Rhodium(II)-Catalyzed Inter- and Intramolecular Enantioselective Cyclopropanations with Alkyl-Diazo(triorganylsilyl)acetates

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The intermolecular cyclopropanation of styrene with ethyl diazo(triethylsilyl)acetate (**1a**) proceeds at room temperature in the presence of chiral Rh^{II} carboxylate catalysts derived from imide-protected amino acids and affords mixtures of *trans*- and *cis*-cyclopropane derivatives **2a** in up to 72% yield but with modest enantioselectivities (< 54%) (*Scheme 1* and *Table 1*). Protiodesilylation of a diastereoisomer mixture **2a** with Bu_4NF is accompanied by epimerization at C(1) (→ **3**). The intramolecular cyclopropanation of allyl diazo(triethylsilyl)acetate (**8a**), in turn, affords optically active 3-oxabicyclo[3.1.0]hexan-2-one (**9a**) with yields of up to 85% and 56% ee (*Scheme 3* and *Table 2*). Similarly, the (2*Z*)-pent-2-enyl derivative **8d** reacts to **9d** in up to 77% yield and 38% ee (*Scheme 3* and *Table 3*). In contrast, the diazo decomposition of (2*E*)-3-phenylprop-2-enyl and 2-methylprop-2-en-1-yl diazo(triethyl-silyl)acetates (**8b** and **8c**, resp.) is unsatisfactory and gives very poor yields of substituted 3-oxabicyclo[3.1.0]hexan-2-ones **9b** and **9c**, respectively (*Table 3*).

1. Introduction. – The photochemical decomposition of diazo(trialkylsilyl)methyl ketones in the absence of reagents affords products derived from either *Wolff* rearrangement or 1,2-alkyl migration of the intermediate carbenes [1]. In the presence of olefins, these carbenes are trapped, and cyclopropanes with high stereospecificity may be isolated [2]. The transition-metal-catalyzed decomposition of alkyl diazo-(trialkylsilyl)acetates in the presence of styrene (= ethenylbenzene) and hex-1-ene has been investigated by *Maas et al.* [3]. The effectiveness of the catalysts followed the order $[Cu(OTf)] > [Ru_2(CO)_4(\mu\text{-}Ac)_2]_n \approx [Rh_2(pfb)_4] >> [Rh_2(OAc)_4]$ (pfb = perfluorobutanoate). The inefficiency of $[Rh_2(OAc)_4]$ in the decomposition of diazo-(trialkylsilyl)acetates has been reported by other authors [4]. In spite of this, Rh^{II} carboxylate catalysts have been used successfully for diazo decomposition of α-silylated diazo esters. *Marsden* and co-workers reported intramolecular CH insertions of silylated diazo esters in the presence of rhodium(II) octanoate in refluxing benzene [5]. Under similar conditions, silylated diazo ketones rearrange to silyl ketenes when exposed to $[Rh_2(O_2CC_7H_{15})_4]$ [6]. *Bolm et al.* described the $[Rh_2(OAc)_4]$-catalyzed decomposition of diazo(trialkylsilyl)acetates in toluene at 40–70° for the preparation of trialkylsilyl-substituted α-amino acids *via* carbene insertion into NH bonds [7].

We have recently investigated Rh^{II}-catalyzed enantioselective intramolecular CH insertions of alkyl diazo(trialkylsilyl)acetates [8]. Reactions carried out with $[Rh_2(OAc)_4]$ required elevated temperatures (refluxing benzene) to effect diazo decomposition. However, we were surprised to find that the Rh^{II} catalysts of *Hashimoto* and *Ikegami* [9][10] were so much more efficient than $[Rh_2(OAc)_4]$ that the reactions could be carried out at 20° in toluene. The *Hashimoto* catalysts use

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phthaloyl-protected amino acids such as phenylalanine and *tert*-leucine (=2-amino-3,3-dimethylbutanoic acid) as ligands for dimeric Rh^{II}. They are sterically more hindered than $[Rh_2(OAc)_4]$, yet they are more reactive. The reasons for this enhanced reactivity were not investigated and are subject to speculation. However, a plausible explanation based on the acidity of the ligands may be advanced: the reactivity of the Rh^{II} catalysts depends strongly upon the pK_a value of the ligand. Thus, Rh^{II} carboxylates are much more efficient in diazo decompositions than Rh^{II} carboxamidates [11]. The pK_a value for *N*-phthaloylglycine is 3.26, *ca.* 1.5 units below that of acetic acid. Other phthaloylated amino acids have a pK_a value in the range of 3.46–3.84 [12]. Conceivably, the presence of four ligands of higher acidity than acetic acid may be at least in part responsible for the enhanced reactivity of Rh^{II} catalysts having phthaloyl-protected amino acids as ligands in comparison to that of $[Rh_2(OAc)_4]$ or other Rh^{II} carboxylates. This enhanced catalyst reactivity is crucial for the successful decomposition of silylated diazo esters under mild conditions.

In the intramolecular CH insertion of alkyl diazo(triethylsilyl)acetates, we have found enantioselectivities of up to 79% at 20°. In this communication, we report results on Rh^{II}-catalyzed inter- and intramolecular cyclopropanations of olefins.

