Catalytic and Photochemical Cyclopropanation of Alkenes with Methyl Diazo(trialkylsilyl)acetates: Steric Effects and Thermodynamic Stabilities of Cyclopropanes

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Diazo esters **1** (N_2=C(SiR_3)COOMe; R = Me (**1a**), Et (**1b**), *i*-Pr (**1c**)) have been decomposed in styrene, 1-hexene, and cyclohexene under Cu, Rh, or Ru catalysis as well as by photochemical means with the objective to evaluate the effectiveness and diastereoselectivity of the respective cyclopropanation reaction. With styrene and 1-hexene as substrates, the ability of the catalysts followed the order CuOTf > $[Ru_2(CO)_4(\mu\text{-}OAc)_2]_n \approx Rh_2(OAc)_4$, but even CuOTf (copper(I) triflate) did not promote cyclopropanation of 1-hexene with the bulky **1c**. Cyclopropanation of cyclohexene with **1a**,**b** succeeded only with the ruthenium catalyst. In all cases, the diastereoisomer having the silyl group anti to the vicinal methyl or phenyl substituent(s) was formed preferentially. In contrast, in the photochemical reactions of **1a**,**c** with styrene and of **1a** with 1-hexene the diastereoisomer having the silyl group syn to the vicinal substituent(s) was formed preferentially. The fluoride-induced desilylation of cyclopropanes **2a**,**c**,**e** was accompanied by a loss of stereochemical integrity. The X-ray crystal structure analysis of the cyclopropane (*E*)-**2f** has been determined. The relative thermodynamic stabilities of various 2-R-1-X-cyclopropanecarboxylates (R = Me, Ph; X = Me, *t*-Bu, SiH_3, $SiMe_3$, Si(*i*-Pr)$_3$) have been calculated by density functional theory methods. These calculations show that for X = $SiMe_3$ and R = Ph the syn−anti energy difference is ca. 0, while for R = Me the anti isomer is more stable.

Introduction

The transition-metal-catalyzed decomposition of a diazo compound in the presence of an alkene is an important method in cyclopropane synthesis.[1] The catalyst metal[2] and its ligands[3−5] usually do not affect the diastereoselectivity of the cyclopropanation reaction to a large extent.[6] For reactions with simple alkyl diazoacetates, the less sterically encumbered trans (or anti or exo) diastereomer is usually obtained as the major product in a ratio of less than 2−3 from monosubstituted alkenes and less than 4 from 1,2-disubstituted alkenes. Preferential formation of the thermodynamically disfavored cis (or syn or endo) isomer is the

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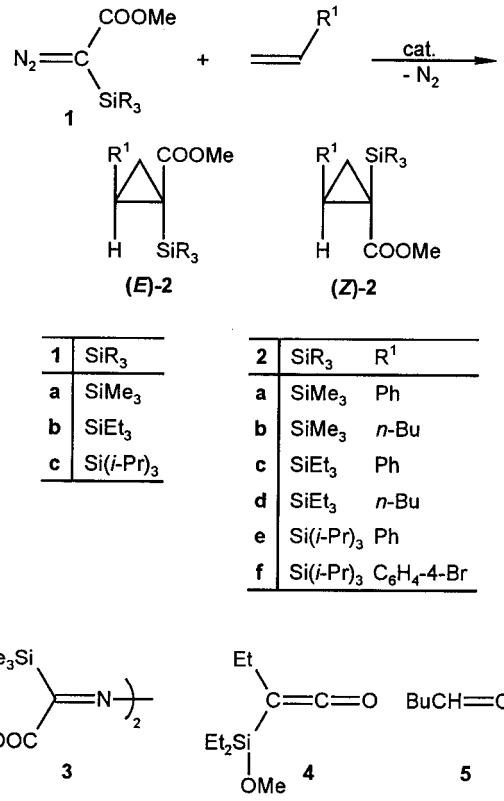
exception.[4b,5] Stereocontrol by the diazo compound has attracted less attention, since most systematic studies have been carried out with simple diazoacetic esters. While the use of a bulky ester residue does not per se guarantee a marked and predictable change of diastereoselectivity, significantly enhanced trans selectivity has been found in special cases, where a bulky diazoacetic ester was combined with the "right" catalyst.[3,7]

Surprisingly little is known about the diastereoselectivity of disubstituted diazo compounds. Only recently, exceptionally high diastereoselectivities (up to 98:2) have been reported for cyclopropanations of monosubstituted alkenes with vinyldiazoacetates[8] and phenyldiazoacetates[8c,9] catalyzed by dinuclear dirhodium prolinates and carboxamidates or by a copper bis(1,3-oxazoline) complex. Therefore, we decided to study to what extent the diastereoselectivity of cyclopropane formation could be controlled by utilizing diazo(trialkylsilyl)acetates having SiR_3 groups with different steric demand. Schöllkopf and co-workers[10] have already studied the photolysis of ethyl diazo(trimethylsilyl)-acetate in the presence of simple alkenes such as isobutene, *cis*- and *trans*-2-butene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene. With *cis*-2-butene, they observed only a 54:46 preference for the cyclopropane which had the Me_3Si group anti to the two vicinal methyl groups. Ruthenium(I)-catalyzed cyclopropanation of mono- and disubstituted alkenes with methyl diazo(trimethylsilyl)acetate also exhibited a preference for the sterically less congested diastereomer.[11]

In cyclopropanation reactions with diazo(trialkylsilyl)-acetates, the choice of the catalyst is expected to be more crucial for the effectiveness of the reaction than in simple diazoacetates, since the diazo carbon atom is not only sterically shielded by the trialkylsilyl group but also rendered less nucleophilic by the π-acceptor character of the SiR_3 group.[12] For smooth decomposition, a rather electrophilic catalyst, such as copper(I) triflate (CuO_3SCF_3 = CuOTf) and rhodium(II) perfluorobutyrate ($Rh_2(pfb)_4$), is therefore required.[13] On the other hand, it was to be expected that these catalysts would be deactivated by olefin coordination, and therefore, the success of the catalytic cyclopropanation could not be predicted. A similar dilemma has been described for the rhodium(II) carboxylate catalyzed decomposition of rather non-nucleophilic diazo compounds in the presence of 2-propanol, where the decomposition rate decreased as the catalyst became more electrophilic; in this case, alcohol coordination to the catalyst is the likely reason.[14]

Scheme 1



1	SiR_3
a	$SiMe_3$
b	$SiEt_3$
c	$Si(i\text{-}Pr)_3$

2	SiR_3	R^1
a	$SiMe_3$	Ph
b	$SiMe_3$	*n*-Bu
c	$SiEt_3$	Ph
d	$SiEt_3$	*n*-Bu
e	$Si(i\text{-}Pr)_3$	Ph
f	$Si(i\text{-}Pr)_3$	C_6H_4-4-Br

