of **28** occurs in much better yield (85%) than



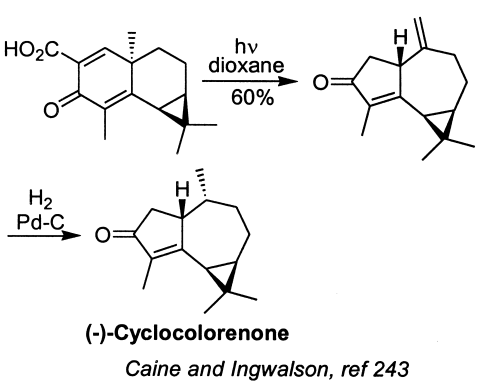
Scheme 64.



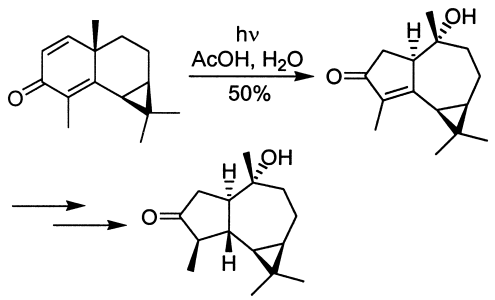
Scheme 65.



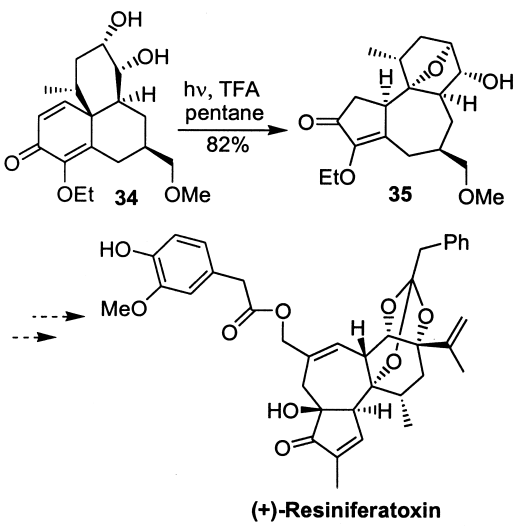
Scheme 66.



Scheme 67.



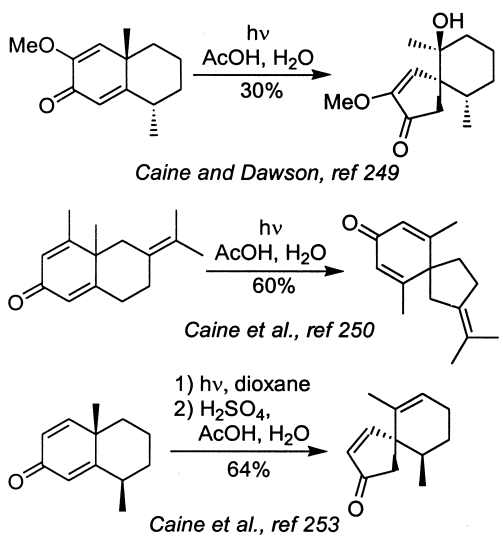
Scheme 68.



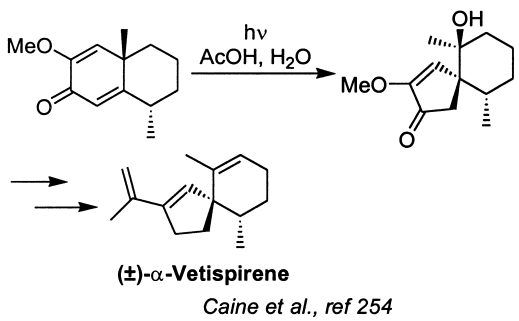
Scheme 69.

that observed utilizing santonin (33-38%), *epi*-santonin **30** (33%) or the santonin derivative **29** (54%).

In the last decades, the photochemically induced ring contraction of cross-conjugated cyclohexadienones has provided a convenient and efficient entry for the preparation of numerous molecules possessing a 5–7-fused ring system,[232–239] including the synthesis of aromadendrene derivatives,[240] α-bulnesene[241,242] (Scheme 66), (−)-cyclocolorenone[243] (Scheme 67) and (−)-4-*epi*-globulol[244] (Scheme 68). Recently, Carreira and his group[245] described the rearrangement of the highly functionalized tricyclic 2,5-cyclohexadienone **34**, leading to the compound **35** in excellent yield, as shown in Scheme 69. The rearrangement product **35** has some of the important features of the (+)-resiniferatoxin, which has pronounced pharmacological activity.



Scheme 70.



Scheme 71.

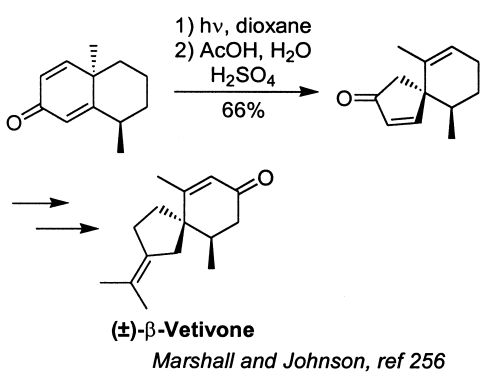
Not only molecules showing the 5,7-fused ring system, as described above, can be obtained from irradiation of 2,5-cyclohexadienones. As exemplified in the following paragraphs, a wide range of ring systems may be constructed by this rearrangement.

Depending on the substituent on the cross-conjugated system of 6–6-fused dienones, a spiro cyclic hydroxyketone may be formed through a photochemical rearrangement,[23,24,246–253] as exemplified in Scheme 70. The total synthesis of spiro-type molecules such as (±)-α-vetispirene[254] (Scheme 71) and (±)-β-vetinone[255,256] (Scheme 72) has been accomplished using this approach.

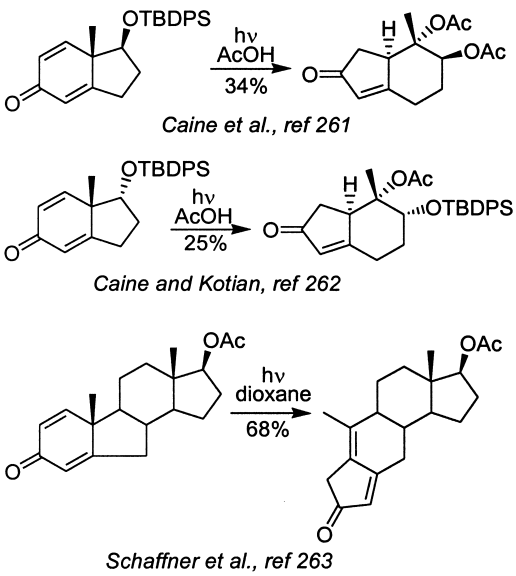
The rearrangement of 6–5-fused dienones has also been explored, leading to 5–6-fused compounds[251,257–263] (Scheme 73). This methodology was applied in the synthesis of oplopanone[264,265] (Scheme 74) and (±)-α-cadinol.[266] The formation of cyclopentanes may also occur by irradiation of substituted-2,5-cyclohexadienones.[267–271]

5.2. Other photochemical ring contractions

Examples of a photodecarbonylation process directed

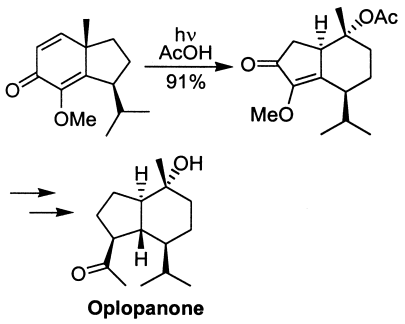


Scheme 72.

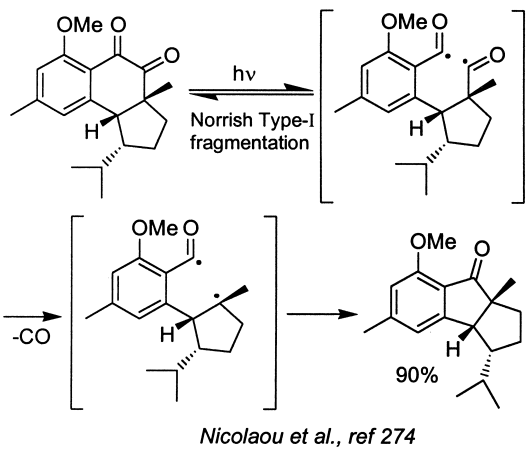


Scheme 73.

