Chemistry of Vinylidenecyclopropanes

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1. Introduction

Vinylidenecyclopropanes (VDCPs) **1**, which have a strained cyclopropyl group connected to an allene moiety and yet are thermally stable and reactive substances in organic chemistry, are versatile intermediates in organic synthesis.[1] The first synthesis of VDCPs **1** can be traced back to 1959.[2]

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Dr. Prof. Min Shi was born in Shanghai, China. He received his B.S. in 1984 (Institute of Chemical Engineering of East China, now named East China University of Science and Technology) and Ph.D. in 1991 (Osaka University, Japan). He had his postdoctoral research experience with Prof. Kenneth M. Nicholas at University of Oklahoma (1995−1996) and worked as an ERATO Researcher in Japan Science and Technology Corporation (JST) (1996−1998). He is currently a group leader of the State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences (SIOC, CAS). His research interest is in photochemistry, total synthesis of natural products, asymmetric synthesis, Morita−Baylis−Hillman reaction, and fixation of CO_2 using transition metal catalyst.

Dr. Li-Xiong Shao was born in Zhejiang Province, China. He received his B.S. degree in Chemistry from Zhejiang University (2001) and Ph.D. from Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences (SIOC, CAS), under the direction of Professor Min Shi (2006). Then he moved to East China University of Science and Technology (ECUST) as an assistant professor (July 2006 through December 2007). He is now doing his independent work in Wenzhou University, Zhejiang Province.

During the past decades, VDCPs **1** have demonstrated special reactivities, which can be tuned by the electronic or steric

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Dr. Jian-Mei Lu was born in Zhejiang Province, China. She received her B.S. degree in Chemistry from East China Normal University (2003) and Ph.D. from Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences (SIOC, CAS), under the direction of Professor Min Shi (2008). Then she moved to Wenzhou University, Zhejiang Province, as an assistant professor.

Dr. Yin Wei was born in 1977 in Henan (P. R. China). She received her Ph.D. from Ludwig-Maximilians-Universität in München (Germany) in 2009 under the direction of Professor Hendrik Zipse. Subsequently, she joined Professor Min Shi's group at Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences (SIOC, CAS), as an assistant professor. She is currently working on theoretical studies of organocatalysis.

effects and nature of the substituents on the skeleton. Thermal, photochemical, Lewis or Brønsted acid, and transition metal catalyzed/mediated skeleton conversions of VDCPs **1** have attracted much attention from mechanistic, theoretical, spectroscopic, and synthetic viewpoints.[3] To further understand the special reactivities of VDCPs, it is helpful to examine the structure and strain energy of VDCP **1a**[4] and to compare it with other simple compounds, such as cyclopropane **2a**,[5] methylenecyclopropane **3a**,[6] and allene **4a**[7] (Figure 1). Compared with cyclopropane **2a** and methylenecyclopropane **3a**, the bond angle of VDCP **1a** is bigger than that of cyclopropane **2a** (62.2° vs 60°) and smaller than that of methylenecyclopropane **3a** (62.2° vs 63.9°). Comparison of simple allene **4a** with **1a** showed that the C1−C1′ double bond is strengthened and the C1′−C2′ double bond becomes weaker (Figure 1). The estimated strain energy of VDCP **1a**[4e] is 50.9 kcal/mol, which is higher than that of cyclopropane **2a** (27.5 kcal/mol) and that of methylenecyclopropane **3a** (40.9 kcal/mol).[5c] This indicates that VDCPs **1** are highly strained and reactive species. As can also be seen from Figure 1, the reactive sites of VDCPs **1** are more than simple cyclopropane **2a**, methylenecyclopropane **3a**, and allene **4a**. Fortunately enough, single crystals of VDCP **1b**

Kazuhiko Mizuno was born in 1947 in Osaka, Japan. He graduated from Osaka University in 1971, where he received his doctorate in 1976 under the supervision of Professor Hiroshi Sakurai. He became a research associate at Osaka Prefecture University in 1976, and he joined Professor Yoshio Otsuji's group. In 1979−1980, he was a postdoctoral fellow at the University of Texas at Dallas under the guidance of Professor Richard A. Caldwell. In 1996, he was promoted to a full Professor at Osaka Prefecture University via a Lecturer and an Associate Professor. His research interests include synthetic and mechanistic organic photochemistry, electron-transfer chemistry, organosilicon chemistry, and organometallic chemistry. He received "Progress Award in Synthetic Organic Chemistry, Japan" (1986), "The Japanese Photochemistry Association Award" (1996), and "The Japanese Photochemistry Association Lectureship Award" (2006). He has published over 220 peer-reviewed international articles in international journals and more than 35 reviews including book chapters. He has served as a president of Japanese Photochemistry Association (JPA) during 2008−2009, a chair of Photochemistry Division in Chemical Society of Japan (CSJ) during 2008−2011, and a division chair of Organometallic Chemistry in Kinki Chemical Society during 2009−2010.

Hajime Maeda was born in Kanazawa, Japan. He graduated from Osaka University in 1992, where he obtained his doctorate in 1997 under the supervision of Professor Noboru Sonoda. He became a research associate at Osaka Prefecture University in 1997, and he worked in the laboratory of Professor Kazuhiko Mizuno. In 2006−2007, he was a visiting scientist at the University of New Mexico and stayed in the group of Professor Patrick S. Mariano. In 2007, he was promoted to Assistant Professor at Osaka Prefecture University. In 2009, he joined in Professor Masahito Segi's group at Kanazawa University as an Associate Professor. His research interests include the development of synthetically useful photochemical reactions and heteroatom chemistry especially that involving group 14 and 16 elements.

and methylenecylopropane **3b** have been obtained to support above discussions. The ORTEP drawings of them are shown in Figures 2[8] and 3[9] and their CIF data are presented in the Supporting Information. Undoubtedly, the chemistry of VDCPs **1** will be much more diverse because of the highly strained cyclopropane ring and the allene moiety.

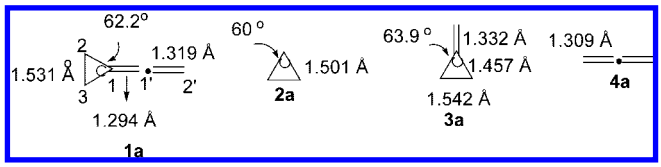


Figure 1.

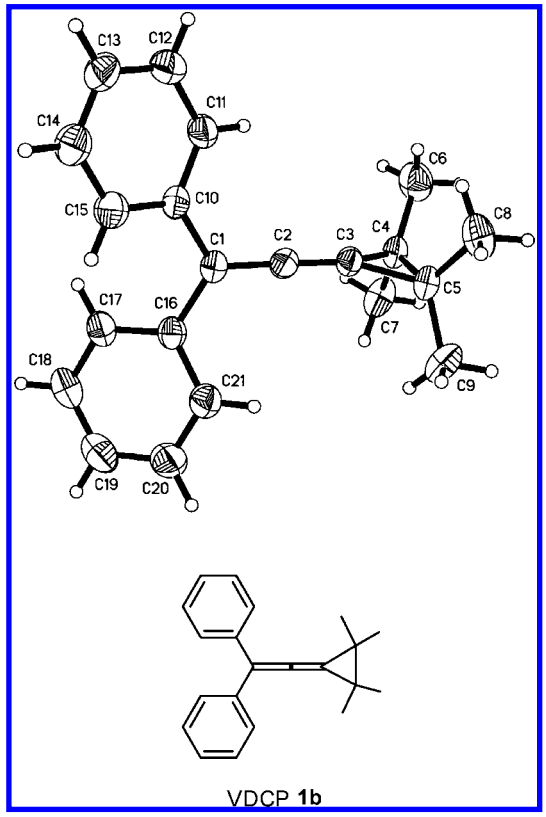


Figure 2. ORTEP drawing of VDCP **1b** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg): $C_1-C_2 = 1.327(2)$, $C_2-C_3 = 1.276(2)$, $C_3-C_4 = 1.488(2)$, $C_3-C_5 = 1.485(2)$, $C_4-C_5 = 1.531(2)$, $C_5-C_3-C_4 = 62.02(11)$.

For a long period of time, VDCPs were considered as highly unstable compounds, and the traditional investigations were focused mainly on the photo- and heat-induced chemistry of VDCPs. However, during the latest years, VDCPs were found to demonstrate good reactivities and selectivities depending on the nature of the electronic and steric effects on the substituents. This review intends to collect systematically the widespread knowledge not only regarding synthetic methods for VDCPs **1**, but also including advances on the chemistry of VDCPs **1**. In order to complete overview of the chemistry of VDCPs, there may be some minor overlap with the contents in the previously published reviews.[10] This review will cover the literature up to the end of 2008.

2. Preparation of VDCPs 1

Generally, VDCPs **1** are prepared through the reaction of alkenes with *in situ* produced alkenylidenecarbenes.[11] These alkenylidenecarbenes can be formed by treating halogenoalkynes,[12] halogenoallenes,[12c,f,i,13] polyhalogenocyclopropanes,[14] and polyhalogenoalkanes[15] with strong bases, which can also be generated by heating of diazoallenes[16] and so on.[17] The general methods for the synthesis of VDCPs **1** are summarized in Scheme 1. The method reported by

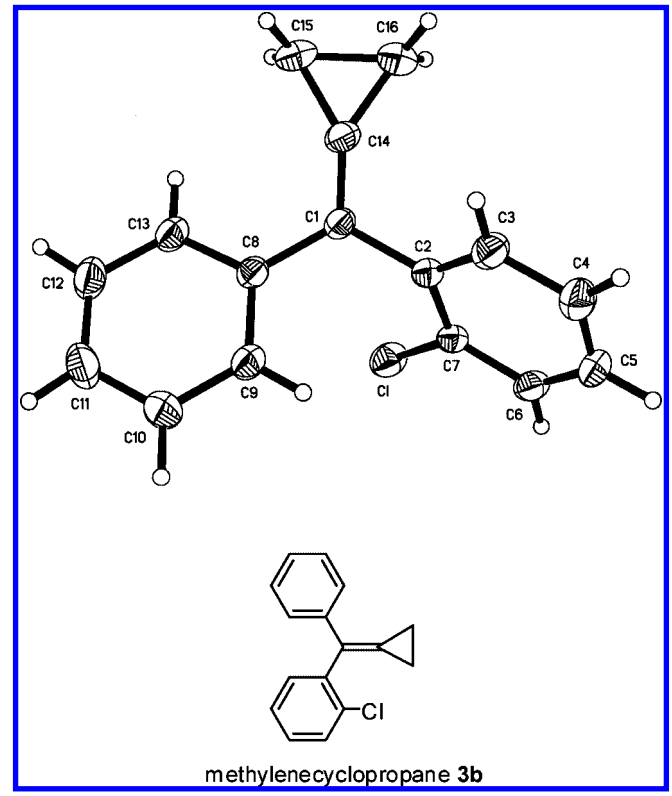
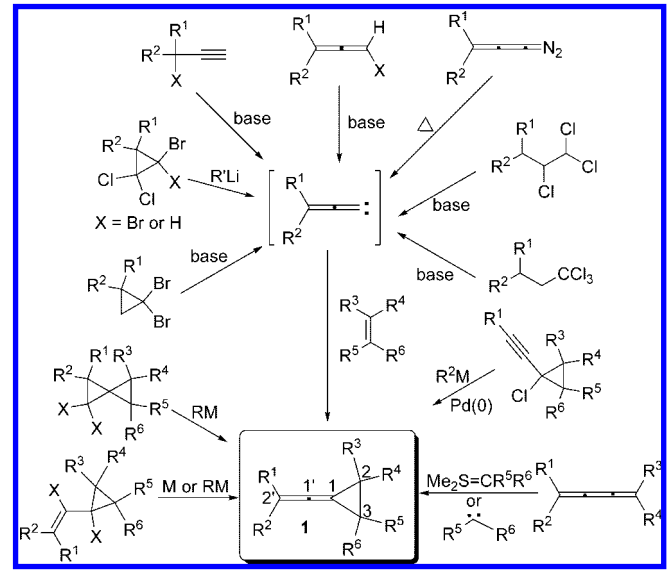


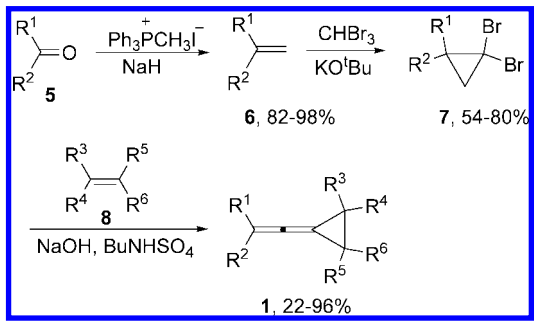
Figure 3. ORTEP drawing of methylenecyclopropane **3b** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg): $C_1-C_{14} = 1.326(3)$, $C_{14}-C_{15} = 1.455(3)$, $C_{15}-C_{16} = 1.528(4)$, $C_{15}-C_{14}-C_{16} = 63.25(19)$.

Scheme 1



Mizuno et al. in 1991[14f] is one of the most popular methods to synthesize various VDCPs, and the general route is shown in Scheme 2. The general procedure includes a Wittig reaction of the corresponding carbonyl compounds **5** to form alkenes **6**.[18] Then, cyclopropanation of alkenes **6** with the in situ generated dibromocarbene gives the 1,1-dibromocyclopropanes **7**.[19] Finally, under phase-transfer conditions, VDCPs **1** can be obtained in acceptable to high yields via the reaction of 1,1-dibromocyclopropanes **7** with various substituted alkenes **8** (Scheme 2).[14f]

Scheme 2

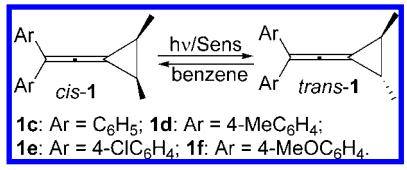


3. Photoinduced Skeleton Rearrangement of VDCPs and Isomerization

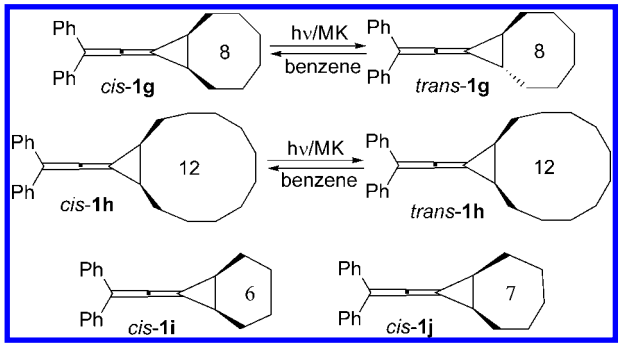
3.1. Photoinduced Cis−Trans Isomerization of VDCPs

Photoirradiation of *cis*- and *trans*-1-diarylvinylidene-2,3-dimethylcyclopropanes **1** in benzene afforded photoisomerized products in a 1:1 photostationary state (PSS) mixture (Scheme 3).[20] The photoisomerization was not quenched by triplet quenchers such as molecular oxygen (O_2) and 2-methyl-1,3-butadiene. Therefore, this photoreaction proceeded through a singlet mechanism. On the other hand, the photoreaction of *cis*-**1c−f** and *trans*-**1c−f** in the presence of triplet sensitizers such as acetophenone (E_T = 309 kJ·mol^{-1}), benzophenone (E_T = 288 kJ·mol^{-1}), thioxanthen-9-one (E_T = 265 kJ·mol^{-1}), Michler's ketone (MK; E_T = 259 kJ·mol^{-1}), and 1-acetonaphthone (E_T = 236 kJ·mol^{-1}) gave a 3:7 PSS mixture of *cis*-**1c−f** and *trans*-**1c−f**, respectively. The triplet-sensitized photoisomerization occurs more efficiently than the direct one. The quantum yield from *cis*-**1c** to *trans*-**1c** in the presence of MK at 366 nm is 0.62. Effects of sensitizers indicated that the triplet energies of *cis*-**1c−f** are estimated as 220−230 kJ·mol^{-1}. The PSS ratios in both direct and triplet-sensitized photoreactions do not depend on the substituents on the *para* position of the phenyl rings but depend on their multiplicity.

Scheme 3



Scheme 4

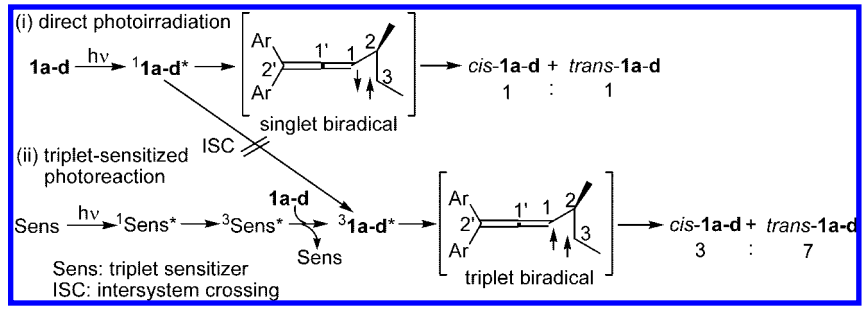


Bicyclic diphenylvinylidenecyclopropanes *cis*-**1g** and *trans*-**1g**, having an eight-membered ring, in the presence of MK were also photoisomerized to give a 1:1 PSS mixture in high efficiency (Scheme 4).[20b,21] Irradiation of *cis*-**1h**, having a twelve-membered ring, in the presence of MK afforded *trans*-**1h** in a similar manner. However, *cis*-diphenylvinylidenebicyclo-[4.1.0]heptane and -[5.1.0]octane, *cis*-**1i,j** did not isomerize to their *trans*-isomers due to the thermodynamic instability of *trans*-**1i,j**.

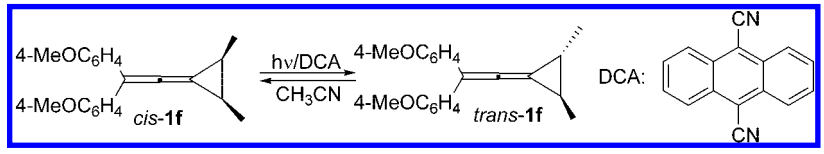
The mechanism for these photoisomerization reactions is shown in Scheme 5. C1−C3 bond cleavage followed by the isomerization from the excited singlet and triplet states of **1** gives the respective PSS mixture. Intersystem crossing (ISC) from the excited singlet state of **1** to the triplet one is quite slow or inefficient. Singlet 1,3-biradical reproduces the cyclopropane ring before ISC to triplet 1,3-biradical occurs. The cleaved bond in both the singlet and the triplet photoisomerization is postulated from the results of photocycloaddition and photorearrangement discussed in the later sections.

The 9,10-dicyanoanthracene (DCA)-sensitized *cis−trans* photoisomerization of electron-rich 1,2-diarylcyclopropanes efficiently proceeds via a radical cation chain transfer mechanism.[10b,20b,22] The photoisomerization of electron-rich *cis*-2′-di-(4-methoxyphenyl)-vinylidene-2,3-dimethylcyclopropane (*cis*-**1f**) in acetonitrile was also sensitized by DCA via photoinduced electron transfer.[23] The photoisomerization efficiently takes place to give a 3:7 PSS mixture of *cis*-**1f** and *trans*-**1f** (Scheme 6). However, the *cis−trans* photoisomerization of less electron-rich VDCPs **1c−e** were sluggish

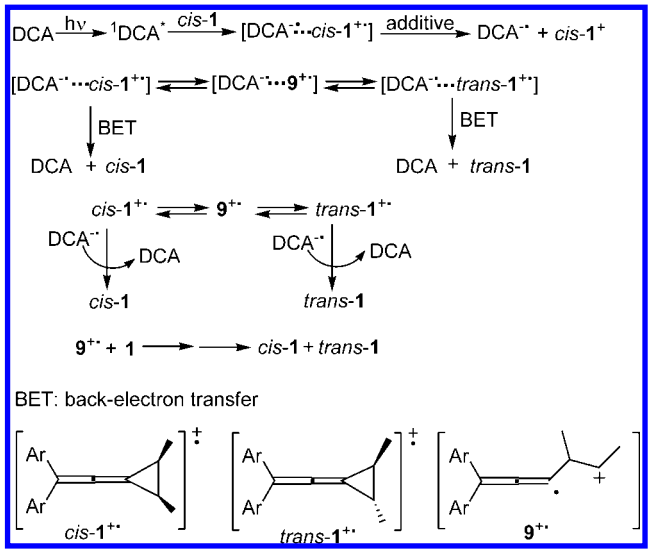
Scheme 5



Scheme 6



Scheme 7



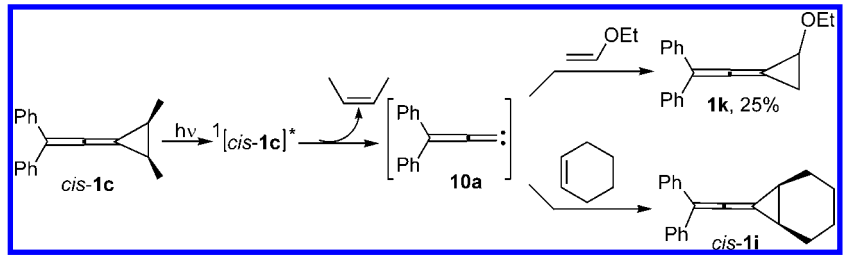
under the same reaction conditions. The photoisomerization is accelerated by O_2 and some additives such as $Mg(ClO_4)_2$ and phenanthrene, which is similar to the photoinduced electron transfer reaction of the DCA−1,2-diarylcyclopropane system.[24]

The proposed mechanism is shown in Scheme 7. The first step is a photoinduced one-electron transfer from *cis*-**1** to the excited singlet state of DCA, ^{1}DCA*, to generate the free radical ions via the radical ion pair [DCA$^{-\bullet}$···*cis*-**1**$^{+\bullet}$]. The key step of this photoisomerization is the dissociation from the radical ion pair to the free radical ions assisted by the additives such as $Mg(ClO_4)_2$. The ring-opening of *cis*-**1**$^{+\bullet}$ generates ring-opened radical cation **9**$^{+\bullet}$ by C1−C3 bond cleavage. The rotation of the C2−C3 bond of **9**$^{+\bullet}$ followed by a back-electron transfer from DCA$^{-\bullet}$ to the opened 1,3-biradical and a rebonding process causes *cis*−*trans* photoisomerization. It is notable here that a chain mechanism in which an electron transfer from neutral *cis*-**1d** to **9**$^{+\bullet}$ takes place is included in the reaction. The back-electron transfer (BET) from DCA$^{-\bullet}$ to *cis*-**1**$^{+\bullet}$ was effectively suppressed by the addition of O_2 and $Mg(ClO_4)_2$. The enhancement of the reaction can be interpreted by the rapid electron transfer from DCA$^{-\bullet}$ to O_2 to afford DCA and $O_2^{-\bullet}$ or by the interaction of DCA$^{-\bullet}$ with Mg(II) ion.

