Organic LETTERS

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Preparation of Optically Active *cis*-Cyclopropane Carboxylates: Cyclopropanation of α-Silyl Stryenes with Aryldiazoacetates and Desilylation of the Resulting Silyl Cyclopropanes

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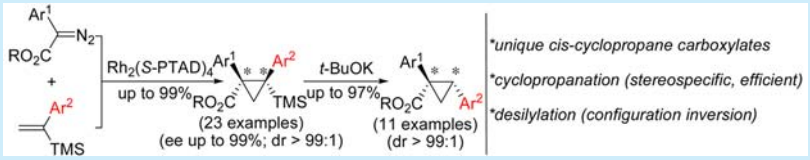
Supporting Information



ABSTRACT: Optically active *cis*-cyclopropane carboxylates are prepared via the Rh_2(*S*-PTAD)$_4$-catalyzed cyclopropanation of α-silyl styrenes with aryl diazoacetates followed by desilylation of the resulting silyl cyclopropane carboxylates. The conjugation of the aryl ring with C═C bond and π stacking are proposed for the stereoselectivity of cyclopropanation, and configuration inversion is observed with the desilylation process.

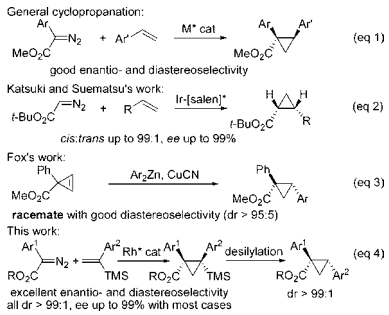
Enantioenriched cyclopropane carboxylates are very important molecules that are generally prepared through the *trans*-selective cyclopropanation of an alkene with a diazo ester (Scheme 1).[1,2] Though considerable efforts have been made toward the *cis*-selective cyclopropanation of alkenes by the Rh, Cu, Ir, and other metal catalysts,[3] much is left to be desired. To date, the best result on the topics was reported by Katsuki's group with the Ir−salen complexes,[4] where only the diazoacetates were used. Asymmetric cyclopropanation of stryenes with Rh−carbenoids from aryl diazoacetates is always *trans*-selective, affording the (*E*)-1,2-diarylcyclopropane carboxylates.[5] The (*Z*)-analogues had been efficiently obtained as the racemates via the carbozincation of cyclopropenes.[6] In this paper, we reported the enantio- and diastereoselective cyclopropanation of α-silyl stryenes with aryl diazoacetates and desilylation of the resulting cyclopropanes for preparation of the optically active *cis*-cyclopropane carboxylates.

Incorporation of a silyl group onto the cyclopropane ring and application of these silylcyclopropanes has attracted considerable interest.[7−13] A range of methods to optically active silyl cyclopropanes were reported,[9−13] but only few catalytic approaches demonstrated their efficiencies in control of enantio- and diastereoselectivities, producing some bifunctional cyclopropanes.[10] Other methods suffered poor to moderate enantioselectivity with significant limitation of substrates. Cyclopropanation of the silylalkenes with diazo compounds had been explored by Ru and Cu catalysts, and only the vinylsilane and diazoacetates were examined.[13]

Following our interest in the β-functionalized cyclopropane carboxylates with restricted conformation,[14,15] the asymmetric cyclopropanation of phenyldiazoacetate **1a** and α-silyl styrene **2a** was explored with the dirhodium catalysts (Table 1). The cyclopropanation reactions using dirhodium carboxylates all afforded **3aa** with absolute control of diastereoselectivity (entries 1−7), and Rh_2(*S*-PTAD)$_4$ was efficient for the conversion. Opposite enantioselectivity was observed when Rh_2(*S*-DOSP)$_4$ was employed for the cyclopropanation reaction,[14,16] and Doyle dirhodium carboxamidates afforded low conversions (entries 8−10).

The optimal conditions (in bold, Table 1) were used for investigation of the aryl diazoacetates (Scheme 2). First, cyclopropanation of **2a** with **1a** was re-examined at ∼0.5 mmol scale, where the yield of **3aa** was improved to 99%, and the enantio- and diastereoselectivity were retainable. Other aryl diazoacetates **1b−n** were all cyclopropanated with **2a**, and the

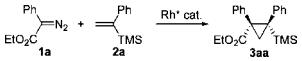
Scheme 1. Stereochemistry of the Cyclopropane Carboxylates