Results and Discussion

Cyclopropanation Reactions. Silyldiazo esters **1a**−**c**, which exhibit significantly different steric bulk of the respective R_3Si group, were chosen for the present study. Copper(I) triflate, $Rh_2(pfb)_4$, and $Rh_2(OAc)_4$ were selected as catalysts; the first two catalysts had already been found to decompose **1a**−**c** smoothly in an inert solvent, whereas $Rh_2(OAc)_4$ had proven to be less well suited and did not decompose **1c**.[13] Diazo esters **1a**−**c** were decomposed by slow addition to styrene or 1-hexene containing these catalysts, to obtain cyclopropanes **2** (Scheme 1). The results are given in Table 1, which also includes experiments utilizing the ruthenium(I) complex $[Ru_2(CO)_4(\mu\text{-}OAc)_2]_n$ (**6**), a compound that has already been shown to catalyze formation of cyclopropanes **2a**,**b** in acceptable yield.[11]

For the reactions sampled in Table 1, the effectiveness of the catalysts for cyclopropanation follows the order CuOTf > $[Ru_2(CO)_4(\mu\text{-}OAc)_2]_n \approx Rh_2(pfb)_4 \gg Rh_2(OAc)_4$. Copper triflate catalyzed each cyclopropanation reaction except for the combination of **1c** with 1-hexene, whereas $Rh_2(OAc)_4$ was only applicable to carbene transfer from **1a** to styrene. The rather low temperature needed for the latter reaction (50 °C) was surprising, since we have observed earlier[13] that **1a** was not decomposed by $Rh_2(OAc)_4$ to an appreciable extent after 3 h in benzene at 80 °C. Use of the rhodium catalysts and of the ruthenium catalyst **6** led to considerable oligo- or polymerization of styrene and 1-hexene. Limitations of the catalytic method were encountered with the sterically most demanding diazo ester **1c**. It is known that both

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Table 1. Cyclopropanation of Styrene and 1-Hexene with Silylated Diazo Esters 1a−c[a]

diazo ester	catalyst (amt (mol %))	*T* (°C)	yield of **2**[b] (%)	(*E*)-**2**: (*Z*)-**2**[c]	other products (amt (%))
		Styrene (R^1 = Ph)			
1a	CuOTf (7.3)	20	82	3.6 (4.0)	
	$Rh_2(OAc)_4$ (6)	50	48	3.4	**3** (14)
	$Rh_2(pfb)_4$ (2.5)	70	53	1.7	
	6 (3.4)	70	67	1.8 (2.2)	
	hν	20	28	0.65	
1b	CuOTf (6.8)	20	61	4.2 (4.7)	
	$Rh_2(OAc)_4$ (6)	90	nr		
	$Rh_2(pfb)_4$ (2.8)	90	<38[d]	∼1.9	
	$Rh_2(pfb)_4$ (2.8)	90[e]			**4**[f]
1c	CuOTf (9)	20	nr		
	CuOTf (9)	20[e]	63	4.7	
	hν	20	30	0.37	
		1-Hexene ($R^1 = C_4H_9$)			
1a	CuOTf (5.6)	20	53	2.9	
	$Rh_2(OAc)_4$ (6)	63	nr		
	$Rh_2(pfb)_4$ (4.5)	20	47	3.2	
	6 (3.2)	63	89	3.2 (3.5)	**5** (5)
	hν	20	73	0.83	
1b	CuOTf (8.2)	20	52	3.0	
	$Rh_2(pfb)_4$ (2.8)	63	nr		
	6 (4.3)	63	57	1.3[g]	
1c	CuOTf	63	nr		
	$Rh_2(pfb)_4$ (2.8)	20	nr		

[a] Reactions were carried out in neat alkene unless stated otherwise. [b] Yields of isolated products are given; nr = no reaction. Cyclopropanes formed from styrene are as follows: **2a** from **1a**, **2c** from **1b**, **2e** from **1c**. Cyclopropanes formed from 1-hexene are as follows: **2b** from **1a**, **2d** from **1b**. [c] Ratios as determined by ^{1}H NMR integration are given first; values obtained by HPLC integration are given in parentheses. [d] Product could not be obtained in analytically pure form. [e] Solvent CH_2Cl_2; styrene to diazoester ratio 5:1. [f] After addition of MeOH, [Et_2(MeO)Si]CH(Et)-COOMe was isolated (48% yield[13]). [g] Determined after distillation.

CuOTf[15] and $Rh_2(pfb)_4$[16] form stable complexes with alkenes, and it can safely be assumed that dissociation of a coordinated alkene molecule followed by association of the diazo compound is necessary to initiate the catalytic process.[1a,b,17] Obviously, the bulky **1c** can no longer replace the 1-hexene ligand at the catalyst metal, whereas with the less strongly coordinating styrene, catalysis by CuOTf becomes effective when the olefin concentration is lowered by dilution with CH_2Cl_2. Catalyst **6** has not been reported to form stable olefin complexes. In this case, we assume that coordination of the bulky diazo ester **1c** to the ruthenium metal with concomitant cleavage of the coordination polymer of **6** is no longer possible.

A different consequence of lowering the alkene concentration by dilution was observed in the $Rh_2(pfb)_4$-catalyzed reaction between **1b** and styrene. With a styrene to diazoacetate ratio of only 5:1, cyclopropanation no longer occurred and ketene **4** was formed by intramolecular transformation of the carbene or metal−carbene intermediate.[13]

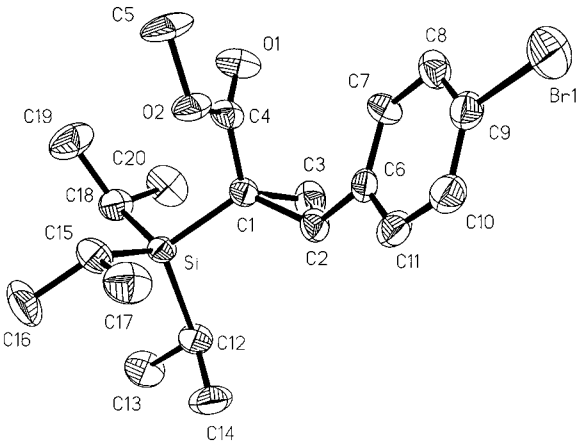

Figure 1. Structure of (*E*)-**2f** in the solid state.

Table 2. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for (*E*)-2f

C1−C2	1.548(6)	C1−C4	1.488(6)
C1−C3	1.501(6)	C1−Si	1.901(4)
C2−C3	1.493(7)	C2−C6	1.492(6)
C2−C1−C3	58.6(3)	C2−C1−C4	115.9(3)
C2−C1−Si	121.4(3)	C4−C1−Si	114.1(3)
C1−C2−C3	59.1(3)	C1−C2−C6	123.0(4)
C3−C2−C6	122.7(4)	C1−C3−C2	62.3(3)
A[a]−C2−C6−C7		−11.8(6)	
B[b]−C1−C4−O1		68.4(6)	

[a] A = midpoint of C1−C3 bond. [b] B = midpoint of C2−C3 bond.