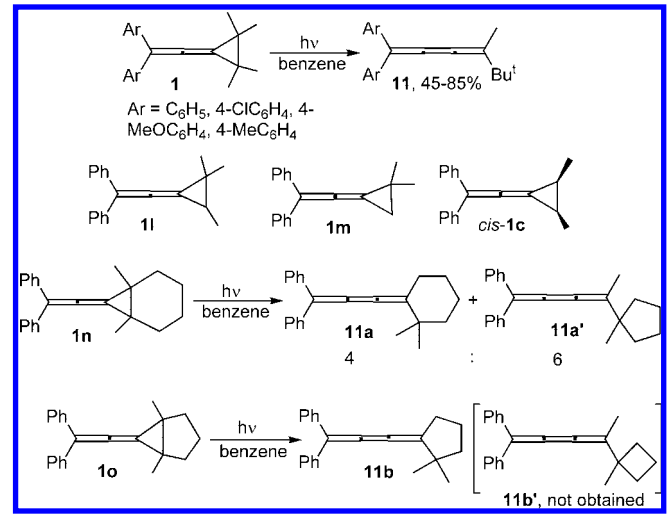
3.2. Photoinduced Generation of Vinylidenecarbenes from VDCPs

Photoirradiation of *cis*-**1c** in methanol through Pyrex filter in the presence of a large excess of ethyl vinyl ether gave 2-ethoxy-1′-(diphenylvinylidene)cyclopropane **1k** in 25% yield (Scheme 8).[21b,25] Similar irradiation of *cis*-**1c** in the presence of cyclohexene gave the corresponding VDCP *cis*-**1i**, although the yield was low. The formation of diphenylvinylidenecarbene **10a** is clearly demonstrated in Scheme 8, and subsequently **10a** could be trapped by electron-rich alkenes to give the desired products. Electrophilic character of this carbene was supported by its reactivity toward these alkenes. This carbene could not be generated by triplet-sensitized photoreaction. Therefore, the vinylidenecarbene **10a** is produced as a competitive process with the formation of 1,2,3-butatriene from the excited singlet state of *cis*-**1c**, which is discussed in the next section.

Scheme 8



Scheme 9



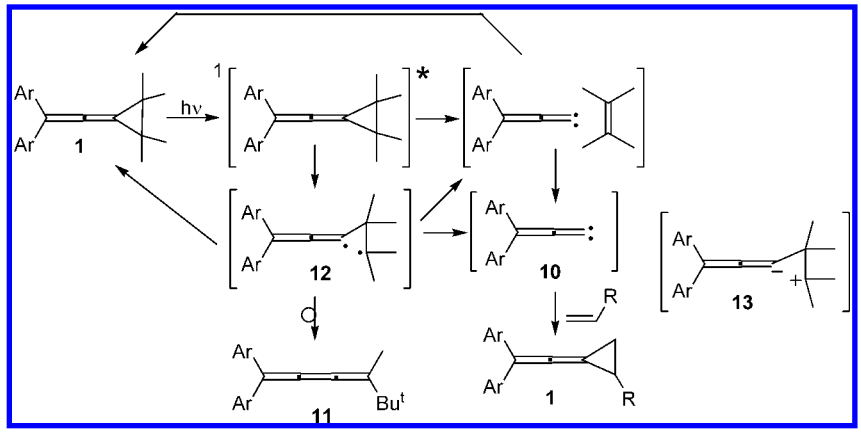
3.3. Photorearrangement of VDCPs

Irradiation of a benzene solution containing 2′-diaryl-2,2,3,3-tetramethylvinylidenecyclopropanes **1** efficiently afforded 1,1-diaryl-4,5,5-trimethyl-1,2,3-hexatriene **11** in high yields, although the quantum yields for the formation of **11** were not high ($\Phi = 0.01-0.02$) (Scheme 9).[25] The photorearrangement of 2,2,3-trimethyl and 2,2- and 2,3-dimethyl derivatives **1l**, **1m**, and *cis*-**1c** also took place, but the rates for the formation of 1,2,3-butatrienes were quite slow. The bicyclic VDCPs **1n** and **1o** also rearranged to the 1,2,3-butatriene derivatives **11a**, **11a′**, and **11b**, respectively.

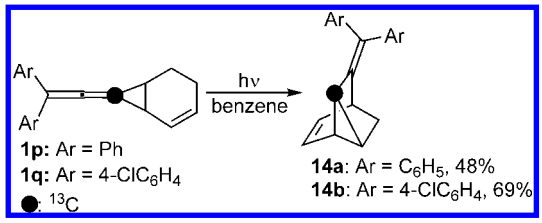
This photorearrangement was not sensitized by triplet sensitizers such as benzophenone and MK and was not quenched by O_2 and 2-methyl-1,3-butadiene; thus the triplet mechanism is ruled out. The singlet mechanism could be used to rationalize these results (Scheme 10). The homolysis of the C1−C3 bond of VDCPs **1** from the excited singlet state of **1** generates the 1,3-singlet biradical intermediate **12**, which rearranges to 1,2,3-butatriene **11** by the migration of an alkyl group. The heterolytic cleavage seems unlikely, because the 1,3-dipolar intermediate **13** is not trapped by methanol under identical reaction conditions.

Irradiation of a benzene solution of 7-diarylvinylidenebicyclo[4.1.0]hept-2-enes (**1p** and **1q**) gave 8-(diarylmethylene)-

Scheme 10



Scheme 11



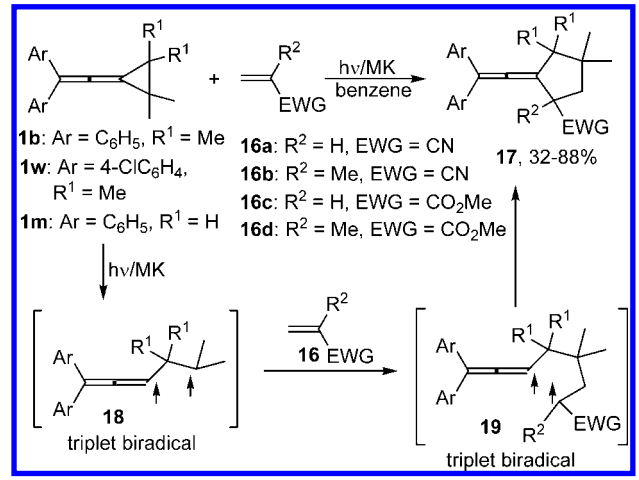
tricyclo[2.2.2.1^{1,5}]oct-2-enes **14** in good yields.[26] Since the photorearrangement was not sensitized by triplet sensitizers such as benzophenone and MK, this photorearrangement might occur from the singlet excited state. The photoreaction of ^{13}C-labeled compound gave only one ^{13}C-labeled rearranged product, and ^{13}C was introduced exclusively into the position shown in Scheme 11.

Irradiation of a benzene solution of *exo*-7-diarylvinylidenetricyclo[4.1.1^{2,5}.0]hept-2-enes (**1r** and **1s**) gave 4-diarylvinylidene-bicyclo[3.2.1]octa-2,6-dienes **15** in moderate to good yields (Scheme 12).[26] However, similar irradiation of the *endo* isomer **1t** and *exo*-7-diphenylvinylidenetricyclo[4.1.1^{2,5}.0]heptane **1u** did not give the corresponding rearranged product. Irradiation of *exo*-7-dimethylvinylidenetricyclo[4.1.1^{2,5}.0]hept-2-ene **1v** through quartz glass by a low-pressure mercury lamp also gave a rearranged product in low yield. In contrast to the above photorearrangement shown in Scheme 11, the photoreaction was sensitized by benzophenone and MK, suggesting that this photoreaction occurs from the excited triplet state. The photoreaction of ^{13}C-labeled compounds **1r** and **1s** clarified the mechanism as shown in Scheme 12.

3.4. [3 + 2] Photocycloaddition of VDCPs with Unsaturated Compounds

Photoirradiation of a benzene solution containing VDCP **1b**, acrylonitrile (**16a**), and MK under argon atmosphere gave

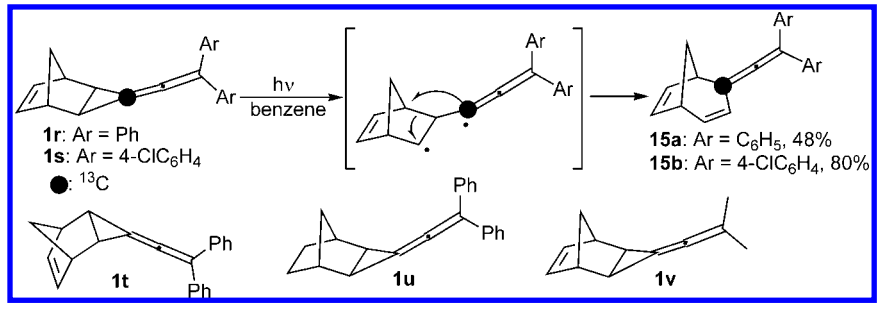
Scheme 13



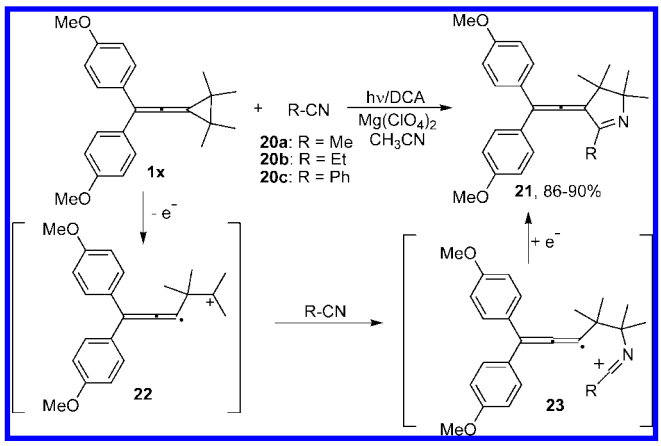
2-cyano-1-diphenylvinylidene-4,4,5,5-tetramethylcyclopentane (**17a**) in 85% isolated yield (Scheme 13).[20b,27] Photoreactions of VDCPs **1b**, **1w**, and **1m** with electron-deficient alkenes **16a**−**d** under similar conditions afforded the corresponding vinylidenecyclopentane derivatives **17**. However, **1b** reacts neither with β-substituted alkenes, such as crotononitrile, 1,2-dicyanoethene, and 2-cyclohexenone, nor with electron-rich alkenes, such as ethyl vinyl ether. The photocycloaddition occurs in a highly regioselective manner even in the reaction of dimethyl derivative **1m**. The photoreaction did not proceed in the absence of triplet sensitizer such as MK. Therefore, a triplet 1,3-biradical mechanism is proposed for the [3 + 2] photocycloaddition. The regioselectivity can be explained by the nucleophilic attack of electron-deficient alkenes to tertiary alkyl radical to generate 1,5-biradicals **19**, which undergo cyclization to afford diarylvinylidenecyclopentanes **17**.

Ritter-type nucleophilic photocycloaddition of cyano group to the cationic carbon of the 1,3-radical cation derived from

Scheme 12



Scheme 14

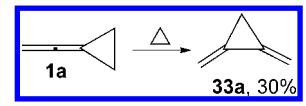


VDCP **1x** generated by photoinduced electron transfer has also been reported by Mizuno et al. (Scheme 14).[20b,28] Irradiation of an acetonitrile solution containing electron-rich VDCP **1x** with nitriles **20** in the presence of DCA and $Mg(ClO_4)_2$ gave 2-alkyl- or 2-phenyl-substituted 3-[2′,2′-bis(4-methoxyphenyl)vinylidene]-4,4,5,5-tetramethyl-1-pyrrolines **21**. The less electron-rich VDCPs **1b** (Ar = Ph) and **1w** (Ar = 4-ClC_6H_4) did not give the corresponding [3 + 2] photocycloadducts. The photoreaction can be explained by the photoinduced electron transfer mechanism. Nitriles attack the ring-opened radical cation **22** derived from **1x**, followed by cyclization to afford products **21**. The [3 + 2] photocycloaddition hardly occurs in the absence of $Mg(ClO_4)_2$. Presumably, the addition of $Mg(ClO_4)_2$ to the reaction system suppresses the back-electron transfer from $DCA^{\bullet-}$ to the radical cation **22** (Scheme 14).

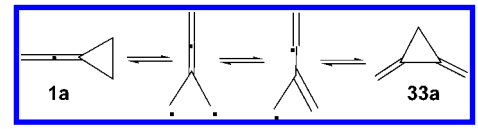
3.5. Photooxygenation of VDCPs

Photooxygenation of strained small ring compounds has received considerable attention from synthetic and mechanistic viewpoints in the last three decades. Akasaka and Ando reported that methylene blue-sensitized photooxygenation of adamantenylidenecyclopropanes **1** in CH_2Cl_2 gave various oxygenated products depending on the substituents on the cyclopropyl ring (Scheme 15).[29] Singlet oxygen is proposed as oxidizing species because addition of 1,4-diazabicyclo[2.2.2]octane as a $^1O_2$ quencher inhibited the reaction. Electrophilic attack of $^1O_2$ on **1** gives peroxyallyl intermediate **25** via perepoxide **24**. Intermediate **25** undergoes ring closure to afford dioxetane **26** or rearranges to form intermediate **30**. Subsequent decomposition of **26** produces adamantanone **27** and ketene **28**. Alternatively, O−O bond cleavage in **26** followed by rearrangement gives **29**. Cyclic ketones **31** and **32** could be produced from intermediate **30** (Scheme 15).

Scheme 16



Scheme 17



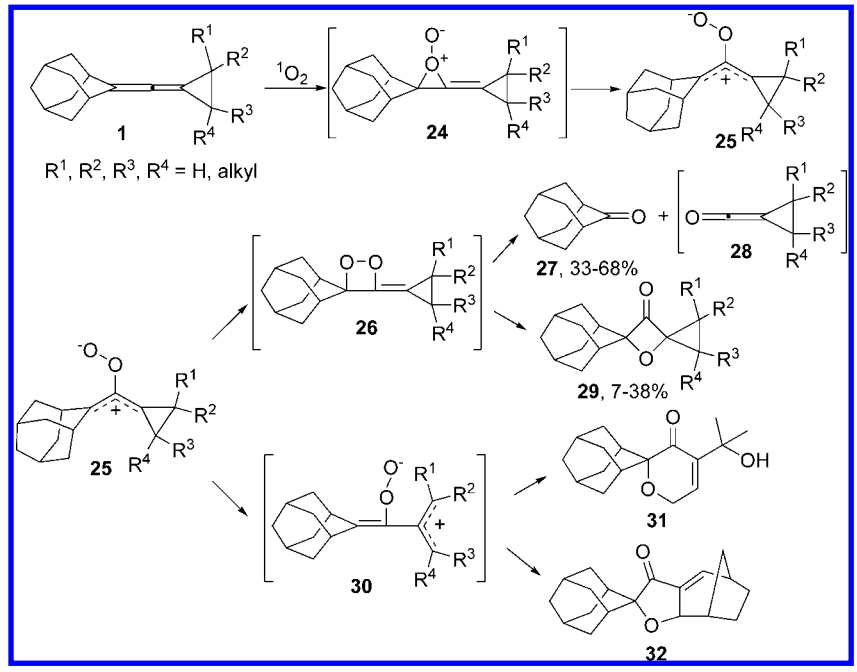
4. Thermal-Induced Reactions of VDCPs

4.1. Rearrangement Reactions of VDCPs upon Heating

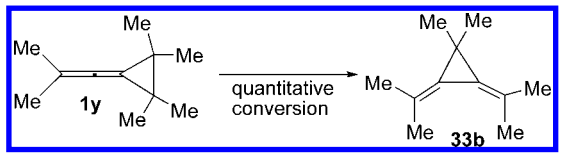
In 1970, Conia et al. reported that upon heating to 320 °C under vacuum for 3 min (static gas-phase technique), VDCP **1a** gave a mixture of **33a** (30%) and recovered **1a** (20%) and polymers, which can be easily separated by gas chromatography (Scheme 16).[30] This simple thermal conversion, observed with its methyl derivatives too,[31] is apparently promoted by a cyclopropane ring cleavage, which leads to a highly delocalized biradical closely related to trimethylenemethane (Scheme 17).

Employing VDCP **1y** as the substrate, which was the methyl derivative of **1a**, some other interesting results were

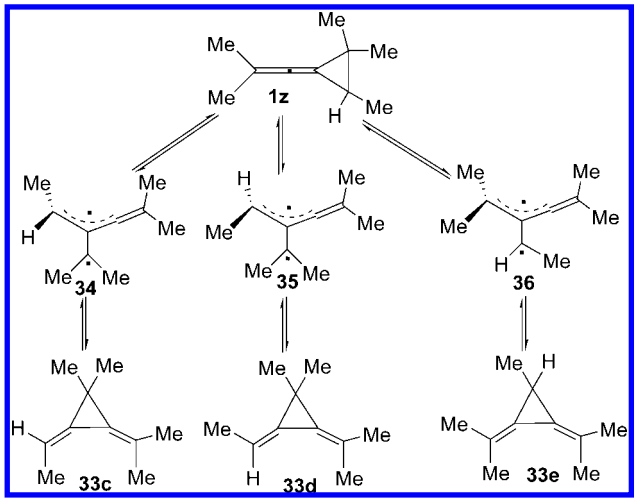
Scheme 15



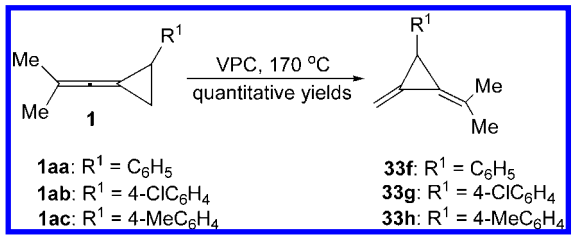
Scheme 18



Scheme 19



Scheme 20



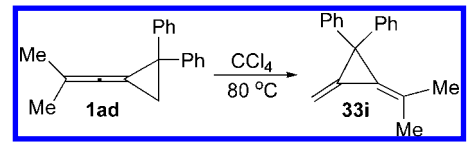
reported by Crandall et al.[32] For example, pyrolysis of **1y**, carried out in a flow system at 360 °C (0.1 mm), gave an almost quantitative conversion to dimethylenecyclopropane **33b** (Scheme 18).

A similar and more instructive conversion was effected by thermolysis of VDCP **1z** in which one methyl group in the cyclopropyl ring of **1y** was replaced by a hydrogen atom. Three isomeric hydrocarbons, **33c**, **33d**, and **33e**, were produced. The ratio of these products varies with temperature; the ratio of **33c/33d/33e** is 10:2:3 at 360 °C and 2:3:6 at 410 °C (Scheme 19). A set of orthogonal diradicals[33] can be invoked to describe this reaction.[32]

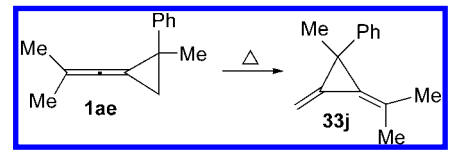
There are many papers reported for similar transformations of aryl derivatives of VDCPs **1** upon heating. For example, Patrick et al. reported a similar but stereoselective thermal rearrangement of 1-(2-methylprop-1-enylidene)-2-arylcyclopropanes **1** to 1-isopropylidene-2-methylene-3-arylcyclopropanes **33**.[34] They found that the rearrangement of VDCPs **1** to products **33** occurs nearly quantitatively on vapor-phase chromatography (VPC) at 170 °C or by heating **1** in mesitylene solution at 130 °C (Scheme 20). A similar type of intermediates as shown in Scheme 17 can also be used to explain the formation of products **33** in this reaction.