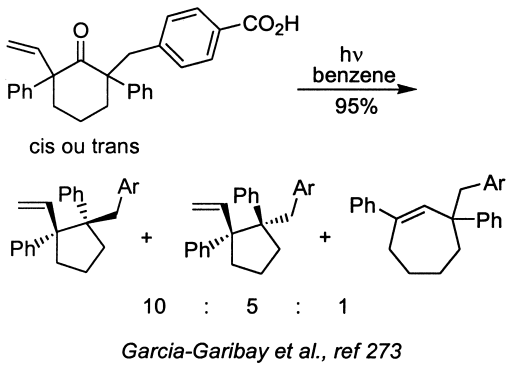
toward the synthesis of cyclopentyl moieties have been recently reported.[272–274] In such a case, the skeletal rearrangement occurs by a Norrish Type-I fragmentation,[202,275] affording ring contraction products in good yield, as shown in Schemes 75 and 76. On the other hand, irradiation of 5,5-dimethylcyclohexane-1,3-dione led to a heterocyclic compound (5,6-dihydropyran-4-ones).[276]



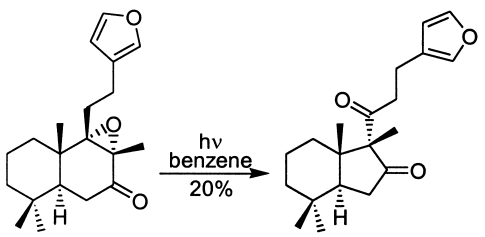
Scheme 74.



Scheme 75.



Scheme 76.



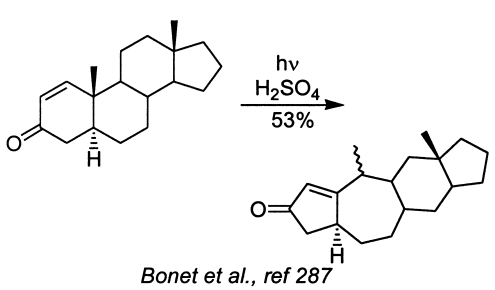
Scheme 77.

Irradiation of α,β-epoxyketones promotes opening of the oxide ring followed by 1,2-rearrangement, culminating in ring contraction.[277–281] An example of this reaction is the photochemical transformation of the labdane diterpene,[282] as shown in Scheme 77. Testosterone has also been synthesized using as a key step the photochemical rearrangement of an epoxy-ketone.[283,284]

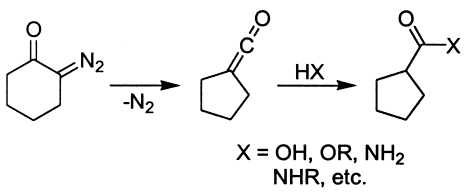
Cyclic enones undergo ring contraction reaction when irradiated under acidic condition,[285–288] as exemplified by 5α-androst-1-en-3-one in Scheme 78.

6. Wolff rearrangements

Under several different conditions, α-diazo ketones can loss nitrogen, leading to carbenes, which furnish ketenes after rearrangement. This sequence of chemical events constitutes the well-established Wolff rearrangement,[289–293] which can be applied to cyclic ketones affording ring contraction products, as illustrated in Scheme 79 for α-diazocyclohexanone. Ketenes may undergo further reactions, such as



Scheme 78.

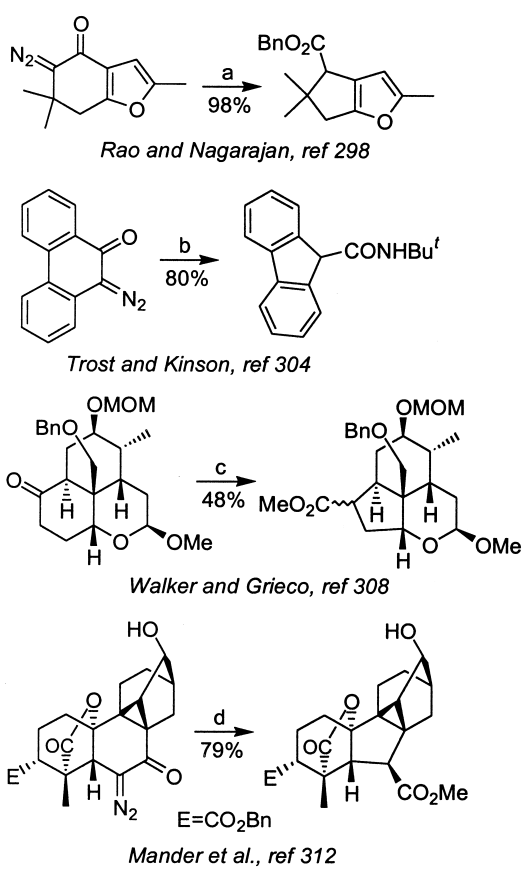


Scheme 79.

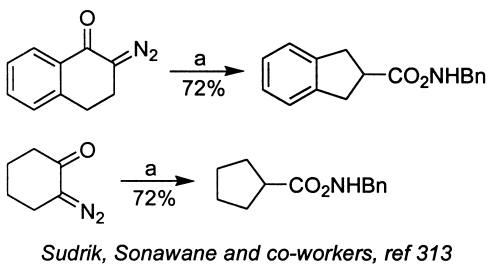
nucleophilic attack (Scheme 79), giving a wide variety of molecules possessing cyclopentyl units. Selected examples of this methodology are presented in the following paragraphs.

The application of the Wolff rearrangement to α-azo-ketones can afford functionalized cyclopentanes,[294,295] as well as a broad range of bicyclic,[294–302] tricyclic[294,303–308] and policyclic compounds.[309–312] Some representative examples of the usefulness of this reaction are shown in Scheme 80. Microwave also promotes the Wolff rearrangement leading to ring contraction products in good yield,[313] as shown in Scheme 81.

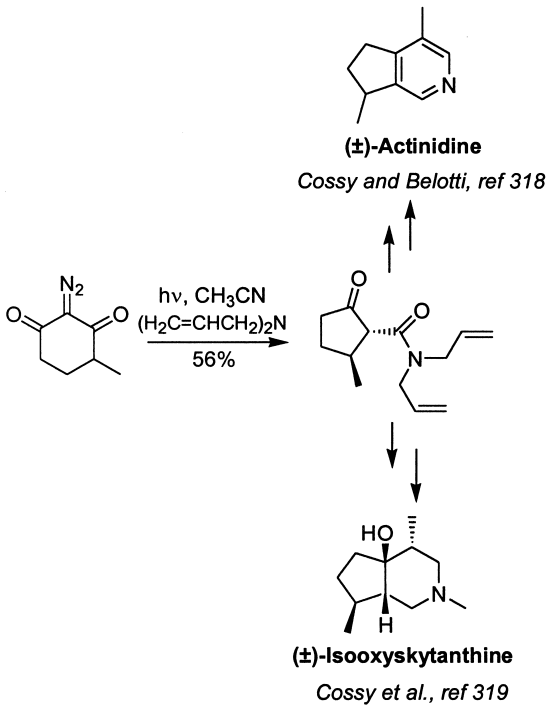
The Wolff rearrangement of 2-azo-1,3-cyclohexadiones can lead to β-dicarbonyl compounds,[314–317] which are versatile building blocks and were applied in the total synthesis of (±)-actidine,[318] (±)-isooxyskytanthine,[318,319] and (±)-velleral,[320] as shown in Schemes 82 and 83. Furthermore,



Scheme 80. *Reagents and conditions*: (a) 180°C, BnOH, 2,4,6-collidine; (b) hν, *t*-BuNH$_2$, C$_6$H$_6$; (c) (i) NaH, HCO$_2$Et, Et$_2$O, EtOH; (ii) TsN$_3$, Et$_2$O; (iii) hν, Et$_2$O, MeOH (d) hν, MeOH.



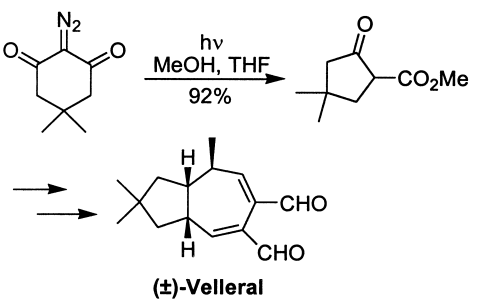
Scheme 81. *Reagents and conditions*: (a) benzylamine, microwave.



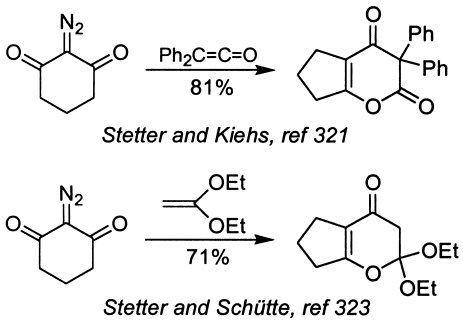
Scheme 82.

the ketenes obtained from 2-azo-1,3-cyclohexadiones can be utilized in cycloaddition reactions, leading to relatively complex structures in a single step,[321–323] as shown in Scheme 84.