Cyclopropanes **2a−f** were obtained as mixtures of diastereomers. The configurational assignment is based mainly on one or more of the following chemical shift differences in the ^{1}H and ^{13}C NMR spectra.[10,11,18] (a) The ^{1}H NMR signals for COO*Me* and SiC*H*, respectively, in **2a**,**c**,**e**,**f** appear at higher field when these groups are cis to the phenyl substituent. (b) The resonance for 2-H in **2a−f** appears at lower field in the *Z* isomers (i.e., with 2-H cis to COOMe). (c) The ^{13}C NMR signal of the ester carbonyl of all *E* isomers is found at higher field than in the *Z* isomers as a consequence of the *γ* effect. The correctness of these assignments was confirmed by a crystal structure determination of the cyclopropane (*E*)-**2f**, which could be separated from the *Z* diastereomer by column chromatography (Figure 1 and Table 2). According to the stereochemical assignments, the *E*-isomer, *in which the SiR_3 group is positioned trans to the vicinal ring substituent R^1, dominated in all cases*. As the results for the CuOTf-catalyzed cyclopropanation of styrene with **1a−c** show, the preference for this isomer did not increase dramatically from $SiMe_3$ to Si-(*i*-Pr)$_3$ (see below for further discussion). The incomplete set of available data shown in Table 1 does not allow us to draw general conclusions concerning the dependence of the diastereoselectivity on the catalyst. Investigations on alkene cyclopropanation using ethyl diazoacetate have shown that copper catalysts in general produce a higher trans selectivity than rhodium catalysts.[2,3] We made the same observation for the cyclopropanation of styrene with **1a** but not for 1-hexene. On the other hand, the diastereoselectivity obtained for both alkenes is very similar for $Rh_2(pfb)_4$ and [Ru_2-

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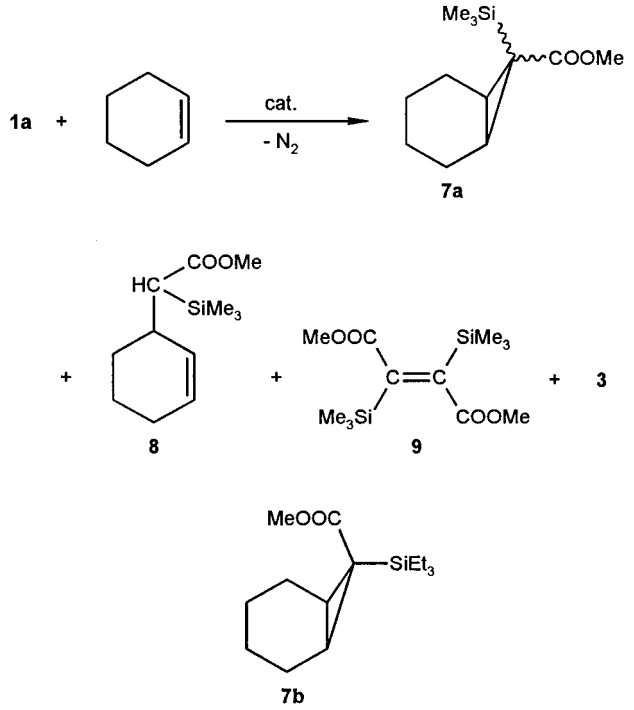
Scheme 2



$(CO)_4(\mu\text{-}OAc)_2]_n$. A control experiment with **2a** (E:Z = 3.6) indicated no geometrical isomerization by $Rh_2(pfb)_4$ at 70 °C.

To evaluate the influence of the catalytic reaction mode on the diastereoselectivity as compared to cyclopropanation with free carbenes, we carried out photolyses of **1a**,**c** in styrene and of **1a** in 1-hexene. We were surprised to find that, in all cases, *the Z isomers of cyclopropanes **2a**,**b**,**e** were formed predominantly*, i.e., with the phenyl or *n*-Bu in **2b** and silyl substituent syn to each other (in contrast to the catalytic reaction mode) and even to a higher extent when the bulky Si(*i*-Pr)$_3$ group was involved, the *Z*:*E* product ratios for **2a**,**e** being 1.5 and 2.7, respectively (Table 1). This result is opposite to Schöllkopf's observations,[10] when he started from **1b** and *cis*-2-butene or 2-methyl-2-butene (see Introduction); moreover, it seems to contrast with the general experience in carbene chemistry,[19] according to which the thermodynamically favored cyclopropane is formed preferentially. To examine this point further, we studied the relative thermodynamic stabilities of diastereomeric pairs of various 2-R-1-X-cyclopropane-1-carboxylates by theoretical calculations (see below).

Decomposition of **1a** by catalytic amounts of CuOTf, Rh(II) carboxylate, or **6** in cyclohexene gave rise to different products (Scheme 2 and Table 3). Bicyclo[4.1.0]-heptanecarboxylate **7a** was obtained only with **6** as catalyst, and as expected,[2−4] the preference for the diastereomer with the bulky $SiMe_3$ group in an exo position (*anti*-$SiMe_3$) was higher than in the case of the monosubstituted alkenes. CuOTf catalysis produced the formal carbene dimers **9**, similar to decomposition of **1a** in an inert solvent.[13] On the other hand, catalysis by

Table 3. Products and Yields of Catalytic Decomposition of 1a,b in Cyclohexene

diazo ester	catalyst (mol %)	temp (°C)	products (yields[a] (%))
1a	CuOTf (8)	20	**9** (36, $E/Z \approx 2.7$)
	$Rh_2(OAc)_4$ (3.7)	83	**8** (32), **3** (4)
	$Rh_2(pfb)_4$ (5.5)	20	**8** (47)
	6 (3.4)	83	**7a** (54[b])
1b	**6** (3.4)	83	**7b** (61[c])

[a] Yields of isolated products are given. [b] 7-*anti*-$SiMe_3$ to 7-*syn*-$SiMe_3$ ratio 7.0. [c] The 7-*anti*-$SiEt_3$ diastereomer was isolated in 95% purity (^{1}H NMR).

$Rh_2(OAc)_4$ or $Rh_2(pfb)_4$ led to product **8** (besides some azine **3**), apparently resulting from allylic C/H insertion. Formation of allylic insertion products is commonly observed as a side reaction during copper-catalyzed decomposition of diazomalonate esters in cyclohexene, but not of simple diazoacetic esters,[20] and it is the major pathway in rhodium-catalyzed reactions of cyclohexene with 2,6-di-*tert*-butyl-4-methylphenyl diazoacetate,[3b] 2-phenyldiazoacetate esters,[21] and diazomalonates.[21] While a number of mechanisms can be envisaged,[1a,b,20,22] addition of a highly electrophilic[23] metal−carbene intermediate (perhaps better viewed as a rhodium-stabilized carbocation) to the alkene and subsequent proton loss appears as a straightforward rationalization in the case of **1a** and the two rhodium(II) carboxylates. The different reactivities of the metal−carbene complex derived from **1a** and catalyst **6** can be related to its reduced electrophilicity, as evidenced by their low propensity to react with the aromatic nucleus.[11]

Ruthenium-catalyzed decomposition of **1b** in cyclohexene gave cyclopropane **7b**, and in contrast to the case for **7a**, the 7-*anti*-$SiEt_3$ isomer was obtained practically exclusively.

Since the catalytic reactions yield cyclopropanes **2a**−**f** with a preference for the diastereomer which has the ester group in a position cis to the vicinal ring substituents R^1, a desilylation reaction[24] with retention of configuration would produce the thermodynamically less stable *cis*-cyclopropanecarboxylate as the major diastereomer.[25] This approach would be stereocomplementary to the direct cyclopropanation of the same alkenes with unsubstituted diazoacetic esters. However, fluoride-induced desilylation of **2a** with CsF, KF, or NBu_4F yielded the cyclopropanecarboxylate **10** with a diastereomer ratio close to 1 (Scheme 3).

