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Journal of Organometallic Chemistry 630 (2001) 57–66

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Rhodium-catalyzed cyclopropanations of allylsilanes and allylstannanes: the role of the silyl/stannyl group in *trans–cis* stereoselection

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Received 4 January 2001; received in revised form 4 May 2001; accepted 5 May 2001

This paper is dedicated with admiration to Professor Myron Rosenblum on his 75th birthday celebration, and on his many important and original contributions to the field of organometallic chemistry

Abstract

The stereochemistry of cyclopropanation reactions between allylsilanes and allylstannanes **6** with four representative diazoalkanes in the presence of rhodium acetate has been studied. Cyclopropanations with ethyl diazoacetate show a preference for the formation of the *trans* cyclopropane esters **7**, whereas the corresponding reactions with (trimethylsilyl)diazomethane favor the *cis* stereoisomers. In both cases, overall stereoselection is low, ranging from 1.3:1 to 2.4:1. The product ratios show a small dependence on the nature of the silyl or stannyl groups, with silyl substituents giving better stereoselection than stannyl, and larger ligands on the metal center leading to lower selectivity. On the other hand, rhodium-catalyzed cyclopropanations using methyl 2-diazo-4-phenyl-3-butenoate or 1-aryldiazoacetates occur with excellent stereocontrol. The stereochemical patterns found in these reactions are in accord with an open transition state model wherein the rhodium carbenoid approaches the allylmetal π-bond from an antiperiplanar orientation with respect to the allylic carbon–ML_3 bond. While the metal center may help stabilize developing β-cationic charge in the transition states, hyperconjugation effects appear to play a minor role, if any, in directing the stereochemical course of cyclopropanation. © 2001 Published by Elsevier Science B.V.

Keywords: Rhodium carbenoids; Allylsilanes; Allylstannanes; Cyclopropanation; Open transition state model

1. Introduction

Rhodium-catalyzed reactions of diazoalkanes with alkenes offer an excellent method for preparing substituted cyclopropane derivatives in high yields under mild reaction conditions [1]. Because of their ready solubility in organic solvents and ability to avoid the formation of undesired side products, complexes of rhodium(II) have become popular catalysts for these types of cycloadditions [2]. The most common types of cyclopropanations are those between alkene substrates **1** and α-diazoacetates **2** to give cyclopropane esters [3] **3**, and the corresponding additions of 2-diazo-3-butenoates [4] **4** to yield vinylcyclopropane esters **5** (Fig. 1). Cyclopropanations of monosubstituted alkenes with simple diazoalkanes or α-diazoacetates **2** generally occur with low diastereoselectivity, while those involving 2-diazo-3-butenoate esters **4** give much higher stereochemical

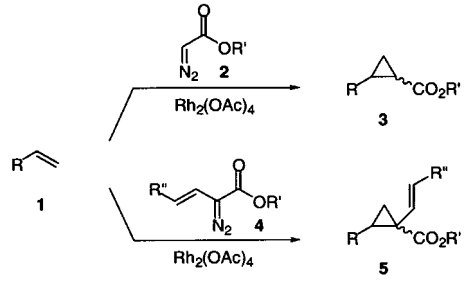

Fig. 1. Cyclopropanation reactions of alkenes.

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0022-328X/01/$ - see front matter © 2001 Published by Elsevier Science B.V.
PII: S0022-328X(01)00938-X

control. Mechanistic models, which rationalize these observations, have been developed and discussed in the literature [3–5].

Despite the wide diversity of double bond compounds [1,6] that have successfully served as substrates in rhodium-promoted cyclopropanations, allylsilanes and allystannanes have to our knowledge not been examined. In fact, we are aware of only one example of an allylsilane undergoing a metal-catalyzed cyclopropanation with a diazo compound, specifically, that of allyltrimethylsilane with ethyl diazoacetate [7]. The conditions described for this reaction entail the dropwise addition of ethyl diazoacetate to a boiling suspension of copper and copper acetate in neat allyltrimethylsilane. The silyl- and stannyl-activated cyclopropane products derived from these reactions can serve as homoallyl anion equivalents in ring-opening processes with electrophiles and thus are useful synthetic reagents [7,8]. During the course of recent investigations [9] on the thermal rearrangement properties of 1-silylmethyl- and 1-stannylmethyl-2-vinylcyclopropanes, we had the opportunity to examine the reactions of allylsilanes and allylstannanes with rhodium carbenoids generated from diazoalkanes. In addition to utilizing the derived adducts, we were interested in examining the possible role that the silyl or stannyl groups might have on the stereochemistry of rhodium(II)-catalyzed cyclopropanation. Current mechanistic models suggest that bulky, branched substituents proximal to the alkene can influence *trans*:*cis* ratios of the cyclopropane products. In addition to potential steric perturbations, silyl and stannyl substituents adjacent to an alkene center can exert powerful β-cation stabilizing effects, which in the case of cyclopropanation, might play a role in guiding the stereochemical course of ring formation. In this report, we summarize our findings and discussions on these particular elements of the reaction.

2. Results

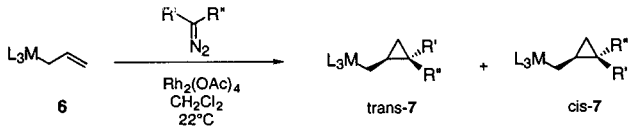
In this study, we examined the rhodium acetate-catalyzed reactions of allylsilanes and allystannanes **6** with four sterically and electronically different types of diazoalkanes, namely, ethyl diazoacetate, (trimethylsilyl)diazomethane, 2-aryldiazoacetates, and methyl 2-diazo-4-phenylbut-3-enoate (Table 1). All of the reactions were done under standard cyclopropanation conditions at room temperature by slow addition of the diazoester to a dilute mixture of the allylmetal reagent and 5 mol% of rhodium acetate in methylene chloride. Upon completion of the reaction, the product mixtures were evaporated and subjected to flash chromatography, with the exception of the triethoxysilylmethyl cyclopropanes, which were unstable and rapidly decomposed upon attempted purification. The instability of these particular cyclopropanes seems to be related to the presence of the ethoxy silyl ligands, which may facilitate acid-promoted opening of the cyclopropyl ring [10]. The relative stereochemistry of the purified cyclopropane diastereomers was established through a combination of standard one-dimensional and two-dimensional NMR experiments. The yields and diastereomeric ratios of the isolated products are given in the Table 1. In general, the reactions were clean and yields of the cyclopropane products were uniformly high. In no cases did we observe the formation of other adducts such as those arising from carbene insertion [11] into the allylic or vinylic C–H bonds of the allylmetal reagent.