Jones has reported that when the diphenyl derivative of VDCPs **1**, such as **1ad**, is heated, the phenyl groups always remain on the cyclopropyl ring and do not migrate to the double bond (Scheme 21).[35]

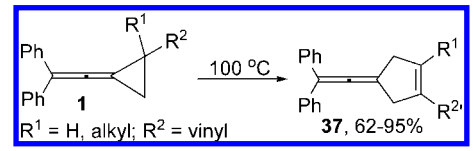
Scheme 21



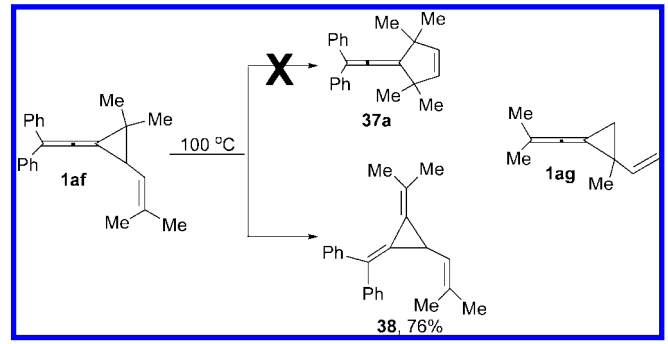
Scheme 22



Scheme 23



Scheme 24



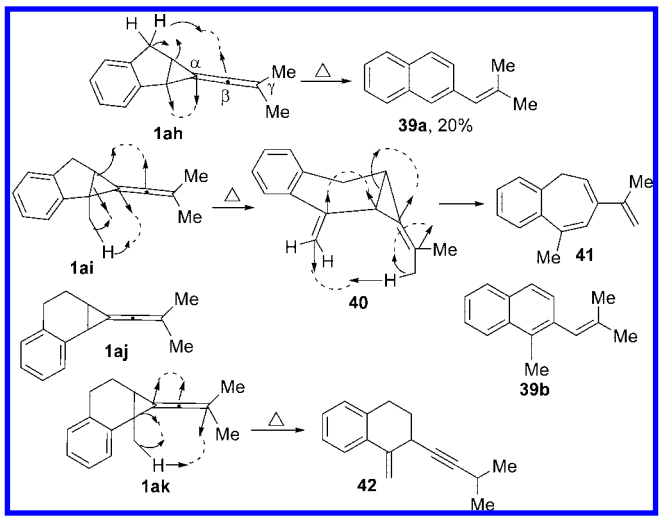
A similar result can be observed when one phenyl group on the cyclopropyl ring of VDCP **1ad** was replaced by a methyl group (Scheme 22).[36]

Heating 2-vinyl derivatives of VDCPs **1** can give the thermal rearrangement products, the cyclopentenes **37**, in up to quantitative yields (Scheme 23).[37]

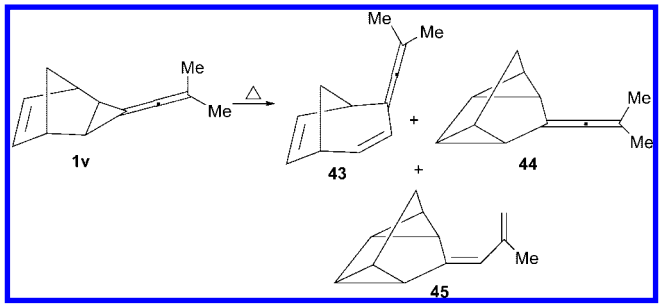
Instead of the expected cyclopentene derivative **37a**, the thermolysis of VDCP **1af** at 100 °C for 4.5 h gave the 1,2-dimethylene-3-vinylcyclopropane **38** in 76% yield, and no rearrangement reaction occurred for 1-(2′-methylpropenylidene)-2-methyl-2-vinylcyclopropane **1ag** even at higher temperature (130 °C) (Scheme 24).[20b]

Sadler et al. reported the thermal rearrangement of the dimethylvinylidene benzobicyclo[*n*.1.0]alkenes ($n = 3, 4$) conveniently obtained in moderate yields as 1:1 adducts of dimethylvinylidenecarbene with indene (**1ah**), 3-methylindene (**1ai**), 1,2-dihydronaphthalene (**1aj**), and 1,2-dihydro-4-methylnaphthalene (**1ak**), respectively.[38] Thermal rearrangement of VDCP **1ah**, effected in refluxing benzene for 24 h gave naphthalene **39a** in 20% yield. Gratifyingly, almost quantitative yield of **39a** was obtained by a low-pressure (ca. 0.01 mmHg) vapor-phase pyrolysis technique in which **1ah** was carried out in a stream of nitrogen through a flow system at 450 °C. Surprisingly, VDCP **1ai** readily rearranged in refluxing benzene to give the bicycloheptene **40** exclusively within 12 h, whereas low-pressure vapor-phase pyrolysis (450 °C) yielded a mixture of the bicycloheptene **40**, the naphthalene **39b**, and the benzocycloheptatriene **41** in the ratio of 2:3:1. Vapor-phase pyrolysis of **40** yielded a mixture of **41** and unreacted **40**, but not **39b** (Scheme 25). The exclusive formation of product **40** at low temperatures and

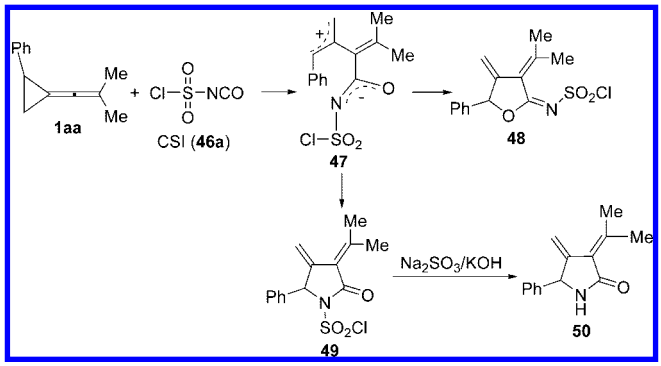
Scheme 25



Scheme 26



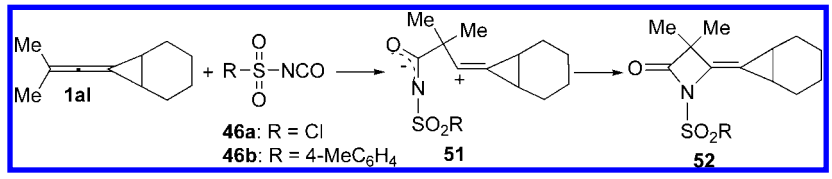
Scheme 27



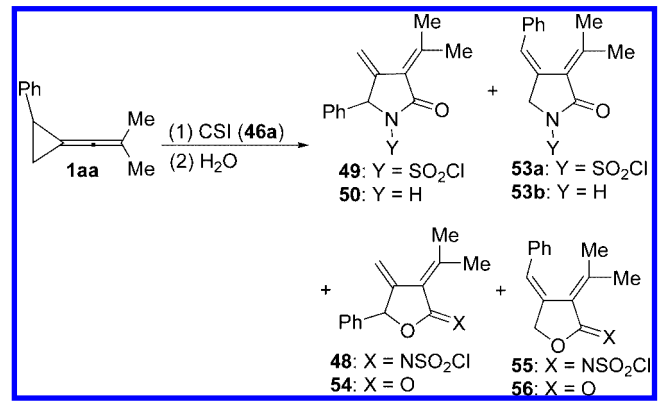
its subsequent conversion into **41** only at higher temperatures indicate that the initial rearrangement of VDCP **1ai** proceeds via either of two separate routes and that the activation energy required for the formation of the thermodynamically favored naphthalene **39b** is greater than that for the formation of the bicycloheptene **40**. Vapor-phase pyrolysis (450 °C) of VDCP **1aj** gave an inseparable complex mixture of products. By contrast, thermal rearrangement of VDCP **1ak** under the same conditions gave good yield of the acetylene **42** (Scheme 25).

Pyrolysis of VDCP **1v** in the gas phase (static) under a pressure of ca. 3 mmHg at 140 °C gave a mixture of products

Scheme 28



Scheme 29



43, **44**, and **45** quantitatively in ratios that varied with the reaction time (Scheme 26).[13e]

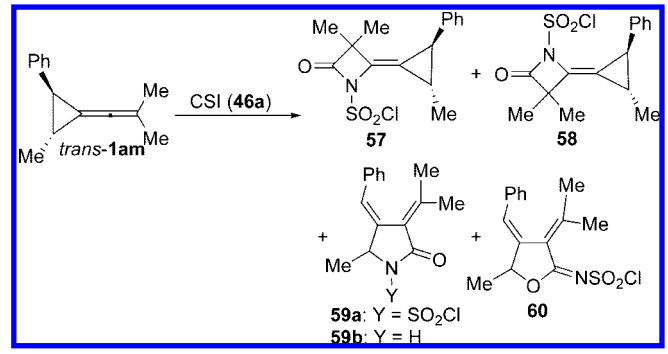
4.2. Thermal-Induced Addition Reactions of VDCPs

Gompper et al. demonstrated that VDCP **1aa** can react with chlorosulfonyl isocyanate CSI (**46a**) to give the [3 + 2] cycloaddition products, tetrahydrofurans and pyrrolidinones (Scheme 27).[39] It is proposed that electrophilic attack of CSI to C1′ of VDCP **1aa** generates zwitterionic intermediate **47**. Subsequent cyclization of O-attack affords product **48**, while N-attack forms **49**, and [3 + 2] cycloaddition products are formed in both cases (Scheme 27).

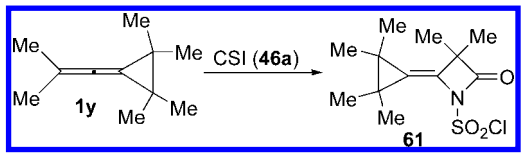
However, if VDCP **1al** was used as the substrate, only [2 + 2] cycloaddition product **52** was obtained (Scheme 28).[39]

Moreover, Pasto et al. found that the reactions of VDCPs **1** with CSI (**46a**) were extremely sensitive to the substituents on the cyclopropyl ring and also to the allene moiety.[40,41] It was reported that electrophilic attack by CSI (**46a**) on VDCPs **1** can occur at C1, C1′, or C2′. Competition between these modes of reaction is expected to be sensitive to steric effects engendered by substituents on VDCPs **1** with the approaching CSI (**46a**), steric effects in the resulting dipolar intermediates, and stabilization affording the cationic center. The factors affecting the stereochemistry about the benzylidene or ethylidene functions in the cyclopropane ring-opened products arise not only in the initial step of the reaction but

Scheme 30



Scheme 31



also in the second step, during which the dipolar intermediates collapse to products. For example, it was reported that the reaction of VDCP **1aa** with CSI (**46a**) produced a mixture of adducts **48**−**50** and **53**−**56** (Scheme 29).[40]

When the reaction of VDCP *trans*-**1am** with CSI (**46a**) was carried out, both the [3 + 2] and [2 + 2] cycloaddition products **57**−**60** were obtained (Scheme 30).[40]

Reaction of VDCP **1y** with CSI (**46a**) occurs exclusively at the C1′−C2′ double bond in a [2 + 2] fashion to afford clean lactam **61** (Scheme 31).[40]

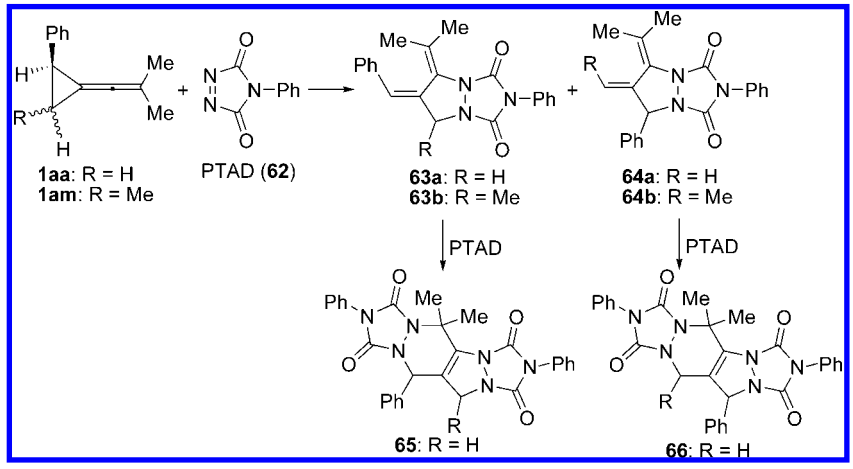
Pasto et al. first investigated the reaction of VDCPs **1** with 4-phenyl-1,2,4-triazoline-3,5-dione PTAD (**62**). It was found that the reaction proceeded very rapidly even at temperature below 25 °C. For the reactions of VDCPs **1aa** and **1am** (*cis*- or *trans*-isomer) with PTAD in a 1:1 molar ratio in dichloromethane, two 1:1 adducts, **63** and **64**, were formed in which both of the products **63a** and **64a** react further with another molecule of PTAD in a hetero-Diels−Alder mode to form the 2:1 adducts **65** and **66**, respectively (Scheme 32).[42]

Kinetic[43] and theoretical studies[44] showed that the reactions of VDCPs **1** with PTAD (**62**) proceeded via a concerted cycloaddition pathway (Scheme 33).

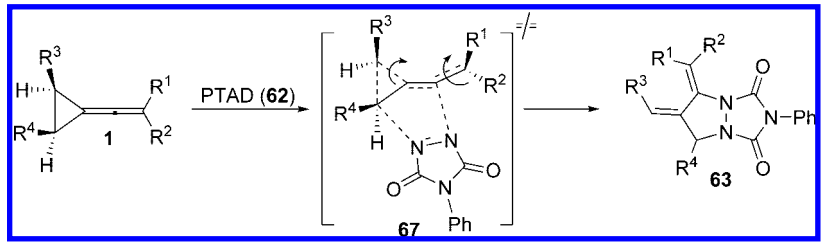
For the reactions of VDCP **1al** with 1-phenyl-pyrrole-2,5-dione **68** and maleic anhydride **69**, no desired [3 + 2] cycloaddition products were obtained. Instead, VDCP **1al** underwent competitive [2 + 2] cycloaddition across the exocyclic double bond to form compounds **70** and **71** and an ene reaction with the remote double bond to form **72**, which reacted further with another molecule of **68** or **69** to give product **73a** or **73b**, respectively (Scheme 34).[45]

The [2 + 2] cycloaddition reactions of VDCPs **1** with electron-deficient alkenes, such as methylenemalonodinitriles

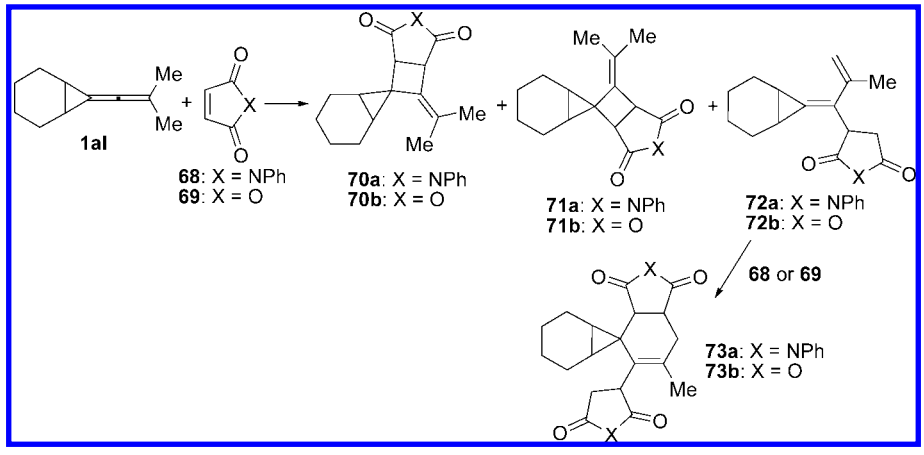
Scheme 32



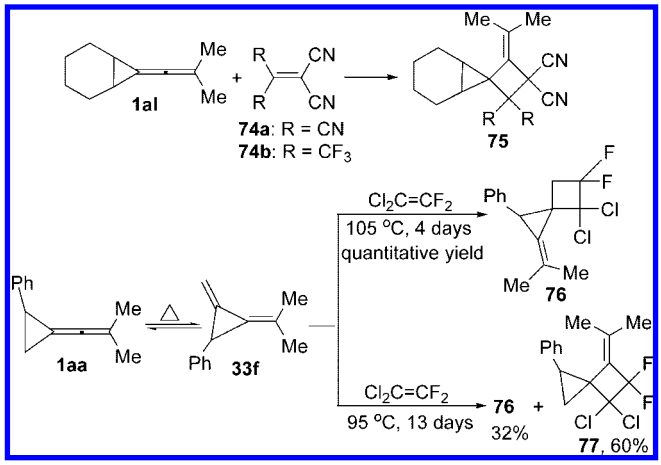
Scheme 33



Scheme 34



Scheme 35



74 and dichlorodifluoroethylene, were also investigated by Gompper et al.[46] and Pasto et al.,[47] and it was believed that the reactions took place via a radical mechanism (Scheme 35).

Based on these results, Sasaki et al. investigated the reactions of VDCPs **1** with electron-deficient acetylenic dienophiles and similar results were reported.[48] For example, the reactions of VDCP **1y** with acetylenes **78** can give the desired [2 + 2] cycloaddition products in acceptable yields (Scheme 36).

4.2.1. Brief Summary of the Photo- or Thermal-Induced Reactions of VDCPs

Generally speaking, the reaction course of photo- or thermal-induced reactions of VDCPs will first proceed via two different patterns: the distal bond and proximal bond cleavage to give biradical intermediates such as **81** and **82** (Scheme 37). Moreover, further oxidation of intermediates **81** and **82** will give radical ions in some cases, for example, intermediate **22** shown in Scheme 14. The further rearrangement or the reaction of these active species can give interesting products.

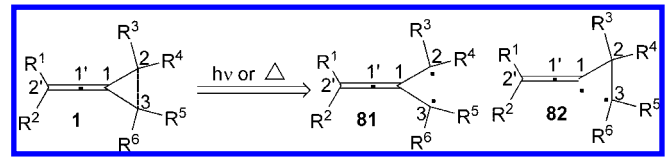
5. Lewis or Brønsted Acid-Mediated Transformations of VDCPs

Leandri et al. reported the first Brønsted acid-catalyzed transformations of VDCPs **1** in 1970, and they found that in wet conditions, 1′,2′-addition of VDCP **1an** can be accomplished by water to give the alcohol **83**, which successively cyclized to the tetrahydrofuran derivative **86** in the presence of Brønsted acid (Scheme 38).[49]

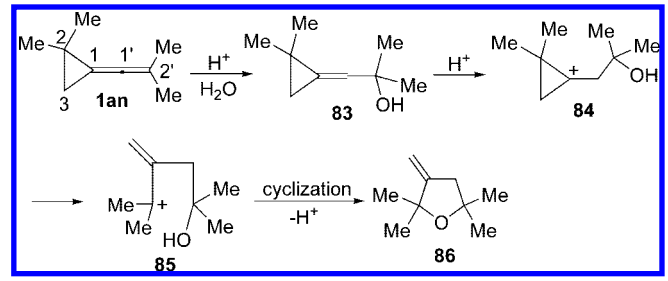
Under anhydrous conditions, Brønsted acid-catalyzed transformations of VDCPs **1** gave compounds **89** as the sole product (Scheme 39).[49]

Fitjer reported isomerization of VDCPs **1** catalyzed by Lewis acid ZnI_2 in 1975.[50] Treatment of VDCPs **1ao** and *trans*-**1ap** with boiling ethereal zinc iodide solution afforded

Scheme 37



Scheme 38

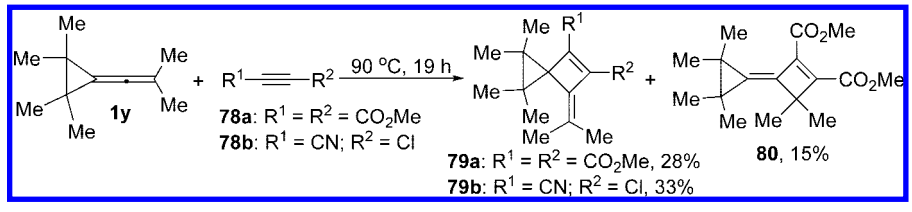


3-isopropylidene-1-methyl-1-cyclobutene **90a** and 3-isopropylidene-1,4-dimethyl-1-cyclobutene **90b** in quantitative yield, respectively, each as the sole reaction product. Isomerization of VDCP *cis*-**1an** gave a mixture of **90b** and 3-ethylidene-5-methyl-1,4-hexadiene **91**. In contrast, VDCPs **1an** and **1z** underwent quantitative isomerization to diisopropylidenecyclopropane **33h** and 1,2-diisopropylidene-3-methylcyclopropane **33e** (Scheme 40).

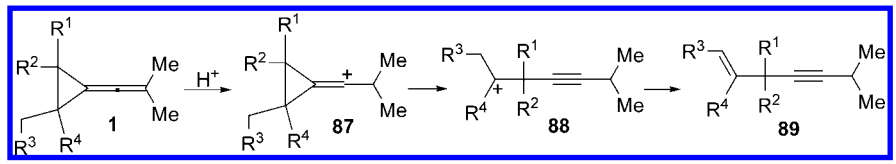
As shown in the case of VDCP **1ao**, the isomerization of VDCPs **1ao** and **1ap** (*trans*- or *cis*-isomer) can only be explained in terms of complex formation via C1 and subsequent [1,2]-alkyl and [1,2]-hydride shifts.[51] In contrast, the isomerization of **1an** and **1z** must proceed by complex formation via C1′, in which cyclopropyl−allyl rearrangement and *trans*-1,3-elimination lead to the formation of products **33k** and **33e**, respectively. Formation of product **91** is presumably attributable to direct opening of the C2−C3 bond of *cis*-**1ap** with subsequent allenylmethyl−butadienyl rearrangement and [1,4]-hydride shift (Scheme 41). Remarkably, it is always the carbon atom displaying the lowest degree of substitution (C3) that undergoes alkyl shift and 1,3-elimination in all the cited isomerizations. This leads to clear-cut reaction courses in all cases.

Pasto et al. reported some transformations of VDCPs **1** mediated by mercury acetate.[52] Acetoxymercuration of VDCP **1aa** followed by reductive demercuration using a great excess of sodium borohydride produced a complex mixture of the monomeric acetates **100** and **101** (60:40 ratio), dimeric diacetates, and bis(acetoxyalkyl)mercury compounds. Disrotatory ring-opening of an intermediate spiromercurinium ion **98** (or possible cyclopropyl cation **99** as a transition state) is expected to occur with outward rotation of the phenyl group, that is, in the least sterically congested manner, to produce an allylic cation, which then reacts with acetate to produce products **100** and **101**. In addition, **101** can be cleanly rearranged to **100** in the presence of strong protic acid (Scheme 42).