2. Results and Discussion. – 2.1. *Intermolecular Cyclopropanation*. The cyclopropanations were carried out with ethyl diazo(triethylsilyl)- and diazo(dimethylphenylsilyl)acetate (**1a** and **1b**, resp.). The acetate **1a** was synthesized in high yield from ethyl diazoacetate and triethylsilyl trifluoromethanesulfonate ($TfOSiEt_3$) [13], and **1b** from chlorodimethylphenylsilane (*Scheme 1*) [3][14]. The decomposition of **1a** with $[Rh_2(OAc)_4]$ in refluxing toluene in the presence of 10 equiv. of styrene afforded the cyclopropane derivative **2a** in 23% yield and a *trans*/*cis* ratio of 74:26 (*Table 1*). This ratio agrees well with that of 3.4:1 reported by *Maas et al.* [3] for methyl diazo(trimethylsilyl)acetate. The relative configurations of the cyclopropane derivatives **2a** were assigned upon comparison of their ^{1}H-NMR spectra with those of the corresponding methyl esters of known configurations. The resonance for H–C(2) in *trans*-**2a** (δ 2.46) is shifted upfield by *ca.* 0.3 ppm relative to that of *cis*-**2a** (δ 2.76). In

Scheme 1

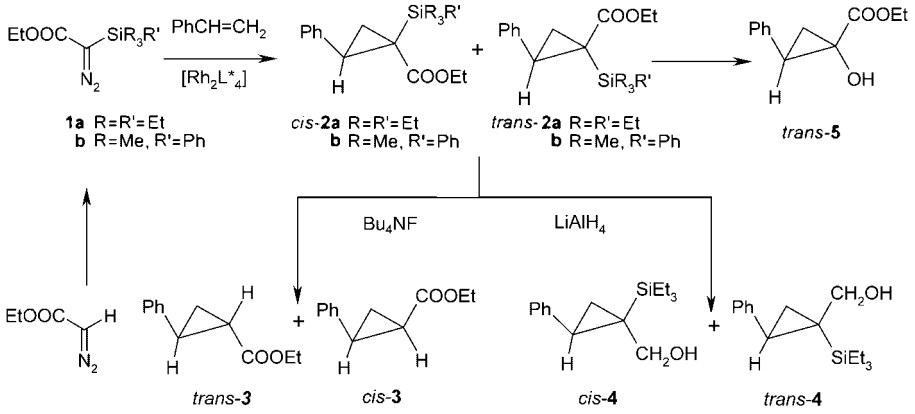


Table 1. *Cyclopropanation of Styrene with Ethyl Diazo(triorganylsilyl)acetates* **1a**,**b**

	Catalyst[a])	Time	Temp.	Solvent	Styrene [equiv.]	Product	Yield [%]	*trans*/*cis*	ee [%]	
									trans	*cis*
1a	$[Rh_2(OAc)_4]$	1 h	reflux	PhMe	10	**2a**	23	74:26	–	–
1a	$[Rh_2\{(S)\text{-nttl}\}_4]$	1.5 h	r.t.	PhMe	5	**2a**	40	82:18	n.d.	n.d.
1a	$[Rh_2\{(S)\text{-nttl}\}_4]$	1.66 h	r.t.	CH_2Cl_2	10	**2a**	40	82:18	n.d.	n.d.
1a	$[Rh_2\{(S)\text{-nttl}\}_4]$	1 h	r.t.	PhMe	10	**2a**	69	82:18	54[b])	27[b])
1a	$[Rh_2\{(S)\text{-pttl}\}_4]$	4 h	r.t.	PhMe	10	**2a**	72	81:19	48[b])	30[b])
1a	$[Rh_2\{(S)\text{-bpttl}\}_4]$	12 h	r.t.	PhMe	10	**2a**	70	77:23	23[b])	n.d.
1a	$[Rh_2\{(R)\text{-bptv}\}_4]$	12 h	r.t.	PhMe	10	**2a**	43	75:25	30[c])	n.d.
1a	$[Rh_2\{(S)\text{-ptpa}\}_4]$	12 h	r.t.	PhMe	10	**2a**	32	68:32	34[b])	41[b])
1b	$[Rh_2(OAc)_4]$	1.5 h	reflux	PhMe	10	**2b**	39	86:14	–	–
1b	$[Rh_2\{(S)\text{-pttl}\}_4]$	0.5 h	r.t.	PhMe	10	**2b**	70	88:12	n.d.	n.d.
1b	$[Rh_2\{(R)\text{-bptv}\}_4]$	12 h	r.t.	PhMe	10	**2b**	68	85:15	n.d.	n.d.