The first series of diazoalkane cycloadditions we examined were those of allylmetals **6** with ethyl diazoacetate (entries 1–5, Table 1). The anticipated *trans* and *cis* cyclopropane esters **7** were afforded in high yield, but with very low diastereoselectivity. The *trans*:*cis* ratios fall well within the ranges expected for diazoacetate couplings with monosubstituted alkenes (below 2.5:1), and show a small dependency on the nature of the silyl/stannyl group. Within the silyl series, for example, *trans*:*cis* selectivity dropped steadily from 2.1:1 to 1.4:1 to 1.2:1 as the silyl ligand L was changed from methyl to phenyl to ethoxy (entries 1–3). From entries 4 and 5 in the table, it appears that stereoselectivity is even lower for the corresponding allylstannane reactions.

The results for the analogous cyclopropanations involving (trimethylsilyl)diazomethane are given in entries 6–10 in Table 1. The electronic and steric properties of the carbenoid center in this case differ markedly from those of the species derived from ethyl diazoacetate. This is reflected by the reversal of *trans*:*cis* stereoselectivities, which now favor the *cis* adduct in each case. The level of stereoselection remains equally low, however, below 1:2.5, with the allylsilanes once again offering slightly better stereocontrol than the allylstannanes.

The third group of reactions we carried out was that of allylmetals **6** with the Davies vinyl-stabilized diazo reagent, methyl 2-diazo-4-phenyl-3-butenoate [12] (entries 11–15). In contrast to the low stereoselectivity obtained in the cyclopropanation reactions of entries 1–10, these *vinylcyclopropanations* show high selectivity for the *trans* vinylcyclopropane **7**. Only allyltrimethylsilane and allyltriphenylsilane (entries 11 and 12) afforded any detectible amounts of the *cis* product, while allyltriethoxysilane, allyltributyltin, and allyltriphenyltin provided the *trans* adduct exclusively. These results are in agreement with earlier reports from Davies who found that rhodium acetate-catalyzed additions of vinyl diazoacetates to alkenes give an unusually high preference for the cyclopropane whose vinyl group is *trans* to the alkyl substituent [3].

Table 1
Rhodium-catalyzed cyclopropanations of allysilanes and allylstannanes **6**



Entry	L_3M	R′	R″	*Trans*:*cis* [a]	Isolated % yields [a]
1	Me_3Si	CO_2Et	H	2.1:1	94
2	Ph_3Si	CO_2Et	H	1.4:1	95
3	$(EtO)_3Si$	CO_2Et	H	1.2:1 [b]	91 [b]
4	Bu_3Sn	CO_2Et	H	1.5:1	94
5	Ph_3Sn	CO_2Et	H	1.2:1	96
6	Me_3Si	$SiMe_3$	H	1:2.0	96
7	Ph_3Si	$SiMe_3$	H	1:2.4	97
8	$(EtO)_3Si$	$SiMe_3$	H	1:2.1 [b]	90 [b]
9	Bu_3Sn	$SiMe_3$	H	1:1.4	95
10	Ph_3Sn	$SiMe_3$	H	1:1.7	96
11	Me_3Si	CO_2Me	CH=CHPh (*E*)	12.7:1	96
12	Ph_3Si	CO_2Me	CH=CHPh (*E*)	9.0:1	90
13	$(EtO)_3Si$	CO_2Me	CH=CHPh (*E*)	Only *trans* [b]	93 [b]
14	Bu_3Sn	CO_2Me	CH=CHPh (*E*)	Only *trans*	93 [c]
15	Ph_3Sn	CO_2Me	CH=CHPh (*E*)	Only *trans*	92
16	Ph_3Si	CO_2Me	Ph	Only *trans*	96
17	Ph_3Si	CO_2Me	4-NO_2Ph	Only *trans*	96
18	Ph_3Sn	CO_2Me	Ph	Only *trans* [b]	90 [b]

[a] Based on isolated material after column chromatography, except where indicated.
[b] Based on crude material obtained after trituration with hexane. Diastereomeric ratios were determined by integration of the signals in the proton NMR spectrum.
[c] Depending on the workup and purification conditions, variable amounts of ring opened, destannylated product can also be obtained.

The final series of reactions we studied were those of allyltriphenylsilane and allyltriphenylstannane with 1-aryl diazoacetates (entries 16–18 in Table 1). Like those of the preceding vinylcyclopropanations, the stereoselectivity of these additions was exceptionally high, giving only the adduct having the ester and CH_2ML_3 substituents *trans* to each other on the cyclopropane ring.

3. Discussion

Rhodium(II)-catalyzed couplings of diazoalkanes with alkenes are thought to proceed via a rhodium-stabilized carbenoid intermediate, an electrophilic species which transfers the carbene component to the alkene centers with retention of the original double bond geometry [1]. The most commonly used stereochemical model for rhodium acetate-promoted cyclopropanation was first postulated by Doyle in 1984, and which is reproduced in Fig. 2 [1]. In the initial step of the reaction, a transient π-complex (**A**) is formed between the rhodium carbenoid and the alkene. Doyle has argued that the rhodium carbenoid coordinates orthogonally to the alkene with respect to the carbon–rhodium bond, such that the alkene substituent R orients away from the rhodium center. π-Complex **A** must then undergo a rotation about the developing C–C bond to bring the carbon–rhodium bond into proper alignment with the alkene center to form the cyclopropane ring. During this rotational process, the alkene becomes polarized such that positive charge character builds up at the more substituted alkene carbon as it swings over the R′ substituent, as shown in transition structure **B**. For carbenoids whose R′ and R″ groups are non-equivalent two different π-complexes can form, each leading to a different diastereomeric cyclopropane adduct. When the carbenoid R′ or R″ group is an ester (or other suitable electron pair donor), cationic charge

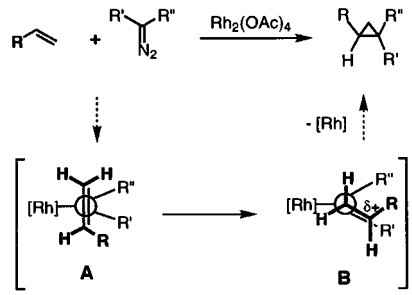


Fig. 2. The Doyle model for Rh(II)-catalyzed diazoalkane cyclopropanation of monoalkylated alkenes.

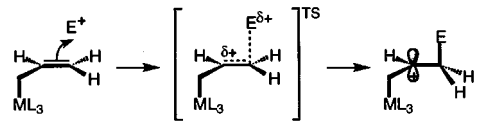


Fig. 3. Stereochemistry of electrophilic addition to an allymetal.