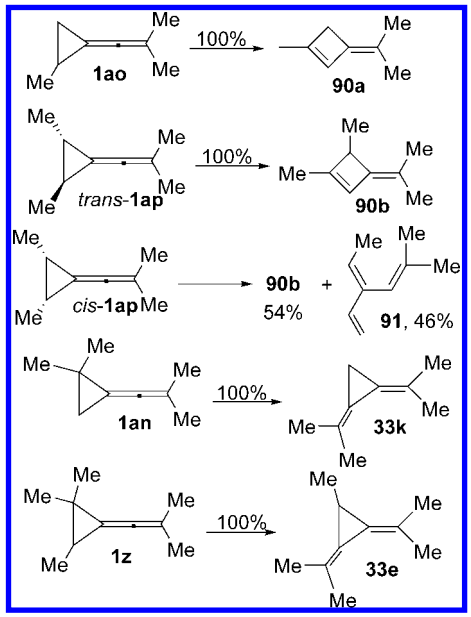
Scheme 36



Scheme 39



Scheme 40

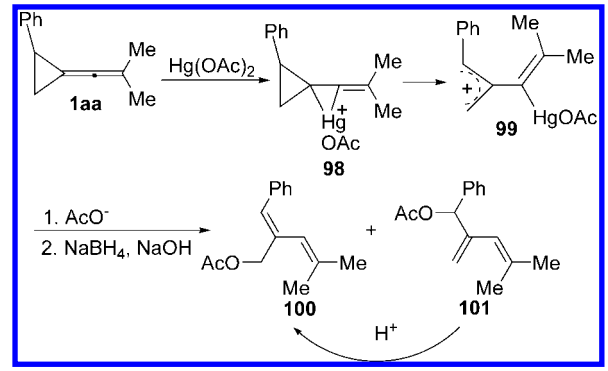


The three diacetates isolated from the acetoxymercuration of **1aa** are proposed to be formed by combination of the free radical formed during the reductive demercuration,[53] and their structures are shown in Figure 4 as **102**, **103**, and **104**. NMR and mass spectroscopic data indicate that the bis(acetoxyalkyl)mercury compounds contain acetoxyalkyl groups corresponding to **102** and **103**, and their partial structures are shown as **105** and **106** (Figure 4).

In addition to the formation of alcohols **107** and **108**, which correspond to the acetates **100** and **101** formed in acetoxymercuration of VDCP **1aa**, hydroxymercuration of **1aa** in 50% aqueous tetrahydrofuran also resulted in the formation of the acetylenic alcohol **109** (small amounts of acetates **100**, **101**, and **110** are also formed) (Scheme 43).

The alcohol **109** and acetate **110** may be formed by initial attack by acetoxymercury cation on one of the ring bonds, either as shown to produce **114** or alternatively on the $-CH_2-C=$ bond to give **115**, both of which would be reduced to **109** and **110** (Scheme 44).[54]

Scheme 42



Acetoxymercuration−demercuration of VDCP **1y** produced a complex mixture from which the five most abundant components were separated by preparative GLC. Identification of the two major components (**116** and **117**) has been achieved from IR, NMR, and MS, while the structures proposed for the minor components (**118**, **119**, and **120**) are based solely on proton Fourier-transform NMR spectra. The fraction containing **120** also contained ~30% of another compound, **121**, whose structure the author could not identify (Scheme 45).[42] The ratio of the products **116/117/118/119/120/121** is approximately 26:100:5:5:15:10.

The formation of **116**, **117**, **118**, and **119** occurs via initial electrophilic attack on the C1−C1′ double bond as illustrated in Scheme 46. The formation of product **120** must occur by attack on the three-membered ring as illustrated for the hydroxymercuration of **1y** (Scheme 46).

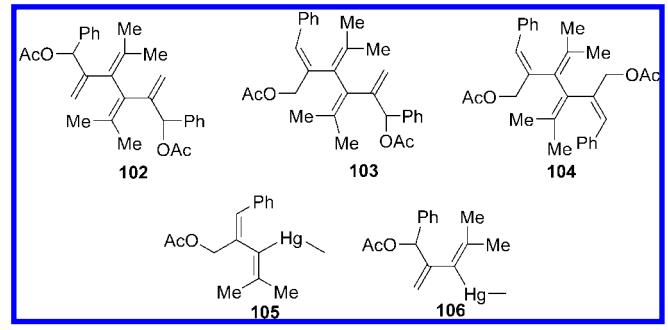
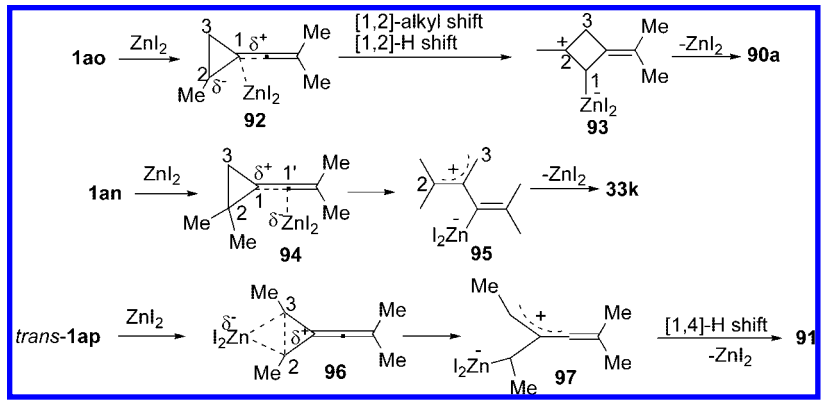
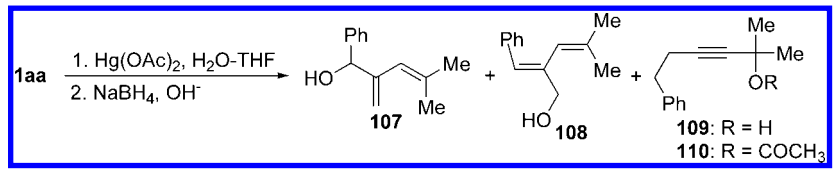


Figure 4.

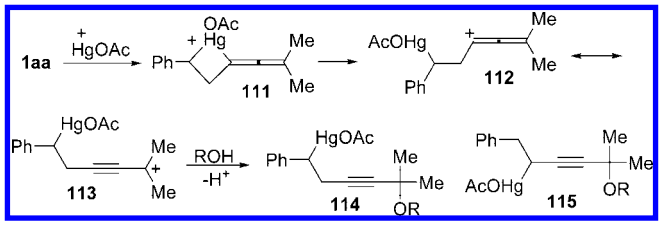
Scheme 41



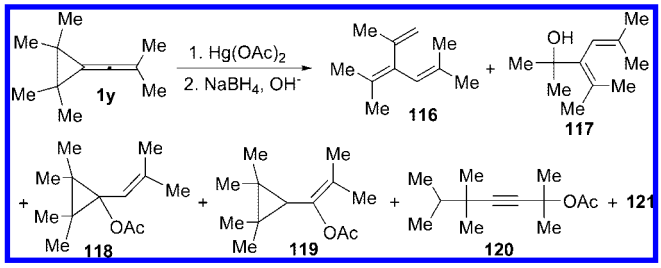
Scheme 43



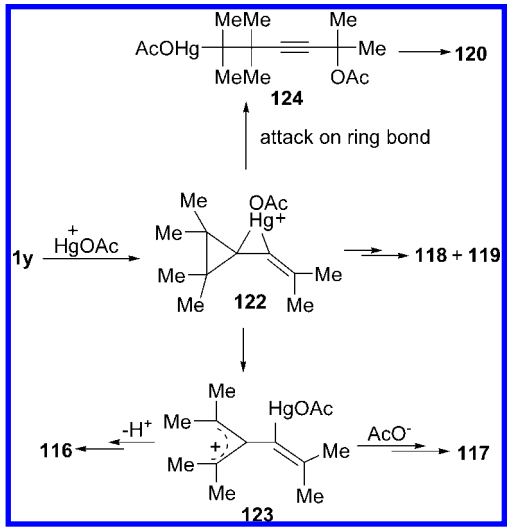
Scheme 44



Scheme 45



Scheme 46



VDCP **1aa** also can react very slowly with acetic acid at 115 °C to produce a 35:65 mixture of **100** and **101**.[52,55] In order to avoid complications arising from thermal rearrangement of **1aa** at temperatures >100 °C, as well as polymerization, catalysis of the acetolysis by *p*-toluenesulfonic (pTS) acid was investigated.[56] In the presence of catalytic amounts of pTS, VDCP **1aa** reacted slowly at 70 °C to produce only product **100**. Heating a sample of pure **101** in acetic acid in the presence of pTS at 105 °C resulted in quantitative rearrangement to **100** (Scheme 47). Thus, product **101** appears to be the kinetically favored product in the acetolysis of VDCP **1aa**, while **100** is the thermodynamically favored one.[36]

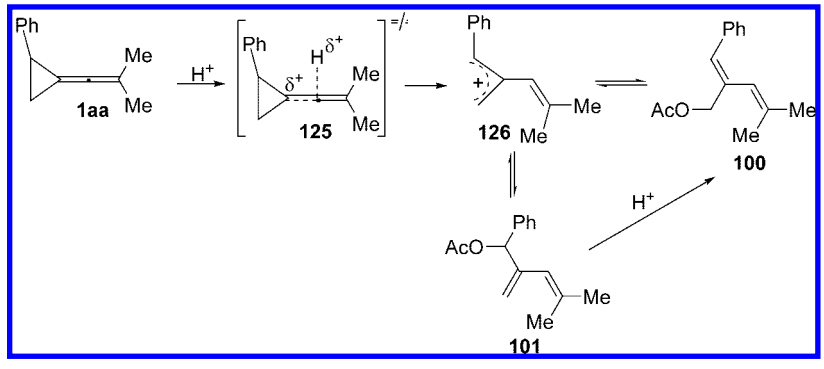
pTS-catalyzed acetolysis of VDCP **1y** produced a 60:40 mixture of **129** and **130**, which can be separated by column chromatography. The formation of **129** and **130** occurred via protonation at C2′ followed by ring opening as illustrated in Scheme 48.

Gompper et al. reported that Brønsted acid HCl- or HBr-mediated reactions of VDCP **1al** led to the formation of the addition products of VDCP **1al** with the Brønsted acid (Scheme 49).[39]

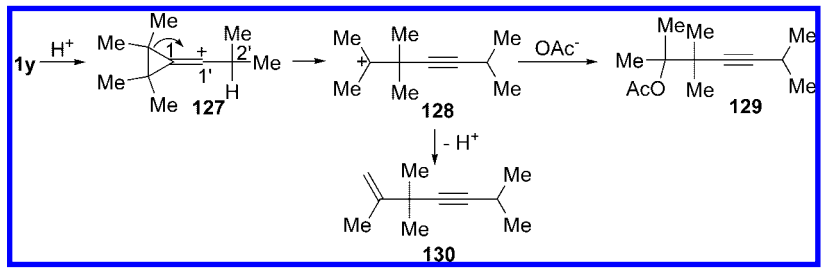
During the last years, Shi and co-workers have reported a series of Lewis acid catalyzed rearrangement reactions of VDCPs **1**. In 2005, Shi et al. first found the Lewis acid catalyzed rearrangement reaction of VDCPs **1**. It was observed that VDCPs **1** could rearrange to naphthalene derivatives **137** in the presence of $Sn(OTf)_2$, in acceptable to high yields under mild conditions (Scheme 50).[57]

Based on this pioneering work, Shi and co-workers investigated thoroughly the Lewis acid catalyzed rearrangement reactions of VDCPs **1** having three substituents on the corresponding cyclopropyl rings.[58] It was found that the reaction products are highly dependent on the substituents on the corresponding cyclopropyl rings and the electronic nature of the aryl groups on VDCPs **1**. For VDCPs **1** bearing two alkyl groups at the C3 position (R^1, R^2, R^3 = aryl; R^4 = H; R^5, R^6 = alkyl), naphthalene derivatives **137** were formed in the presence of Lewis acid $Eu(OTf)_3$ in DCE at 40 °C. For VDCPs **1** in which R^1, R^2, R^3 = aryl and R^4, R^5 = alkyl (*syn*/*anti* isomeric mixture), the corresponding *6a*H-benzo[*c*]-fluorine derivatives **138** were obtained in the *syn*-configuration via a double intramolecular Friedel−Crafts reaction using the substrates without electron-withdrawing substituents on aryl groups or the corresponding indene derivatives **139** were formed via an intramolecular Friedel−Crafts

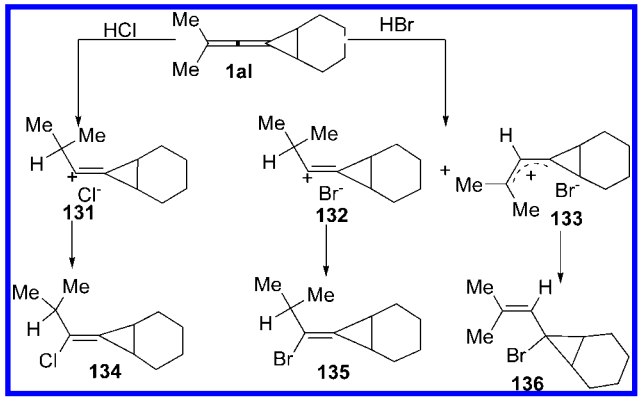
Scheme 47



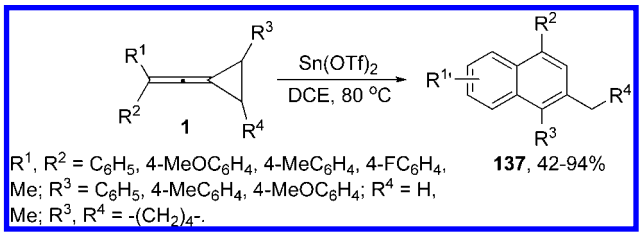
Scheme 48



Scheme 49



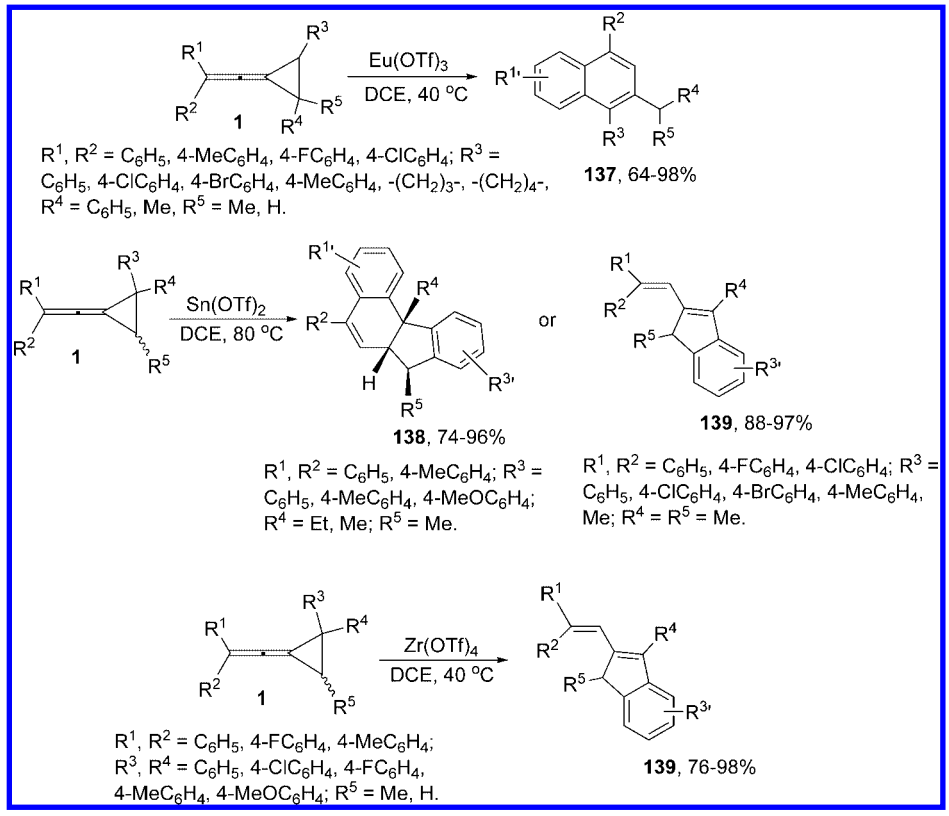
Scheme 50



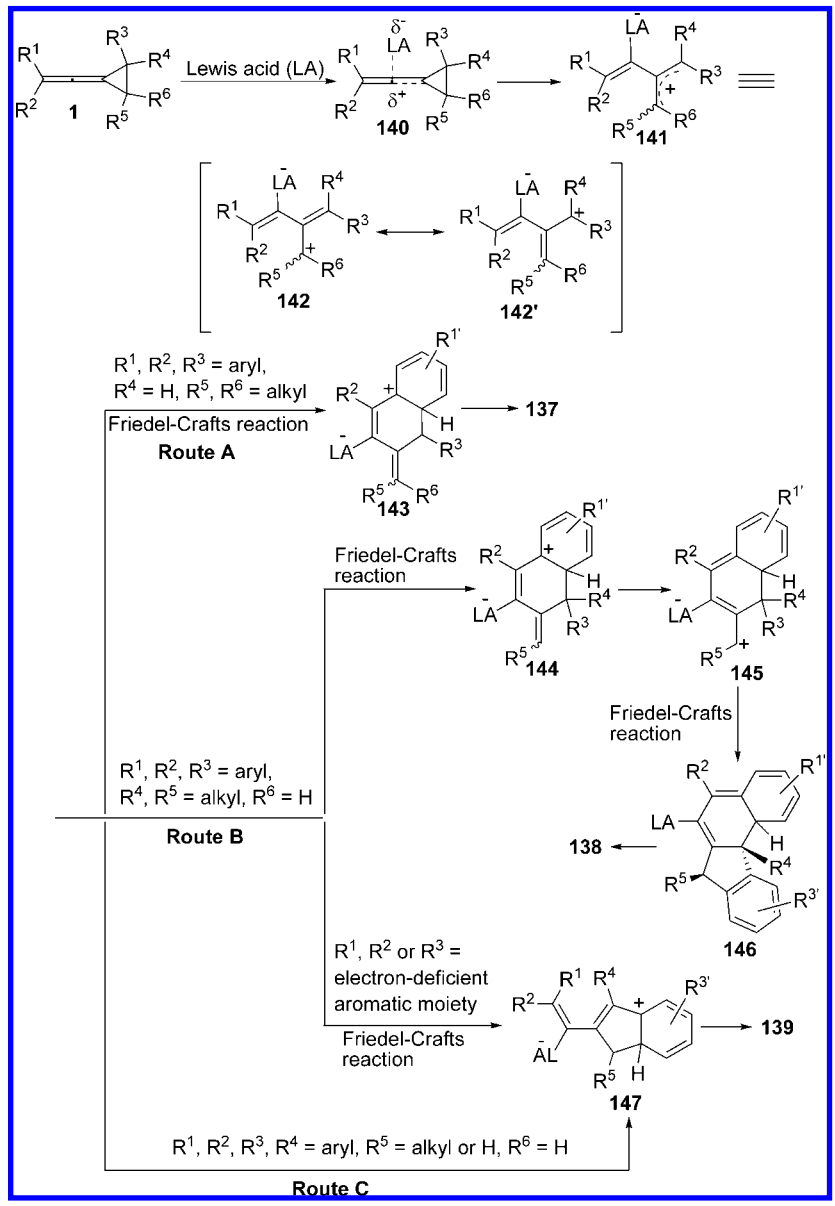
reaction as long as one electron-deficient aryl group was attached. For VDCPs **1** in which R^1, R^2, R^3, R^4 = aryl and R^5 = alkyl or H, the corresponding indene derivatives **139** were obtained exclusively via a sterically demanding intramolecular Friedel−Crafts reaction (Scheme 51).