[a]) See *Fig. 1* for the ligand structures. [b]) Absolute configuration of major component: *trans*-**2a**, (1*S*,2*R*); *cis*-**2a**, (1*R*,2*R*). [c]) Absolute configuration of major component: *trans*-**2a**, (1*R*,2*S*), *cis*-**2a**, (1*S*,2*S*).

addition, the methylene group of the ester function of *trans*-**2a**, which is situated *cis* to the Ph group, appears at higher field (δ 3.80) than in *cis*-**2a** (δ 4.22), where it is *trans*. The preference for formation of *trans*-**2a** where the Ph and COOEt groups are *cis* is of some interest since in the cyclopropanation with ethyl diazoacetate, the *trans*-isomer usually predominates. However, upon protiodesilylation with Bu_4NF, epimerization occurred, and the desilylated cyclopropane **3** was isolated as a 70:30 *trans*/*cis* mixture, even when the reaction was carried out at $-78°$.

The cyclopropanation of styrene with **1a** was then carried out in the presence of chiral Rh^{II} carboxylate catalysts of the *Hashimoto* type, and the results are reported in *Table 1* (for structures and abbreviations of catalysts, see *Fig. 1*).With $[Rh_2\{(S)\text{-nttl}\}_4]$ or $[Rh_2\{(S)\text{-pttl}\}_4]$ as the catalyst in toluene, the reaction proceeded smoothly at room temperature. With a 10-fold excess of styrene, yields of 69 and 72% of cyclopropane derivatives **2a** were obtained, respectively. The yield of **2a** decreased significantly when the excess of styrene was reduced to five-fold or when the reaction was carried out in CH_2Cl_2. GC Separation of the enantiomers of the cyclopropane derivatives **2a** failed, but could be achieved upon their reduction with $LiAlH_4$ to a diastereomer *trans*/*cis* mixture **4**. The relative configuration of the diastereoisomers **4** was verified by comparison of the NMR signals of the CH_2OH group with those reported in the literature for the trimethylsilyl analogues of **4** [3]. Separation of the enantiomers was not perfect; however, the modest enantioselectivities achieved in these reactions (up to 54% for *trans*-**2a** and up to 41% for *cis*-**2a**) do not warrant the development of a more appropriate analytical method at this time. The alcohols **4** failed to undergo protiodesilylation upon exposure to Bu_4NF even upon prolonged reaction times.

For the determination of the absolute configuration of **2a**, a 83:17 mixture of (1*R*,2*R*)-ethyl 2-phenylcyclopropane-1-carboxylate (*trans*-**3**) and of its isomer *cis*-**3** having (1*R*,2*S*)-configuration was synthesized by Cu-catalyzed cyclopropanation of styrene with ethyl diazoacetate in the presence of the chiral bis[dihydrooxazole] ligand **6** [15] (*Scheme 2*). Comparison of the retention times (*β-Dex* column) with that of the isomer mixture **3** obtained after desilylation of the cyclopropane derivatives **2a**

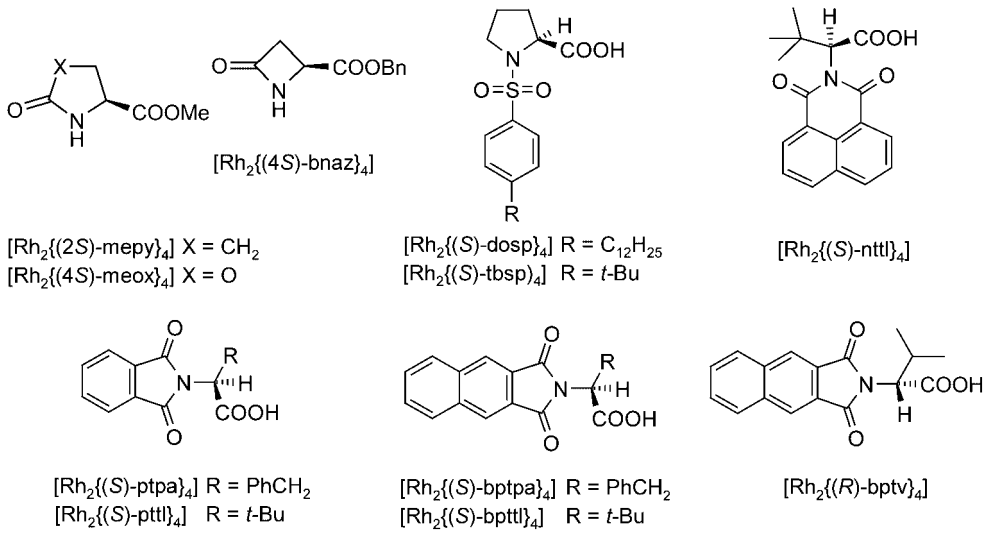
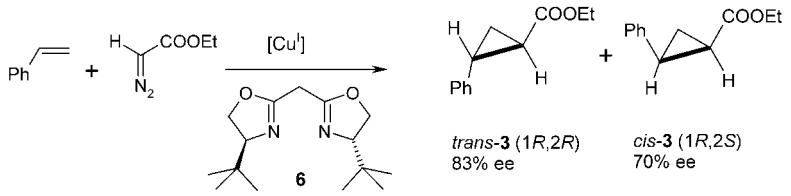


Fig. 1. *Ligands and abbreviations of the corresponding Rh^{II} catalysts*

Scheme 2



(isolated from the reaction with [Rh$_2${(*S*)-pttl}$_4$] and [Rh$_2${(*S*)-nttl}$_4$]), allowed assignment of the (1*S*,2*S*)-configuration of the major enantiomer of *trans*-**3** and the (1*R*,2*S*)-configuration to the major isomer of *cis*-**3**. Application of the CIP rules affords *cis*-**2a** with predominant (1*R*,2*R*) and *trans*-**2a** with predominant (1*S*,2*R*) configuration.