These findings probably reflect the fact that the stereochemical information was lost at the stage of an anionic intermediate, for which the structures of an ester enolate or of rapidly interconverting pyramidal cyclopropyl anions can be proposed.[26] Our DFT calcula-

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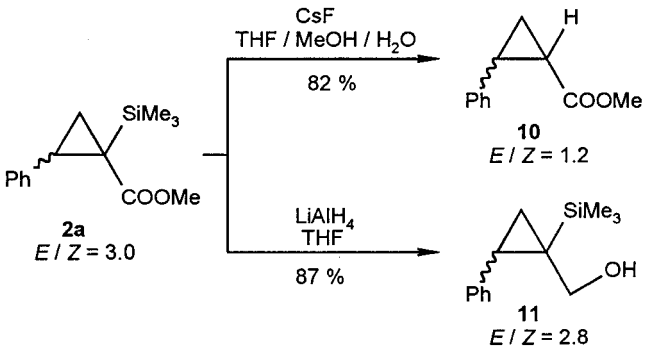
Scheme 3

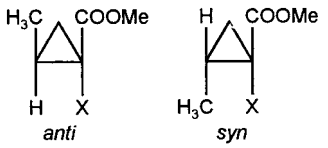


tions (see below) indicate that the structure of the anion of methyl 1-cyclopropanecarboxylate is pyramidal but the barrier for its inversion is only 1.9 kcal/mol, as compared to 15.5 kcal/mol for the parent cyclopropyl anion. Analogous results were obtained when **2c** and **2e** were desilylated with NBu_4F in THF. On the other hand, reduction of **2a** with $LiAlH_4$ gave a diastereomeric mixture of alcohols **11** with virtually complete retention of stereochemistry.

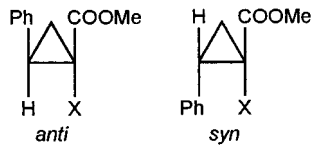
Calculations of Thermodynamic Stability and Geometries of 1,2-Disubstituted Cyclopropanecarboxylates. A. Methods. Calculations were carried out using density functional methods[27] (DFT) with the hybrid B3LYP functional[28] and the polarized 6-31G** basis set.[29] For some systems conventional molecular orbital ab initio calculations at the HF/6-31G* level[29] were also performed. All caclulations were carried out using the Gaussian 98 series of programs.[30] The geometries of all species were fully optimized using the B3LYP method and the polarized 6-31G** basis set (denoted as B3LYP/6-31G**//B3LYP/6-31G**). Frequency calculations were used to characterize the stationary points as minima and to obtain zero-point vibrational energies (ZPEs). For the discussion we use the B3LYP/6-31G**//B3LYP/6-31G** energies corrected for unscaled zero-point energy differences, referred to in the text as the B3LYP results. For comparison we have also calculated all species using the MM2[31a,b] and MM3[31c] force-field methods. The calculated absolute energies and the ZPEs of all calculated species are given in the Supporting Information.

B. Relative Thermodynamic Stability of the Isomeric Products. To model the relative stabilities of the stereoisomeric (*E*)-and (*Z*)-cyclopropanes **2** quantitatively, we have calculated the relative stabilities of the model compounds **12a**−**e** and **13a**−**e**. Compounds **12a**−**e** model the products in the addition of **1** to 1-hexene (i.e., **2b**,**d**), where a methyl group models the *n*-butyl substituent used in the experiments. This modeling is justified, as the steric sizes of methyl and *n*-butyl, as expressed by their *A* (or E_s) values[32] (see below), are similar. Compounds **13a**−**e** model the products in the addition of **1** to styrene (i.e., **2a**,**c**,**e)** as well as 4-bromostyrene (i.e., **2f**). In addition to the experimental systems we have also examined **12** and **13** with X = CH_3, SiH_3, *t*-Bu (i.e. **12a**/**13a**, **12b/13b**, and **12d/13d**, respectively). Furthermore, we have also calculated the *E*/*Z* pairs of several 1-methyl-2-X-cyclopropanes (**14**) and 1-phenyl-2-X-cyclopropanes (**15**), in which the carboxylate group present in **12** and **13** is omitted. In **14** and **15** the energy difference between the syn and anti isomers provides a direct measure of the interactions between X and the methyl (in **14**) and phenyl (in **15**), relative to their interactions with hydrogens.

The results of the density functional B3LYP/6-31G** calculations as well as the force-field calculations for **12**−**15** are presented in Table 4. Since the *E*,*Z* nomenclature is not uniform in the series of compounds studied (e.g., when X is changed from methyl to silyl, the *E* isomer becomes the *Z* isomer and vice versa), we use the anti/syn designation (anti indicating that X is trans to the methyl in **12** or to the phenyl in **13**, respectively), as shown in the formulas



12 **a**: X = CH_3; **b**: X = SiH_3
c: X = $Si(CH_3)_3$; **d**: X = $C(CH_3)_3$



13 **a**: X = CH_3; **b**: X = SiH_3
c: X = $Si(CH_3)_3$; **d**: X = $C(CH_3)_3$

The data in Table 4 show that for the relatively small CH_3 and SiH_3 substituents X, the *syn* isomer (in which X is syn to a methyl (in **12**) or to a phenyl (in **13**)) is more stable than the anti isomer, where the methyl (or

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Table 4. Calculated Relative Energies (kcal/mol) of 1-R-2-X-cyclopropane-1-carboxylates and 1-R-2-X-cyclopropanes[a]

			ΔE(syn−anti)		
structure	R	X	B3LYP[b]	MM2	MM3(96)
12a	CH_3	CH_3	−0.2	0.4	0.2
12b	CH_3	SiH_3	−0.2 (−0.4[c])	0.5	−0.1
12c	CH_3	$SiMe_3$	1.3	1.3	1.2
12d	CH_3	*t*-Bu	3.3	4.3	3.5
12e	CH_3	Si(*i*-Pr)$_3$	2.5	5.9	3.9
13a	Ph	CH_3	−1.8	0.1	1.0
13b	Ph	SiH_3	−1.4	0.2	0.4
13c	Ph	$SiMe_3$	−0.1	0.6	0.8
13d	Ph	*t*-Bu	2.3	2.0	2.3
13e	Ph	Si(*i*-Pr)$_3$	5.5[d]	6.6	6.7
14a	CH_3	CH_3	1.5	1.5	1.4
14b	CH_3	SiH_3	1.4	1.2	1.5
14c	CH_3	$SiMe_3$	2.1	1.9	2.8
14d	CH_3	*t*-Bu	4.2	4.7	4.5
14e	CH_3	Si(*i*-Pr)$_3$	3.5 (3.6[d])	6.8	6.4
14f	CH_3	$SiEt_3$	2.0 (2.1[d])	3.4	3.7
14g	CH_3	Ph	0.8	0.4	1.3
14h	CH_3	COOMe	1.3	0.5	1.0
15a	Ph	CH_3	0.8	0.4	1.3
15b	Ph	SiH_3	0.9	0.2	1.1
15c	Ph	$SiMe_3$	2.3	1.8	1.8
15d	Ph	*t*-Bu	3.0	2.3	3.2
15e	Ph	Si(*i*-Pr)$_3$	4.5	6.8	5.7
15f	Ph	$SiEt_3$	2.3[d]	2.8	2.9
15g	Ph	COOMe	2.8[d]	0.7	1.0
15h	Ph	Ph	2.6[d]	0.8	0.9

[a] A positive value indicates that the anti isomer is more stable than the syn isomer. [b] At B3LYP/6-31G**//B3LYP/6-31G** including unscaled zero point energy (ZPE) corrections. [c] At HF/6-31G*//HF/6-31G* including unscaled ZPE corrections. [d] At B3LYP/6-31G*//B3LYP/6-31G* including unscaled ZPE corrections.