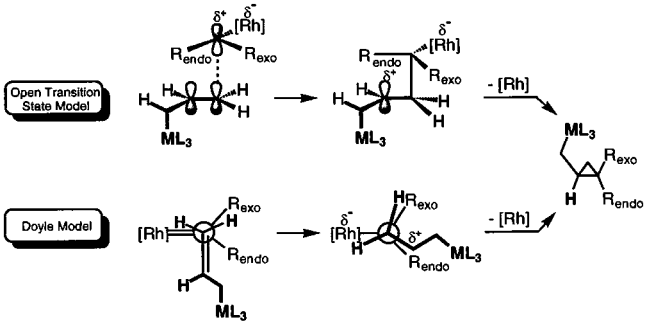


Fig. 4. Comparison of the open transition state model (above) and Doyle model (below) for rhodium–carbenoid additions to an allymetal.

developing in the transition state can be stabilized through electrostatic interaction with the eclipsing R′ moiety in **B**, thus delivering the *trans* adduct as the major product. Substituents that do not have this stabilization capability prefer to occupy the R″ site to minimize unfavorable steric interactions, thus giving the *cis* product predominantly [13].

Application of the Doyle model to the reactions of the allylsilanes and allystannanes with ethyl diazoacetate (entries 1–5 in Table 1) would suggest that the allylic metal group ($R = CH_2ML_3$) could also play a role in promoting electropositive charge development at the alkene center in the transition states, and thereby possibly reduce to some degree the through-space stabilizing effect of the carbenoid ester group ($R' =$ ester). Silyl and stannyl substituents are effective at stabilizing electropositive character at a β-carbon [14] through orbital hyperconjugation [15], and this effect can be influenced by the ligands on the silyl or stannyl center which attenuate the electron donating ability of the metal–carbon bond [16–18]. Mayr [16] and Brook [17] have determined that the β-cation stabilizing ability of silyl and stannyl groups increases in the order of $(RO)_3Si < Ar_3Si < R_3Si < (RO)_3Sn < Ar_3Sn < R_3Sn$. This corresponds with the steady drop in *trans*:*cis* selectivity we see in the allylsilane cyclopropanation reactions upon changing the silyl ligands (entries 1–3). However, given that the amount of the *trans* product in these cyclopropanations diminishes even further when the silyl center is replaced with stannyl (entries 4 and 5), it would appear that hyperconjugation effects do not decisively influence stereochemistry of these carbenoid additions [19]. Since developing positive charge in the transition states leading to the *trans* and *cis* products should be stabilized equally well by the β-silyl/stannyl group, differences in steric interactions within these two transition states could be of greater importance. Destabilizing forces between R and R′ should increase as the metal center and its ligands become larger, thus decreasing the relative amount of the trans adduct. This could explain the diminishing *trans* selectivity found for entries 1–5 in Table 1. However, the fact that the *trans*:*cis* product ratios do not significantly change suggests that the steric effects of the silyl/stannyl moieties must play a minimal role in stereoregulation of the cyclopropanation process [20].

To provide a clearer picture as to why this might be the case, we postulate an alternative depiction for the cycloaddition process that is based on the well-known open transition state model for allylsilane/stannane additions to aldehyde–Lewis acid complexes [21]. According to this model, attack of the electrophile (E +) occurs from the less shielded face of the allylmetal π-system and antiperiplanar to the allylic carbon–metal bond (Fig. 3). This orientation allows developing cationic charge in the transition state to be stabilized through hyperconjugation with the adjacent ML_3 moiety. Adaptation of the open transition state model to the rhodium-catalyzed cyclopropanations of allylsilanes/stannanes, shown in Fig. 4, suggests that the rhodium carbenoid can orient its substituents either *endo* and *exo* to the allylmetal π-system during the addition process. This arrangement is effectively equivalent to that in the Doyle model for the alkene–rhodium carbenoid π-complex, where the substituents R_{endo} and R_{exo} in the open transition state model correspond to R′ and R″ in the Doyle model, respectively. Substituents on the carbenoid that can stabilize cationic charge in the transition state (e.g. CO_2Et), either through electrostatic or secondary orbital interactions, would prefer to occupy the R_{endo} position and give the *trans* product. Conversely, a sterically repulsive group would favor the more open R_{exo} orientation, affording the *cis* stereoadduct. Indeed, our model reactions of allylmetals **6** with the sterically hindered (trimethylsilyl)diazomethane (entries 6–10 in Table 1) confirm that the favored product is the *cis* cyclopropane ($R_{endo} = H$, $R_{exo} = SiMe_3$ in Fig. 4). The overall low level of stereochemical control exerted by the allylic silyl and stannyl moieties in these additions supports the notion that the bulky ML_3 group must lie well outside the congested regions of the transition state, and distal to the site where C–C bond formation is occurring.

To account for the unusually high stereochemical control in the rhodium-catalyzed vinylcyclopropanations (entries 11–15, Table 1), we cite the earlier proposal [3] by Davies that the transition state leading to the disfavored (minor) adduct suffers serious *destabiliz-*

ing interactions between the alkene substituent and the vinyl moiety, while the transition state leading to the favored (major) cyclopropane product experiences *stabilizing* interactions between the ester and the cationic center (Fig. 5) [22]. For the trimethylsilyl and triphenylsilyl systems (entries 11 and 12), the small amount of *cis* product formed may be due to a still tolerable amount of steric interactions in the transition state leading to the disfavored *cis* compound, which become prohibitive when ML_3 is $Si(OEt)_3$ or SnL_3.

A similar argument can be invoked to explain the complete stereochemical control observed in entries 16–18 of Table 1 for the reactions of allyltriphenylsilane and allyltriphenylstannane with 2-aryl substituted diazoacetates. Here, the additions yield exclusively adducts having the CH_2ML_3 and ester groups *trans* on the ring. Application of the Doyle/Davies models would indicate that steric repulsion between the CH_2ML_3 moiety and the carbenoid aryl ring in the π-complex (and subsequent transition state) leading to the disfavored cyclopropane product would be severe (Fig. 6).

In conclusion, these investigations indicate that the factors which typically govern *trans*:*cis* stereoselection

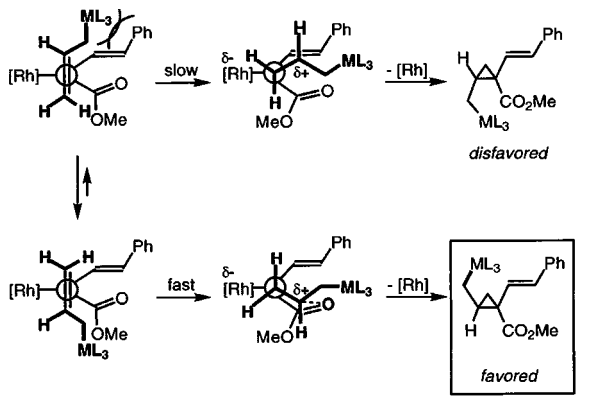


Fig. 5. Pathways for $Rh_2(OAc)_4$-catalyzed cyclopropanation of allylmetals **6** with methyl 2-diazo-4-phenyl-3-butenoate.