Note that, because epimerization occurred at C(1) upon protiodesilylation of the *trans*/*cis*-mixture **2a**, *trans*- and *cis*-**3** have the same ee. The expected ee of *trans*-**3** resulting from reaction with [Rh$_2${(*S*)-pttl}$_4$], assuming total equilibration of the epimers, is 43%, close to the observed value of 45% (*Fig. 2*). For catalysis with [Rh$_2${(*S*)-nttl}$_4$], the calculated and experimental values are 49 and 51%, respectively (*Fig. 2*).

Some cyclopropanations were carried out with ethyl diazo(dimethylphenylsilyl)-acetate (**1b**) to afford cyclopropane derivatives **2b** as a *ca.* 88:15 *trans*/*cis* stereoisomer mixture. As before, the enantiomers of **2b** were not separable. Protiodesilylation of *trans*/*cis* **2b** 88:12 gave a mixture of (1*S*,2*S*)-*trans*-**3** (31%, 15% ee) and (1*R*,2*S*)-*cis*-**3** (18%, 13% ee). Accordingly, the absolute configuration of *trans*-**2b** is (1*S*,2*R*), and that of *cis*-**2b** is (1*R*,2*R*). Determination of the ee of the isomers **2b** *via* reduction to the

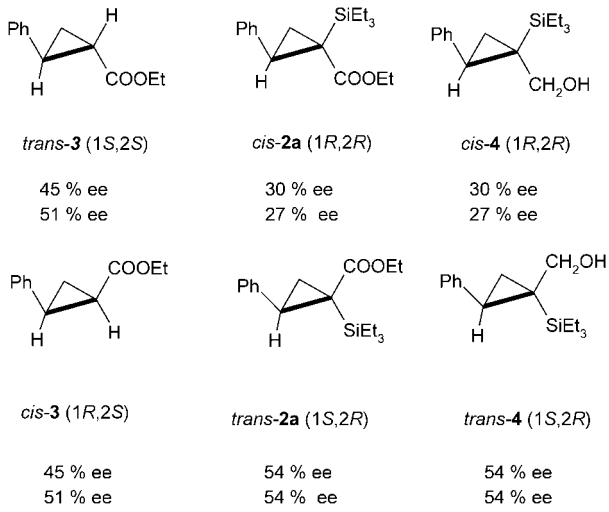


Fig. 2. *Enantiomer excesses* (ee) *of* **2a**, **3**, *and* **4**

corresponding alcohols failed. The 88:15 *trans*/*cis*-mixture **2b** resulting from reaction with $[Rh_2\{(R)\text{-bptv}\}_4]$ was converted to the known [16] alcohol *trans*-**5** in a mediocre yield of 24% with mercuric acetate/peracetic acid (*Scheme 1*). The *cis*-isomer was not detectable in the reaction mixture. Furthermore, the enantiomers of **5** could not be separated.

2.2. *Intramolecular Cyclopropanation*. The intramolecular cyclopropanation of allylic diazoacetates in the presence of chiral Rh^{II} carboxamidate catalysts, such as $[Rh_2\{(S)\text{-mepy}\}_4]$, was the first successful application of Rh^{II} carboxamidate catalysts and provided enantioselectivities close to 100% [17]. We have now investigated the analogous reaction with several (triethylsilyl)-substituted allyl diazoacetates with the objective of opening enantioselective access to functionalized *cis*-disubstituted cyclopropane derivatives. The diazo esters **7a**–**d** required as precursors are known (*Scheme 3*). They were synthesized from the corresponding alcohols and the acetone adduct of ketene, as described previously [18]. Details and full characterization are found elsewhere [19]. Silylation of the diazo esters to afford **8a**–**d** was effected with $TfOSiEt_3$ in the presence of diisopropylethylamine ($^iPr_2NEt$) [20].

The diazo decomposition of the silylated ester **8a** was investigated with a large selection of catalysts (*Table 2*). $[Rh_2(OAc)_4]$ and the Rh^{II} carboxamidate catalysts were inefficient even at elevated temperatures and provided only poor yields of cyclopropane derivative **9a**. Satisfactory results were obtained, however, with Rh^{II} carboxylates derived from protected amino acids in toluene at room temperature. The structure of **9a** was established by comparison of its spectral data with those of the corresponding trimethylsilyl analogue, which are available in the literature [21]. The highest yield of 85% resulted from the reaction catalyzed by $[Rh_2\{(S)\text{-tbsp}\}_4]$, thus demonstrating that sulfonylated proline is as efficient as the *Hashimoto*-type ligands. The highest enantioselectivity in toluene (54%) was obtained with $[Rh_2\{(S)\text{-bpttl}\}_4]$,