Table 5. Experimental *A* Values (kcal/mol) of Relevant Groups[a,b]

R	*A* value	R	*A* value
H	0.0	SiH_3	1.45, 1.52
COOMe	1.2−1.3	$SiMe_3$	2.5
Me	1.74	*t*-Bu	4.7, 4.9
Et	1.79	Si(*i*-Pr)$_3$	3.2[c]
Ph	2.8		

[a] Free energy difference between equatorial and axial 1-R-cyclohexanes. [b] Reference 32. [c] Calculated using the MM2* force field.[31b]

phenyl) is syn to the COOMe group. The syn−anti energy difference is small for R = methyl (−0.2 kcal/mol in **12)**, but it is significantly larger for R = Ph (−1.4 kcal/mol for X = SiH_3 and −1.8 kcal/mol for X = CH_3 in **13)**. These results are somewhat unexpected in view of the *A* values of the relevant groups, which follow the order phenyl > methyl > silyl > COOMe (Table 5). Thus, the calculations predict that, in **13a**, the phenyl substituent prefers by 1.8 kcal/mol to be syn to a CH_3 group at C-1 (*A* = 1.74 kcal/mol), rather than to the "smaller" COOMe group (*A* = 1.2−1.3 kcal/mol). Thus, the steric interactions exerted by groups in the axial and equatorial positions of substituted cyclohexanes (which form the basis for the *A* scale) are not good measures for their steric interactions in **12** or **13**. This may be due to conjugative effects associated with interactions of the COOMe substituent with the cyclopropane ring. Support for this interpretation is found upon examining the preferred conformation of the COOMe group in the anti vs syn isomers. Thus, in the syn isomers of **12a**,**b** and **13a**,**b**, where the carboxylate group is syn to the small hydrogen and thus can adopt the best conformation for conjugation with the cyclopropyl ring, the carboxylate group adopts a gauche conformation in which the electron-deficient 2p(C) carbonyl orbital is properly aligned to overlap with one of the cyclopropyl C−C bonds (the O1−C4−C1−C2 dihedral angle θ is 33−35°, and the atom numbering is according to Figure 1). In the anti isomer the syn alkyl or phenyl groups force the carboxylate to rotate to 46−65°, reducing the conjugation with the cyclopropyl ring and thus raising its energy. In the parent methyl cyclopropanecarboxylate, the calculated barrier for rotation of the carboxylate group is quite high (6.2 kcal/mol), indicating the significant interaction between the carboxylate group and the cyclopropane ring and the angle dependence of this interaction. Rotation of the COOMe group from θ = 33° to θ = 60° requires ca. 1 kcal/mol.

When the size of the X group is increased, i.e., with X = $SiMe_3$ and *t*-Bu, the energy of the syn isomer (where the R···X steric interactions occur) is raised relative to that of the anti isomer. For the 2-methyl series **12**, *anti*-**12c** (X = Me_3Si) is 1.3 kcal/mol more stable than *syn*-**12c**. For the bulkier X = *t*-Bu (**12d**), Δ*E*(syn−anti) increases to 3.3 kcal/mol. In the 2-phenyl series **13,** *syn*-**13b (**X = SiH_3) is 1.4 kcal/mol more stable than *anti*-**13b**, while for **13c** (X = $SiMe_3$) Δ*E*(syn−anti) is nearly zero and with X = *t*-Bu, *anti*-**13d** is more stable than *syn*-**13d** by 2.3 kcal/mol. In both **12** and **13** substitution of X = SiH_3 by $SiMe_3$ destabilizes the syn isomer relative to the anti isomer by ca. 1.4 kcal/mol and substitution of X = $SiMe_3$ by the larger *t*-Bu increases Δ*E*(syn−anti) by 2.3 kcal/mol. The fact that, for each of the substituents, the preference for the anti isomer is smaller by ca. 1.2−1.5 kcal/mol for the phenyl-substituted cyclopropanes **13** than for the analogous methyl-substituted cyclopropanes **12**, seems confusing at first sight in view of the larger *A* value of a phenyl group (2.8 kcal/mol) as compared to that of a methyl group (1.74 kcal/mol). However, in the environment of the cyclopropyl ring the phenyl ring apparently exhibits a smaller effective volume due to its highly unsymmetrical shape, in contrast to the spherically symmetric methyl group. These unusual "effective sizes", where the methyl group is larger than the phenyl group, is merely another demonstration of the fact that the transfer of measures of steric sizes of groups from one molecular system to a different one may be misleading.

What is the effective steric size of the Si(*i*-Pr)$_3$ group, the largest group used in the experimental study? Although the volume of the Si(*i*-Pr)$_3$ group is much larger than that of the Me_3Si group, the calculations reveal that when attached to a cyclopropyl ring the effective sizes of the Si(*i*-Pr)$_3$ and $SiMe_3$ groups are not very different. Thus, in **12e**, the syn−anti energy difference is only 2.8 kcal/mol, 1.5 kcal/mol larger than for X = $SiMe_3$. Furthermore, the syn−anti energy difference in **12e** is 0.5 kcal/mol smaller than for X = *t*-Bu, although the volume of Si(*i*-Pr)$_3$ is much larger than that of the *t*-Bu group. The same trend is found in 1-methyl-2-X-cyclopropanes (**14**), the Δ*E*(syn−anti) values being 2.1, 3.6, and 4.3 kcal/mol for X = $SiMe_3$, Si(*i*-Pr)$_3$, *t*-Bu, respectively. Force-field MM2[31a] and MM2*[31b] calculations show that also the *A* value of the Si(*i*-Pr)$_3$ group of 3.2 kcal/mol (0.7 kcal/mol larger than that of $SiMe_3$) is 1.5−1.7 kcal/mol *smaller* than that of

t-Bu. When the other group on the cyclopropyl ring is a phenyl, the Si(*i*-Pr)$_3$ group shows a larger steric size than *t*-Bu by 1.5 kcal/mol: i.e., ΔE(syn−anti) is 3.8 kcal/mol for **13e** and 2.3 kcal/mol for **13d**. The MM2 and MM3 force-field values are in general similar to the B3LYP results for all systems, except for the systems substituted with a Si(*i*-Pr)$_3$ group (i.e. **12e**, **13e**, **14e**, and **15e**), for which the force-field methods overestimate (more so the MM2 method) by ca. 2−3 kcal/mol (Table 4) the steric effect of the Si(*i*-Pr)$_3$ group.