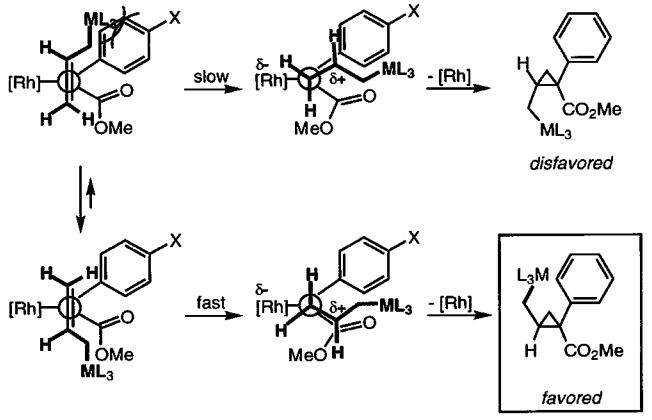


Fig. 6. Pathways for $Rh_2(OAc)_4$-catalyzed cyclopropanation of allylmetals **6** with methyl 2-diazo-2-arylacetates.

in rhodium-catalyzed cyclopropanations of alkenes remain dominant for the corresponding reactions involving allylsilane and allystannane substrates. Although the silyl/stannyl centers and their ligands do provide a secondary influence on *trans*:*cis* product ratios, these affects are relatively small and appear to be primarily steric in nature. Our results can best be explained by the combination of the Doyle and open transition state models, which places the allylic silyl/stannyl moiety outside the sterically congested regions and well away from where bond formation is occurring in the transition state. This precludes the ML_3 group from playing a more prominent role in controlling the reaction stereochemistry. Hyperconjugative stabilization of positive charge by the silyl and stannyl substituents in the transition state may be a contributing factor in the reactions, but does not play a significant role in regulating the *trans*:*cis* stereoselection. These concepts may be extended to related metal-catalyzed cyclopropanation reactions involving other types of alkene substrates bearing allylic substitution.

4. Experimental

4.1. General

All organic reagents were purchased from Aldrich Chemical Company and used without further purification. Solvents were obtained from Fisher Scientific Company. CH_2Cl_2 was distilled from CaH_2 under nitrogen immediately before use. All reactions were performed under an argon or nitrogen atmosphere using glassware and syringes that had been pre-dried overnight at 120 °C. Thin layer chromatography (TLC) was carried out using EM Reagent plates with a fluorescence indicator (SiO_2-60, F-254). Products were purified by flash chromatography using J.T. Baker flash chromatography silica gel (40 μ). ^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ solution on Varian Inova-500, Inova-400, and VXR-300 instruments or Bruker AMX-360 and AMX-250 spectrometers. For sequential ^{1}H-NMR assignments, one-dimensional nuclear Overhauser enhancement difference spectroscopy (1D NOE), two-dimensional correlation spectroscopy (2D COSY), two-dimensional rotating frame Overhauser enhancement spectroscopy (2D ROESY), and two-dimensional total correlation spectroscopy (2D TOCSY) experiments were performed. 1D NOE difference spectra were recorded on a Varian Inova-500 and a Bruker AMX-360 using multiple irradiation with 32 scans each. 2D spectra were acquired in a phase sensitive mode using time proportional phase increments (TPPI), a phase sensitive four-quadrant transformation, on a Bruker AMX-360. 1024 data points were acquired over a 3.6 kHz spectral width for 128 increments. Eight to sixty-four scans plus two to four dummy scans were

acquired per increment. 2D data sets were multiplied in both dimensions by a sinebell squared function and zero filled to 512 in both dimensions. The IR spectra were measured in CH_2Cl_2 solution on a Perkin–Elmer Paragon 1000 Series Model FT Infrared Spectrophotometer. Mass spectra were run using chemical ionization (CI) with isobutane as the ionizing gas. High-resolution mass spectra were obtained using either CI with perfluorokerosene as an internal standard or electron impact (EI). Elemental analyses were performed by Atlantic Microlabs, Inc., Norcross, GA.

4.2. Preparation of cyclopropyl esters

A solution of ethyl diazoacetate (173 mg, 1.51 mmol) in 1 ml of CH_2Cl_2 was added dropwise over 5 h to a 1 ml CH_2Cl_2 solution of allyltriphenylsilane (500 mg, 1.66 mmol) and rhodium(II) acetate (3.3 mg, 7.6 μmol) at room temperature (r.t.) under nitrogen. The solution was stirred for an additional 1 h at r.t. and then evaporated. The *cis* and *trans* isomers of 1-ethoxycarbonyl-2-(triphenylsilylmethyl)cyclopropane were separated by column chromatography with a mixed solvent gradient of petroleum ether and CH_2Cl_2 to give 231 mg (40%) of *cis*-1-ethoxycarbonyl-2-(triphenylsilylmethyl)-cyclopropane and 323 mg (55%) of *trans*-1-ethoxycarbonyl-2-(triphenylsilylmethyl)cyclopropane as white solids.

4.2.1. cis-1-Ethoxycarbonyl-2-(triphenylsilylmethyl)-cyclopropane

Melting point: 61–62 °C. ^{1}H-NMR (500 MHz) δ 7.55 (dd, 6H, $J = 7.5$, 1.5 Hz), 7.41 (tt, 3H, $J = 7.5$, 1.5 Hz), 7.36 (t, 6H, $J = 7.5$ Hz), 4.09 (dq, 1H, $J = 10.5$, 7.0 Hz), 3.95 (dq, 1H, $J = 10.5$, 7.0 Hz), 1.71 (m, 2H), 1.63 (m, 1H), 1.41 (m, 1H), 1.22 (t, 3H, $J = 7.0$ Hz), 0.95 (m, 1H), 0.84 (m, 1H). ^{13}C-NMR (125 MHz) δ 175.0, 136.5, 135.3, 130.4, 128.7, 61.0, 23.6, 19.3, 18.8, 18.7, 15.1. IR 1723 cm^{-1}. EIMS; m/z 386.2 ([M$^+$]). Anal. Found: C, 77.80; H, 6.84. Calc. for $C_{25}H_{26}O_2Si$: C, 77.68; H, 6.78%.

4.2.2. trans-1-Ethoxycarbonyl-2-(triphenylsilylmethyl)-cyclopropane

Melting point: 73–74 °C. ^{1}H-NMR (500 MHz) δ 7.54 (dt, 6H, $J = 7.0$, 1.0 Hz), 7.42 (tt, 3H, $J = 7.0$, 1.0 Hz), 7.37 (t, 6H, $J = 7.0$ Hz), 4.03 (m, 2H), 1.62 (dd, 1H, $J = 14.5$, 6.0 Hz), 1.52 (m, 1H), 1.32 (dd, 1H, $J = 14.5$, 7.5 Hz), 1.30 (m, 1H), 1.22 (t, 3H, $J = 7.0$ Hz), 1.10 (m, 1H), 0.60 (m, 1H). ^{13}C-NMR (125 MHz) δ 173.6, 136.5, 135.5, 130.2, 128.6, 61.0, 20.3, 18.4, 16.4, 15.1, 11.5. Anal. Found: C, 77.53; H, 6.81. Calc. for $C_{25}H_{26}O_2Si$: C, 77.68; H, 6.78%.