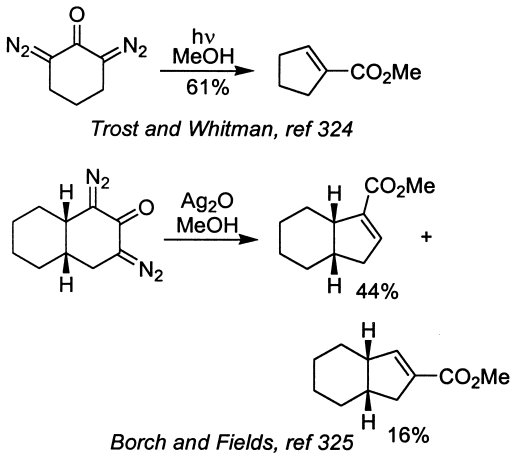
Cyclopentyl units bearing an unsaturated ester moiety can be obtained from α,α′-*bis*(diazo)ketones, as shown for cyclohexanones[324] and for decalones[325] in Scheme 85. Non-equivalent diazo groups can also be used in Wolff



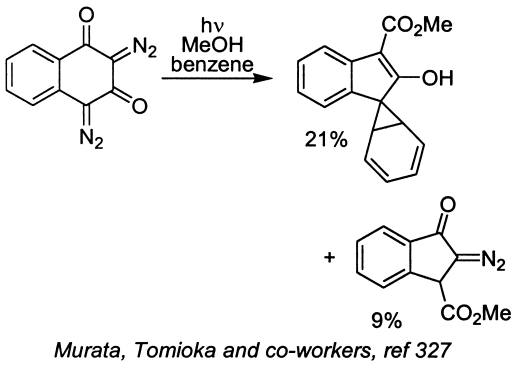
Scheme 83.



Scheme 84.



Scheme 85.



Scheme 86.

rearrangements,[326,327] albeit the yields so far obtained were low, as exemplified in Scheme 86.

7. Conclusion

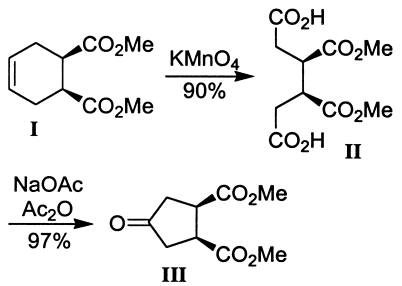
This review has attempted to highlight several approaches concerning the construction of cyclopentyl units utilizing ring contraction reactions, including a number of interesting applications to the synthesis of natural products possessing a broad range of different cyclic systems. Such a strategy constitutes a powerful method in total syntheses because molecular complexity is greatly increased in several of the mentioned skeletal rearrangements, leading to compounds not easily accessed by other methods. We hope this review stimulates further applications of the well-established ring contraction reactions, as well as the development of new rearrangement strategies.

Acknowledgements

The author thanks FAPESP for continuous support and Prof. Helena M. C. Ferraz for fruitful discussions.

References

1. For examples of total synthesis, see: Corey, E. J.; Cheng, X.-M. *The Logic of Chemical Synthesis*, Wiley: New York, 1989.
2. For examples of marine natural products, see: Faulkner, D. J. *Nat. Prod. Rep.* **2002**, *19*, 1.
3. For examples of sesquiterpenoids, see: Fraga, B. M. *Nat. Prod. Rep.* **2001**, *18*, 650.
4. For examples of monoterpenoids, see: Grayson, D. H. *Nat. Prod. Rep.* **2000**, *17*, 385.
5. For examples of diterpenoids, see: Hanson, J. R. *Nat. Prod. Rep.* **2002**, *19*, 125.
6. For examples of triterpenoids, see: Connoly, J. D.; Hill, R. A. *Nat. Prod. Rep.* **2001**, *18*, 560.
7. For a review concerning ring contraction reactions, see: Redmore, D.; Gutsche, C. D. *Carbocyclic Ring Contraction Reactions*, Hart, H., Karabastos, G. J., Eds.; Academic: New York, London, 1971; Vol. 3, p 1.
8. The two-step transformation of the cyclohexene **I** into the cyclopentanone **III** (Molander, G. A., Quirmbach, M. S., Silva, L. F., Jr.; Spencer, K. C., Balsells, *J. Org. Lett.* **2001**, *3*, 2257) is an example of a synthetic sequence that is not included in this review, because it occurs through an isolable intermediate (**II**) containing fewer rings than the starting material (**I**).[7]



9. For a review concerning Wagner–Meerwein rearrangements, see: Hanson, J. R. *Wagner–Meerwein Rearrangements*, Trost, B. M., Ed.; Pergamon: New York, 1991; Vol. 3, p 705.
10. Heathcock, C. H.; Ratcliffe, R. *Chem. Commun.* **1968**, 994.
11. González, A. G.; Galindo, A.; Mansilla, H. *Tetrahedron* **1980**, *36*, 2015.
12. Heathcock, C. H.; Ratcliffe, R. *J. Am. Chem. Soc.* **1971**, *93*, 1746.
13. Mehta, G.; Singh, B. P. *Tetrahedron Lett.* **1975**, 4495.
14. Kato, M.; Kosugi, H.; Yoshikoshi, A. *Chem. Commun.* **1970**, 185.
15. Kato, M.; Kosugi, H.; Yoshikoshi, A. *Chem. Commun.* **1970**, 934.
16. Ando, M.; Akahane, A.; Yamaoka, H.; Takase, K. *J. Org. Chem.* **1982**, *47*, 3909.