What can be concluded from the calculations regarding the interpretation of the experimental results? For the experimentally studied system **1a** with X = SiMe$_3$, if product stability alone dictates the stereochemistry of the products, we would expect to obtain mostly (*E*)-**2b** in the reaction with 1-hexene and a roughly 1:1 mixture of (*E*)- and (*Z*)-**2a** in the reaction with styrene. Experimentally, a small excess of the *Z* product is observed in the photochemical reactions of **1a** with both 1-hexene and styrene. This noncorrespondence between the observed products and the relative thermodynamic stability of the *E* and *Z* products indicates an early transition state (TS) (i.e., a TS where the steric repulsions in the products are not well developed). This conclusion is further supported by the experimental fact that the *E*/*Z* (anti/syn) product ratio even *decreases* for the larger Si(*i*-Pr)$_3$ group (although, as pointed out above, only by ca. 1 kcal/mol); i.e., in the photochemical reaction of **1c** with styrene the (*E*)-**2**/(*Z*)-**2** (*anti*-**2**/*syn*-**2**) product ratio is 0.37, indicating clearly in view of the significantly higher thermodynamic stability of (*E*)-**2e**, relative to (*Z*)-**2e** (calculated to be 5.5 kcal/mol, i.e. **13e** in Table 4), that the R^1 and SiR$_3$ groups are not close in space in the TS of the reaction. At this point we have no convincing explanation for the stereochemistry of the photochemical cyclopropanation reaction and we plan further experimental and computational studies to clarify this point.

Conclusions

We have shown that for the effectiveness of cyclopropanation of styrene, 1-hexene, and cyclohexene with diazo(trialkylsilyl)acetates **1** (**a**, SiMe$_3$; **b**, SiEt$_3$; **c**, Si(*i*-Pr)$_3$), the influence of several reaction parameters—method of decomposition, nature of catalyst, and olefin concentration—is much more crucial than for simple alkyl diazoacetates. For cyclopropanation of styrene and 1-hexene, copper(I) triflate appears to be the best catalyst, but it also reaches its limits when the most bulky diazoacetate (**1c**) is applied. The complex [Ru$_2$(CO)$_4$(μ-OAc)$_2$]$_n$ was found to be well suited for cyclopropanation reactions involving **1a**,**b**; in particular, it was the only one that catalyzed the cyclopropanation of cyclohexene while the rhodium carboxylate catalysts gave rise to the allylic C−H insertion product.

In contrast to the photochemical cyclopropanations of styrene and 1-hexene, which yield predominantly the *Z* isomers of **2a**,**b**,**e**, the catalyzed version yields the thermodynamically favored *E* diastereomer (according to DFT calculations) with all three olefins studied. The diastereomer ratio is rather sensitive to the steric bulk of the trialkylsilyl group of **1** when cyclohexene is cyclopropanated but surprisingly is hardly sensitive to the size of the SiMe$_3$, SiEt$_3$, and Si(*i*-Pr)$_3$ groups, in the case of the two monosubstituted alkenes studied. Density functional theory calculations show clearly that the observed product diastereomer ratios do not reflect the relative stabilities of the isomeric *E* and *Z* products: i.e., the reactions are not thermodynamically controlled. This is not unexpected for the transition-metal-catalyzed reactions, where both trans- and cis-selective cyclopropanations are known and where it is assumed that the interaction between the metal−carbene intermediate and alkene can take a stereochemical course that may be governed by a combination of several different steric factors and electronic factors as well (see, for example, refs 17a and 33). On the other hand, the preference for the sterically more congested diastereomer in the case of photochemical cyclopropanation reactions with **1a**−**c** is surprising. Although we are not aware of a systematic study of this issue, the examples reported in the literature give the impression that, in general, free carbenes react with alkenes to give the sterically less congested cyclopropane preferentially (but often at a ratio not far from 1). Our preliminary results call for a more detailed experimental and theoretical study, and it appears that diazo(trialkylsilyl)acetates, bearing silyl groups of tunable steric demand, are the appropriate candidates.

Experimental Section

General Information. ^{1}H NMR spectra: Bruker WP 200 (200 MHz), Bruker AM 400 (400 MHz), and AMX 500 (500 MHz) instruments; chloroform (δ 7.24) or dichloromethane (δ 5.32) as internal standard. ^{13}C NMR spectra: Bruker AM 400 (100.6 MHz) and AMX 500 (125.8 MHz) instruments; chloroform as internal standard (δ 77.0). All NMR spectra were recorded in CDCl$_3$. IR spectra: Perkin-Elmer IR 397 instrument; wavenumbers (cm^{-1}) are given. Elemental analyses: Perkin-Elmer EA 240 instrument. The following compounds were prepared by published procedures: **1a**,[34] **1b**,[13] **1c**,[34] Cu(O$_3$SCF$_3$)·0.5C$_6$H$_6$,[15a] Rh$_2$(C$_3$F$_7$COO)$_4$,[35] and [Ru$_2$(CO)$_4$(μ-OAc)$_2$]$_n$ (**6**).[36]

Catalytic Decomposition of 1a−c in an Alkene: General Procedure. Under an argon atmosphere, a solution of diazo ester **1** (2−5 mmol) in the alkene (ca. 10 mL) was added dropwise over a period of 2−3 h to the same alkene (10 mL) containing the catalyst (3−8 mol %), and the mixture was stirred until the evolution of dinitrogen had ceased (5−12 h). This mixture was filtered over a pad of neutral Al$_2$O$_3$ to remove the catalyst (inefficient in the case of Rh$_2$(pfb)$_4$). Excess alkene was distilled off (eventually also oligomers that had been formed), and the products were isolated by vacuum distillation (Kugelrohr), column chromatography (Merck Lobar columns, LiChroprep Si-60, 40−63 μm), or a combination of both. The cyclopropanation of styrene, 1-hexene, and cyclohexene with **1a** catalyzed by **6** has already been described.[11]

The diastereomer ratios of the cyclopropanes **2** and **7** were determined by integration of appropriate ^{1}H NMR signals. In some cases (Table 1), these ratios were also determined by analytical HPLC (Merck/Hitachi LiChromatograph with L-6200 gradient pump and UV detector; column LiChrospher RP-18 Merck; eluent acetonitrile (Chromasolv, Riedel de Haen)/water), assuming the same response factors for both diaster-

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eomers. In those cases where the diastereomer ratio of isolated cyclopropanes could be compared with the (approximate) ratio found in the product mixture before chromatographic or distillative workup, no substantial difference could be detected.

Photochemical Cyclopropanation with 1a and 1c: General Procedure. A solution of the diazo ester (2−3 mmol) in the alkene (45 mL) was irradiated with a high-pressure mercury lamp (Philips HPK 125 W, λ = 300 nm) until evolution of N_2 had ceased. The alkene was distilled off (styrene, 40−50 °C/0.01 mbar; 1-hexene, 20 °C/0.01 mbar), and the cyclopropane was isolated by Kugelrohr distillation (**2a**, 70 °C/0.01 mbar; **2b**, 75 °C/0.02 mbar; **2e**, 90 °C/0.01 mbar).