Scheme 3

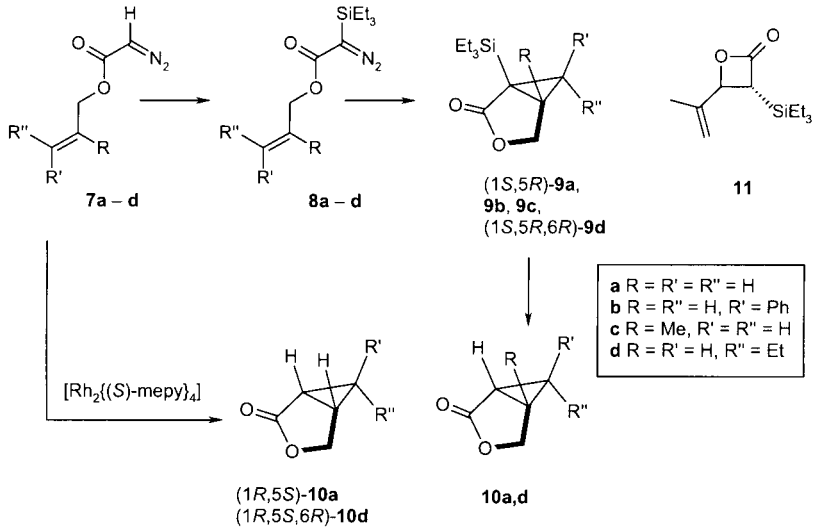


Table 2. *Intramolecular Cyclopropanation of Allyl Diazo(triethylsilyl)acetate* (**8a**)[a])

Catalyst[b])	Time	Temp.	Solvent	Yield [%] of **9a**	ee [%]	Conf.
$[Rh_2(OAc)_4]$	1.5 h	reflux	PhMe	32	–	–
$[Rh_2\{(S)\text{-mepy}\}_4]$	12 h	reflux	PhMe	0	–	–
$[Rh_2\{(S)\text{-meox}\}_4]$	15 h	reflux	PhMe	5	0	–
$[Rh_2\{(S)\text{-bnaz}\}_4]$	4 h	reflux	PhMe	17	4	(1*R*,5*S*)
$[Rh_2\{(S)\text{-pttl}\}_4]$	2.5 h	r.t.	PhMe	79	24	(1*S*,5*R*)
$[Rh_2\{(S)\text{-nttl}\}_4]$	3 h	r.t.	PhMe	74	18	(1*S*,5*R*)
$[Rh_2\{(S)\text{-ptpa}\}_4]$	2 h	r.t.	PhMe	62	11	(1*S*,5*R*)
$[Rh_2\{(S)\text{-tbsp}\}_4]$	3.5 h	r.t.	PhMe	85	18	(1*R*,5*S*)
$[Rh_2\{(S)\text{-dosp}\}_4]$	2.5 h	r.t.	PhMe	64	18	(1*R*,5*S*)
$[Rh_2\{(R)\text{-bptv}\}_4]$	2.25 h	r.t.	PhMe	76	11	(1*R*,5*S*)
$[Rh_2\{(R)\text{-bptv}\}_4]$	2 h	r.t.	$PhCF_3$	78	14	(1*R*,5*S*)
$[Rh_2\{(S)\text{-bptpa}\}_4]$	1.5 h	r.t.	PhMe	76	53	(1*S*,5*R*)
$[Rh_2\{(S)\text{-bptpa}\}_4]$	12 h	r.t.	$PhCF_3$	82	56	(1*S*,5*R*)
$[Rh_2\{(S)\text{-bpttl}\}_4]$	2.5 h	r.t.	PhMe	76	54	(1*S*,5*R*)
$[Rh_2\{(S)\text{-bpttl}\}_4]$	6 h	−78°	PhMe	0	–	–
$[Rh_2\{(S)\text{-bpttl}\}_4]$	2 h	0°	PhMe	78	17	(1*S*,5*R*)
$[Rh_2\{(S)\text{-bpttl}\}_4]$	3 h	r.t.	CH_2Cl_2	82	15	(1*S*,5*R*)
$[Rh_2\{(S)\text{-bpttl}\}_4]$	3 h	r.t.	pentane	62	16	(1*S*,5*R*)
$[Rh_2\{(S)\text{-bpttl}\}_4]$	3 h	r.t.	$PhCF_3$	75	53	(1*S*,5*R*)

[a]) With 2% of catalyst. [b]) See *Fig. 1* for the ligand structures.

although $[Rh_2\{(S)\text{-bptpa}\}_4]$ was comparable with 53%. Surprisingly, with $[Rh_2\{(S)\text{-bpttl}\}_4]$, the ee at 0° was lower (17%) than at room temperature, and no reaction occurred at −78°. Among the various solvents tried, toluene and α,α,α-trifluorotoluene (=(trifluoromethyl)benzene) afforded the best results, while CH_2Cl_2 and pentane were unsatisfactory. The absolute configuration of **9a** was assigned by its

conversion to **10a** by protiodesilylation with Bu_4NF and comparison of its GC retention time with that of authentic (1*R*,5*S*)-**10a**, which was prepared directly with 97% ee from **7a** in the presence of [Rh_2(*S*)-mepy$\}_4$] [17]. The majority of catalysts afforded silylated cyclopropanes **9a** of configuration (1*S*,5*R*), which led to (1*R*,5*S*)-**10a** upon protiodesilylation.