17. Ando, M.; Kusaka, H.; Ohara, H.; Takase, K.; Yamaoka, H.; Yanagi, Y. *J. Org. Chem.* **1989**, *54*, 1952.
18. Ando, M.; Ibayashi, K.; Minami, N.; Nakamura, T.; Isogai, K.; Yoshimura, H. *J. Nat. Prod.* **1994**, *57*, 433.
19. Bell, R. P. L.; Wijnberg, J. B. P. A.; de Groot, A. *J. Org. Chem.* **2001**, *66*, 2350.
20. Hendrickson, J. B.; Ganter, C.; Dorman, D.; Link, H. *Tetrahedron Lett.* **1968**, 2235.
21. Howard, B. M.; Fenical, W. *J. Org. Chem.* **1977**, *42*, 2518.
22. Marshall, J. A.; Partridge, J. J. *Tetrahedron* **1969**, *25*, 2159.
23. For a review concerning the synthesis of spiro compounds by rearrangement, see: Krapcho, A. P. *Synthesis* **1976**, 425.
24. For a review concerning the synthesis of spiro compounds, see: Sannigrahi, M. *Tetrahedron* **1999**, *55*, 9007.
25. Hwu, J. R.; Wetzel, J. M. *J. Org. Chem.* **1992**, *57*, 922.
26. Novák, L.; Kovács, P.; Kolonits, P.; Orovecz, O.; Fekete, J.; Szántay, C. *Synthesis* **2000**, 809.
27. Sato, T.; Hayashi, M.; Hayata, T. *Tetrahedron* **1992**, *48*, 4099.
28. For a review concerning pinacol rearrangement, see: Rickborn, B. *The Pinacol Rearrangement*, Trost, B. M., Ed.; Pergamon: New York, 1991; Vol. 3, p 721.
29. Kita, Y.; Yoshida, Y.; Mihara, S.; Fang, D.-F.; Higuchi, K.; Furukawa, A.; Fujioka, H. *Tetrahedron Lett.* **1997**, *38*, 8315.
30. Kita, Y.; Yoshida, Y.; Mihara, S.; Furukawa, A.; Higuchi, K.; Fang, D.-F.; Fujioka, H. *Tetrahedron* **1998**, *54*, 14689.
31. Hariprakasha, H. K.; SubbaRao, G. S. R. *Tetrahedron Lett.* **1997**, *38*, 5343.
32. Janaki, S. N.; Rao, G. S. R. S. *J. Chem. Soc., Perkin Trans. 1* **1997**, 195.
33. Tapondjou, L. A.; Ngounou, F. N.; Lontsi, D.; Sondegam, B. L.; Connolly, J. D. *Tetrahedron* **1998**, *54*, 2099.
34. Büchi, G.; Hofheinz, W.; Paulktelis, J. V. *J. Am. Chem. Soc.* **1966**, *88*, 4113.
35. Büchi, G.; Hofheinz, W.; Paukstelis, J. V. *J. Am. Chem. Soc.* **1969**, *91*, 6473.
36. Barili, P. L.; Berti, G.; Macchia, B.; Macchia, F.; Monti, L. *J. Chem. Soc. C* **1970**, 1168.
37. For a review concerning semipinacol rearrangements, see: Coveney, D. J. *The Semipinacol and Other Rearrangements*, Trost, B. M., Ed.; Pergamon: New York, 1991; Vol. 3, p 777.
38. Cremlyn, R. J. W.; Garmaise, D. L.; Shoppee, C. W. *J. Chem. Soc.* **1953**, 1847.
39. Nace, H. R.; Crosby, G. A. *J. Org. Chem.* **1968**, *33*, 834.
40. For a review concerning concerning mechanisms of epoxide reactions, see: Parker, R. E.; Isaacs, N. S. *Chem. Rev.* **1959**, 737.
41. For a review concerning epoxide reactions, see: Smith, J. G. *Synthesis* **1984**, 629.
42. For a review concerning epoxide rearrangements, see: Rickborn, B. *Acid-catalyzed Rearrangements of Epoxides*, Trost, B. M., Ed.; Pergamon: New York, 1991; Vol. 3, p 733.
43. For a review concerning the construction of molecules with quaternary carbon stereocenters, see: Corey, E. J.; Guzman-Perez, A. *Angew. Chem. Int. Ed.* **1998**, *37*, 388.
44. Rickborn, B.; Gerkin, R. M. *J. Am. Chem. Soc.* **1968**, *90*, 4193.
45. Suga, H.; Miyake, H. *Synthesis* **1988**, 394.
46. Gerkin, R. M.; Rickborn, B. *J. Am. Chem. Soc.* **1967**, *89*, 5850.
47. Rickborn, B.; Gerkin, R. M. *J. Am Chem. Soc.* **1971**, *93*, 1693.
48. Harada, T.; Mukaiyama, T. *Chem. Lett.* **1992**, 1901.
49. Harada, T.; Mukaiyama, T. *Bull. Chem. Soc. Jpn* **1993**, *66*, 882.
50. House, H. O.; Wasson, R. L. *J. Am. Chem. Soc.* **1957**, *79*, 1488.
51. Magnuson, G.; Thorén, S. *J. Org. Chem.* **1973**, *38*, 1380.
52. Rao, P. N.; Uroda, J. C. *Tetrahedron Lett.* **1964**, 1117.
53. Maruoka, K.; Nagahara, S.; Ooi, T.; Yamamoto, H. *Tetrahedron Lett.* **1989**, *30*, 5607.
54. Nagahara, S.; Maruoka, K.; Yamamoto, H. *Chem. Lett.* **1992**, 1193.
55. Maruoka, K.; Murase, N.; Bureau, R.; Ooi, T.; Yamamoto, H. *Tetrahedron* **1994**, *50*, 3663.
56. Kita, Y.; Yoshida, Y.; Kitagaki, S.; Mihara, S.; Fang, D.-F.; Furukawa, A.; Higuchi, K.; Fujioka, H. *Tetrahedron* **1999**, *55*, 4979.
57. Sudha, R.; Narasimhan, K. M.; Saraswathy, V. G.; Sankararaman, S. *J. Org. Chem.* **1996**, *61*, 1877.
58. Ranu, B. C.; Jana, U. *J. Org. Chem.* **1998**, *63*, 8212.
59. Lewis, J. B.; Hedrick, G. W. *J. Org. Chem.* **1965**, *30*, 4271.
60. Bach, R. D.; Klix, R. C. *Tetrahedron Lett* **1985**, *26*, 985.
61. Obuchi, K.; Hayashibe, S.; Asaoka, M.; Takei, H. *Bull. Chem. Soc. Jpn* **1992**, *65*, 3206.
62. (a) Constantino, M. G.; Donate, P. M.; Frederico, D.; Carvalho, T. V.; Cardoso, L. E.; Zukerman-Schpector, J. *Synth. Commun.* **2000**, *30*, 3327. For other contributions from the same group, see: (b) Constantino, Jr. M. G.; Lacerda, V.; Aragão, V. *Molecules* **2001**, *6*, 770. (c) Constantino, M. G.; Prado, M. C. *Quim. Nova* **1991**, *14*, 22.
63. Wilgus, III., H. S.; Oftedahl, E. N.; Musliner, W. J.; Gates, Jr. J. W. *J. Org. Chem.* **1967**, *32*, 3208.
64. Hudrlik, P. F.; Misra, R. N.; Withers, G. P.; Hudrlik, A. M.; Rona, R. J.; Arcoleo, J. P. *Tetrahedron Lett.* **1976**, 1453.
65. Kunisch, F.; Hobert, K.; Welzel, P. *Tetrahedron Lett.* **1985**, *26*, 6039.
66. Maruoka, K.; Ooi, T.; Yamamoto, H. *J. Am. Chem. Soc.* **1989**, *111*, 6431.
67. Maruoka, K.; Ooi, T.; Nagahara, S.; Yamamoto, H. *Tetrahedron* **1991**, *47*, 6983.
68. Asaoka, M.; Hayashibe, S.; Sonoda, S.; Takei, H. *Tetrahedron Lett.* **1990**, *31*, 4761.
69. Asaoka, M.; Hayashibe, S.; Sonoda, S.; Takei, H. *Tetrahedron* **1991**, *47*, 6967.
70. Kita, Y.; Furukawa, A.; Futamura, J.; Ueda, K.; Sawama, Y.; Hamamoto, H.; Fujioka, H. *J. Org. Chem.* **2001**, *66*, 8779.
71. Kita, Y.; Furukawa, A.; Futamura, J.; Higuchi, K.; Ueda, K.; Fujioka, H. *Tetrahedron Lett.* **2000**, *41*, 2133.
72. Kita, Y.; Furukawa, A.; Futamura, J.; Higuchi, K.; Ueda, K.; Fujioka, H. *Tetrahedron* **2001**, *57*, 815.
73. Coxon, J. M.; Hartshorn, M. P.; Kirk, D. N. *Tetrahedron* **1964**, *20*, 2531.
74. Hikino, H.; Suzuki, N.; Takemoto, T. *Chem. Pharm. Bull.* **1966**, *14*, 1441.
75. Hart, H.; Shih, E. M. *J. Org. Chem.* **1975**, *40*, 1128.
76. Yamano, Y.; Tode, C.; Ito, M. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1337.
77. Yamano, Y.; Tode, C.; Ito, M. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2569.
78. Neef, G.; Baesler, S.; Depke, G.; Vierhufe, H. *Tetrahedron Lett.* **1999**, *40*, 7969.
79. Srikrishna, A.; Nagamani, S. A. *J. Chem. Soc., Perkin Trans. 1* **1999**, 3393.
80. Bach, R. D.; Tubergen, M. W.; Klix, R. C. *Tetrahedron Lett.* **1986**, *27*, 3565.