Methyl (*E*)- and (*Z*)-2-Phenyl-1-(triethylsilyl)-1-cyclopropanecarboxylate (2c). These isomers were obtained from **1b** and styrene. Bp: 90 °C/0.01 mbar (Kugelrohr). ^{1}H NMR (400 MHz): (*E*)-**2c**, δ 0.76 (dq, $SiCH_2$), 1.10 (t, CH_2CH_3), 1.26 (dd, J = 7.8, 4.9 Hz, 1 H), 1.99 (dd, J = 6.5, 4.9 Hz, 1 H), 2.48 (pseudo-t, 2-H), 3.38 (OMe); (*Z*)-**2c**, δ 0.38 (m, $Si-CH_2$), 0.87 (t, $SiCH_2CH_3$), 1.49 (dd, J = 6.9, 4.3 Hz, 1 H), 1.81 (dd, J = 8.9, 4.3 Hz, 1 H), 2.78 (dd, 2-H), 3.77 (OMe). ^{13}C NMR: (*E*)-**2c**, δ 2.7, 7.4, 13.7, 22.0, 27.5, 51.1, 126.1−128.2, 129.8, 172.6; (*Z*)-**2c**, δ 3.6 ($SiCH_2$), 7.5 (CH_2CH_3), 15.8 (C-3), 19.1 (C-1), 31.4 (C-2), 51.6 (OMe), 126.1−128.2, 137.4 (aromatic ipso C), 176.1 (C=O). IR (film): 1710 cm^{-1} (C=O). Anal. Calcd for $C_{17}H_{26}O_2Si$ (290.5): C, 70.29; H, 9.02. Found: C, 69.7; H, 9.0.

Methyl (*E*)- and (*Z*)-2-Butyl-1-(triethylsilyl)-1-cyclopropanecarboxylate (2d). These isomers were obtained from **1b** and 1-hexene. Bp: 90 °C/0.01 mbar (Kugelrohr). Partial separation of the diastereomers was achieved by column chromatography. ^{1}H NMR (400 MHz): (*E*)-**2d**, δ 0.55 (dq, $SiCH_2$), 0.82−0.88 (t and m, 4 H), 0.93 (t, $SiCH_2CH_3$), ca. 1.00−1.40 (m, 8 H), 3.62 (OMe); (*Z*)-**2d**, δ 0.62 (q, $SiCH_2$), 1.38 (dd, 1 H), 1.62 (m_c, 1 H, 2-H), 3.59 (OMe); the remaining signals overlap with those of the *E* isomer at δ 0.82−0.93 and 1.00−1.40. ^{13}C NMR: (*E*)-**2d**, δ 2.8, 7.4, 13.9, 15.3 (J = 161.3 Hz, C-3), 16.5 (C-1), 22.5/28.9/31.6 ($-(CH_2)_3-$), 23.9 (C-2), 51.2, 174.6; (*Z*)-**2d**, δ 4.6 ($Si-CH_2$), 7.6 ($SiCH_2CH_3$), 13.9 ($C_3H_6CH_3$), 17.9 (J = 162.9 Hz, C-3), 22.4 (C-2), 23.9 (C-1), 28.9/30.8/32.0 ($-(CH_2)_3-$), 51.4 (OMe), 176.8 (C=O). IR (film): 1710 cm^{-1} (C=O). Anal. Calcd for $C_{15}H_{30}O_2Si$ (270.5): C, 66.61; H, 11.18. Found: C, 66.4; H, 11.0.

Methyl (*E*)- and (*Z*)-2-Phenyl-1-(triisopropylsilyl)-1-cyclopropanecarboxylate (2e). These isomers were obtained from **1c** and styrene. Bp: 90 °C/0.01 mbar. ^{1}H NMR (400 MHz): (*E*)-**2e**, δ ca. 0.95−1.10 (m, 21 H, $CHMe_2$), 1.25 (dd, J = 7.9, 5.2 Hz, 1 H), 1.90 (dd, J = 6.5, 5.2 Hz, 1 H), 2.53 (dd, J = 7.9, 6.5 Hz, 2-H), 3.18 (s, OMe); (*Z*)-**2e**, δ 0.72 and 0.92 (2 × d, diastereotopic $CHMe_2$), 0.75−0.90 (m, $CHMe_2$), 1.51 (dd, J = 7.2, 4.5 Hz, 1 H), 1.71 (dd, J = 9.0, 4.5 Hz, 1 H), 2.60 (dd, J = 9.0, 7.2 Hz, 2-H), 3.60 (s, OMe); ^{13}C NMR: (*E*)-**2e**, δ 11.8 (Si−CH), 14.1 (C-3), 19.0 ($CHCH_3$), 22.5 (C-1), 27.3 (C-2), 51.1 (OMe), 126.4−129.9 (aromatic CH), 137.6 (aromatic ipso-C), 172.6 (C=O); (*Z*)-**2e**, δ 12.4, 15.6, 19.0, 20.4, 31.4, 51.6, 126.4−129.9, 138.2, 176.5. IR (film): 1708 cm^{-1} (C=O). Anal. Calcd for $C_{20}H_{32}O_2Si$ (332.5): C, 72.2; H, 9.7. Found: C, 71.6; H, 9.6.

Methyl (*E*)- and (*Z*)-2-(4-Bromophenyl)-1-(triisopropylsilyl)-1-cyclopropanecarboxylate (2f). A solution of **1c** (0.82 g. 3.2 mmol) and of 4-bromostyrene (1.83 g, 10.0 mmol) in dichloromethane (20 mL) was added dropwise over 6 h to a solution of the same alkene (1.83 g, 10 mmol) and of copper(I) triflate (80 mg) in dichloromethane (20 mL). After filtration over a pad of neutral alumina, the mixture was separated by column chromatography (silica gel, petroleum ether/ethyl acetate (97:3)) to give first unchanged bromostyrene and then pure, crystalline (*E*)-**2f** (0.20 g, 15%, mp 69 °C) followed by a mixture of (*E*)- and (*Z*)-**2f** (0.20 g, 15%, *E*:*Z* = 3.3, mp 54−69 °C) and a fraction (0.10 g) with (*Z*)-**2f** as the major component. Spectral and analytical data of (*E*)-**2f**: ^{1}H NMR (500 MHz) δ 1.05−1.25 (m, 21 H, $CHMe_2$), 1.34 (dd, J = 7.9, 5.3 Hz, 1 H, 3-H_1), 1.92 (dd, J = 6.3, 5.3 Hz, 1 H, 3-H_1), 2.53 (dd, J = 7.9, 6.3 Hz, 1 H, 2-H), 3.29 (s, OMe), 7.05/7.36 (AA′BB′, 4 H, C_6H_4); IR (film) 1708 cm^{-1} (C=O); ^{13}C NMR (125.8 MHz) δ 11.8 (Si−CH), 14.3 (C-3), 18.96 ($CHCH_3$), 19.0 ($CHCH_3$), 22.7 (C-1), 26.7 (C-2), 51.2 (OMe), 120.3, 129.8, 131.0, 136.7, 172.4 (C=O). Anal. Calcd for $C_{20}H_{31}BrO_2Si$ (411.1): C, 58.38; H, 7.59. Found: C, 58.09; H, 7.95. ^{1}H NMR data for (*Z*)-**2f** in the diastereomeric mixture: δ 1.55 (dd, J = 7.7, 5.1 Hz, 3-H_1), 1.78 (dd, J = 9.2, 5.1 Hz, 1 H, 3-H_1), 2.59 (dd, J = 9.2, 7.7 Hz, 2-H), 3.68 (s, 3 H, OMe), 7.18/7.36 (AA′BB′, 4 H, C_6H_4).