The results are disappointing in comparison to those obtained with unsilylated allylic diazo esters **7**, where enantioselectivities of $>98\%$ have been observed with [$Rh_2\{$(*S*)-mepy$\}_4$]. Unfortunately, as mentioned above, the Rh^{II} carboxamidate catalysts, which perform best with unsilylated allyl diazoacetates **7**, are not sufficiently reactive to decompose the silylated analogues. Similarily, no diazo decomposition occurred with the *ortho*-metallated [Rh^{II}(phosphine)] complexes of *Lahuerta et al.* [22].

The intramolecular cyclopropanations of the silylated diazo esters **8b**,**c** were less satisfactory. The cinnamyl derivative **8b** reacted with [$Rh_2\{$(*S*)-nttl$\}_4$] and [$Rh_2\{$(*S*)-bpttl$\}_4$] to afford the cyclopropane **9b** in only 9 and 10% yield, respectively (*Table 3*). The '*exo*'-orientation of the Ph substituent in **9b** was assigned on the grounds of the coupling constant of 4.5 Hz for H–C(6), typical for vicinal *trans*-coupling of cyclopropane protons [23]. This is consistent with the generally observed stereospecific cyclopropanation of allylic diazo esters in the presence of Rh^{II} or Cu catalysts. An analogous *trans*-coupling of 3.7 Hz has been reported for the desilylated **10b** [24].

Table 3. *Intramolecular Cyclopropanation of Silylated Diazoacetates* **8b**–**d** *in PhMe*

	Catalyst[a])	Time	Temp.	Product	Yield [%]	ee [%]	Conf.	Other product
8b	[$Rh_2\{$(*S*)-nttl$\}_4$]	2.5 h	r.t.	**9b**	9	n.d.	n.d.	–
8b	[$Rh_2\{$(*S*)-bpttl$\}_4$]	2.5 h	r.t.	**9b**	10	n.d.	n.d.	–
8c	[Rh_2(OAc)$_4$]	1 h	reflux	**9c**	9	–	–	–
8c	[$Rh_2\{$(*S*)-nttl$\}_4$]	3.5 h	r.t.	**9c**	20	30	n.d.	**11** (18%)
8d	[Rh_2(OAc)$_4$]	1.5 h	reflux	**9d**	36	–	–	–
8d	[$Rh_2\{$(*S*)-pttl$\}_4$]	2 h	r.t.	**9d**	77	31	(1*S*,5*R*,6*R*)	–
8d	[$Rh_2\{$(*S*)-nttl$\}_4$]	1 h	r.t.	**9d**	76	38	(1*S*,5*R*,6*R*)	–
8d	[$Rh_2\{$(*S*)-bpttl$\}_4$]	12 h	r.t.	**9d**	69	28	(1*S*,5*R*,6*R*)	–

[a]) See *Fig. 1* for the ligand structures.

The diazo decomposition of **8b** was accompanied by formation of secondary products, the structure of which could not be established. However, a β-lactone may be implicated (see below). Owing to the poor yield of **9b** and to difficulties in the enantiomer separation, the reaction of **8b** was not pursued. The diazo decomposition of the 2-methyl substituted diazo acetate **8c**, in turn, proceeded to **9c** in mediocre yield of *ca.* 20% with up to 30% ee, and was accompanied by formation of β-lactone **11** (15–18% yield). In contrast, the reaction proceeded well with the (2*Z*)-pent-2-enyl diazo ester **8d**, which resulted in yields of *ca.* 70% of cyclopropane derivative **9d**. The structure of **9d** was confirmed *via* its protiodesilylation with Bu_4NF in THF to afford known **10d**, which was used for the determination of the ee. The absolute configuration of **9d** was determined to be (1*S*,5*R*,6*R*) by comparison of the GC retention times of the

desilylated **10d** (1*R*,5*S*,6*R*) with those of an authentic sample of (1*R*,5*S*,6*R*)-**10d** prepared from **7d** in the presence of [Rh_2{(*S*)-mepy}$_4$] [17].

3. Conclusions. – The present results show that the diazo decomposition of α-silylated diazo acetates may be carried out under mild conditions and affords acceptable yields of cyclopropane derivatives. The Rh^{II}-catalysts presently available do not allow to reach enantioselectivities comparable to those resulting from the unsilylated analogues. In addition, the protiodesilylation of silylated cyclopropanecarboxylates proceeds with epimerization, unless epimerization is precluded for skeletal reasons, and the oxydative replacement of silyl groups adjacent to carbonyl functions proceeds with poor yields. These problems have yet to be overcome to make silylated diazo esters attractive reagents for enantioselective carbene transfer.