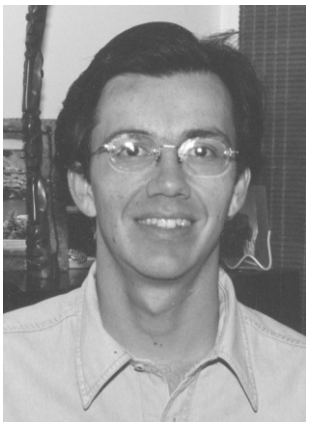
81. Kita, Y.; Kitagaki, S.; Yoshida, S.; Mihara, S.; Fang, D.-F.; Fujioka, H. *Tetrahedron Lett.* **1997**, *38*, 1061.
82. Kita, Y.; Kitagaki, S.; Yoshida, Y.; Mihara, S.; Fang, D.-F.; Kondo, M.; Okamoto, S.; Imai, R.; Akai, S.; Fujioka, H. *J. Org. Chem.* **1997**, *62*, 4991.
83. Gerlach, H.; Müller, W. *Helv. Chim. Acta* **1972**, *55*, 2277.
84. Fujioka, H.; Kitagaki, S.; Imai, R.; Kondo, M.; Okamoto, S.; Yoshida, Y.; Akai, S.; Kita, Y. *Tetrahedron Lett.* **1995**, *36*, 3219.
85. (a) Kita, Y.; Kitagaki, S.; Imai, R.; Okamoto, S.; Mihara, S.; Yoshida, Y.; Akai, S.; Fujioka, H. *Tetrahedron Lett.* **1996**, *37*, 1817. (b) Kita, Y.; Higuchi, K.; Yoshida, Y.; Iio, K.; Kitagaki, S.; Ueda, K.; Akai, S.; Fujioka, H. *J. Am. Chem. Soc.* **2001**, *123*, 3214. (c) Kita, Y.; Higuchi, K.; Yoshida, Y.; Iio, K.; Kitagaki, S.; Akai, S.; Fujioka, H. *Angew. Chem. Int. Ed.* **1999**, *38*, 683.
86. Favorskii, A. E. *J. Russ. Phys. Chem. Soc.* **1894**, *26*, 590.
87. For a review concerning Favorskii rearrangement, see: Akhrem, A. A.; Ustynyuk, T. K.; Titov, Y. A. *Russ. Chem. Rev.* **1970**, *39*, 732.
88. For a review concerning Favorskii rearrangement in bridged cyclic compounds, see: Chenier, P. J. *J. Chem. Educ.* **1978**, *55*, 286.
89. For a review concerning Favorskii rearrangement, see: Mann, J. *The Favorskii Rearrangement*, Trost, B. M., Ed.; Pergamon: New York, 1991; Vol. 3, p 839.
90. For a review concerning Favorskii rearrangement in haloketones, see: Kende, A. S. *Org. React.* **1960**, *11*, 261.
91. Goheen, D. W.; Vaughan, W. R. *Org. Synth.* **1959**, *39*, 37.
92. House, H. O.; Frank, G. A. *J. Org. Chem.* **1965**, *30*, 2948.
93. Smissman, E. E.; Lemke, T. L.; Kristiansen, O. *J. Am. Chem. Soc.* **1966**, *88*, 334.
94. Bordwell, F. G.; Strong, J. G. *J. Org. Chem.* **1973**, *38*, 579.
95. Grunewald, G. L.; Ye, Q. *J. Org. Chem.* **1988**, *53*, 4021.
96. Rupe, H.; Schäfer, K. *Helv. Chim. Acta* **1928**, *30*, 463.
97. Wolinsky, J.; Wolf, H.; Gibson, T. *J. Org. Chem.* **1963**, *28*, 274.
98. Wolinsky, J.; Chan, D. *J. Org. Chem.* **1965**, *30*, 41.
99. Wolinsky, J.; Chollar, B.; Baird, M. D. *J. Am. Chem. Soc.* **1962**, *84*, 2775.
100. Achmad, S. A.; Cavill, G. W. K. *Aust. J. Chem.* **1963**, *16*, 858.
101. Yates, P.; Jorgenson, M. J.; Singh, P. *J. Am. Chem. Soc.* **1969**, *91*, 4739.
102. Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*. 5th ed. Longman: London, 1989.
103. Wolinsky, J.; Gibson, T.; Chan, D.; Wolf, H. *Tetrahedron* **1965**, *21*, 1247.
104. Marx, J. N.; Norman, L. R. *J. Org. Chem.* **1975**, *40*, 1602.
105. Jamison, T. F.; Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 4353.
106. Bintz-Giudicelli, C.; Weymann, O.; Uguen, D.; De Cian, A.; Fischer, J. *Tetrahedron Lett.* **1997**, *38*, 2841.
107. Kurosawa, S.; Bando, M.; Mori, K. *Eur. J. Org. Chem.* **2001**, 4395.
108. Nangia, A.; Prasuma, G. *Tetrahedron* **1996**, *52*, 3435.
109. Asaka, T.; Kamikawa, T.; Kubota, T. *Tetrahedron* **1974**, *30*, 3257.
110. Lee, E.; Yoon, C. H. *J. Chem. Soc., Chem. Commun.* **1994**, 479.
111. Gonzáles, A. G.; Fraga, B. M.; Hernández, M. G.; Luis, J. G. *Tetrahedron Lett.* **1978**, 3499.
112. Fraga, B. M.; Hernández, M. G.; Arraez, J. D.; Luis, J. G. *Tetrahedron* **1994**, *50*, 12643.
113. For the synthesis of gibberelin derivatives by ring contraction using a microbial transformation, see: Barrero, A. F.; Oltra, J. E.; Cerdá-Olmedo, E.; Ávalos, J.; Justicia, J. *J. Nat. Prod.* **2001**, *64*, 222.
114. Barbee, T. R.; Guy, H.; Heeg, M. J.; Albizati, K. F. *J. Org. Chem.* **1991**, *56*, 6773.
115. Tsuboi, S.; Nagae, H.; Yamato, H.; Takeda, A. *Bull. Chem. Soc. Jpn* **1987**, *60*, 836.
116. Sakai, T.; Amano, E.; Kawabata, A.; Takeda, A. *J. Org. Chem.* **1980**, *45*, 43.
117. Sato, K.; Kojima, Y.; Sato, H. *J. Org. Chem.* **1970**, *35*, 2374.
118. Sato, K.; Inoue, S.; Ohashi, M.; Kuranami, S.-I. *Chem. Lett.* **1975**, 405.
119. Sato, K.; Inoue, S.; Kuranami, S.-I. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1666.
120. Keana, J. F. W.; Seyedrezai, S. E. *J. Org. Chem.* **1982**, *47*, 347.
121. De Kimpe, N.; D'Hondt, L.; Moens, L. *Tetrahedron* **1992**, *48*, 3183.
122. Bordwell, F. G.; Almy, J. *J. Org. Chem.* **1973**, *38*, 571.
123. Llera, J. M.; Fraser-Reid, B. *J. Org. Chem.* **1989**, *54*, 5544.
124. De Angelis, F.; Feroci, M.; Inesi, A. *Bull. Soc. Chim. Fr.* **1993**, *130*, 712.
125. Satoh, T.; Oguro, K.; Shishikura, J.-I.; Kanetaka, N.; Okada, R.; Yamakawa, K. *Tetrahedron Lett.* **1992**, *33*, 1455.
126. Satoh, T.; Oguro, K.; Shishikura, J.-I.; Kanetaka, N.; Okada, R.; Yamakawa, K. *Bull. Chem. Soc. Jpn* **1993**, *66*, 2339.
127. Samaranayake, G.; Magri, N. F.; Jitrangsri, C.; Kingston, D. G. I. *J. Org. Chem.* **1991**, *56*, 5114.
128. Yu, C.; Liu, Z. *Tetrahedron Lett.* **1997**, *38*, 4133.
129. Chen, S.-H.; Huang, S.; Roth, G. P. *Tetrahedron Lett.* **1995**, *36*, 8933.
130. Chen, S.-H.; Huang, S.; Wei, J.; Farina, V. *Tetrahedron* **1993**, *49*, 2805.
131. Hosoyama, H.; Shigemori, H.; Kobayashi, J. *Tetrahedron Lett.* **1999**, *40*, 2149.
132. Sun, D.-A.; Sauriol, F.; Mamer, O.; Zamir, L. O. *Bioorg. Med. Chem.* **2001**, *9*, 793.
133. Kobayashi, T.; Kurono, M.; Sato, H.; Nakanishi, K. *J. Am. Chem. Soc.* **1972**, *98*, 2863.
134. Hamon, D. P. G.; Tuck, K. L. *Chem. Commun.* **1997**, 941.
135. Wendler, N. L.; Hirschmann, R. F.; Slates, H. L.; Walker, R. W. *J. Am. Chem. Soc.* **1955**, *77*, 1632.
136. Mazur, Y.; Nussim, M. *J. Am. Chem. Soc.* **1961**, *83*, 3911.
137. Marshall, J. A.; Brady, S. F. *Tetrahedron Lett.* **1969**, 1387.
138. Wijnberg, J. B. P. A.; de Groot, A. *Tetrahedron Lett.* **1987**, *28*, 3007.
139. Orru, R. V. A.; Wijnberg, J. B. P. A.; Bouwman, C. T.; de Groot, A. *J. Org. Chem.* **1994**, *59*, 374.
140. Wijnberg, J. B. P. A.; Jenniskens, L. H. D.; Brunekreef, G. A.; de Groot, A. *J. Org. Chem.* **1990**, *55*, 941.
141. Jenniskens, L. H. D.; Wijnberg, J. B. P. A.; de Groot, A. *J. Org. Chem.* **1991**, *56*, 6585.
142. Bell, R. P. L.; Sobolev, A.; Wijnberg, J. B. P. A.; de Groot, A. *J. Org. Chem.* **1998**, *63*, 122.
143. Koike, T.; Yamazaki, K.; Fukumoto, N.; Yashiro, K.; Takeuchi, N.; Tobinaga, S. *Chem. Pharm. Bull.* **1996**, *44*, 646.
144. Piet, D. P.; Orru, R. V. A.; Jenniskens, L. H. D.; van de Haar, C.; van Beek, T. A.; Franssen, M. C. R.; Wijnberg, J. B. P. A.; de Groot, A. *Chem. Pharm. Bull.* **1996**, *44*, 1400.