4.2.3. cis- and trans-1-Ethoxycarbonyl-2-(triethoxysilylmethyl)cyclopropane

Crude yellow oil, 399 mg (91%), *trans*:*cis* = 1.2:1, unstable to column chromatography. ^{1}H-NMR (360 MHz) δ 4.22 (m, *cis*, 1H), 4.14 (m, *cis*, 1H), 4.08 (m, *trans*, 2H), 3.80 (m, *cis*/*trans*, 6H), 1.66 (m, *cis*, 1H), 1.35 (m, *trans*, 2H), 1.32 (m, *trans*, 1H), 1.28 (m, *cis*, 2H), 1.20 (m, *cis*/*trans*, 12H), 1.40 (m, *cis*, 1H), 0.90 (m, *trans*, 1H), 0.88 (m, *cis*, 1H), 0.83 (m, *trans*, 1H), 0.70 (m, *trans*, 1H), 0.58 (dd, *cis*, 1H, $J = 15.2$, 7.5 Hz). ^{13}C-NMR (90 MHz) δ 174.6 (*trans*), 173.1 (*cis*), 133.8 (*cis*), 130.0 (*trans*), 60.4 (*trans*), 60.3 (*cis*), 58.6 (*trans*), 58.5 (*cis*), 22.3 (*trans*), 19.3(*cis*), 18.4 (*cis*/*trans*), 17.5 (*trans*), 17.4 (*cis*), 16.5 (*trans*), 15.3 (*cis*), 15.1 (*trans*), 14.5 (*cis*), 14.4 (*trans*), 8.3 (*cis*). HRMS; m/z: Found: 291.1611. Calc. for $C_{17}H_{25}O_2Si$: 291.1620 [M + 1].

4.2.4. cis-1-Ethoxycarbonyl-2-(tributylstannylmethyl)-cyclopropane

Colorless oil, 234 mg (38%). ^{1}H-NMR (360 MHz) δ 4.08 (m, 2H), 1.65 (m, 1H), 1.56 (m, 2H), 1.43 (m, 4H), 1.27 (m, 9H), 1.51 (m, 1H), 0.97 (m, 3H), 0.83 (m, 15H). ^{13}C-NMR (90 MHz) δ 174.1, 60.0, 29.2, 27.4, 21.1, 20.8, 15.8, 14.3, 8.9, 6.4.

4.2.5. trans-1-Ethoxycarbonyl-2-(tributylstannylmethyl)-cyclopropane

Colorless oil, 344 mg (56%). ^{1}H-NMR (360 MHz) δ 4.11 (q, 2H, $J = 7.1$ Hz), 1.60 (m, 2H), 1.46 (m, 6H), 1.41 (m, 1H), 1.32 (m, 6H), 1.26 (m, 12H), 1.01 (dd, 1H, $J = 12.9$, 6.1 Hz), 0.90 (t, 15H, $J = 7.3$ Hz), 0.81 (1m, H), 0.67 (m, 2H). ^{13}C-NMR (90 MHz) δ 174.6, 60.4, 29.4, 27.6, 24.4, 22.4, 19.1, 14.5, 13.9, 13.5, 9.2.

4.2.6. cis-1-Ethoxycarbonyl-2-(triphenylstannylmethyl)-cyclopropane

Colorless oil, 310 mg (43%). ^{1}H-NMR (360 MHz) δ 7.57 (m, 6H), 7.39 (m, 9H), 4.08 (m, 1H), 3.94 (m, 1H), 1.82 (m, 1H), 1.72 (m, 1H), 1.58 (m, 2H), 1.20 (t, 3H, $J = 7.2$ Hz), 1.02 (m, 1H), 0.95 (m, 1H). ^{13}C-NMR (90 MHz) δ 172.8, 138.8, 137.3, 129.0, 129.0, 128.7, 21.5, 20.2, 16.5, 14.8, 9.1. CIMS; m/z: 478.2 ([M + 1]).

4.2.7. trans-1-Ethoxycarbonyl-2-(triphenylstannylmethyl)cyclopropane

White solid, 382 mg (53%); m.p: 85–86 °C. ^{1}H-NMR (360 MHz) δ 7.56 (m, 6H), 7.38 (m, 9H), 4.03 (m, 2H), 1.69 (m, 2H), 1.41 (m, 2H), 1.24 (m, 1H), 1.21 (t, 3H, $J = 7.1$ Hz), 0.74 (m, 1H). ^{13}C-NMR (90 MHz) δ 174.1, 138.5, 137.2, 129.1, 128.8, 24.5, 21.3, 19.1, 15.8, 14.4. CIMS; m/z: 478.2 ([M + 1]).

4.3. Procedure for the preparation of trimethylsilyl-substituted cyclopropanes

(Trimethylsilyl)diazomethane (2 M in hexane, 1 ml, 2.0 mmol) was added dropwise over 5 h into a 1 ml

CH_2Cl_2 solution of allyltrimethylsilane (215 mg, 2.2 mmol) and rhodium(II) acetate (3.3 mg, 7.6 mmol) at r.t. under nitrogen. The solution was stirred further for 1 h at r.t. and then concentrated. The crude sample was purified by column chromatography with pentane to give 385 mg (96%) of 1-trimethylsilyl-2-(trimethylsilylmethyl)cyclopropane (*trans*:*cis* = 1:2.0) as a colorless oil. ^{1}H-NMR (360 MHz) δ 0.99 (m, *trans*, 1H), 0.93 (m, *trans*, 1H), 0.78 (m, *trans*, 1H), 0.69 (dd, *cis*, 1H, J = 14.4, 6.1 Hz), 0.56 (m, *cis*, 1H), 0.43 (dd, *cis*, 1H, J = 14.4, 7.6 Hz), 0.36 (tt, *cis*, 1H, J = 7.2, 3.2 Hz), 0.22 (m, *cis*, 1H), 0.03 (s, *cis*, 18H), −0.06 (s, *trans*, 18H), −0.44 (tt, *trans*, 1H, J = 9.0, 8.3 Hz), –0.68 (tt, *cis*, 1H, J = 9.7, 6.1 Hz). ^{13}C-NMR (90 MHz) δ 24.0 (*cis*), 19.8 (*trans*), 12.0 (*trans*), 11.2 (*cis*), 10.8 (*cis*), 10.7 (*trans*), 6.5 (*cis*), 3.7 (*trans*), 0.2 (*trans*), −1.1 (*cis*), −1.4 (*trans*) −2.0 (*cis*). Anal. Found: C, 60.02; H, 11.83. Calc. for $C_{10}H_{24}Si_2$: C, 59.91; H, 12.07%.