Plausible mechanisms for the formation of naphthalene, *6a*H-benzo[*c*]fluorine, and indene derivatives are shown in Scheme 52: the coordination of VDCPs **1** to Lewis acid initially gave 1-cyclopropylvinyl cation **140**, a vinyl group stabilized cyclopropyl cation,[59] which results in the formation of cyclopropyl ring-opened cationic intermediate **141** or its resonance-stabilized zwitterionic intermediate **142** and **142′**, which is stabilized by the aromatic R^3 group in most cases. The intramolecular Friedel−Crafts reaction[60] produces the cyclized intermediate **143**, from which the thermodynamically favored naphthalene derivatives **137** are formed via successive 1,3-carbocation rearrangement, 1,4-proton shift along with release of Lewis acid, or deprotonation and 1,3-proton shift (Scheme 52, route A).[61] *6a*H-Benzo[*c*]fluorine derivatives **138** can be obtained via a double Friedel−Crafts reaction as shown in route B in Scheme 52.[58a] The formation of indene derivatives **139** is illustrated in route C in Scheme 52.[58b]

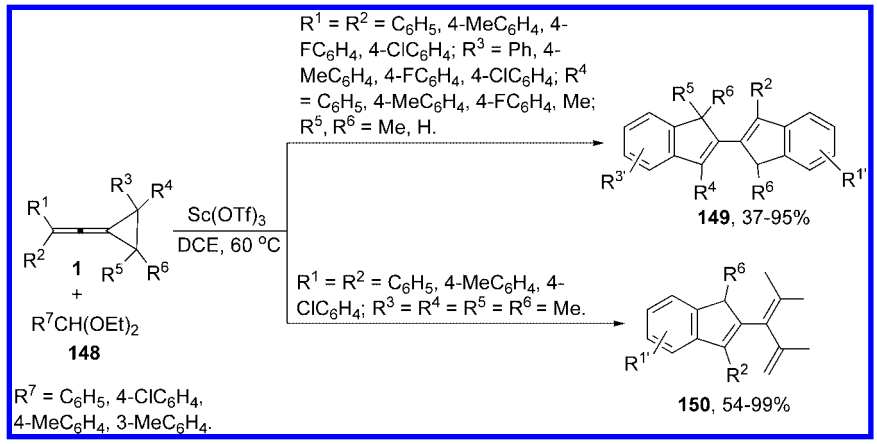
Scheme 51



Scheme 52

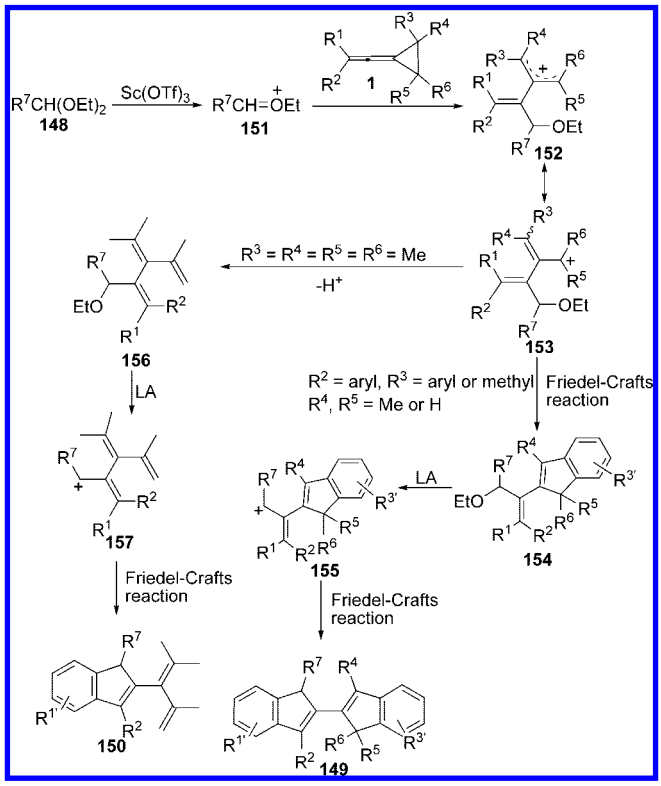


Scheme 53



Meanwhile, a facile synthetic protocol was also established for the preparation of indene derivatives **149** and **150** from Lewis acid $Sc(OTf)_3$ catalyzed reactions of VDCPs **1** with acetals **148**. This reaction is believed to proceed via regioselective addition of oxonium intermediate to VDCPs **1** and the subsequent intramolecular Friedel−Crafts reaction. It was found that the electronic nature of substituents strongly influenced the reaction results, even leading to different products (Scheme 53).[62] Namely, when R^3 and R^4 are aryl groups and R^5 and R^6 = Me or H, indene derivatives **149**

Scheme 54



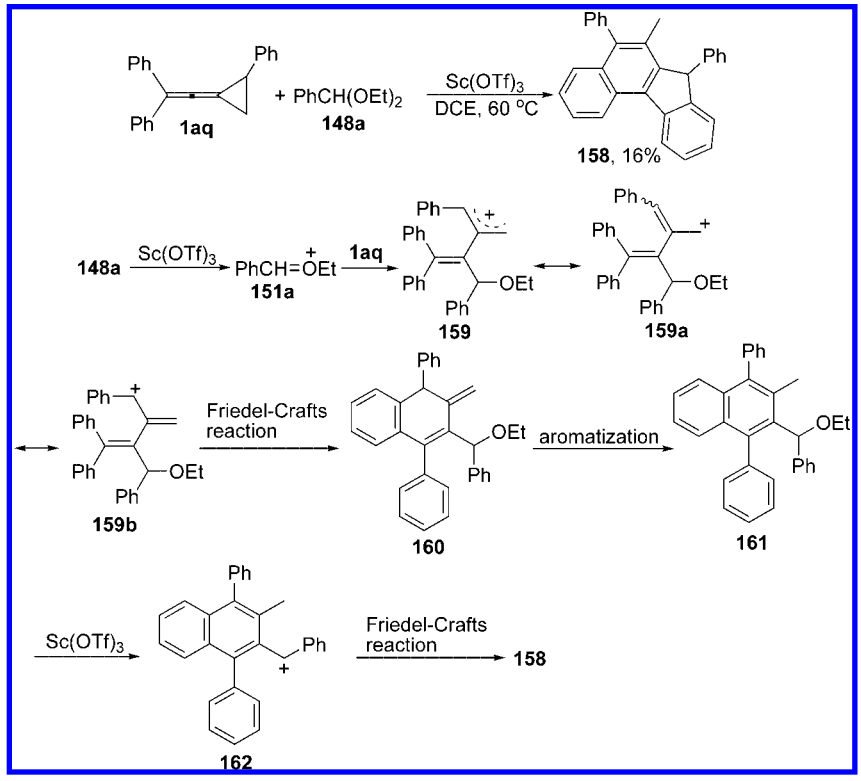
can be formed singly; while when $R^3 = R^4 = R^5 = R^6 =$ Me, indene derivatives **150** were obtained exclusively.

A plausible mechanism for the formation of indene derivatives **149** and **150** is outlined in Scheme 54. Initially, the acetals **148** react with Lewis acid $Sc(OTf)_3$ (LA) to generate oxonium intermediate **151**.[63] The reaction of intermediate **151** with VDCPs **1** produces the cyclopropyl ring-opened π-allylic cationic intermediate **152** or the resonance-stabilized cationic intermediate **153**, which undergoes intramolecular Friedel−Crafts reaction to give intermediate **154** when R^2 is aryl group, R^3 is aryl or methyl group, R^4 and R^5 are methyl group or hydrogen atom. When R^2, R^3, R^4, and R^5 are methyl groups, deprotonation of intermediate **153** takes place to afford the corresponding intermediate **156**. In the presence of $Sc(OTf)_3$ (LA), intermediate **154** or **156** releases one ethoxy anion to give the corresponding cationic intermediate **155** or **157**.[64] The subsequent intramolecular Friedel−Crafts reaction of **155** and **157** produces the indene derivatives **149** and **150**, respectively (Scheme 54).

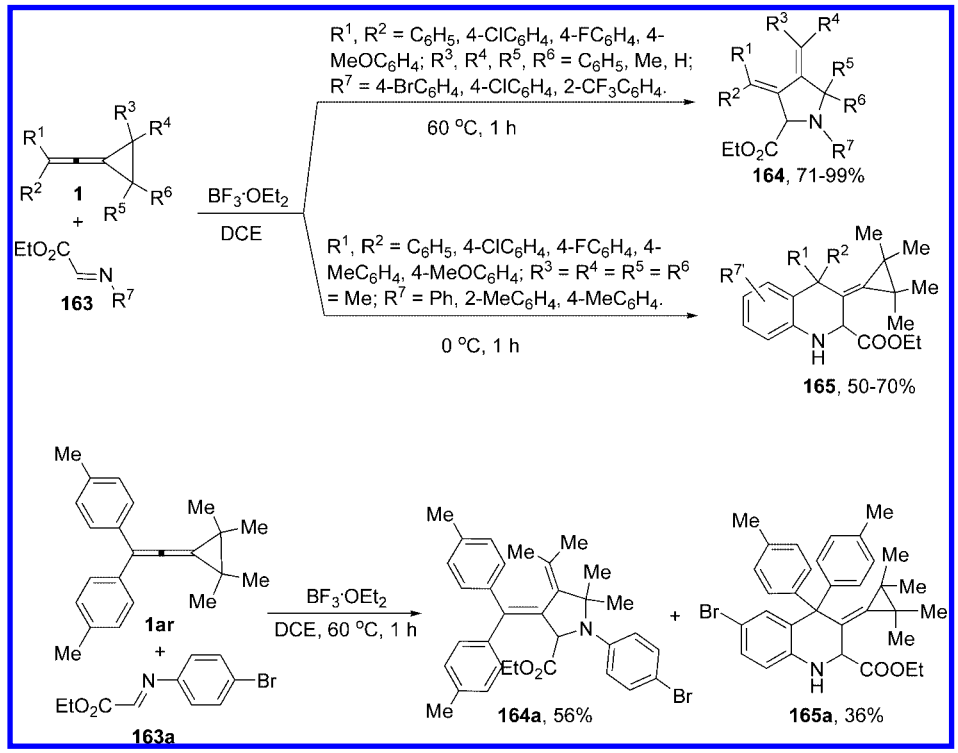
Interestingly, the substrate VDCP **1aq**, with only one phenyl group at the cyclopropyl ring, demonstrated a special reactivity under identical reaction conditions. A new product 6-methyl-5,7-diphenyl-7*H*-benzo[*c*]fluorine **158** along with another unidentified byproduct was obtained although the yield (16%) was rather low (Scheme 55). In order to rationalize this observation, a new mechanism is proposed in Scheme 55. Similar to the previous example, the cyclopropyl ring-opened π-allylic cationic intermediate **159** is formed from the reaction of the corresponding cationic intermediate **151a** with **1aq**. Because the corresponding resonance-stabilized cationic intermediate **159a** is less stable than cationic intermediate **152** shown in Scheme 54, the resonance-stabilized cationic intermediate **159b** should be the major intermediate, which undergoes intramolecular Friedel−Crafts reaction to give intermediate **160**. Aromatization of **160** produces the thermodynamically favored naphthalene intermediate **161**, which, also similar to the previous example, produces intermediate **162** in the presence of $Sc(OTf)_3$. Then, the final product **158** was formed similarly via intramolecular Friedel−Crafts reaction (Scheme 55).

Later on, the scope of Lewis acid catalyzed reaction of VDCPs **1** was extended with respect to a series of ethyl

Scheme 55



Scheme 56

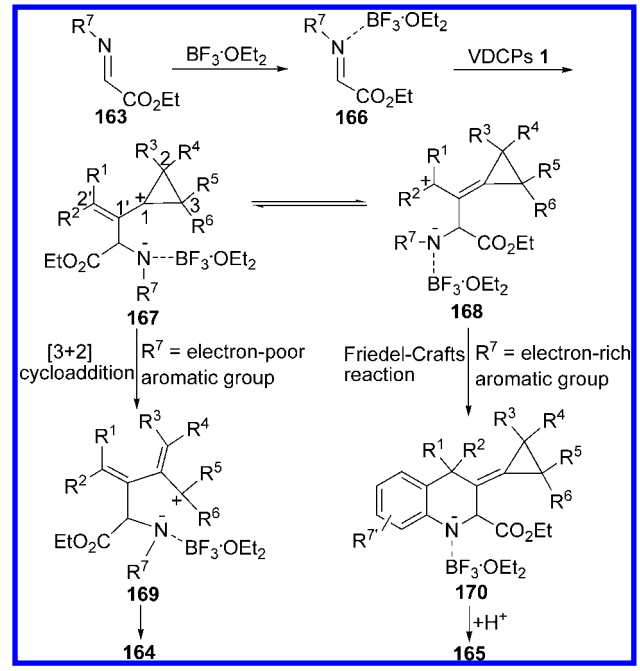


(arylimino)acetates **163**, which led to a facile synthesis protocol of pyrrolidine and 1,2,3,4-tetrahydroquinoline derivatives. A number of pyrrolidines **164** and 1,2,3,4-tetrahydroquinoline derivatives **165** can be obtained selectively in moderate to good yields by the reaction of VDCPs **1** with ethyl (arylimino)acetates **163** in the presence of Lewis acid $BF_3 \cdot OEt_2$ depending on the electronic nature of both **163** and R^1 or R^2 aromatic groups of **1** (Scheme 56).[65−67] Generally, when the R^7 group on **163** is an electron-poor aromatic group, the pyrrolidines **164** will be formed solely; while when R^7 is an electron-rich aromatic group, the 1,2,3,4-tetrahydroquinolines **165** will be obtained as the sole products. Meanwhile, if R^1 and R^2 are both electron-rich aromatic groups ($R^1 = R^2 = 4\text{-}MeC_6H_4$ as the example in this case), both of the products **164a** and **165a** can be obtained despite R^7 being an electron-poor or -rich group (Scheme 56).

Plausible mechanisms for the formation of pyrrolidines **164** and 1,2,3,4-tetrahydroquinolines **165** are outlined in Scheme 57. First, ethyl (arylimino)acetate **163** is activated by $BF_3 \cdot OEt_2$ to afford intermediate **166**, which subsequently adds to C1′ of VDCPs **1** to give the corresponding allylic carbocationic intermediates **167** and **168**.[68] Intermediate **169**, derived from **167** via a cyclopropyl ring-opening process, undergoes cyclization to give the corresponding [3 + 2] cycloaddition product **164** when R^7 is an electron-poor aromatic group. Alternatively, if R^7 is an electron-rich aromatic group, intramolecular Friedel−Crafts reaction takes place from intermediate **168** to give intermediate **170**,[69] which finally furnishes product **165** (Scheme 57).[70]

Based on the results of VDCPs **1** with acetals **148** and ethyl (arylimino)acetates **163**, the reactions of VDCPs **1** with activated carbonyl compounds **171** were also investigated, and it was found that a number of functionalized tetrahydrofurans **172** and 3,6-dihydropyrans **173** can be formed in moderate to good yields selectively in the presence of Lewis acid (Scheme 58).[71] In these reactions, tetrahydrofurans **172**

Scheme 57

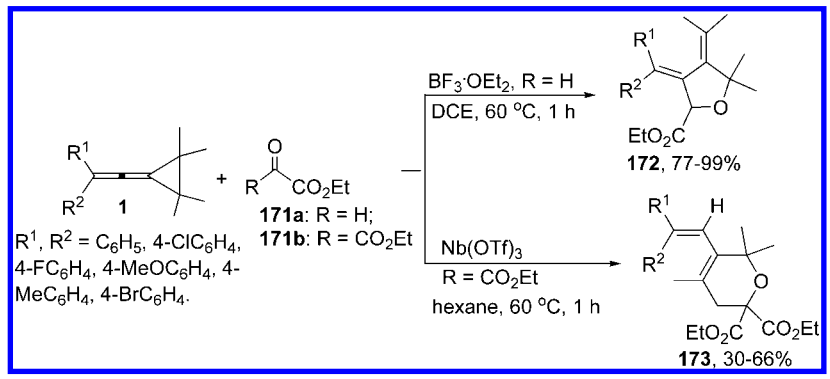


were obtained in 77−99% yields in the reactions of VDCPs **1** with oxo-acetic acid ethyl ester **171a**; however, 3,6-dihydropyrans **173** were formed in 30−66% yields in the reactions of VDCPs **1** with 2-oxo-malonic acid diethyl ester **171b**.

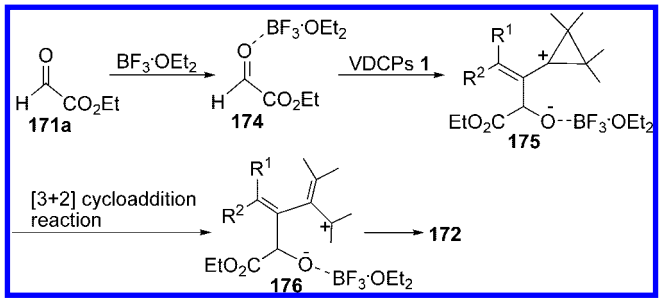
The formation of tetrahydrofuran derivatives **172** is suggested as follows: intermediate **174**, generated from **171a** (R = H) and $BF_3 \cdot OEt_2$, reacts with VDCPs **1** to produce intermediate **175**, which undergoes a ring-opening process to afford intermediate **176**. Cyclization of intermediate **176** furnishes [3 + 2] cycloadducts **172** (Scheme 59).

The formation of 3,6-dihydropyran derivatives **173** is illustrated in the Scheme 60. The coordination of VDCPs **1**

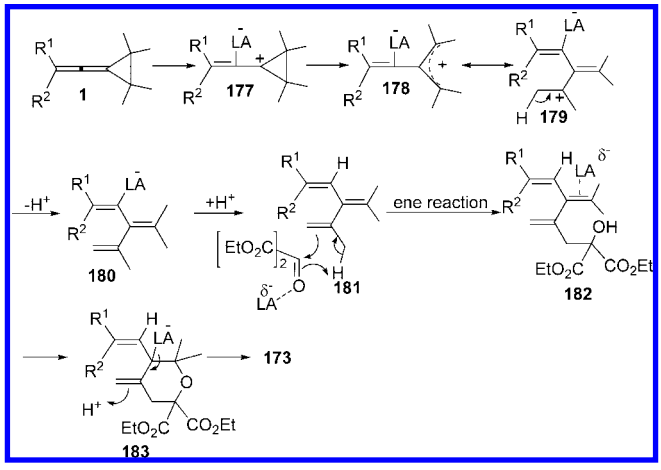
Scheme 58



Scheme 59



Scheme 60

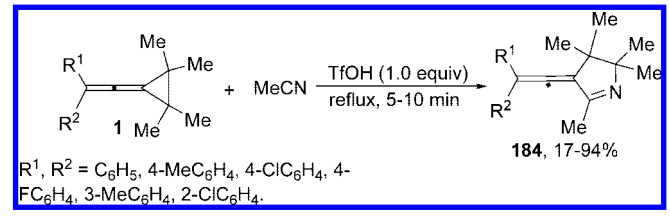


to the Lewis acid initially gives the vinyl group stabilized cyclopropyl cationic intermediate **177**, which results in the formation of cyclopropane ring-opened zwitterionic intermediate **178** or the resonance-stabilized zwitterionic intermediate **179**. Deprotonation of intermediate **179** and reprotonation of intermediate **180** give triene **181**. The carbonyl−ene reaction[72] of triene **181** with diethyl ketomalonate **171b** (R = CO_2Et), which is activated by Lewis acid, generates homoallylic alcohol **182**. The subsequent ring closure of homoallylic alcohol **182** and protonation of intermediate **183** produce the product **173** (Scheme 60).

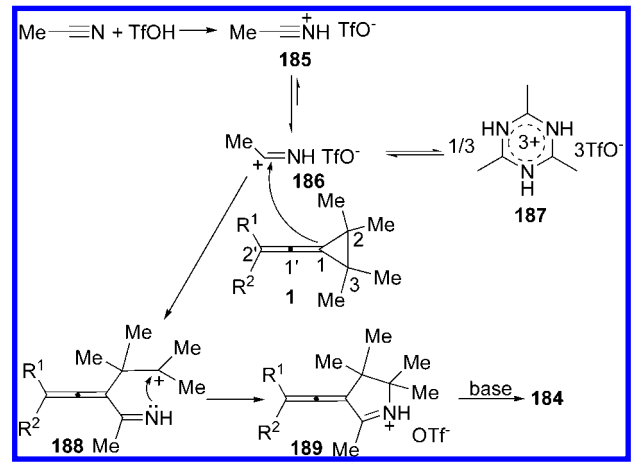
The Brønsted acid TfOH catalyzed reactions of VDCPs **1** with MeCN were also carried out in Shi's group, and it was reported that the [3 + 2] cycloaddition products, the 3,4-dihydro-2*H*-pyrrole derivatives **184**, can be obtained in moderate to excellent yields under reflux within a short time (Scheme 61).[73,74] In these reactions, all substituents on the cyclopropyl ring of VDCPs **1** should be methyl groups.

A plausible mechanism for this transformation is outlined in Scheme 62. First, there is an equilibrium among inter-

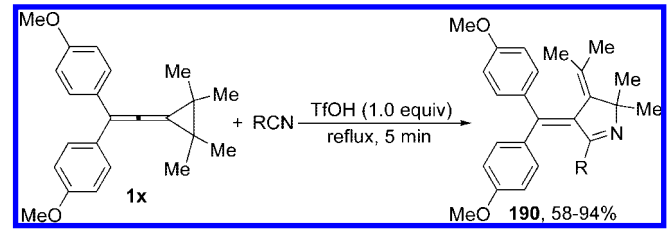
Scheme 61



Scheme 62



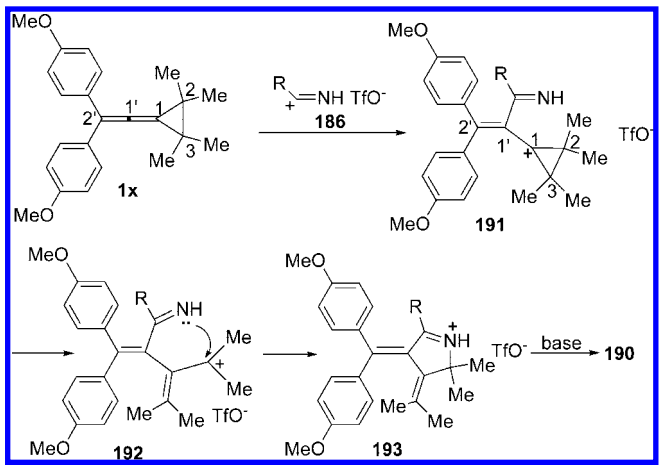
Scheme 63



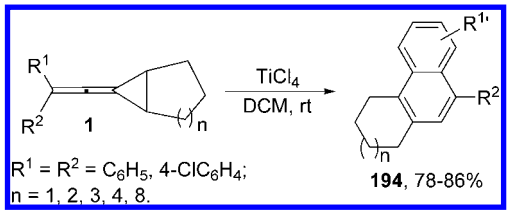
mediates **185**, **186**, and **187** in the reaction of acetonitrile with TfOH according to the previous literature.[75] Intermediate **186** undergoes an electrophilic attack to the C1 position of VDCPs **1** to afford the corresponding ring-opened cationic intermediate **188**, which undergoes the subsequent intramolecular cyclization reaction to give cationic intermediate **189**. Treatment of **189** with a base furnishes products **184** (Scheme 62).

For strongly electron-donating 4-methoxyphenyl group substituted VDCP **1x** ($R^1 = R^2 = 4\text{-}MeOC_6H_4$, $R^3 = R^4 = R^5 = R^6 = Me$), 3,4-dihydro-2*H*-pyrrole derivatives **190** were formed in good yields under the same reaction conditions (Scheme 63).