Received: July 19, 2016
Published: August 16, 2016

DOI: 10.1021/acs.orglett.6b02117
Org. Lett. 2016, 18, 4356−4359

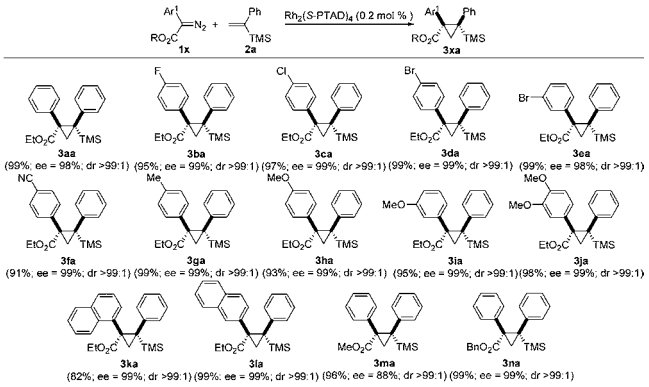
Table 1. Asymmetric Cyclopropanation of α-Silyl Styrene 1a with Phenyldiazoacetate 2a[a]



entry	catalyst	time (min)	yield[b] (%)	dr[c]	ee[d]
1	Rh_2(*S*-DOSP)$_4$	30	43	>99:1	−34
2	Rh_2(*R*-TBSP)$_4$	60	46	>99:1	38
3	**Rh_2(*S*-PTAD)$_4$**	**30**	**92**	**>99:1**	**98**
4	Rh_2(*S*-PTPA)$_4$	30	77	>99:1	99
5	Rh_2(*S*-PTTL)$_4$	30	85	>99:1	98
6	Rh_2(*S*-TCPTTL)$_4$	30	65	>99:1	73
7	Rh_2(*S*-TFPTTL)$_4$	30	42	>99:1	85
8	Rh_2(4*S*-MPPIM)$_4$	16 h	trace		
9	Rh_2(4*S*-MEOX)$_4$	16 h	trace		
10	Rh_2(5*R*-MEPY)$_4$	16 h	trace		

[a]Cyclopropanation of **1a** (52.8 mg, 0.3 mmol) and **2a** (19.0 mg, 0.1 mmol) with Rh catalyst (0.0002 mmol) in hexane (0.1 mL) at ∼15 °C. [b]Isolated yield after purification. [c]Determined by ^{1}H NMR of the crude reaction mixture. [d]Determined by chiral HPLC.

Scheme 2. Scope of the Aryl Diazoacetates[a]



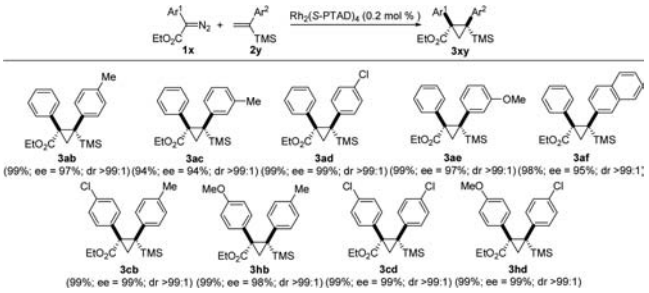
[a]Cyclopropanation of α-silyl styrene **2a** (1.5 mmol) with aryl diazoacetate **1x** (0.5 mmol) in hexane (0.5 mL) with Rh_2(*S*-PTAD)$_4$ (1.6 mg, 0.001 mmol) at ∼15 °C for 30 min.

conversion was nearly immune to the substituents on the aryl group of the aryl diazoacetates. The silyl cyclopropane carboxylates **3aa**−**na** except **3ma** were obtained in excellent yields, diastereoselecitivity (dr >99:1), and enantioselectivity (98%−99% ee). The enantioselectivity for **3ma** (88% ee) indicated the reaction was sensitive to the size of the ester group.

The α-silyl styrenes were next explored, and the results are summarized in Scheme 3. All of the corresponding cyclopropane carboxylates were obtained with excellent diastereoselectivity (dr >99:1). It indicated that introduction of an electron-donating group at the phenyl ring of α-silyl styrene would slightly decrease the enantioselectivity. If a methyl group was attached at the *ortho*-position of the phenyl ring, the cyclopropanation reaction completely failed (not shown in Scheme 3), while its analogues **3ab** and **3ac** with the methyl group at the *para*- and *meta*-position of phenyl ring were produced with excellent yields. Furthermore, cyclopropanation of α-silyl *para*-methylstyrene and α-silyl *para*-chlorostyrene, with aryl diazoacetates **1c** and **1h**, respectively, afforded four β-silyl cyclopropanecarboxylates with excellent enantio- and diastereoselectivity.