4.3.1. cis-and trans-1-(Trimethylsilyl)-2-(triphenylsilylmethyl)cyclopropane

Colorless oil, 750 mg (97%), *trans*:*cis* = 1:2.4. ^{1}H-NMR (360 MHz) δ 7.6 (m, *cis*/*trans*, 6H), 7.42 (m, *cis*/*trans*, 9H), 1.95 (dd, *trans*, 1H, J = 14.4, 2.2 Hz), 1.57 (dd, *cis*, 1H, J = 14.8, 6.1 Hz), 1.47 (dd, *cis*, 1H, J = 14.8, 6.5 Hz), 1.19 (m *trans*, 1H), 1.04 (dd, *trans*, 1H, J = 14.4, 10.8 Hz), 0.80 (m, *cis*, 1H), 0.73 (m, *trans*, 1H), 0.37 (m, *cis*, 1H), 0.31 (m, *cis*, 1H), 0.09 (s, *trans*, 9H), 0.03 (m, *trans*, 1H), −0.17 (s, *cis*, 9H), −0.34 (m, *trans*, 1H), −0.51 (m, *cis*, 1H). ^{13}C-NMR (90 MHz) δ 136.0 (*trans*), 135.9 (*cis*), 135.6 (*cis*), 135.5 (*trans*), 129.6 (*cis*/*trans*), 128.0 (*cis*/*trans*), 20.7 (*cis*), 16.8 (*trans*), 12.0 (*trans*), 11.9 (*trans*), 11.7 (*cis*), 11.1 (*cis*), 7.9 (*cis*), 4.9 (*trans*), 0.2 (*trans*), −2.2 (*cis*). Anal. Found: C, 77.91; H, 8.02. Calc. for $C_{25}H_{30}Si_2$: C, 77.65; H, 7.82%.

4.3.2. cis- and trans-1-(Tributylstannylmethyl)-2-(trimethylsilyl)cyclopropane

Colorless oil, 793 mg (95%), *trans*:*cis* = 1:1.4. ^{1}H-NMR (360 MHz) δ 1.50 (m, *cis*/*trans*, 6H), 1.31 (m, *cis*/*trans*, 6H), 1.19 (m, *cis*, 1H), 0.90 (m, *cis*/*trans*, 15H), 0.73 (m, *trans*, 1H), 0.40 (m, *trans*, 2H), 0.23 (m, *cis*, 1H), 0.05 (s, *trans*, 9H), −0.03 (m, *cis*, 2H), −0.37 (m, *trans*, 1H), −0.69 (m, *cis*, 1H). ^{13}C-NMR (90 MHz) δ 29.5 (*cis*/*trans*), 27.9 (*cis*/*trans*), 16.6 (*cis*), 15.0 (*trans*), 14.2 (*cis*), 14.0 (*cis*/*trans*), 12.8 (*trans*), 12.6 (*cis*), 11.7 (*trans*), 9.2 (*cis*/*trans*), 9.1 (*cis*), 6.8 (*trans*), 0.3 (*trans*), −1.9 (*cis*). CIMS; m/z: 418.2 ([M + 1]).

4.3.3. cis- and trans-1-(Trimethylsilyl)-2-(triphenylstannylmethyl)cyclopropane

Colorless oil, 916 mg (96%), *trans*:*cis* = 1:1.7. ^{1}H-NMR (360 MHz) δ 7.61 (m, *cis*/*trans*, 6H), 7.41 (m, *cis*/*trans*, 9H), 2.04 (dd, *trans*, 1H, J = 12.6, 2.9 Hz), 1.73 (dd, *cis*, 1H, J = 13.0, 6.5 Hz), 1.58 (dd, *cis*, 1H, J = 13.0, 7.6 Hz), 1.37 (m, *trans*, 1H), 1.20 (t, *trans*, 1H, J = 12.6 Hz), 1.01 (m, *cis*, 1H), 0.43 (m, *cis*, 1H), 0.40 (m, *trans*, 1H), 0.12 (s, *trans*, 9H), −0.15 (s, *cis*, 9H), −0.22 (m, *trans*, 1H), −0.45 (m, *cis*, 1H). ^{13}C-NMR (90 MHz) δ 139.5 (*cis*), 139.4 (*trans*), 137.3 (*cis*/*trans*), 129.0 (*cis*/*trans*), 128.6 (*cis*/*trans*), 18.9 (*cis*), 15.3 (*trans*), 14.7 (*trans*), 13.7 (*cis*), 12.9 (*cis*), 12.1 (*cis*), 9.9 (*trans*), 7.5 (*cis*), 0.3 (*trans*), −2.2 (*cis*). CIMS; m/z: 478.2 ([M + 1]).

4.4. Procedure for the preparation of 1-(2-phenylethenyl)- and 1-aryl-substituted cyclopropanes esters

A solution of methyl 2-diazo-4-phenyl-3-butenoate (483 mg, 2.39 mmol) dissolved in 1 ml of CH_2Cl_2 was added dropwise over 5 h into a 1 ml CH_2Cl_2 solution of allyltrimethylsilane (300 mg, 2.63 mmol) and rhodium(II) acetate (5.3 mg, 11.9 mmol) at r.t. under nitrogen. The solution was stirred for 1 h at r.t. and then concentrated. The residue was triturated with 5 ml of hexanes and filtered, and the solvent was removed under reduced pressure. The diastereomers were separated by column chromatography with a mixed solvent gradient of petroleum ether and CH_2Cl_2 to afford 616 mg (89%) of *E*-(1*R**,2*R**)-1-methoxycarbonyl-1-(2-phenylethenyl) - 2 - (trimethylsilylmethyl)cyclopropane and 46 mg (7%) of *E*-(1*S**,2*R**)-1-methoxycarbonyl-1-(2-phenylethenyl)-2-(trimethylsilylmethyl)cyclopropane as colorless oils.

4.4.1. E-(1R*,2R*)-1-Methoxycarbonyl-1-(2-phenylethenyl)-2-(trimethylsilylmethyl)cyclopropane

^{1}H-NMR (500 MHz) δ 7.43 (d, 2H, J = 7.5 Hz), 7.33 (t, 2H, J = 7.5 Hz), 7.24 (t, 1H, J = 7.5 Hz), 6.66 (d, 1H, J = 16.0 Hz), 6.31 (d, 1H, J = 16.0 Hz), 3.71 (s, 3H), 1.69 (m, 2H), 1.04 (m, 1H), 0.76 (dd, 1H, J = 16.0, 4.0 Hz), 0.33 (m, 1H), 0.03 (s, 9H). ^{13}C-NMR (90 MHz) δ d 175.2, 137.3, 132.0, 128.7, 127.6, 126.5, 125.2, 52.3, 31.0, 28.8, 21.1, 15.7, −1.3. IR 1749 cm^{-1}. CIMS (isobutene); m/z: 289.2 ([M + 1]). HRMS (CI, isobutane) Found: 289.1599. Calc. for $C_{17}H_{25}O_2Si$ 289.1625 [M + 1].