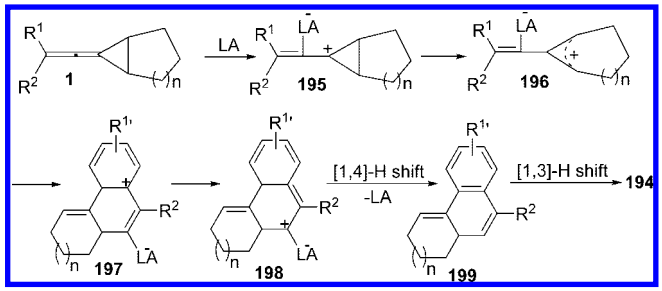
Scheme 64



Scheme 65



Scheme 66



Scheme 64 shows the plausible mechanism for this [3 + 2] cycloaddition reaction of VDCP **1x** with nitriles mediated by TfOH. Electrophilic attack of intermediate **186** to the C1′ of VDCP **1x** gives intermediate **191**, which immediately undergoes a ring-opening process to afford intermediate **192**. Intramolecular cyclization takes place to give intermediate **193**, which furnishes product **190** by treatment with a base (Scheme 64). Maybe the strongly electron-donating 4-methoxyphenyl group on VDCP **1x** increases the electron density at C1′, facilitating the electrophilic attack of cationic intermediate **186**. Therefore, the reaction takes place in a different pathway.

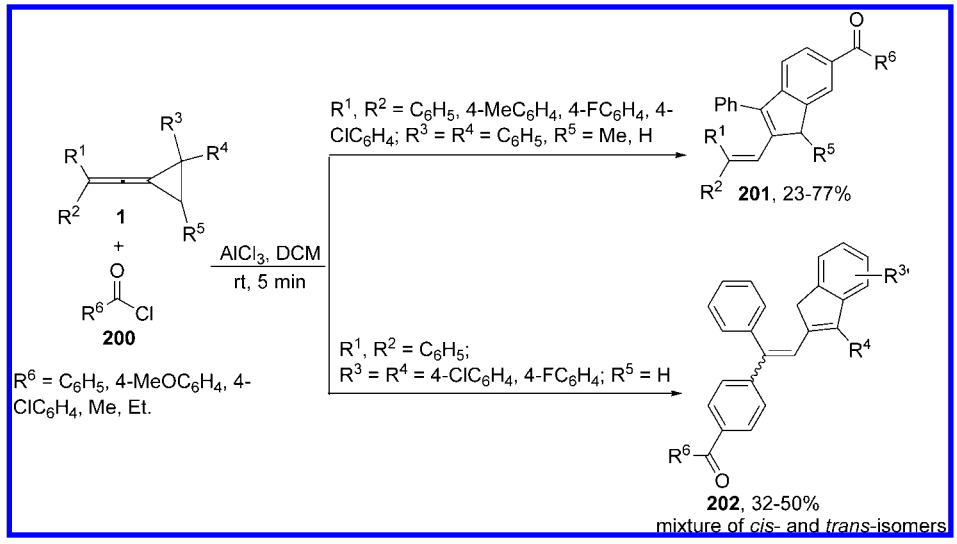
In the early 2008, Huang et al. reported a Lewis acid $TiCl_4$ mediated ring-expansion reaction of bicyclic VDCPs **1** for the formation of medium- and large-size naphthalenacarbocycle derivatives **194** (Scheme 65).[76]

A plausible mechanism for this ring-expansion reaction is shown in Scheme 66. Coordination of VDCPs **1** to Lewis acid gives intermediate **195**, which produces the ring-expansion intermediate **196**. The intramolecular Friedel−Crafts reaction of **196** gives the cyclized intermediate **197**, which is smoothly transformed to intermediate **198** through further rearrangement. The Lewis acid catalyst is released via a 1,4-proton shift to give the corresponding intermediate **199**, while further 1,3-proton shift finally affords products **194** (Scheme 66).

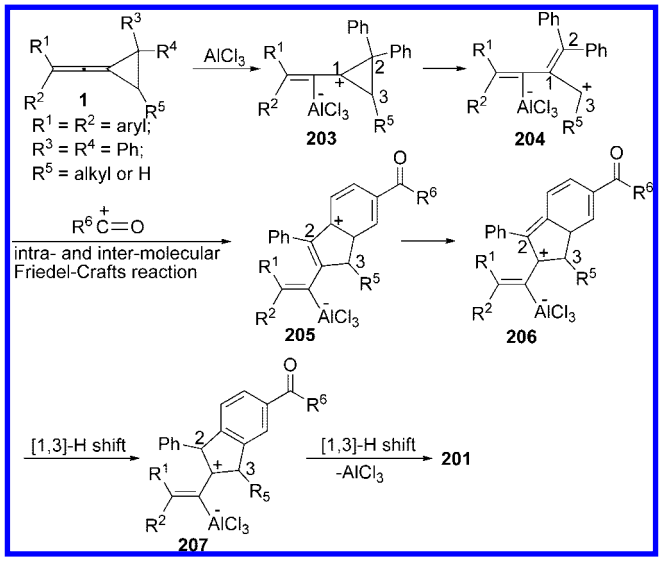
In the Lewis acid mediated chemistry of VDCPs **1**, it was also reported that $AlCl_3$-mediated tandem Friedel−Crafts reaction of VDCPs **1** with acyl chlorides **200** afforded the corresponding products **201** or **202** in moderate to good yields under mild conditions within short reaction time (Scheme 67).[77,78] The control experiment showed that products **201** and **202** can be derived from the corresponding rearrangement products of VDCPs **1**.[57,58]

A plausible mechanism for these transformations is outlined in Scheme 68 with the formation of products **201** as the example. The coordination of VDCPs **1** with $AlCl_3$ produces the initial zwitterionic intermediate **203**, from which the corresponding cyclopropyl ring-opened zwitterionic intermediate **204** is formed. Intramolecular Friedel−Crafts reaction with the aromatic group at the C2 position and the intermolecular Friedel−Crafts reaction with the *in situ* generated acyl cation in the presence of $AlCl_3$ take place at the same time to produce zwitterionic intermediate **205**, which affords the corresponding zwitterionic intermediate **206** via allylic rearrangement. Subsequently two 1,3-proton shifts along with the release of Lewis acid via zwitterionic intermediate **207** afford the corresponding indene derivatives **201** (Scheme 68).

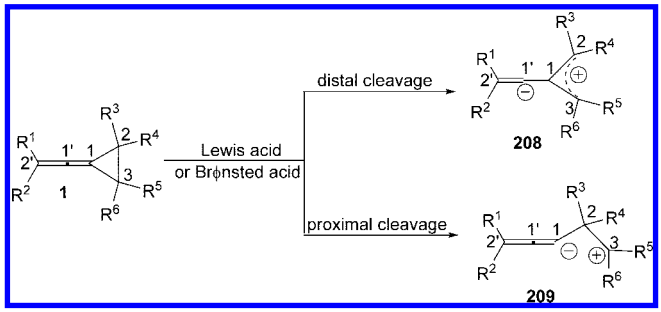
Scheme 67



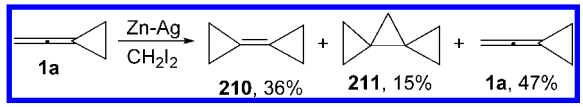
Scheme 68



Scheme 69



Scheme 70



5.1. Brief Summary for the Lewis or Brønsted Acid-Mediated Reactions of VDCPs

The reaction course of VDCPs promoted by Lewis or Brønsted acid can be categorized into the following two patterns: the distal bond and proximal bond cleavage. As can be seen from Scheme 69, zwitterionic ions **208** and **209** were formed with these two bond cleavages, respectively. To obtain stable zwitterionic ions as **208** and **209**, the substituents as R^3, R^4, R^5, and R^6 on the cyclopropyl ring cannot be hydrogen atom at the same time in this case.

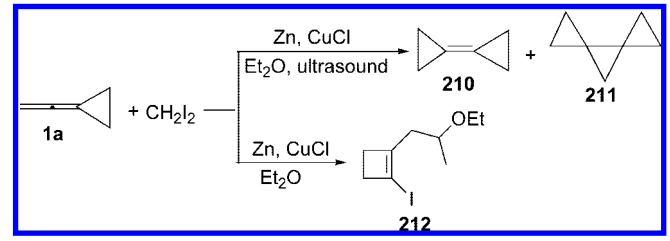
6. Transition Metal-Catalyzed Transformations of VDCPs

Compared with the photoinduced or Lewis acid or Brønsted acid mediated reactions, much less attention was paid to the transition metal-catalyzed transformations of VDCPs **1**.

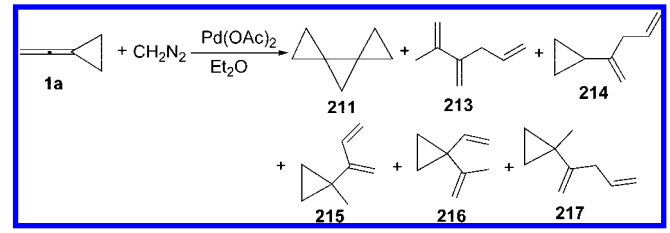
The Simmons−Smith reaction[79] provides a convenient synthesis of cyclopropane derivatives. In 1972, Conia et al. reported a zinc−silver couple-mediated Simmons−Smith reaction of VDCP **1a** to give the cyclopropanated products **210** and **211** in moderate total yields (Scheme 70).[80]

In 1987, Zefirov et al. reported a Simmons−Smith cyclopropanation of VDCP **1a** with ultrasonic technology, and it was found that both of the Simmons−Smith cyclopropanation adducts **210** and **211** and the rearrangement adduct **212** can be obtained with varying reaction conditions (Scheme 71).[81]

Scheme 71



Scheme 72



The same year, Zefirov et al. also found a $Pd(OAc)_2$-catalyzed polymethylenation of VDCP **1a** by diazomethane (Scheme 72).[82]

$RhCl(PPh_3)_3$-catalyzed reactions of VDCPs **1** with butenoic acid or its alkaline salts proceeded smoothly in ethanol at 70−75 °C to give products **218** in acceptable to good yields with products **219**, which consist of bibasic acids, as the byproduct in less than 10% yield (Scheme 73).[83]

A possible method for the formation of products **218** and **219** is illustrated in Scheme 74. First, coordination of RhCl with VDCPs **1** and butenoic acid alkaline salt takes place via two different pathways to give intermediates **220** and **223**, respectively. Subsequent cyclometalation from these two intermediates gives intermediates **221** and **224**. β-carbon scission of intermediate **221** results in another metallocyclic intermediate **222**, which affords products **218** via β-hydride elimination and release of RhCl (path A in Scheme 74). In another method, η^1-intermediate **224** is transformed to η^3-intermediate **225**, which results in intermediate **226** via β-hydride elimination and successive hydrometalation with another molecular butenoic acid alkaline salt. Finally, products **219** are obtained from **226** via intramolecular carbometalation and release of RhCl (path B in Scheme 74).

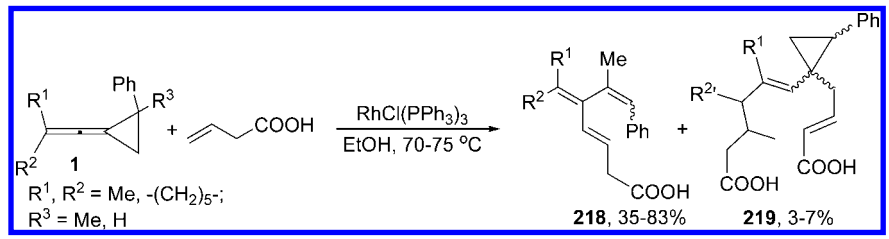
In 1994, Hwu et al. reported a novel coupling reaction of Fischer chromiumcarbene complexes **227** with VDCPs **1**, leading to allylidenecyclopropanes **228**. This reaction is the first example of a double-bond migration of allenes involving the chromiumcarbene carbon center (Scheme 75).[84]

This reaction is believed to proceed via initial [2 + 2] cycloaddition to give chromacyclobutane **229**, followed by β-hydride elimination into intermediate **230**. Subsequent reductive elimination affords the final products **228** (Scheme 76).

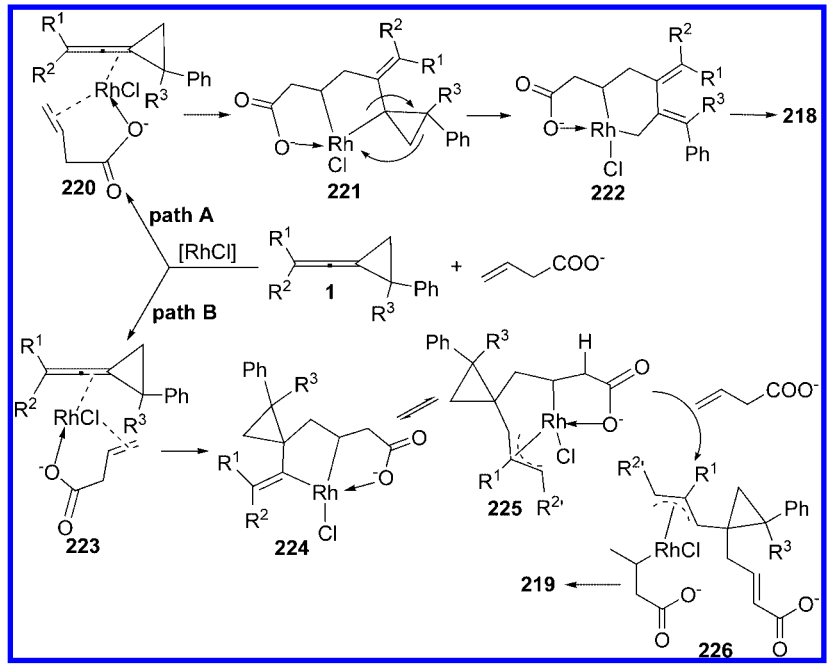
In 2006, Shi's group first reported the palladium(0)-catalyzed reactions of VDCPs **1**. They disclosed that the palladium(0)-catalyzed reactions of VDCPs **1** with acetic acid can proceed efficiently to give the corresponding cyclopropane ring-opened acetylated dienes **231** in moderate to good yields in the presence of DPEphos ligand under mild reaction conditions (Scheme 77).[85]

A plausible mechanism for the formation of products **231** is outlined based on the previous investigations and deute-

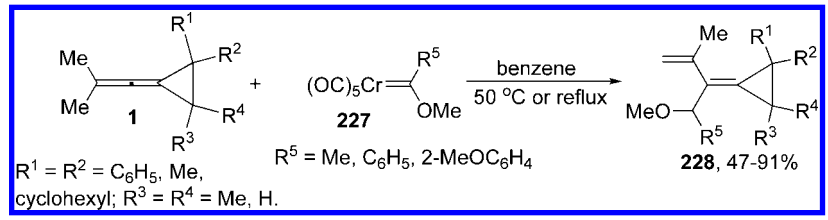
Scheme 73



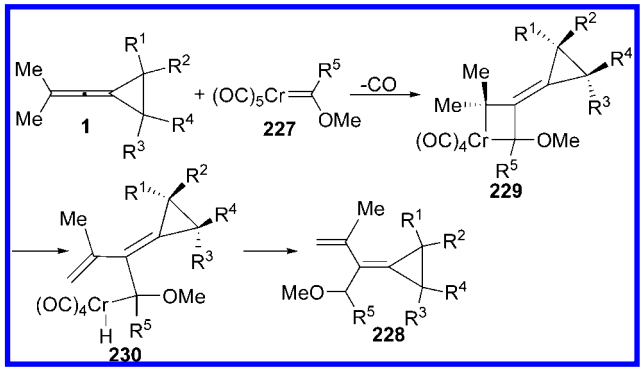
Scheme 74



Scheme 75

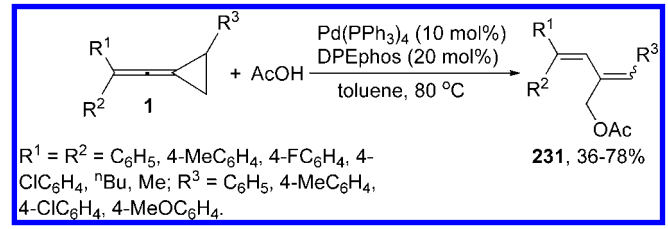


Scheme 76



rium labeling experiment:[86,87] the initial step is a regioselective hydropalladation of VDCPs **1** with hydridopalladium species **232**, generated from oxidative addition of Pd(0) with acetic acid, to afford intermediate **233**. Intermediate **233** undergoes β-carbon elimination to give two π-allyl-palladium intermediates **234** and **235**. Intermediate **234** should be the major conformer because of the steric repulsion between the

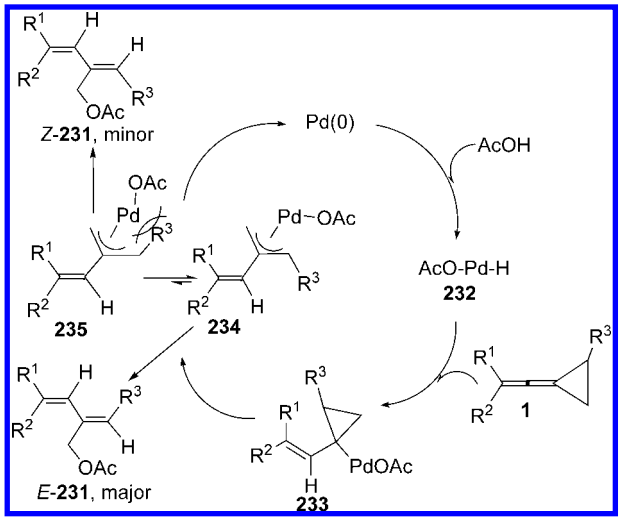
Scheme 77



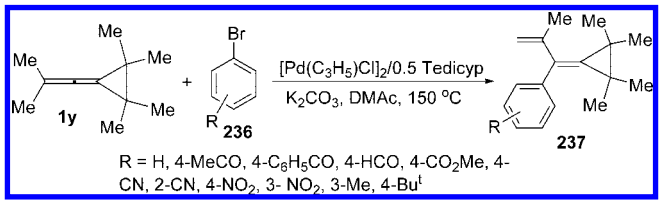
R^3 group and palladium metal center in intermediate **235**. Reductive elimination of intermediates **234** and **235** gives the corresponding product **231** as mixtures of *E*- and *Z*-isomers, with *E*-**231** derived from intermediate **234** as the major one, along with the regeneration of Pd(0) catalyst (Scheme 78).

Subsequently, Santelli et al. reported a Heck reaction[88] of VDCP **1y** with various bromobenzenes **236** to give 1-aryl-2-methyl-1-(2,2,3,3-tetramethylcyclopropylidene)propenes **237** using *cis*,*cis*,*cis*-1,2,3,4-tetrakis(diphenylphosphinomethyl)cyclopentane (Tedicyp) as the ligand (Scheme 79).[89] This reaction can tolerate both electron-poor and electron-

Scheme 78



Scheme 79



rich aryl bromides and achieve the construction of highly complex structures.

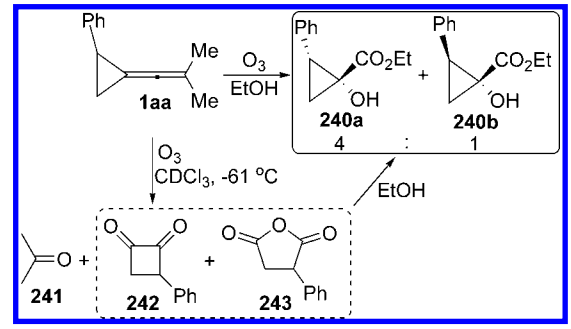
Scheme 80 summarizes the mechanism of the Heck reaction involving VDCP **1y** and aryl bromides. First, oxidative addition of aryl bromides to palladium gives intermediate **238**. Insertion of intermediate **238** to the C1′−C2′ double bond of **1y** leads to intermediate **239**, which liberates products **237** and HPdBr after β-hydride elimination. A reductive elimination assisted by a base regenerates Pd(0) to furnish the catalytic cycle (Scheme 80).

7. Oxidation and Reduction Reactions of VDCPs

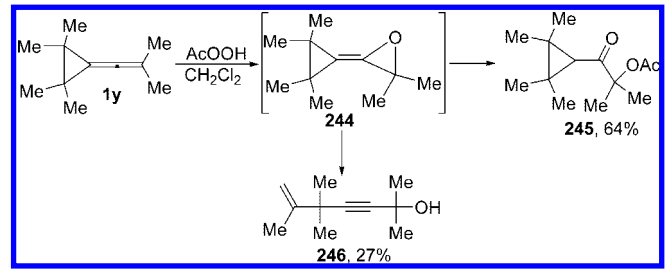
7.1. Oxidation Reactions of VDCPs

In 1961, Hartzler et al. reported the ozonolysis reaction of VDCP **1aa** in ethanol, in which cyclopropyl hydroxylester **240** was formed in good yield (Scheme 81).[12k] Crandall et al. examined this transformation in detail, and it was reported that the addition of VDCP **1aa** to a saturated solution of ozone (1.0 equiv) in $CDCl_3$ at −61 °C gave acetone **241**, 3-phenylcyclobutane-1,2-dione **242**, and phenylsuccinic anhydride **243**. Treatment of the latter two compounds with excess ethanol can give the esters, which clearly indicates that these two compounds are precursors to the esters (Scheme 81).[90]

Scheme 81



Scheme 82

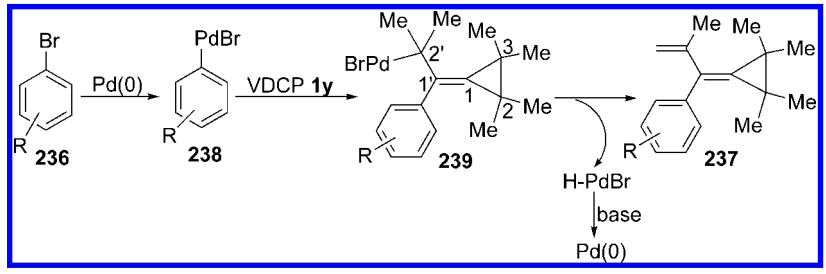


The peracid oxidation reaction of VDCP **1y** was first reported by Crandall et al. in 1968.[56] Treatment of VDCP **1y** with 1 equiv of peracetic acid in cold dichloromethane solution containing suspended sodium carbonate afforded two major products **245** and **246**, with a third unidentified minor component. The reaction is postulated to proceed via the allene oxide intermediate **244** derived from selective attack of peracid at the C1′−C2′ double bond of VDCP **1y**. The addition of acetic acid to **244** yields **245** via its enol. Alternatively, protonated **244** can fragment with cleavage of both epoxide and cyclopropyl ring to establish the acetylenic function in the open-chain, cationic precursor to product **246** (Scheme 82).