145. (a) Sander, B.; Andresen, S.; Reichow, S.; Dubois, K.; Agosta, W. C.; Margaretha, P. *Helv. Chim. Acta* **1996**, *79*, 1428. (b) Tanaka, H.; Kozuki, Y.; Ogasawara, K. *Tetrahedron Lett.* **2002**, *43*, 4175.
146. Fu, J.-M.; Snieckus, V. *Can. J. Chem.* **2000**, *78*, 905.
147. For a review concerning benzil-benzilic rearrangements, see: Gill, G. B. *Benzil-Benzilic Acid Rearrangements*, Trost, B. M., Ed.; Pergamon: New York, 1991; Vol. 3, p 821.
148. For a review concerning thallium compounds, see: McKillop, A.; Taylor, E. C. *Compounds of Thallium in Organic Synthesis*, Wilkinson, G., Ed.; Pergamon: New York, 1982; Vol. 7, p 465.
149. For a review concerning thallium(III) in organic synthesis, see: Ferraz, H. M. C.; Silva, Jr. L. F.; Vieira, T. O. *Synthesis* **1999**, 2001.
150. For a review concerning thallium(III)-mediated ring contraction reactions, see: Ferraz, H. M. C.; Silva, Jr. L. F. *Quim. Nova* **2000**, *23*, 216.
151. Thallium trinitrate (TTN) corresponds to 62%, thallium triacetate (TTA) to 21% and other salts to 17%, considering all the publications concerning the use of thallium(III) salts to promote ring contraction reactions from 1962 until 2001. For some examples of TTN-promoted oxidation, see: Vieira, T. O. *Synlett* **2002**, 1017.
152. Ferraz, H. M. C.; Silva, Jr. L. F. *Tetrahedron Lett.* **1997**, *38*, 1899.
153. Ferraz, H. M. C.; Silva, Jr. L. F. *J. Org. Chem.* **1998**, *63*, 1716.
154. Ferraz, H. M. C.; Silva, Jr. L. F. *J. Braz. Chem. Soc.* **2001**, *12*, 548. Ref. 328.
155. McKillop, A.; Hunt, J. D.; Taylor, E. C. *J. Org. Chem.* **1972**, *37*, 3381.
156. Ferraz, H. M. C.; Silva, Jr. L. F.; Aguilar, A. M.; Vieira, T. O. *J. Braz. Chem. Soc.* **2001**, *12*, 680. Ref. 328.
157. Ferraz, H. M. C.; Silva, Jr. L. F.; Vieira, T. O. *Tetrahedron* **2001**, *57*, 1709.
158. Bohlmann, F.; Zdero, C.; Le Van, N. *Phytochemistry* **1979**, *18*, 99.
159. Ho, T.-L.; Lee, K.-Y.; Chen, C.-K. *J. Org. Chem.* **1997**, *62*, 3365.
160. Capon, R. J.; MacLeod, J. K.; Scammels, P. J. *Tetrahedron* **1986**, *42*, 6545.
161. Ferraz, H. M. C.; Santos, A. P.; Silva, Jr. L. F.; Vieira, T. O. *Synth. Commun.* **2000**, *30*, 751.
162. Ferraz, H. M. C.; Silva, Jr. L. F. *Tetrahedron* **2001**, *57*, 9939.
163. Ferraz, H. M. C.; Silva, Jr. L. F. *Synthesis* **2002**, 1033.
164. Ferraz, H. M. C.; Longo, Jr. L. S.; Zukerman-Schpector, J. *J. Org. Chem.* **2002**, *67*, 3518.
165. For a review concerning the reaction of nitrogen compounds with mercury(II), thallium(III) and lead(IV), see: Butler, R. N. *Chem. Rev.* **1984**, *84*, 249.
166. For a review concerning acyloxylation methods, including lead(IV)-mediated reactions, see: Rawlinson, D. J.; Sosnovsky, G. *Synthesis* **1973**, 567.
167. Mathew, F.; Myrboh, B. *Synth. Commun.* **1996**, *26*, 1097.
168. Cekovic, Z.; Bosnjak, J.; Cvetkovic, M. *Tetrahedron Lett.* **1980**, *21*, 2675.
169. It is of note that similar diastereoselectivity was observed in studies toward the construction of hydrindane derivatives utilizing TTN and LTA (cf. Schemes 47 and 56).
170. Horwell, D. C.; Howson, W.; Ratcliffe, G.; Willems, H. *Bioorg. Med. Chem. Lett.* **1994**, *4*, 2825.
171. Horwell, D. C.; Howson, W.; Ratcliffe, G. S.; Willems, H. M. G. *Bioorg. Med. Chem.* **1996**, *4*, 33.
172. Nongrum, F. M.; Myrboh, B. *Synthesis* **1987**, 845.
173. Miura, H.; Fujimoto, Y.; Tatsuno, T. *Synthesis* **1979**, 898.
174. Henbest, H. B.; Jones, D. N.; Slater, G. P. *J. Chem. Soc. C* **1967**, 756.
175. Robinson, D. L.; Theobald, D. W. *Tetrahedron* **1968**, *24*, 5227.
176. Murai, A.; Nishizakura, K.; Katsui, N.; Masamune, T. *Bull. Chem. Soc. Jpn* **1977**, *50*, 1206.
177. Nag, S. K.; Bose, S. N. *Indian J. Chem., Sect. B* **1990**, *29*, 160.
178. Shafiullah, D.; Ali, H. *Synthesis* **1979**, 124.
179. Debono, M.; Molloy, R. M. *J. Org. Chem.* **1969**, *34*, 1454.
180. For a review concerning synthetic applications of hypervalent iodine, see: Wirth, T.; Hirt, U. H. *Synthesis* **1999**, 1271.
181. For a review concerning hypervalent iodine, see: Varvoglis, A. *Tetrahedron* **1997**, *53*, 1179.
182. For a review concerning iodine(III)- and thallium(III)-mediated oxidative rearrangements, see: Prakash, O. *Aldrichimica Acta* **1995**, *28*, 63.
183. Daum, S. J. *Tetrahedron Lett.* **1984**, *25*, 4725.
184. Moriarty, R. M.; Prakash, I.; Musallam, H. A. *Tetrahedron Lett.* **1984**, *25*, 5867.
185. Moriarty, R. M.; Enache, L. A.; Zhao, L.; Gilardi, R.; Mattson, M. V.; Prakash, O. *J. Med. Chem.* **1998**, *41*, 468.
186. (a) Varma, R. S.; Kumar, D. *Synthesis* **1999**, 1288. (b) Spyroudis, S.; Xanthopoulou, N. *J. Org. Chem.* **2002**, *67*, 4612.
187. Hara, S.; Nakahigashi, J.; Ishi-i, K.; Fukuhara, T.; Yoneda, N. *Tetrahedron Lett.* **1998**, *39*, 2589.
188. Sawaguchi, M.; Hara, S.; Yoneda, N. *J. Fluor. Chem.* **2000**, *105*, 313.
189. Karpov, V. M.; Mezhenkova, T. V.; Platonov, V. E. *J. Fluor. Chem.* **1996**, *77*, 101.
190. For a review concerning iodine compounds, where the ring contraction of cyclohexene is mentioned, see: Stang, P. J.; Zhdankin, V. V. *Chem. Rev.* **1996**, *96*, 1123.
191. Payne, G. B.; Smith, C. W. *J. Org. Chem.* **1957**, *22*, 1680.
192. Payne, G. B. *J. Org. Chem.* **1961**, *26*, 4793.
193. Giroud, A.-M.; Rassat, A.; Witz, P.; Ourisson, G. *Bull. Soc. Chim. Fr.* **1965**, 3240.
194. Caspi, E.; Shimizu, Y.; Balasubrahmanyam, S. N. *Tetrahedron* **1964**, *20*, 1271.
195. Kartha, C. C.; Chakravarti, K. K. *Tetrahedron* **1965**, *21*, 139.
196. Giurg, M.; Mlochowski, J. *Synth. Commun.* **1999**, *29*, 2281.
197. For a book concerning photochemistry in organic synthesis, see: Coyle, J. D. *Photochemistry in Organic Synthesis*. The Royal Society of Chemistrry: London, 1986; p 333.
198. For a review concerning photochemical rearrangements, see: Barton, D. H. R. *Helv. Chim. Acta* **1959**, *62*, 2604.
199. For a review concerning photochemical rearrangements of cyclic ketones, see: Schaffner, K. *Photochemical Rearrangements of Conjugated Cyclic Ketones: The Present State of Investigations*, Noyes, W. A. Jr., Hammond, G. S., Pitts, J. N. Jr., Eds.; Wiley: New York, 1966; Vol. 4, p 81.
200. For a review concerning mechanisms of photochemical transformations, see: Schuster, D. I. *Acc. Chem. Res.* **1978**, *11*, 65.
201. For a review concerning historial sketches of photochemistry, see: Roth, H. D. *Pure Appl. Chem.* **2001**, *73*, 395.
202. For a review concerning photochemistry of carbonyl compounds, see: Sventon, J. S. *J. Chem. Educ.* **1969**, *46*, 217.