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Experimental Part

1. *General*. See [25]. The catalysts (see *Fig. 1*) were synthesized according to published procedures: [Rh_2{(*S*)-mepy}$_4$] [26], [Rh_2{(*S*)-meox}$_4$] [27], [Rh_2{(*S*)-bnaz}$_4$] [11c], [Rh_2{(*S*)-ptpa}$_4$] [9], [Rh_2{(*S*)-pttl}$_4$] [9], [Rh_2{(*S*)-pttl}$_4$] [10], [Rh_2{(*S*)-bptpa}$_4$] [10], [Rh_2{(*R*)-bptv}$_4$] [10], [Rh_2{(*S*)-tbsp}$_4$] [28], [Rh_2{(*S*)-dosp}$_4$] [29], and [Rh_2{(*S*)-nttl}$_4$] [30].

2. *Intermolecular Cyclopropanation of Styrene.* 2.1. *Ethyl Diazo(triethylsilyl)acetate* (**1a**) [31] was synthesized from ethyl diazoacetate and $TfOSiEt_3$ according to [18]. IR (film): 2957*s*, 2094*w*, 1677*m*, 1271*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.75 (*q*, *J* = 8.1, 6 H); 0.98 (*t*, *J* = 8.3, 9 H); 1.26 (*t*, *J* = 7.2, 1 H); 4.18 (*q*, *J* = 7.2, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 3.2 (*t*); 7.0 (*q*); 14.4 (*q*); 60.6 (*t*); 69.6 (*s*). MS: 228 (5, M^+), 200 (7), 199 (48), 183 (10), 171 (15), 143 (12), 131 (100), 115 (30), 103 (61), 99 (17), 87(67), 75(39), 59(43). HR-MS: 228.1310 ($C_{10}H_{20}O_2N_2Si^+$; calc. 228.1294).

2.2. *Ethyl Diazo(dimethylphenylsilyl)acetate* (**1b**) [3][12]. To ethyl diazoacetate (6.0 mmol) in Et_2O (15 ml) was added, at 0°, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 1.34 ml, 8.9 mmol) and chlorodimethylphenylsilane (380 µl, 8.9 mmol). After 20 h of stirring at r.t., Et_2O (25 ml) was added, and the mixture was washed with H_2O (25 ml). The org. layer was dried ($MgSO_4$) and evaporated: **1b** (1.44 g, 98%). Yellow oil after FC (SiO_2, pentane/AcOEt 80:20). IR (film): 2983*w*, 2088*s*, 1682*s*, 1257*s*, 1073*m*, 820*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.57 (*s*, 6 H); 1.23 (*t*, *J* = 7.14, 3 H); 4.18 (*q*, *J* = 7.0, 2 H); 7.20–7.30 (*m*, 5 H); 7.42–7.45 (*m*, 3 H); 7.61–7.65 (*m*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): −3.0 (*q*); 14.2 (*t*); 60.6 (*t*); 127.9 (*d*); 129.8 (*d*); 133.7 (*d*); 135.3 (*d*); 169.0 (*s*). MS: 248 (7, M^+), 205 (33), 177 (51), 135 (80), 103 (76), 75 (100), 59 (23). HR-MS: 248.0980 ($C_{12}H_{16}O_2N_2Si^+$; calc. 248.0981).

2.3. *Cyclopropanation of Styrene. General Procedure.* To the Rh^{II} catalyst (2 mol-%) under Ar, styrene (920 µl, 8.0 mmol) and the silylated diazo acetate **1a**,**b** (0.85 mmol were added). The mixture was heated to the temp. indicated in *Table 1* until decomposition of the diazo ester was completed (*ca.* 2 h). The solvent was evaporated, and the crude cyclopropane derivative was purified by FC. The diastereoisomers were not separated, but their NMR data could be extracted from mixtures.

Ethyl cis- *and* trans-*2-Phenyl-1-(triethylsilyl)cyclopropane-1-carboxylate* (**2a**). Separation of diastereoisomers by GC (anal. β-*Dex*, 5 min 140°, then 1°/min for 10 min to 180°): t_R 36.2 (*trans*-**2a**) and 36.6 (*cis*-**2a**). **2a**: IR (film): 2958*w*, 2878*w*, 1714*s*, 1461*m*, 1208*m*, 1004*m*, 698*s*. MS: 304 (7, M^+), 275 (15), 231 (19), 135 (19), 131 (100), 115 (40), 87 (70), 75 (35), 59 (37). HR-MS: 304.1849 ($C_{18}H_{28}O_2Si^+$; calc. 304.1858).

trans-**2a**: ^{1}H-NMR (300 MHz, $CDCl_3$): 0.68–0.76 (*m*, 6 H); 1.08 (*t*, *J* = 7.7, 9 H); 1.20–1.26 (*m*, 1 H); 1.36 (*t*, *J* = 7.0, 3 H); 1.96 (*dd*, *J* = 6.4, 4.9, 1 H); 2.46 (*t*, *J* = 7.2, 1 H); 3.80 (*qd*, *J* = 7.2, 0.8, 2 H); 7.20–7.32 (*m*, 5 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 2.8 (*t*); 7.6 (*q*); 13.5 (*t*); 13.9 (*q*); 27.5 (*d*); 60.1 (*t*); 126.4 (*d*); 126.9 (*d*); 128.5 (*d*); 137.5 (*s*); 172.3 (*s*).