Table 6. Data for Crystal Structure Analysis of (*E*)-2f

empirical formula	$C_{20}H_{31}BrO_2Si$
fw	411.45
cryst dimens, mm	0.62 × 0.42 × 0.23
temp, K	183(2)
cryst syst	monoclinic
space group (No.)	$P2_1/c$ (14)
a, Å	14.601(1)
b, Å	8.862(1)
c, Å	17.278(2)
α, deg	90
β, deg	108.04(1)
γ, deg	90
Z	4
D_{calcd}, g cm^{-3}	1.286
θ range (min/max), deg	1.47/22.50
μ(Mo Kα), cm^{-1}	19.9
no. of measd data	3627
no. of unique data	2773
R_{int}	0.0297
no. of obsd data ($I > 2\sigma(I)$)	2185
no. of ref params	228
R1 (obsd/all data)[a]	0.0459/0.0644
wR2 (obsd/all data)[a]	0.1155/0.1368

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]]^{1/2}$.

Dimethyl 2,3-Diaza-1,4-bis(trimethylsilyl)butadiene-1,4-dicarboxylate (3). The yellow oil obtained after Kugelrohr distillation at 90 °C/0.03 mbar solidified on standing at 4 °C. ^{1}H NMR (200 MHz): δ 0.24 (s, $SiMe_3$), 3.75 (s, OMe). Further purification was not possible, due to the small amount of material available. Anal. Calcd for $C_{12}H_{24}N_2O_4Si_2$ (316.5): C, 45.54; H, 7.64; N, 8.84. Found: C, 46.2; H, 7.7; N, 7.5.

Methyl 7-*anti*-(Triethylsilyl)bicyclo[4.1.0]heptane-7-carboxylate (7b). After removal of excess cyclohexene at 20 °C/0.3 mbar, the product was isolated by column chromatography (eluent ether/petroleum ether (3:7)) and Kugelrohr distillation at 150 °C/0.3 mbar; yield 61%. ^{1}H NMR (400 MHz): δ 0.44 (q, $SiCH_2$), 0.83−0.91 (t and m, CH_2CH_3 and 1,6-H), 1.03−1.15 (m, 4 H), 1.80 (m_c, 4 H), 3.56 (s, OMe). ^{13}C NMR: δ 2.3 ($SiCH_2$), 7.2 (CH_2CH_3), 17.0 (C-1,6), 20.4 and 20.8 (C-2,3,4,5), 20.6 (C-7), 50.8 (OMe), 173.0 (C=O). Anal. Calcd for $C_{15}H_{28}O_2Si$ (268.5): C, 67.11; H, 10.51. Found: C, 66.9; H, 10.4.

Methyl α-(2-Cyclohexenyl)-α-(trimethylsilyl)acetate (8). This product was obtained as a 1.4:1 mixture of diastereomers; bp 60 °C/0.02 mbar (Kugelrohr). ^{1}H NMR (400 MHz): δ 0.09 (s, 9 H, $SiMe_3$), 0.9−2.1 (m, 6 H, $-(CH_2)_3-$), 2.01/1.91 (2 × d, 1 H, CHCO), 2.63 (m, 1 H, 1-H of cyclohexenyl), 3.60/3.61 (3 H, OMe), 5.43−5.72 (m, 2 H, CH=CH). ^{13}C NMR (major /minor isomer): δ −1.5/−1.3 ($SiMe_3$), 20.5/21.1 (t), 25.1/24.1 (t), 29.3/29.3 (t), 34.7/35.0 (C-1), 43.5/44.1 (CHCO), 50.7/50.8 (OMe), 131.3/128.3 and 130.0/127.2 (CH=CH), 175.3/175.3 (C=O). IR (film): 1728 (C=O), 1438, 1252, 843 cm^{-1}. Anal. Calcd for $C_{12}H_{22}O_2Si$ (226.4): C, 63.66; H, 9.79. Found: C, 63.5; H, 9.6.

Desilylation of 2a. A solution of CsF (162 mg, 1.07 mmol) in THF/methanol (10 mL, 1:1) was added to a solution of **2a** (231 mg, 0.93 mmol, *E*:*Z* = 3.0) in THF/methanol/water (20 mL, 4:4:1). After 72 h, the solvent was evaporated, and the residue was dissolved in ether (5 mL). This solution was washed with water and dried, and methyl 2-phenylcyclopropanecarboxylate (**10**, *E*:*Z* = 1.2) was isolated by Kugelrohr distillation at 60 °C/0.01 mbar; yield 83%. The ^{1}H and ^{13}C NMR

values were in agreement with literature data.[9,18a] Anal. Calcd for $C_{11}H_{12}O_2$ (176.2): C, 74.98; H, 6.87. Found: C, 75.1; H, 6.9.

(*E*)- and (*Z*)-(2-Phenyl-1-(trimethylsilyl)cyclopropyl)-methanol (11). A solution of **2a** (0.46 g, 1.85 mmol, *E*:*Z* = 3.0) in ether (30 mL) was added to $LiAlH_4$ (0.21 g, 5.56 mmol) in ether (30 mL), and the mixture was refluxed for 5 h. After cooling, excess $LiAlH_4$ was destroyed with water, and the precipitate that had formed was dissolved by addition of KOH pellets. The product was extracted with ether (3 × 10 mL) and isolated by Kugelrohr distillation at 75 °C/0.04 mbar: yield 87%; mixture of diastereomers, *E*:*Z* = 2.8. ^{1}H NMR (400 MHz): (*E*)-**11**, δ 0.16 ($SiMe_3$), 0.97 (dd, J = 7.6, 4.9 Hz, 1 H), 1.09 (t, 1 H), 2.24 (dd, J = 7.6, 5.8 Hz, 2-H), 3.25/3.55 (AB, J = 11.7 Hz, CH_2OH); (*Z*)-**11**, δ −0.19 (s, 9 H), 0.89 (dd, 1 H), 1.16 (t, 1 H), 2.24 (m, 2 H), 3.30/3.89 (AB, J = 11.7 Hz, 2 H). ^{13}C NMR: (*E*)-**11**, δ −2.5 ($SiMe_3$), 11.8 (C-3), 17.5 (C-1), 24.3 (C-2), 65.5 (*C*H_2OH), 128.1−129.8, 138.3 (ipso-C, Ph); (*Z*)-**11**, δ −1.0, 11.4, 18.5, 28.1, 71.5, 128.1−129.8, 139.6. IR (film): 3500 cm^{-1} (br, OH), 1265/1250 s, 1038 s. Anal. Calcd for $C_{13}H_{20}OSi$ (220.3): C, 70.8; H, 9.1. Found: C, 70.9; H, 9.2.

X-ray Crystal Structure Analysis of (*E*)-2f. Crystals were obtained from low-boiling petroleum ether. The reflection data were collected on a Siemens P4 diffractometer at room temperature. The structure was solved and refined with the SHELXTL software (Bruker ARX GmbH, Karlsruhe, Germany). Crystal data and refinement results are given in Table 6 and selected values of bond geometry in Table 2. Further technical details as well as positional and thermal parameters are found in the Supporting Information.

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Supporting Information Available: Tables giving details of the data collection and structure solution, positional and thermal parameters, and bond distances and angles for (*E*)-**2f** and tables of calculated absolute energies and zero-point vibrational energies (ZPEs) of all calculated species. This material is available free of charge via the Internet at http://pubs.acs.org.

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