We were very glad that the asymmetric cyclopropanation of α-silyl styrene herein addressed both excellent enantio- and diastereoselectivity. The ester group was regarded as a *trans*-directing group in the Rh-catalyzed cyclopropanation of alkenes.[5] To our great surprise, the ester group here faced to the same direction of the silyl group according to the single-crystal X-ray crystallography of **3da**,[17] which was different from the expected structure.

Scheme 3. Scope of the α-Silyl Styrenes[a]

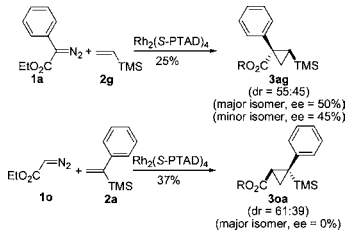


[a]Cyclopropanation of α-silyl styrenes **2y** (1.5 mmol) with aryl diazoacetates **1x** (0.5 mmol) in hexane (0.5 mL) with Rh_2(*S*-PTAD)$_4$ (1.6 mg, 0.001 mmol) at ∼15 °C for 30 min.

A similar intriguing stereocontrol had been reported with the cyclopropanation reaction of 1,1-diarylethylenes by the Davies group, and good diastereoselectivity was observed even when two aryl rings substituted with the alkene were very similar in size.[18] The better conjugation of electron-rich aryl ring with the C═C bond was proposed to support their good diastereoselectivity. Here, the conjugation effect should also contribute to the diastereocontrol of the cyclopropanation of α-silyl styrenes. Considering the excellent diastereoselectivity in this paper, we thought that the two aromatic rings, one from the α-silyl styrene and the other from the aryl diazoacetate, might had some tight interaction.

Two more experiments, cyclopropanation of vinylsilane **2g** with **1a** and cyclopropanation of **2a** with ethyl diazoacetate **1o**, were carried out to see if the diastereoselectivity would be kept when one of the aryl rings was removed from the system (Scheme 4). Both reactions gave the silyl cyclopropane carboxylates **3ag**

Scheme 4. Diastereoselectivity in the Cyclopropanation of 1a with 2g and 1o with 2a



and **3oa** with poor stereocontrol and poor yields, which indicated that the π stacking interaction[19] between the two aromatic rings could possibly exist.

Rh_2(*S*-PTAD)$_4$ and Rh_2(*S*-PTTL)$_4$ are both derived from *N*-phthaloylamino acids, and the differences between the two catalysts are the substituents at the α-carbon of leucine. The two catalysts had demonstrated their efficiencies with the cyclopropanation reaction (Table 1, entries 3 and 5). Several groups reported that a "chiral crown" conformation of Rh_2(*S*-PTTL)$_4$ was observed with its X-ray crystal structure,[20] where an approximate C_2-symmetric chiral cavity with Rh catalyst face was generated. Four phthalimido groups were oriented on the same face, but they were not equal in space. A similar cavity of

DOI: 10.1021/acs.orglett.6b02117
Org. Lett. 2016, 18, 4356−4359

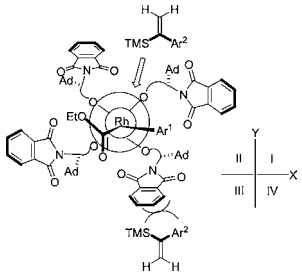
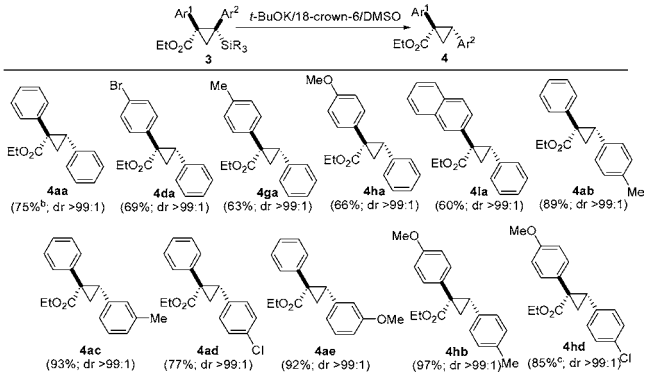


Figure 1. Possible induction model for cyclopropanation of α-silyl styrene with aryl diazoacetates.

Rh_2(*S*-PTAD)$_4$ was proposed for illustration of the stereoselectivity (Figure 1). With the catalyst face, quadrants I and III are less sterically encumbered than quadrants II and IV. According to Fox's research,[20a] the carbene would be aligned with the *X*-axis, and then approach of the α-silyl styrene to the Rh−carbenoid would proceed through an end-on model[5a] from quadrant I. The bulky silyl group might point to the vertical phthalimido group in quadrant II, and then the Ar^2 ring and the C=C bond could possess a coplanar conformation, resulting in better conjugation. On the contrary, if the Ar^2 ring closer to quadrant II was applied, the required orthogonal conformation of Ar^2 ring and C=C bond would destroy the conjugation. Furthermore, with the coplanar conformation, the possible Pi stacking of Ar^1 ring and Ar^2 ring could come into being, and it might stabilize the transition states. The conjugation effect and Pi stacking interaction would dominate the product with two aromatic rings pointing in the same direction.