203. For a review concerning photochemical reactions, see: Zimmerman, H. E. *Pure Appl. Chem.* **1965**, 493.
204. For a review concerning photochemistry in Helvetica Chimica Acta, see: Heimgartner, H.; Hansen, H.-J. *Helv. Chim. Acta* **1993**, *76*, 1027.
205. For a review concerning photochemical reactions in the synthesis of natural products, see: Sammes, P. G. Q. *Rev. Chem. Soc.* **1970**, *24*, 37.
206. For a review concerning photochemical reactions in the synthesis of natural products, see: Kossanyi, J. *Pure Appl. Chem.* **1979**, *51*, 181.
207. Barton, D. H. R.; de Mayo, P.; Shafiq, M. *J. Chem. Soc.* **1957**, 929.
208. Barton, D. H. R.; de Mayo, P.; Shafiq, M. *J. Chem. Soc.* **1958**, 140.
209. Barton, D. H. R.; de Mayo, P.; Shafiq, M. *J. Chem. Soc.* **1958**, 3314.
210. Barton, D. H. R.; McGhie, J. F.; Rosenberger, M. *J. Chem. Soc.* **1961**, 1215.
211. Barton, D. H. R.; Levisalles, J. E. D.; Pinhey, J. T. *J. Chem. Soc.* **1962**, 3472.
212. Barton, D. H. R.; Pinhey, J. T.; Wells, R. J. *J. Chem. Soc.* **1964**, 2518.
213. Arigoni, D.; Bosshard, H.; Bruderer, H.; Büchi, G.; Jeger, O.; Krebaum, L. J. *Helv. Chim. Acta* **1957**, *40*, 1732.
214. Zimmerman, H. E.; Schuster, D. I. *J. Am. Chem. Soc.* **1962**, *84*, 4527.
215. Marx, J. N.; White, E. H. *Tetrahedron* **1969**, *25*, 2117.
216. Marx, J. N.; McGaughey, S. M. *Tetrahedron* **1972**, *28*, 3583.
217. White, E. H.; Eguchi, S.; Marx, J. N. *Tetrahedron* **1969**, *25*, 2099.
218. Greene, A. E. *Tetrahedron Lett.* **1978**, 851.
219. Edgar, M. T.; Greene, A. E.; Crabbé, P. *J. Org. Chem.* **1979**, *44*, 159.
220. Greene, A. E. *J. Am. Chem. Soc.* **1980**, *102*, 5337.
221. Delair, P.; Kann, N.; Greene, A. E. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1651.
222. Bargues, V.; Blay, G.; Cardona, L.; García, B.; Pedro, J. R. *Tetrahedron* **1998**, *54*, 1845.
223. Blay, G.; Cardona, L.; García, B.; Lahoz, L.; Monje, B.; Pedro, J. R. *Tetrahedron* **2000**, *56*, 6331.
224. Blay, G.; Cardona, L.; García, B.; Lahoz, L.; Pedro, J. R. *J. Org. Chem.* **2001**, *66*, 7700.
225. Blay, G.; Bargues, V.; Cardona, L.; García, B.; Pedro, J. R. *Tetrahedron* **2001**, *57*, 9719.
226. Lauridsen, A.; Cornett, C.; Vulpius, T.; Moldt, P.; Christensen, S. B. *Acta Chem. Scand.* **1996**, *50*, 150.
227. Blay, G.; Cardona, M. L.; García, B.; Pedro, J. R. *J. Org. Chem.* **1991**, *56*, 6172.
228. Blay, G.; Bargues, V.; Cardona, L.; García, B.; Pedro, J. R. *J. Org. Chem.* **2000**, *65*, 6703.
229. Blay, G.; Bargues, V.; Cardona, L.; Collado, A. M.; García, B.; Muñoz, M. C.; Pedro, J. R. *J. Org. Chem.* **2000**, *65*, 2138.
230. Greene, A. E.; Edgar, M. T. *J. Org. Chem.* **1989**, *54*, 1468.
231. Metz, P.; Bertels, S.; Fröhlich, R. *J. Am. Chem. Soc.* **1993**, *115*, 12595.
232. Kropp, P. J. *J. Org. Chem.* **1964**, *29*, 3110.
233. Caine, D.; Dawson, J. B. *J. Org. Chem.* **1964**, *29*, 3108.
234. Piers, E.; Cheng, K. F. *Can. J. Chem.* **1967**, *45*, 1591.
235. Caine, D.; Deutsch, H.; Gupton, J. T.; III, *J. Org. Chem.* **1978**, *43*, 343.
236. Caine, D.; Debardeleben, Jr. J. F. *Tetrahedron Lett.* **1965**, 4585.
237. Caine, D.; Debardeleben, Jr. J. F.; Dawson, J. B. *Tetrahedron Lett.* **1966**, 3627.
238. Shiozaki, M.; Mori, K.; Hiraoka, T.; Matsui, M. *Tetrahedron* **1974**, *30*, 2647.
239. Shiozaki, M.; Mori, K.; Matsui, M.; Hiraoka, T. *Tetrahedron Lett.* **1972**, 657.
240. Streith, J.; Blind, A. *Bull. Soc. Chim. Fr.* **1968**, 2133.
241. Piers, E.; Cheng, K. F. *Chem. Commun.* **1969**, 562.
242. Piers, E.; Cheng, K. F. *Can. J. Chem.* **1970**, *48*, 2234.
243. Caine, D.; Ingwalson, P. F. *J. Org. Chem.* **1972**, *37*, 3751.
244. Caine, D.; Gupton, J. T.; III, *J. Org. Chem.* **1975**, *40*, 809.
245. Jackson, S. R.; Johnson, M. G.; Mikami, M.; Shiokawa, S.; Carreira, E. M. *Angew. Chem. Int. Ed.* **2001**, *40*, 2694.
246. Kropp, P. J.; Erman, W. F. *J. Am. Chem. Soc.* **1963**, *85*, 2456.
247. Kropp, P. J. *J. Am. Chem. Soc.* **1964**, *86*, 4053.
248. Kropp, P. J. *J. Am. Chem. Soc.* **1965**, *87*, 3914.
249. Caine, D.; Dawson, J. B. *Chem. Commun.* **1970**, 1232.
250. Caine, D.; Chu, C.-Y.; Graham, S. L. *J. Org. Chem.* **1980**, *45*, 3790.
251. Caine, D.; Brake, P. F.; DeBardelen, Jr. J. F.; Dawson, J. B. *J. Org. Chem.* **1973**, *38*, 967.
252. Caine, D.; Chu, C.-Y. *Tetrahedron Lett.* **1974**, 703.
253. Caine, D.; Boucugnani, A. A.; Pennington, W. R. *J. Org. Chem.* **1976**, *41*, 3632.
254. Caine, D.; Boucugnani, A. A.; Chao, S. T.; Dawson, J. B.; Ingwalson, P. F. *J. Org. Chem.* **1976**, *41*, 1539.
255. Marshall, J. A.; Johnson, P. C. *Chem. Commun.* **1968**, 391.
256. Marshall, J. A.; Johnson, P. C. *J. Org. Chem.* **1970**, *35*, 192.
257. Caine, D.; Gupton, III., J. T.; Ming, K.; Powers, III., W. J. *J. Chem. Soc., Chem. Commun.* **1973**, 469.
258. Pfister, J.; Wehrli, H.; Schaffner, K. *Helv. Chim. Acta* **1967**, *50*, 166.
259. Caine, D.; Powers, III., W. J.; Alejandre, A. M. *Tetrahedron Lett.* **1968**, 6071.
260. Caine, D.; Alejandre, A. M.; Ming, K.; Powers, W. J.; III, *J. Org. Chem.* **1972**, *37*, 706.
261. Caine, D.; Kotian, P. L.; McGuiness, M. D. *J. Org. Chem.* **1991**, *56*, 6307.
262. Caine, D.; Kotian, P. L. *J. Org. Chem.* **1992**, *57*, 6587.
263. Bozzato, G.; Throndsen, H. P.; Schaffner, K.; Jeger, O. *J. Am. Chem. Soc.* **1964**, *86*, 2073.
264. Caine, D.; Tuller, F. N. *J. Am. Chem. Soc.* **1971**, *93*, 6311.
265. Caine, D.; Tuller, F. N. *J. Org. Chem.* **1973**, *38*, 3663.
266. Caine, D.; Frobese, A. S. *Tetrahedron Lett.* **1977**, 3107.
267. Childs, R. F.; Hine, K. E.; Hung, F. A. *Can. J. Chem.* **1979**, *57*, 1442.
268. (a) Zimmerman, H. E.; Jian-hua, X.; King, R. K.; Caufield, C. E. *J. Am. Chem. Soc.* **1985**, *107*, 7724. (b) Zimmerman, H. E.; Nesterov, E. E. *J. Am. Chem. Soc.* **2002**, *124*, 2818.
269. Schultz, A. G.; Hardinger, S. A. *J. Org. Chem.* **1991**, *56*, 1105.
270. Schultz, A. G.; Lockwood, Jr. L. O. *J. Org. Chem.* **2000**, *65*, 6354.
271. Hart, H.; Peng, C.; Shih, E. *J. Org. Chem.* **1977**, *42*, 3635.
272. Choi, T.; Cizmeciyan, D.; Khan, S. I.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **1995**, *117*, 12893.
273. Ng, D.; Yang, Z.; Garcia-Garibay, M. A. *Tetrahedron Lett.* **2001**, *42*, 9113.
274. Nicolaou, K. C.; Gray, D.; Tae, J. *Angew. Chem. Int. Ed.* **2001**, *40*, 3679.
275. Bamford, C. H.; Norrish, R. G. W. *J. Chem. Soc.* **1938**, 1521.
276. Saito, K.; Yuki, H.; Ohyama, T.; Nakane, R.; Nagumo, K.; Sato, T. *Can. J. Chem.* **1981**, *59*, 1717.