4.4.2. E-(1S*,2R*)-1-Methoxycarbonyl-1-(2-phenylethenyl)-2-(trimethylsilylmethyl)cyclopropane

^{1}H-NMR (500 MHz) δ 7.36 (d, 2H, J = 7.0 Hz), 7.30 (t, 2H, J = 7.0 Hz), 7.21 (tt, 1H, J = 7.5, 1.5 Hz), 6.90 (d, 1H, J = 16.5 Hz), 6.19 (d, 1H, J = 16.5 Hz), 3.75 (s, 3H), 1.50 (m, 2H), 1.33 (m, 1H), 0.91 (dd, 1H, J = 15.0, 5.0 Hz), 0.73 (dd, 1H, J = 15.0, 10.5 Hz), 0.05 (s, 9H). ^{13}C-NMR (90 MHz) δ 172.6, 137.5, 130.0, 128.7, 127.3, 126.5, 126.3, 52.16, 32.1, 32.0, 22.5, 15.4, −1.3.

4.4.3. E-(1R,2R*)-1-Methoxycarbonyl-1-(2-phenylethenyl)-2-(triphenylsilylmethyl)cyclopropane*

Colorless oil, 924 mg (81%). ^{1}H-NMR (500 MHz) δ 7.52 (dd, 6H, $J = 8.0$, 1.0 Hz), 7.44 (tt, 3H, $J = 8.0$, 1.5 Hz), 7.37 (m, 11H), 6.28 (d, 1H, $J = 16.0$ Hz), 6.24 (d, 1H, $J = 16.0$ Hz), 3.64 (s, 3H), 1.92 (m, 1H), 1.55 (dd, 1H, $J = 9.0$, 5.0 Hz), 1.52 (dd, 1H, $J = 15.0$, 6.0 Hz), 1.37 (dd, 1H, $J = 15.0$, 8.0 Hz), 0.99 (dd, 1H, $J = 6.5$, 5.0 Hz). ^{13}C-NMR (125 MHz) δ 175.5, 137.6, 136.4, 135.1, 132.8, 130.3, 129.2, 128.6, 128.2, 127.1, 125.4, 52.8, 32.3, 28.3, 21.9, 13.0. IR 1723 cm^{-1}. Anal. Found: C, 81.23; H, 6.01. Calc. for $C_{32}H_{30}O_2Si$: C, 80.97; H, 6.37%.

4.4.4. E-(1S,2R*)-1-Methoxycarbonyl-1-(2-phenylethenyl)-2-(triphenylsilylmethyl)cyclopropane*

Colorless oil, 97 mg (9%). ^{1}H-NMR (360 MHz) δ 7.55 (m, 6H), 7.38 (m, 9H), 7.18 (m, 1H), 6.72 (d, 1H, $J = 16.1$ Hz), 6.04 (d, 1H, $J = 16.1$ Hz), 3.65 (s, 3H), 1.82 (dd, 1H, $J = 14.8$, 4.8 Hz), 1.66 (dd, 1H, $J = 14.8$, 8.9 Hz), 1.49 (m, 1H), 1.39 (m, 2H). ^{13}C-NMR (90 MHz) δ 172.5, 137.4, 136.0, 134.7, 129.8, 129.6, 128.7, 128.1, 127.4, 126.9, 126.3, 52.3, 32.6, 30.9, 23.2, 12.1.

4.4.5. E-(1R,2R*)-1-Methoxycarbonyl-1-(2-phenylethenyl)-2-(triethoxysilylmethyl)cyclopropane*

Crude yellow oil, 313 mg (93%), unstable to column chromatography. ^{1}H-NMR (400 MHz) δ 7.39 (d, 2H, $J = 7.6$ Hz), 7.30 (t, 2H, $J = 7.6$ Hz), 7.22 (t, 1H, $J = 7.6$ Hz), 6.66 (d, 1H, $J = 16.0$ Hz), 6.30 (d, 1H, $J = 16.0$ Hz), 3.81 (q, 6H, $J = 7.2$ Hz), 3.68 (s, 3H), 1.77 (m, 1H), 1.67 (dd, 1H, $J = 9.2$, 4.8 Hz), 1.21 (t, 3H, $J = 7.2$ Hz), 1.11 (dd, 1H, $J = 6.8$, 4.4 Hz), 0.83 (dd, 1H, $J = 15.2$, 5.6 Hz), 0.49 (dd, 1H, $J = 15.2$, 10.0 Hz). ^{13}C-NMR (90 MHz) δ 174.7, 137.0, 132.0, 128.4, 127.3, 126.2, 124.7, 58.4, 52.0, 31.1, 26.5, 20.6, 18.2, 9.7. IR 1718 cm^{-1}. HRMS (CI, isobutane). Found: 379.1939. Calc. for $C_{20}H_{31}O_5Si$: 379.1932 [M + 1].

4.4.6. E-(1R,2R*)-1-(Methoxycarbonyl)-1-(2-phenylethenyl)-2-(tributylstannylmethyl)cyclopropane*

Colorless oil, 418 mg (93%). ^{1}H-NMR (360 MHz) δ 7.42 (d, 2H, $J = 7.6$ Hz), 7.31 (t, 2H, $J = 7.6$ Hz), 7.23 (d, 1H, $J = 7.6$ Hz), 6.67 (d, 1H, $J = 16.0$ Hz), 6.31 (d, 1H, $J = 16.0$ Hz), 3.69 (s, 3H), 1.84 (m, 1H), 1.70 (dd, 1H, $J = 9.0$, 4.3 Hz), 1.46 (m, 6H), 1.28 (m, 9H), 1.03 (dd, 1H, $J = 6.8$, 4.7 Hz), 1.92 (m, 1H), 0.87 (m, 12H), 0.69 (dd, 1H, $J = 12.6$, 10.8 Hz). ^{13}C-NMR (90 MHz) δ 174.6, 131.8, 128.6, 127.4, 126.3, 126.1, 124.8, 52.5, 33.1, 32.0, 29.2, 27.1, 22.0, 13.8, 9.2, 7.8. IR 1723 cm^{-1}. CIMS; m/z: 506.3 ([M + 1]).