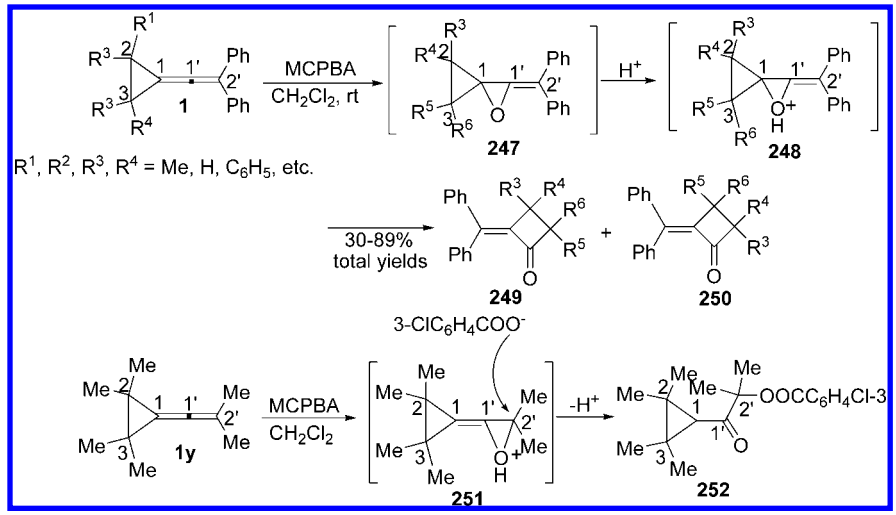
In 1992, Mizuno et al. reported the regioselective MCPBA oxidation reactions of VDCPs **1**, and the results indicate that the regioselectivity in the epoxidation reactions strongly depends on the substituents on C2′ of VDCPs **1**. When R^1 and R^2 are both aryl groups, 2-methylene-cyclobutan-1-ones **249** and **250** are formed singly, while when R^1 and R^2 are both alkyl groups, cyclopropyl keto ester derivatives **252** are obtained exclusively (Scheme 83).[91,92] Proposed mechanisms for these transformations are also illustrated in Scheme 83. Differences between these two oxidation reactions may be ascribed to the steric and electronic effects of the phenyl groups in C2′ of VDCPs **1**: it is worth noting that phenyl groups at the C2′ position cannot be coplanar with the C1′−C2′ plane for steric reasons.

Oxygenation of VDCPs **1** with dimethyldioxirane in CH_2Cl_2 in the presence of 18-crown-6 gave methylenecyclopropanes **253**. Further oxygenation of **253** with dimeth-

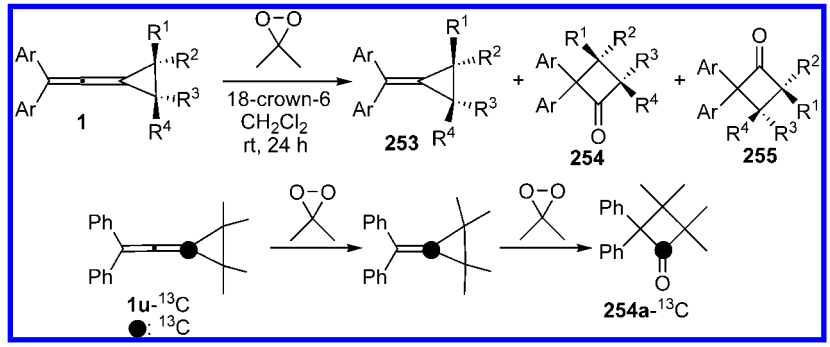
Scheme 80



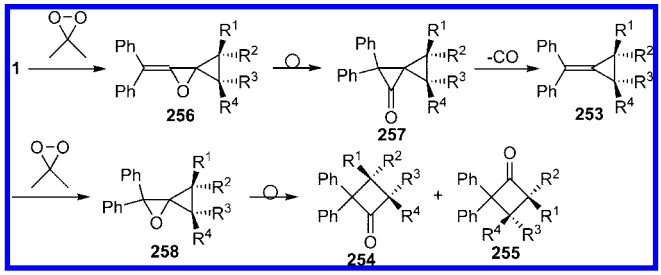
Scheme 83



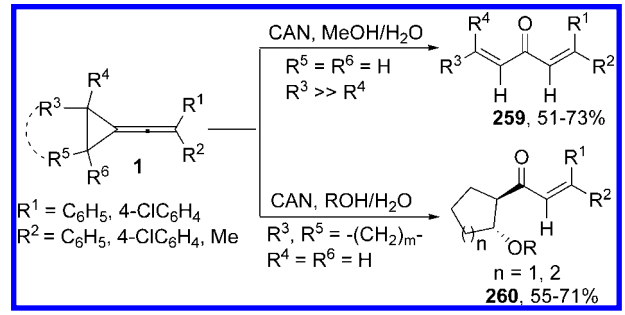
Scheme 84



Scheme 85



Scheme 86



yldioxirane gave cyclobutanones **254** and **255** (Scheme 84). Based on the results of a ^{13}C isotope experiment (Scheme 84), the mechanism is proposed as shown in Scheme 85.

In 2008, Huang et al. reported cerium(IV) ammonium nitrate (CAN)-mediated oxidative rearrangement reactions of VDCPs **1**, which resulted in unsymmetrical divinyl ketones **259** and functional enone derivatives **260** in moderate to good yields with excellent regio- and stereoselectivities (Scheme 86).[93]

A plausible mechanism for these transformations is shown in Scheme 87. VDCPs **1**, in the presence of Ce(IV), undergo oxidative electron transfer to afford cationic radical **261**.[94] The following nucleophilic attack of the solvent as MeOH at the cyclopropyl ring may cause the rearrangement to produce the ring-opened radical intermediate **262**.[78,95] Intermediate **262** can be further oxidized by another molecule of CAN to give cation **263**, which is quenched by water in the solvent to produce intermediate **264**. Subsequent enol rearrangement of the corresponding intermediate **264** affords product **260** or intermediate **265**. Further elimination of a molecule of MeOH from **265** furnishes product **259**. For **260**, the *trans*-isomer in a sterically hindered ring does not progress to the corresponding divinyl ketones (Scheme 87).

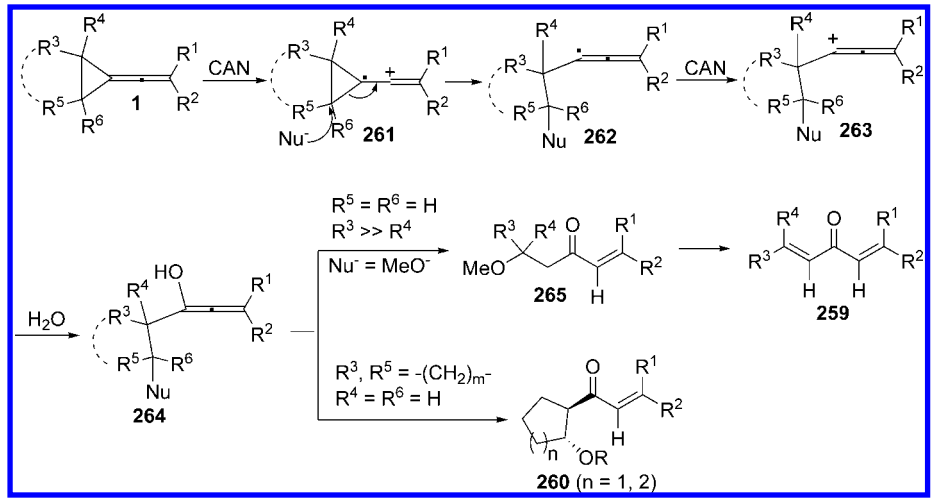
7.2. Reduction Reactions of VDCPs

Treatment of VDCP **1as** with excess sodium in liquid ammonia resulted in regiospecific reduction of the C1−C1′ double bond and led to a 1:1 mixture of cis and trans isomers of vinylcyclopropane **266** (Scheme 88).[92]

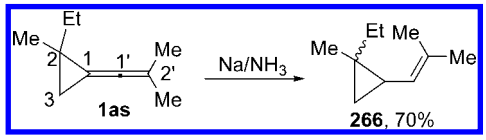
By contrast, reduction of VDCP **1at**, which contains a vinyl group in the cyclopropyl ring, largely led to dihydromycene **271** and a small amount of the positional isomer **272** (Scheme 89).[92]

Crombie et al. also reported the transition metal catalyzed hydrogenation of VDCPs **1** in 1998.[96] It was reported that hydrogenation of VDCPs **1** over platinum mainly led to double bond saturation, while hydrogenation over palladium involved predominantly ring hydrogenolysis. For example, hydrogenation of VDCP **1al** gave **273** as the major product

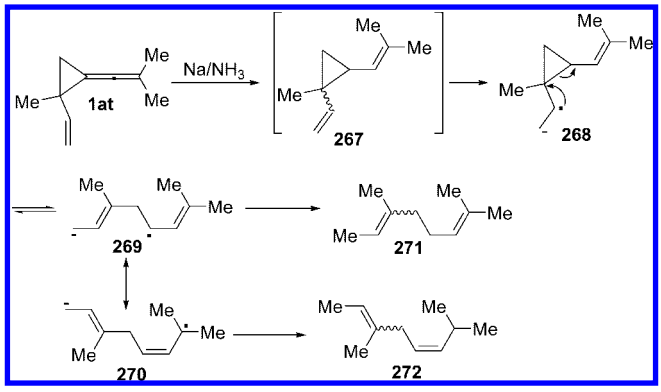
Scheme 87



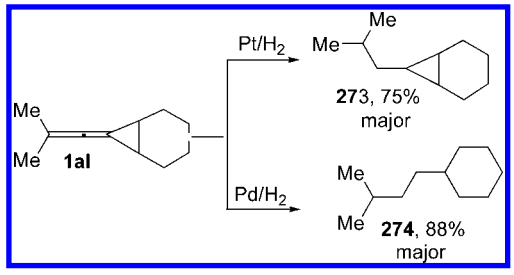
Scheme 88



Scheme 89



Scheme 90



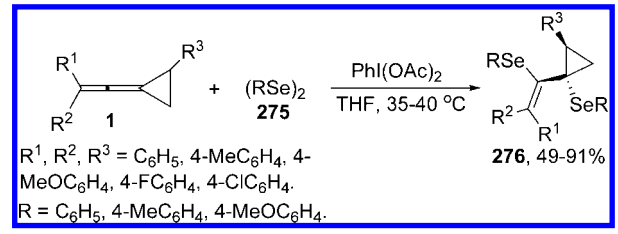
in the presence of Pt catalyst, while **274** was obtained as the major product in the presence of Pd catalyst (Scheme 90).

8. Miscellaneous Analogues

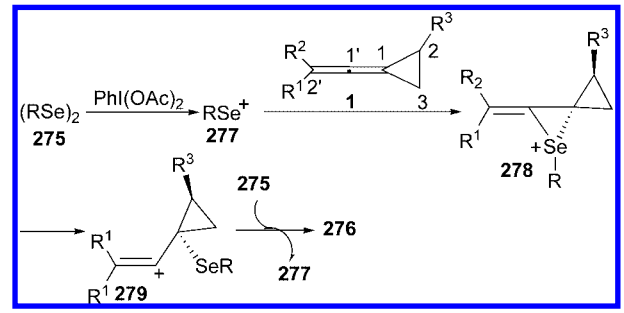
An interesting addition reaction of VDCPs **1** with diaryl diselenide **275** catalyzed by iodosobenzene diacetate was first reported by Shi's group. The corresponding addition products **276** could be obtained in moderate to good yields under mild conditions (Scheme 91).[97]

Further studies showed that these reactions can also take place in the presence of radical scavengers such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and 2,6-di-*tert*-butyl-4-methylphenol (BHT). In addition, it was also found that

Scheme 91



Scheme 92

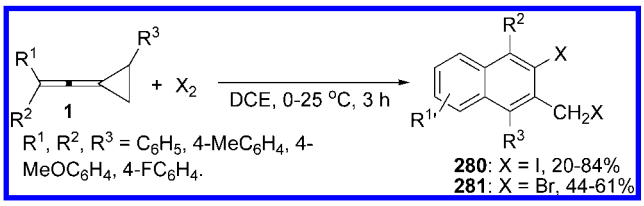


the yields of the above reactions decreased drastically in the presence of H_2O. These control experiments clearly suggest that the above reactions proceed via the corresponding cationic intermediate. A plausible mechanism for this transformation is shown as follows: the hypervalent iodine reagent [$PhI(OAc)_2$] oxidatively cleaves the Se−Se bond of diaryl diselenide to generate *in situ* a very reactive electrophilic selenium species **277** (initiation),[98,99] which adds to the C1−C1′ double bond of VDCPs **1** from the opposite side of the R^3 group, presumably due to the steric repulsion between R^3 and RSe^+ groups, to give the cationic intermediate **278**. The rearrangement of intermediate **278** produces another cationic intermediate **279**,[54] which affords products **276** and regenerates the electrophilic selenium species from the reaction with another molecule of diaryl diselenide to accomplish the catalytic cycle (Scheme 92).

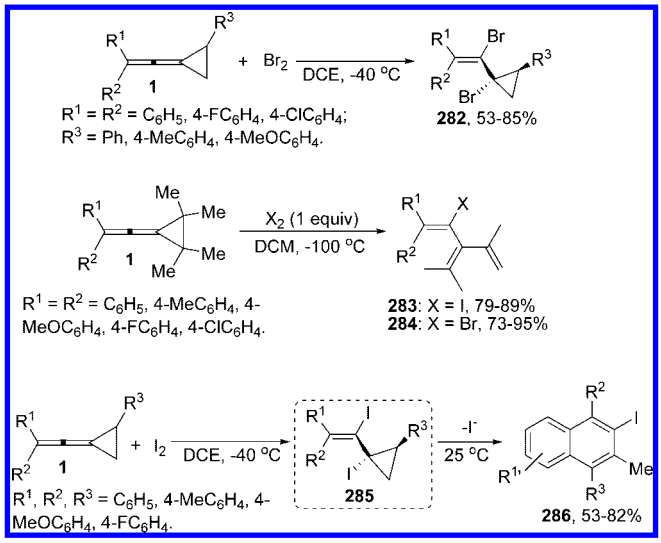
It was also found that VDCPs **1** can undergo ring-opening reactions upon treatment with iodine or bromine at 0−25 °C in DCE to give the corresponding iodinated or brominated naphthalene derivatives **280** or **281** in good to high yields within 3 h (Scheme 93).[100]

In the continuing research, it was observed that reactions of VDCPs **1** with an equimolar amount of bromine or iodine can produce the corresponding addition products **282**−**284**,

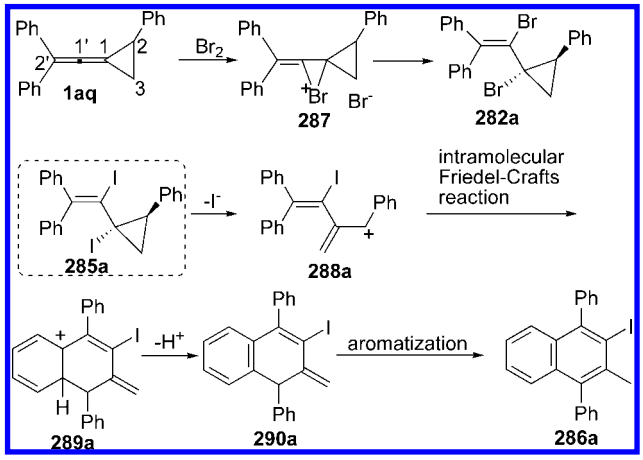
Scheme 93



Scheme 94



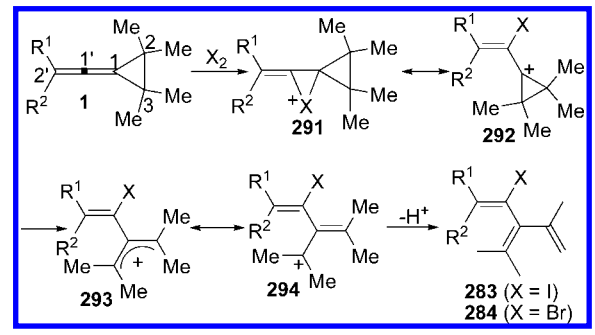
Scheme 95



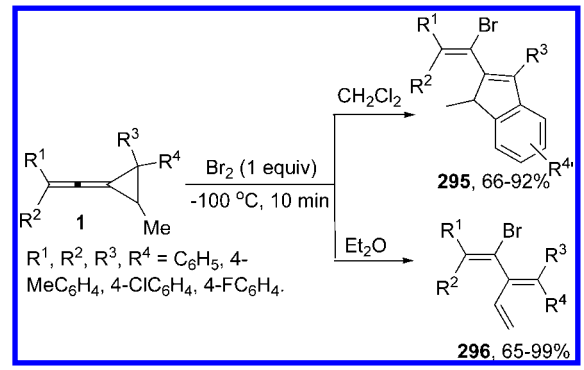
depending on the nature of VDCPs, in moderate to good yields at −40 and −100 °C, respectively. In addition, the reactions of VDCPs **1** with equimolar amounts of iodine gave the corresponding iodinated naphthalene derivatives **286** presumably derived from the corresponding addition products **285** at 25 °C (Scheme 94).[101]

A plausible mechanism for the formation of products **282**, **283**, and **286** is outlined in Scheme 95 with VDCP **1aq** as the model substrate. The addition of halogen (Br_2) to the C1−C1′ double bond of VDCP **1aq** gives the cationic cyclized intermediate **287**, which is stabilized by a cyclopropyl ring. The backside attack of the formed corresponding anion Br^- to the intermediate **287** produces the *anti*-addition products **282a**. In the case of addition reaction with iodine, the corresponding addition product **285a** is labile and can release one iodine anion to give the corresponding ring-opened cationic intermediate **288a** at room temperature.[99] The intramolecular Friedel−Crafts reaction affords the intermediate **289a**, which furnishes the product **286a** presumably via aromatization of another intermediate **290a** (Scheme 95).

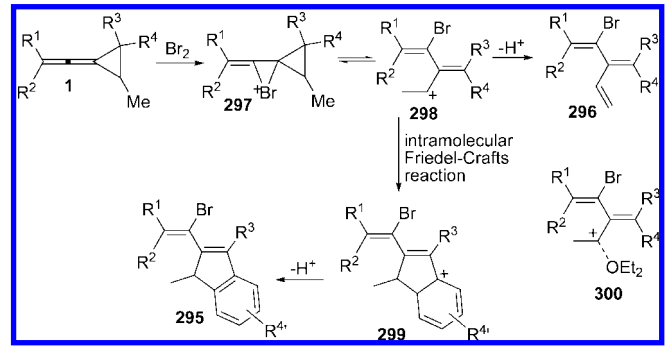
Scheme 96



Scheme 97



Scheme 98

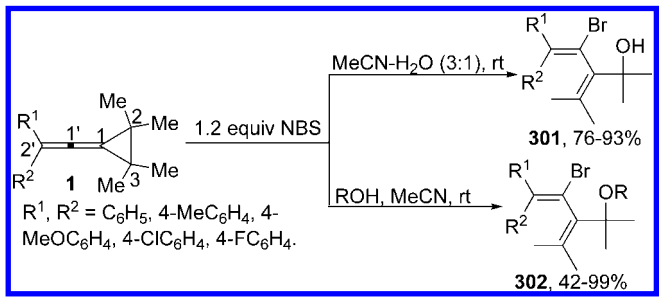


Scheme 96 summarizes a plausible mechanism for the formation of products **283** or **284**. The addition of halogen (X_2) to the C1−C1′ double bond of VDCPs **1** produces the corresponding cationic intermediate **291** or its resonance-stabilized cationic intermediate **292**, which gives the corresponding ring-opened cationic intermediates **293** and **294**. Elimination of a proton takes place to afford the corresponding products **283** or **284** via cationic intermediate **294** (Scheme 96).