277. Wehrli, H.; Lehmann, C.; Schaffner, K.; Jeger, O. *Helv. Chim. Acta* **1964**, *47*, 1336.
278. Wehrli, H.; Lehmann, C.; Keller, P.; Bonet, J. J.; Schaffner, K.; Jeger, O. *Helv. Chim. Acta* **1966**, *49*, 2218.
279. Wehrli, H.; Lehmann, C.; Iizuka, T.; Schaffner, K.; Jeger, O. *Helv. Chim. Acta* **1967**, *50*, 2403.
280. For a review concerning photochemical transformations of epoxyketones, see: Jeger, O.; Schaffner, K.; Wehrli, H. *Pure Appl. Chem.* **1965**, 555.
281. For a review concerning photochemistry of ketones, see: Schaffner, K.; Jeger, O. *Tetrahedron* **1974**, *30*, 1891.
282. Fontana, G.; Savona, G.; Vivona, N.; Rodríguez, B. *Eur. J. Org. Chem.* **1999**, 2011.
283. Murai, A.; Iwasa, N.; Masamune, T. *Chem. Lett.* **1977**, 235.
284. Murai, A.; Iwasa, N.; Masamune, T. *Bull. Chem. Soc. Jpn* **1980**, *53*, 259.
285. Bellus, D.; Kearns, D. R.; Schaffner, K. *Helv. Chim. Acta* **1969**, *52*, 971.
286. Cornell, D. G.; Filipescu, N. *J. Org. Chem.* **1977**, *42*, 3331.
287. Lupón, P.; Ferrer, J. C.; Piniella, J. F.; Bonet, J.-J. *J. Chem. Soc., Chem. Commun.* **1983**, 718.
288. Pfenninger, E.; Poel, D. E.; Berse, C.; Wehrli, H.; Schaffner, K.; Jeger, O. *Helv. Chim. Acta* **1968**, *51*, 772.
289. For a review concerning carbene reactions, see: Kirmse, W. *Angew. Chem.* **1959**, *71*, 537.
290. For a review concerning Wolff rearrangements, see: Meier, H.; Zeller, K.-P. *Angew. Chem. Int. Ed.* **1975**, *14*, 32.
291. For a review concerning oxoketenes, see: Wentrup, C.; Heilmayer, W.; Kollenz, G. *Synthesis* **1994**, 1219.
292. For a review concerning diazocarbonyl compounds, see: Ye, T.; McKervey, M. A. *Chem. Rev.* **1994**, *94*, 1091.
293. For a review concerning Wolff rearrangements, see: Gill, G. B. *The Wolff Rearrangement*, Trost, B. M., Ed.; Pergamon: New York, 1991; Vol. 3, p 887.
294. Qiao, G. G.; Andraos, J.; Wentrup, C. *J. Am. Chem. Soc.* **1996**, *118*, 5634.
295. Allen, A. D.; Porter, J.; Tahmassebi, D.; Tidwell, T. T. *J. Org. Chem.* **2001**, *66*, 7420.
296. Pacansky, J.; Coufal, H. *J. Am. Chem. Soc.* **1980**, *102*, 410.
297. Hacker, N. P.; Turro, N. J. *Tetrahedron Lett.* **1982**, *23*, 1771.
298. Rao, Y. K.; Nagarajan, M. *J. Org. Chem.* **1989**, *54*, 5678.
299. Nikolaev, V. A.; Popik, V. V. *Tetrahedron Lett.* **1992**, *33*, 4483.
300. Barra, M.; Fisher, T. A.; Cernigliaro, G. J.; Sinta, R.; Scaiano, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 2630.
301. Vleggaar, J. J. M.; Huizer, A. H.; Kraakman, P. A.; Nijssen, W. P. M.; Visser, R. J.; Varma, C. A. G. O. *J. Am. Chem. Soc.* **1994**, *116*, 11754.
302. Uyehara, T.; Takehara, N.; Ueno, M.; Sato, T. *Bull. Chem. Soc. Jpn* **1995**, *68*, 2687.
303. Trost, B. M.; Kinson, P. L. *Tetrahedron Lett.* **1973**, 2675.
304. Trost, B. M.; Kinson, P. L. *J. Am. Chem. Soc.* **1975**, *97*, 2438.
305. Chapman, O. L.; Gano, J.; West, P. R.; Regitz, M.; Maas, G. *J. Am. Chem. Soc.* **1981**, *103*, 7033.
306. McMahon, R. J.; Chapman, O. L.; Hayes, R. A.; Hess, T. C.; Krimmer, H.-P. *J. Am. Chem. Soc.* **1985**, *107*, 7597.
307. Andraos, J.; Chiang, Y.; Kresge, A. J.; Popik, V. V. *J. Am. Chem. Soc.* **1997**, *119*, 8417.
308. Walker, D. P.; Grieco, P. A. *J. Am. Chem. Soc.* **1999**, *121*, 9891.
309. Mander, L. N.; Pyne, S. G. *J. Am. Chem. Soc.* **1979**, *101*, 3373.
310. Fessner, W.-D.; Prinzbach, H.; Rihs, G. *Tetrahedron Lett.* **1983**, *24*, 5857.
311. Fessner, W.-D.; Sedelmeier, G.; Spurr, P. R.; Rihs, G.; Prinzbach, H. *J. Am. Chem. Soc.* **1987**, *109*, 4626.
312. King, G. R.; Mander, L. N.; Monck, N. J. T.; Morris, J. C.; Zhang, H. *J. Am. Chem. Soc.* **1997**, *119*, 3828.
313. Sudrik, S. G.; Chavan, S. P.; Chandrakumar, K. R. S.; Pal, S.; Date, S. K.; Chavan, S. P.; Sonawane, H. R. *J. Org. Chem.* **2002**, *67*, 1574.
314. Kunisch, F.; Hobert, K.; Welzel, P. *Tetrahedron Lett.* **1985**, *26*, 5433.
315. Leung-Toung, R.; Wentrup, C. *J. Org. Chem.* **1992**, *57*, 4850.
316. Allen, A. D.; Cheng, B.; Fenwick, M. H.; Huang, W.-W.; Missiha, S.; Tahmassebi, D.; Tidwell, T. T. *Org. Lett.* **1999**, *1*, 693.
317. Allen, A. D.; Cheng, B.; Fenwick, M. H.; Givehchi, B.; Henry-Riyad, H.; Nikolaev, V. A.; Shikhova, E. A.; Tahmassebi, D.; Tidwell, T. T.; Wang, S. *J. Org. Chem.* **2001**, *66*, 2611.
318. Cossy, J.; Belotti, D. *Tetrahedron Lett.* **1988**, *29*, 6113.
319. Cossy, J.; Belotti, D.; Leblanc, C. *J. Org. Chem.* **1993**, *58*, 2351.
320. Froborg, J.; Magnusson, G. *J. Am. Chem. Soc.* **1978**, *100*, 6728.
321. Stetter, H.; Kiehs, K. *Chem. Ber.* **1965**, *98*, 1181.
322. Stetter, H.; Kiehs, K. *Chem. Ber.* **1965**, *98*, 2099.
323. Stetter, H.; Schütte, M. *Chem. Ber.* **1975**, *108*, 3314.
324. Trost, B. M.; Whitman, P. J. *J. Am. Chem. Soc.* **1974**, *96*, 7421.
325. Borch, R. F.; Fields, D. L. *J. Org. Chem.* **1969**, *5*, 1480.
326. Murata, S.; Kobayashi, J.; Kongou, C.; Miyata, M.; Matsushita, T.; Tomioka, H. *J. Am. Chem. Soc.* **1998**, *120*, 9088.
327. Murata, S.; Kobayashi, J.; Kongou, C.; Miyata, M.; Matsushita, T.; Tomioka, H. *J. Org. Chem.* **2000**, *65*, 6082.
328. Available free of charge at http://jbcs.sbq.org.br.

Biographical sketch



Luiz F. Silva, Jr. was born in São Paulo, Brazil, in 1971. He studied chemistry at the University of São Paulo, where he received his BSc in 1993. In 1994, he joined the group of Professor Helena M. C. Ferraz, at the University of São Paulo, receiving his PhD in 1999. During his thesis, he was involved in ring contraction reactions promoted by thallium(III) salts. He then worked for 1 year as a FAPESP postdoctoral research associate toward the total synthesis of variecolin with Professor Gary A. Molander, at the University of Pennsylvania at Philadelphia. He returned to Brazil and worked for two more years as a FAPESP postdoctoral research associate with Professor H. M. C. Ferraz. In April of 2002, he accepted an appointment at the University of São Paulo, as Assistant Professor of Chemistry. His current research interests are focus on the total synthesis of natural products and the development of thallium(III) promoted reactions. Besides chemistry, he also enjoys sport and high mountain climbing.