4.4.7. E-(1R,2R*)-1-(Methoxycarbonyl)-1-(2-phenylethenyl)-2-(triphenylstannylmethyl)-cyclopropane*

Colorless oil, 463 mg (92%). ^{1}H-NMR (360 MHz) δ 7.50 (m, 6H), 7.31 (m, 14H), 6.49 (d, 1H, $J = 16.2$ Hz), 6.29 (d, 1H, $J = 16.2$ Hz), 3.59 (s, 3H), 2.04 (m, 1H), 1.59 (m, 2H), 1.51 (dd, 1H, $J = 8.3$, 6.2 Hz), 1.09 (dd, 1H, $J = 6.2$, 4.8 Hz). ^{13}C-NMR (90 MHz) δ 174.5, 138.4, 137.2, 132.4, 129.2, 129.0, 128.8, 127.6, 126.6, 124.4, 52.2, 33.0, 30.3, 22.2, 10.6. IR 1723 cm^{-1}. CIMS; m/z: 566.3 ([M + 1]).

4.4.8. (1R,2R*)-1-Methoxycarbonyl-1-phenyl-2-(triphenylsilylmethyl)cyclopropane*

Colorless oil, 450 mg (96%). ^{1}H-NMR (360 MHz) δ 7.47–7.18 (m, 20H), 3.53 (s, 3H), 2.05 (m, 1H), 1.64 (ABm, 2H), 0.89 (dd, 1H, $J =$ 6.5, 4.3 Hz), 0.42 (dd, 1H, $J = 14.8$, 11.2 Hz). Anal. Found: C, 80.54; H, 6.49. Calc. for $C_{30}H_{28}O_2Si$: C, 80.32; H, 6.29%.

4.4.9. (1R,2R*)-1-Methoxycarbonyl-1-(4-nitrophenyl)-2-(triphenylsilylmethyl)cyclopropane*

Colorless oil, 380 mg (96%). ^{1}H-NMR (360 MHz) δ 8.15 (d, 2H, $J = 10.8$ Hz), 7.42–7.21 (m, 17H), 3.51 (s, 3H), 2.09 (m, 1H), 1.68 (m, 1H), 1.52 (m, 1H), 0.87 (dd, 1H, $J = 6.5$, 4.3 Hz), 0.30 (dd, 1H, $J = 14.8$, 11.0 Hz). Anal. Found: C, 72.69; H, 5.73. Calc. for $C_{30}H_{27}O_4NSi$: C, 73.00; H, 5.51%.

4.4.10. (1R,2R*)-1-Methoxycarbonyl-1-phenyl-2-(triphenylstannylmethyl)cyclopropane*

Colorless oil, 240 mg (90%). ^{1}H-NMR (360 MHz) δ 7.48–7.16 (m, 20H), 3.52 (s, 3H), 2.11 (m, 1H), 1.70 (m, 1H), 1.55 (m, 1H), 1.00 (dd, 1H, $J = 6.3$, 4.5 Hz), 0.55 (dd, 1H, $J = 14.5$, 10.8 Hz). CIMS; m/z: 540.3 ([M + 1]).

Acknowledgements

E.T. thanks the Spanish Ministerio de Educacion y Cultura for a grant (SAB1999-0001), and Professor Jose Barluenga (University of Oviedo, Spain) and members of his research group for their hospitality and helpful discussions during the preparation of this manuscript. We also thank the Department of Chemistry at University of South Florida for funds to carry out this research.

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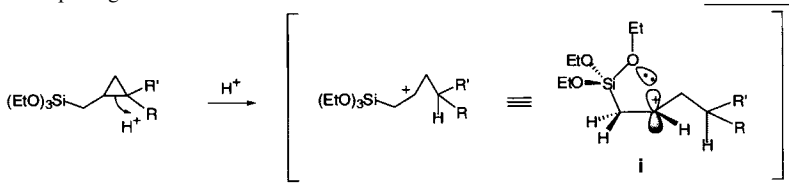

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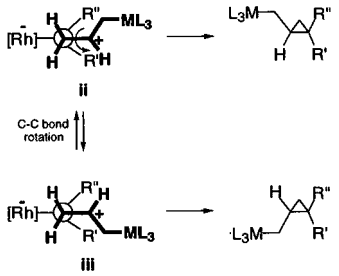
[19] An alternative explanation for the poor stereochemical control in these reactions may be that there is formation of a stable zwitterionic intermediate **ii**, whose lifetime may be sufficiently long to permit C–C bond rotation to **iii** to lead to the other cyclopropane diastereomer. This possibility seems unlikely, however, since reactions carried out in polar versus non-polar solvents, or in the presence of nucleophilic trapping agents, failed to alter product ratios or afford any demetalated side products derived from such zwitterionic structures.



[20] Previous studies on the rhodium acetate-catalyzed cyclopropanation of monosubstituted alkenes with diazoacetates indicate that *trans*:*cis* selectivity can be increased by enlarging the steric dimensions of the alkene and ester substituents. Generally, these steric effects are limited to cases where the two groups are highly branched. See: M.P. Doyle, V. Bagheri, T.J. Wandless, N.K. Harn, D.A. Brinker, C.T. Eagle, K.L. Loh, J. Am. Chem. Soc. 112 (1990) 1906.

[21] For representative examples and discussions of the open transition state model applied to allylsilane and allylstannane additions to carbonyl compounds, see: (a) S.E. Denmark, E.J. Weber, J. Am. Chem. Soc., 106 (1984) 7970;
(b) S.E. Denmark, E.J. Weber, J. Helv. Chim. Acta. 66 (1983) 1655;
(c) T. Hayashi, K. Kabeta, I. Hamaachi, M. Kumada, Tetrahedron Lett. 24 (1983) 2865;
(d) Y. Yamamoto, H. Yatagai, Y. Ishikawa, N. Maeda, K. Maruyama, Tetrahedron 40 (1984) 2239;
(e) Y. Yamamoto, H. Yatagai, Y. Naruta, K. Maruyama, J. Am. Chem. Soc. 102 (1980) 7107;
(f) H. Sakurai, Pure Appl. Chem. 54 (1982) 1;
(g) R.W. Hoffmann, Angew. Chem. Int. Ed. Engl. 21 (1982) 555;
(h) A. Hosomi, H. Sakurai, Tetrahedron Lett. 17 (1976) 1295;
(i) G.E. Keck, D.E. Abbott, E.P. Boden, E.J. Ehnolm, Tetrahedron Lett. 25 (1984) 3927;
(j) W.R. Roush, K. Ando, D.B. Powers, A.D. Palkowitz, R.L. Halterman, J. Am. Chem. Soc. 112 (1990) 6339.

[22] This effect can apparently be reduced when highly electron-rich alkenes (e.g. enol ethers) are employed as substrates, giving lower *trans*:*cis* selectivities than those of unactivated alkenes (e.g. 1-hexene). Refer: H.M.L. Davies, B. Hu, J. Org. Chem. 57 (1992) 3186.