Desilylation of the α-silyl α-alkyl cyclopropanes had been reported by the group of Inomata and Ukaji,[9g] affording a mixture of diastereomers of cyclopropane carboxylates. The major isomer was assigned as the corresponding cyclopropane with configuration retention. Treatment of **3aa** with TBAF in THF afforded a mixture of *cis*/*trans* cyclopropane carboxylate (89:11) in 98% yield, and the major isomer (*Z*)-**4aa** was obtained with configuration inversion. Further desilylation of **3aa** (0.20 mmol) with KO^{t}Bu/18-crown-6 in DMSO delivered (*Z*)-**4aa** as the only isomer in 75% yield (Scheme 5). The enantiomeric excess for **4aa** was expected to be excellent as only one of the two stereocenters of **3aa** was involved in the desilylation process, and the precognition was confirmed by chiral HPLC analysis (98% ee for **4aa**). Then a range of silylcyclopropanes were desilylated under the conditions, and only the (*Z*)-cyclopropane carboxylates were observed and separated. In some cases, the yields were slightly moderate, which was thought be due to part saponification of the ester group under the strong basic conditions. It should be noted that the (*E*)-**4aa** could be hydrolyzed to the corresponding (*E*)-cyclopropane carboxylic acid, and then it would be lost in the basic aqueous phase. Further careful treatment of **3aa** (0.40 mmol) with the optimized conditions gave (*Z*)-**4aa** in 82% yield and a mixture of cyclopropane carboxylic acid diastereomers (*E*/*Z* < 1/7) in 13% yield, which indicated that the diastereoselectivity of the desilylation reaction was very excellent (dr >98:2). Finally, the structure of **4hd** was unambiguously confirmed by X-ray crystallography.

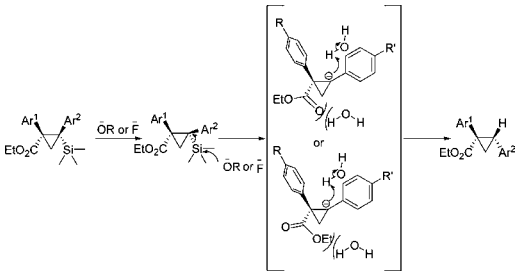
Scheme 5. Desilylation of β-Silyl Cyclopropanes 3[a]



[a]Desilylation of **3** (0.20 mmol) with *t*-BuOK (26.9 mg, 0.24 mmol) and 18-crown-6 (15.8 mg, 0.06 mmol) in DMSO (1.0 mL) at ~15 °C for 10 min. [b]Desilylation for 1 min. [c]Desilylation of **3hd** at 0.27 mmol scale.

The possible desilylation process was proposed through the following two stages: (1) desilylation of the silyl cyclopropane carboxylate **3** would generate a planar carbanion stabilized by the cyclopropyl ring[21] and a benzyl group, where the planar conformation would strengthen the conjugation of the carbanion and Ar^2 ring;[22] (2) protonation of the carbanion might proceed from the above side of the cyclopropane ring, affording the (*Z*)-1,2-diarylcyclopropane carboxylate with configuration retention, and the down side should be blocked by the carbonyl group or the alkoxyl group of the ester (Scheme 6).

Scheme 6. Possible Mechanism of Desilylation of the Silyl Cyclopropane Carboxylate



In summary, we have demonstrated the asymmetric cyclopropanation of α-silyl styrenes with aryl diazoacetates and desilylation of the resulting silylcyclopropanes with configuration inversion. This strategy might be very useful for preparation of chiral (*Z*)-1,2-diarylcyclopropane carboxylates, which was very difficult to address previously.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02117.

Experimental procedures and spectroscopic data and copies of NMR spectra for all new compounds (PDF)
X-ray crystallographic data for compound **3da** (CIF)
X-ray crystallographic data for compound **4hd** (CIF)

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Notes

The authors declare no competing financial interest.

DOI: 10.1021/acs.orglett.6b02117
Org. Lett. 2016, 18, 4356−4359

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Nos. 21262024 and 21202074), the Program for New Century Excellent Talents in University (NCET-13-0874), and the Research Starting Funds for Imported Talents of Ningxia University (BQD2015001).

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DOI: 10.1021/acs.orglett.6b02117
Org. Lett. 2016, 18, 4356−4359