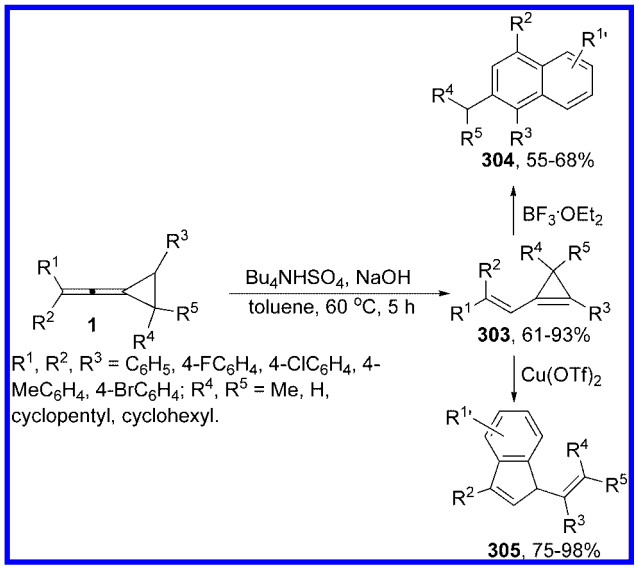
Interestingly, a drastic solvent effect was found to result in different products during the investigation of the reactions of VDCPs **1** with bromine. The brominated indene derivatives **295** were obtained in good to high yields in DCM at −100 °C; however, the brominated conjugate triene derivatives **296** were obtained in diethyl ether at the same temperature (Scheme 97).[102]

A plausible mechanism for these transformations is shown in Scheme 98. The addition of bromine (Br_2) to the C1−C1′ double bond of VDCPs **1** produces the corresponding cationic intermediate **297**,[59b,101] which successively gives the corresponding ring-opened cationic intermediate **298**. Then, elimination of a proton takes place to give the corresponding

Scheme 99



Scheme 100



brominated conjugated triene derivatives **296**. Intramolecular Friedel−Crafts reaction of intermediate **298** produces intermediate **299**, which subsequently gives the corresponding brominated indene derivative **295** via deprotonation (Scheme 98). In diethyl ether, an oxygen atom-containing solvent, the key intermediate **298** might be coordinated by an oxygen atom to give an oxonium ion **300**, which blocks out the intramolecular Friedel−Crafts reaction.[103] Therefore, the proton elimination exclusively takes place to give the corresponding brominated conjugate triene derivative **296** in ether solution (Scheme 98).

VDCPs **1** can also undergo hydrobromination or alkoxybromination in the presence of *N*-bromosuccinimide (NBS) and water or alcohols to give the corresponding vinylbromohydrin **301** and vinylbromoalkoxy derivatives **302** in moderate to excellent yields at room temperature (Scheme 99).[104] Formation of products **301** and **302** can also be rationalized as being derived from the same intermediate as **293** shown in Scheme 96.

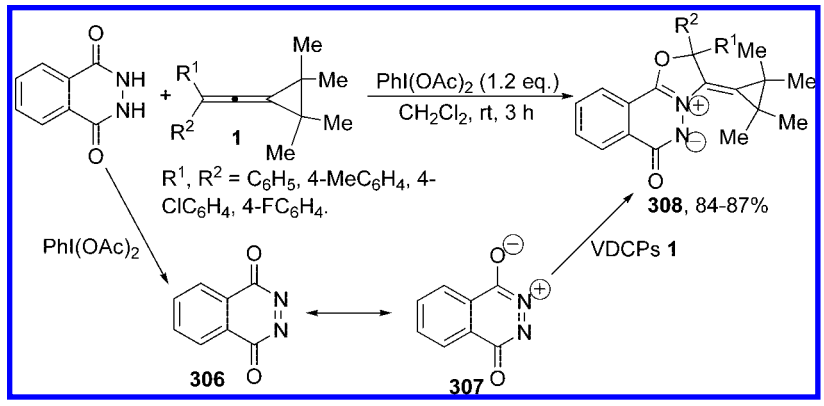
VDCPs **1** can be isomerized to vinylcyclopropenes **303** in good to high yields within 5 h under basic conditions, which can also undergo Lewis acid catalyzed rearrangement reactions to give the corresponding naphthalenes **304** or indenes **305**, respectively (Scheme 100).[105]

Iodobenzene diacetate-mediated reactions of VDCPs **1** with phthalhydrazide can give the corresponding [3 + 2] cycloaddition products in good yields under mild reaction conditions.[106] It was believed that in these reactions, phthalhydrazide was transformed to a 1,3-dipole intermediate in the presence of iodobenzene diacetate. First, iodobenzene diacetate oxidized phthalhydrazide to phthalazine-1,4-dione **306**,[107] which was an equivalent of 1,3-dipole intermediate **307**. The 1,3-dipole intermediate **307** reacted with the C1−C1′ double bond of highly strained VDCPs **1** to give the corresponding cycloaddition products **308** (Scheme 101).

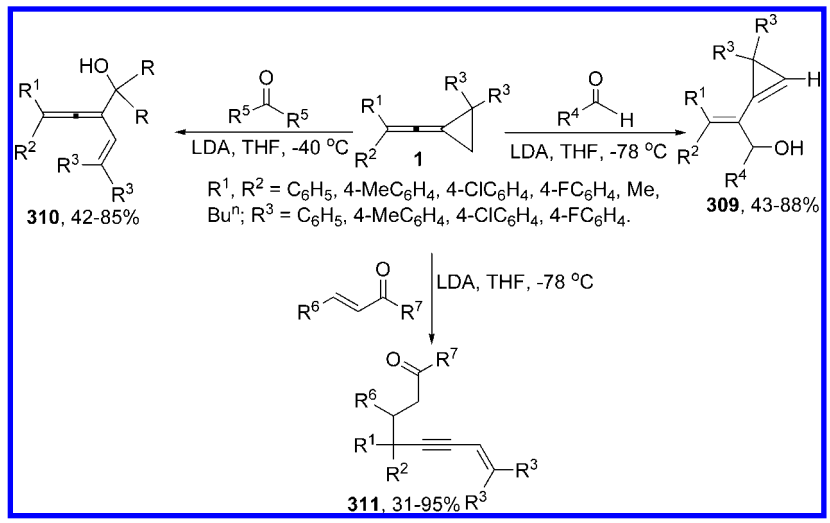
Highly selective addition reactions of VDCPs **1** were realized by treatment with LDA in THF and quenching with aldehydes, ketones, and enones. A number of vinylcyclopropenes **309**, allenol **310**, and 1,3-enynes **311** can be obtained selectively in moderate to good yields depending on the nature of different electrophiles (Scheme 102).[108]

A plausible mechanism for the formation of products **309**, **310**, and **311** is outlined in Scheme 103. Initially, the lithiation of the cyclopropyl ring of VDCPs **1** gives the corresponding cyclopropyl carbanion intermediate **312** by treatment with LDA.[109] When aldehyde is used as an electrophile (E^+), anionic intermediate **313** is formed through 1,3-shift[110] via carbanion **312**, which reacts with the aldehyde to give intermediate **314** and subsequently furnishes product **309**. Intermediate **312** can also undergo a ring-opening reaction to produce allenic carbanion **315**.[111] When ketone is used as an electrophile (E^+), allenol **310** is obtained by the reaction of **315** with the ketone through intermediate **316** (Scheme 103, path a). Furthermore, intermediate **315** can also undergo rearrangement to form propargylic carbanion **317**.[112] When enone is used as an electrophile (E^+), intermediate **318** is formed through 1,4-addition of **317** to enone (Scheme 103, path b). Protonation of intermediate **318** produces the corresponding 1,3-enyne **311**. This highly selective synthesis of vinylcyclopropenes **309**, allenols **310**, and 1,3-enynes **311** by the addition of the lithiated VDCPs **1** with aldehydes, ketones, and enones in THF may be due to the electronic nature of the employed electrophiles and intermediates **312**, **313**, **315**, and **317**. In addition, the reaction temperature may also affect the stability of the involved

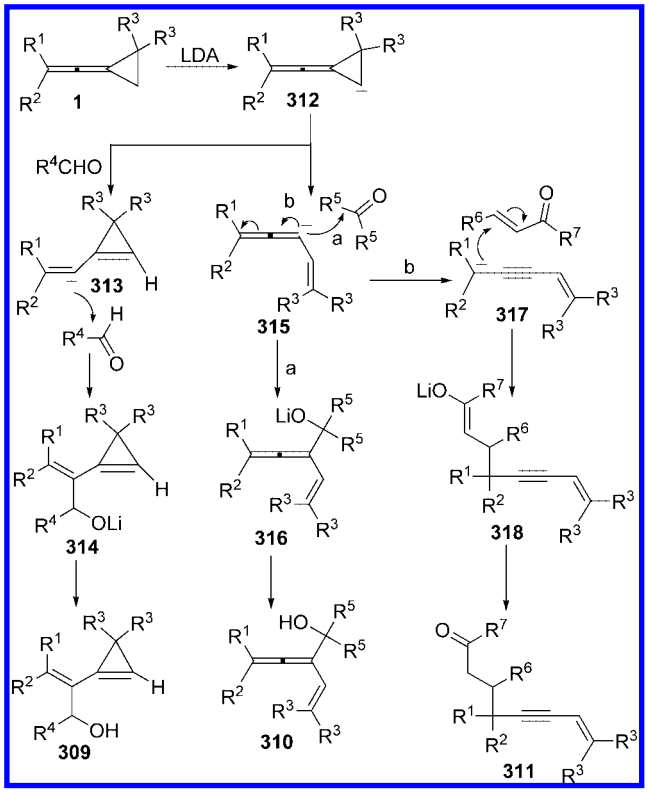
Scheme 101



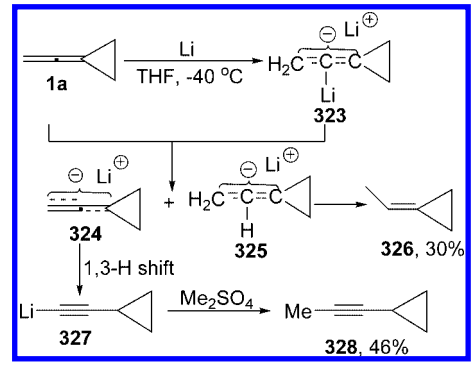
Scheme 102



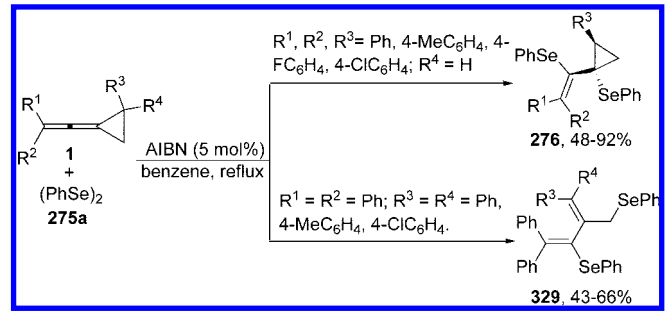
Scheme 103



Scheme 105



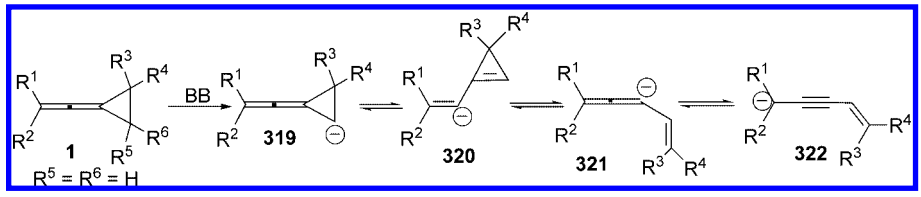
Scheme 106



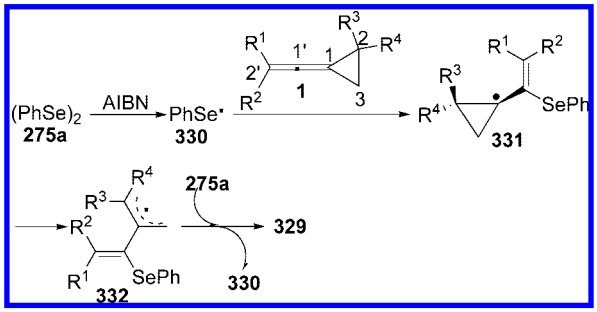
intermediates. In these reactions, there may be equilibrium among the lithiated anions **319**−**322**. To carry out these reactions smoothly, the substituents on one carbon of the cyclopropyl ring should both be hydrogen atoms ($R^5 = R^6 = H$); at the same time, R^3 and R^4 can both be aryl or alkyl groups or one can be an aryl group and the other an alkyl group and neither of them can be a hydrogen atom (Scheme 104).[108,113]

In 2002, Maercker et al. found the reaction of VDCP **1a** with lithium metal during an investigation into the reactivity of substituted allenes toward lithium metal.[114] It was reported that VDCP **1a** was reacted with lithium dust in THF at −40 °C for 1 h, the excess of lithium was filtered off, and dimethyl sulfate was added to trap the corresponding carbanion. Gas chromatography using *n*-decane as internal standard showed that only two reaction products, ethylidenecyclopropane **326** and 1-cyclopropyl-1-propyne **328**, were obtained in 76% yield with a ratio of about 1.5:1; interestingly, no cyclopropyl

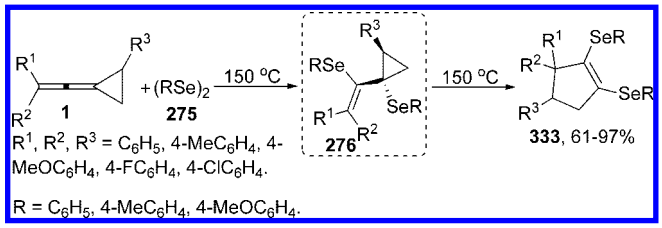
Scheme 104



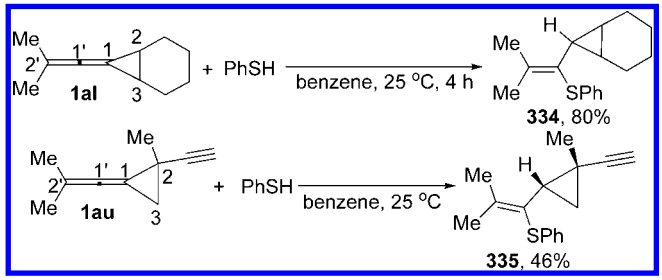
Scheme 107



Scheme 108



Scheme 109



ring-opened products were obtained (Scheme 105). In these transformations, first, VDCP **1a** was lithiated to give intermediate **323**, which metalated the starting materials VDCP **1a** affording allyl lithium **325**, and hydrolysis of intermediate **325** furnishes product **326**. The primary metalation intermediate **324** through a known 1,3-hydride shift[112] gives intermediate **327**. Product **328** is obtained by quenching intermediate **327** with dimethyl sulfate (Scheme 105).

It was found that the reactions of VDCPs **1** with diphenyl diselenide **275a** could also take place in the presence of AIBN to produce the corresponding products **276** or **329** in moderate to good yields under mild conditions (Scheme 106).[115]

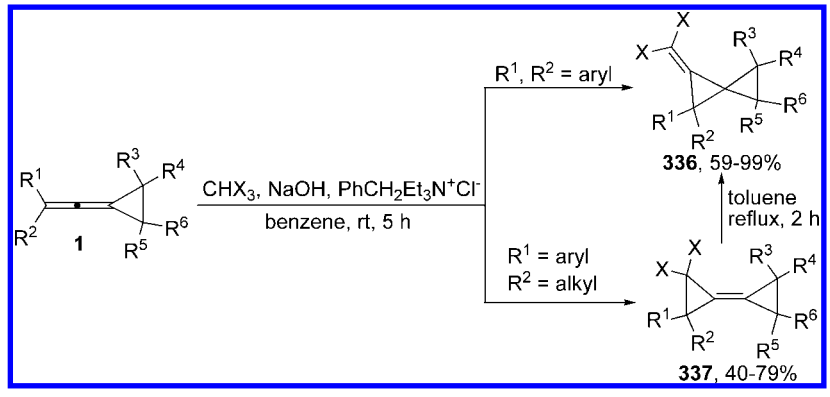
In a similar manner to the aforementioned cationic mechanism for the formation of products **276**, the formation of products **329** can be rationalized by radical mechanism, and Scheme 107 shows the detailed mechanism. The phenylseleno radical **330** is generated by cleavage of diphenyl diselenide with AIBN and then adds to the C1−C1′ double bond of VDCPs **1** from the opposite side of the R^3 group, presumably due to the steric repulsion between the R^3 and PhSe• groups, to form the corresponding radical intermediate **331**.[42e] The cyclopropane radical intermediate **331** undergoes ring opening to give allylic radical intermediate **332** because substitution by the two aryl rings in the 3-position of the allylic radical leads to a greater resonance stabilization than those observed in simple allylic radicals.[116] Radical intermediate **332** reacts with another molecule of diphenyl diselenide **275a** to produce the corresponding ring-opened products **329** with regeneration of the radical **330** (Scheme 107). The two *gem*-aryl groups on the cyclopropane ring of **1** are essential for the ring-opening reaction to occur in this case.

VDCPs **1** can also undergo the reaction with diaryl diselenide **275** upon heating at 150 °C to give the corresponding 1,2-diarylselenocyclopentene derivatives **333** in good to excellent yields, in which the cyclized product is confirmed to be formed from the rearrangement of the normal addition products **276** upon heating (Scheme 108).[117]

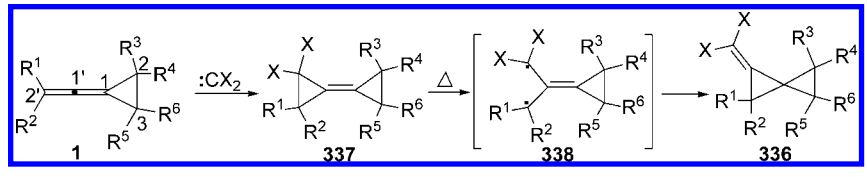
In 1982, Crombie et al. reported the addition reactions of thiophenol with VDCPs **1**, which produced the corresponding vinyl sulfide adducts in high regioselectivity and stereoselectivity.[54b,118] For example, treatment of VDCP **1al** with thiophenol resulted in highly regioselective and stereoselective addition to the C1−C1′ double bond to give the *endo*-sulfide **334**; in a similar manner, reaction between thiophenol and VDCP **1au** also proceeded regioselectively to produce the vinyl sulfide **335** (Scheme 109).

Mizuno et al. reported the cyclopropanation reactions of VDCPs **1** in 2003 with CHX_3 as the precursor of carbene. It was reported that reactions of diaryl-substituted VDCPs **1** with dibromocarbene and dichlorocarbene exclusively gave

Scheme 110



Scheme 111



1-(dihalomethylene)spiropentanes **336** in high yields, while reactions of monoaryl-substituted VDCPs **1** with dihalocarbenes afforded cyclopropylidenecyclopropanes **337** as the major product with the formation of a small amount of 1-(dihalomethylene)spiropentanes **336**. It was also observed that the cyclopropylidenecyclopropanes **337** can be easily converted to the corresponding 1-(dihalomethylene)spiropentanes **336** quantitatively in refluxing toluene for 2 h (Scheme 110).[119]

Based on the above results, a possible reaction pathway for the formation of products **336** and **337** is illustrated in Scheme 111. The first step is the regioselective addition of dihalocarbene to the C1′−C2′ double bond of VDCPs **1** to give the cyclopropylidenecyclopropanes **337**. Then products **337** rearrange to the spiropentane derivatives **336** via trimethylenemethane intermediate **338** generated by homolytic C−C bond cleavage of the cyclopropylidenecyclopropanes **337** (Scheme 111). The difference between products derived from diaryl derivatives and those from monoaryl derivatives of VDCPs **1** clearly indicates that the rearrangement from **337** to **336** proceeds efficiently at room temperature when both R^1 and R^2 are aryl groups because relatively stable biradical intermediate **338** is formed in this case, whereas the rearrangement of **337** to **336** requires more elevated temperature when only one of R^1 and R^2 is an aryl group and the other is an alkyl group.

9. Concluding Remarks and Perspectives of VDCPs

Compared with the chemistry of cyclopropanes and methylenecyclopropanes, which has been extensively studied and well established during the past decades,[120,121] vinylidenecyclopropanes (VDCPs), as another important class of highly strained small-ring compounds, have not been well documented. Traditionally, great attention and many efforts have been focused on the photo- and thermal-induced chemistry of VDCPs. However, the situation has been dramatically changed in recent years since Lewis acid or Brønsted acid catalyzed or mediated chemistry of VDCPs has been thoroughly investigated, and many new reactions of VDCPs have been discovered, showing significant usefulness in organic synthesis. The chemistry of VDCPs greatly depends on the substituents at the allene and cyclopropyl moiety. It is believed that with continued investigations in this area, many new reactions and more useful chemistry of VDCPs including application of these products or reactions for the synthesis of natural products will be found in the near future.

10. Abbreviations

PSS	photostationary state
MK	Michler's ketone, 4,4′-bis(dimethylamino)benzophenone
DPEphos	bis[(2-diphenylphosphino)phenyl] ether
CSI	chlorosulfonyl isocyanate
PTAD	4-phenyl-1,2,4-triazoline-3,5-dione
MCPBA	3-chloroperoxybenzoic acid
CAN	cerium(IV) ammonium nitrate
AIBN	azobisisobutyronitrile
LDA	lithium dimethylamide

11. Acknowledgments

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12. Supporting Information Available

Crystallographic information files for compounds **1b** and **3b**, as well as estimated strain energy of **1a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) The crystal data for **1b** have been deposited in CCDC with number 764959. Empirical formula: $C_{21}H_{22}$. Formula weight: 274.39. Crystal color, habit: colorless, prismatic. Crystal system: triclinic. Lattice type: primitive. Lattice parameters: a = 10.3256(10) Å, b = 11.1547(11) Å, c = 15.7258(15) Å, α = 108.462(2)°, β = 93.591(2)°, γ = 91.936(2)°, V = 1711.9(3) Å^3. Space group: $P\bar{1}$. Z = 4. D_{calcd} = 1.065 g/cm^3. F_{000} = 592. Diffractometer: Rigaku AFC7R. Residuals, R, Rw: 0.0519, 0.1198.
(9) The crystal data for **3b** have been deposited in CCDC with number 223481. Empirical formula: $C_{16}H_{13}Cl$. Formula weight: 240.71. Crystal color, habit: colorless, prismatic. Crystal system: triclinic. Lattice type: primitive. Lattice parameters: a = 7.673(2) Å, b = 8.574(3) Å, c = 9.724(3) Å, α = 99.406(5)°, β = 93.714(5)°, γ = 93.823(6)°, V = 627.8(3) Å^3. Space group: $P\bar{1}$. Z = 2; D_{calcd} = 1.273 g/cm^3. F_{000} = 252. Diffractometer: Rigaku AFC7R. Residuals, R, Rw: 0.0516, 0.0954.
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