cis-**2a**: ^{1}H-NMR (300 MHz, $CDCl_3$): 0.25–0.48 (*m*, 6 H); 0.85 (*t*, *J* = 7.9, 9 H); 0.92 (*t*, *J* = 7.1, 3 H); 1.44–1.48 (*m*, 1 H); 1.80 (*dd*, *J* = 8.8, 4.0, 2 H); 2.76 (*dd*, *J* = 7.0, 8.8, 1 H); 4.22 (*qd*, *J* = 7.1, 0.8, 2 H); 7.20–7.32 (*m*, 5 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 3.8 (*t*); 7.7 (*q*); 14.3 (*q*); 16.0 (*t*); 31.6 (*d*); 60.7 (*t*); 127.9 (*d*); 128.0 (*d*); 130.0 (*d*); 138.3(*s*); 172.3 (*s*).

Ethyl cis-*and* trans-1-*(Dimethylphenylsilyl)-2-phenylcyclopropane-1-carboxylate* (**2b**). Separation of diastereoisomers by GC (anal. *permabond*, 5 min 120°, then 1°/min for 30 min to 180°): t_R 63.5 (*cis*) and 64.4 (*trans*). **2b**: IR (film): 2971*w*, 1716*s*, 1427*m*, 1275*s*, 1108*s*. MS: 324 (9, M^+), 246 (9), 144 (12), 136 (14), 135 (100), 107 (14), 103 (21), 75 (11). HR-MS: 324.1545 ($C_{20}H_{24}O_2Si^+$; calc. 324.1546).

trans-**2b**: ^{1}H-NMR (300 MHz, $CDCl_3$): 0.52 (*s*, 3 H); 0.55 (*s*, 3 H); 0.89 (*t*, *J* = 7.17, 3 H); 1.15–1.20 (*m*, 1 H); 2.02 (*m*, 1 H); 2.45 (*t*, *J* = 8.3, 1 H); 3.77 (*dd*, *J* = 1.1, 7.17, 2 H); 7.20–7.30 (*m*, 5 H); 7.42–7.44 (*m*, 5 H); 7.64–7.67 (*m*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): −3.6 (*q*); −2.1 (*q*); 13.9 (*t*); 14.4 (*t*); 22.6 (*s*); 28.2 (*d*); 60.2 (*t*); 126.4 (*d*); 127.7 (*d*); 127.8 (*d*); 128.7 (*d*); 129.3 (*d*); 134.2 (*d*); 136.7 (*s*); 137.0 (*s*); 172.0 (*s*).

cis-**2b**: ^{1}H-NMR (300 MHz, $CDCl_3$): 0.52 (*s*, 3 H); 0.55 (*s*, 3 H); 0.89 (*t*, *J* = 7.2, 3 H); 1.61 (*dd*, *J* = 4.0, 6.8, 1 H); 1.88 (*dd*, *J* = 4.0, 8.9, 1 H); 2.89 (*dd*, *J* = 6.8, 8.7, 1 H); 4.14 (*q*, *J* = 7.2, 2 H); 7.20–7.30 (*m*, 5 H); 7.42–7.44 (*m*, 5 H); 7.64–7.67 (*m*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): −2.6 (*q*); −2.1 (*q*); 13.9 (*t*); 16.1 (*t*); 19.8 (*s*); 32.5 (*d*); 60.2 (*t*); 126.8 (*d*); 127.3 (*d*); 127.9 (*d*); 128.5 (*d*); 130.0 (*d*); 133.9 (*d*); 136.7 (*s*); 137.0 (*s*); 172.0 (*s*).

2.4. *Desilylation of* **2a** and **2b**: *Ethyl* trans- *and* cis-*2-Phenylcyclopropane-1-carboxylate* (**3**). To a 81:19 mixture of *trans*(48% ee)- and *cis*(30% ee)-**2a** (142 mg, 0.56 mmol) in THF (3.0 ml) was added 1M Bu_4NF (1.0 ml) in THF at −78°. The temp. was allowed to reach r.t. After stirring for 2–4 h, the mixture was quenched with H_2O (2.0 ml) and extracted with CH_2Cl_2. The org. layer was dried ($MgSO_4$) and evaporated and the residue purified by FC (SiO_2, pentane/AcOEt 97:3); 70:30 mixture of (1*S*,2*S*)-*trans*-**3** (45% ee) and (1*R*,2*S*)-*cis*-**3** (45% ee) in 81% yield.

Similarly, starting from a mixture of *trans*(54% ee)- and *cis*(27% ee)-**2a** 4:1, *trans*- and *cis*-**3** were obtained in a 82:18 ratio and with 51% ee (*trans*-**3**) and 49% ee (*cis*-**3**), resp.

The same procedure was applied to the *trans*/*cis*-**2b** 88:12 (100.5 mg, 0.31 mmol) from reaction with $[Rh_2\{(S)\text{-pptl}\}_4]$), which afforded (1*S*,2*S*)-*trans*-**3** (31%, 15% ee) and (1*R*,2*S*)-*cis*-**3** (18%, 13% ee).

trans-**3**: Enantiomer separation by GC (see below). IR (film): 2982*w*, 1725*s*, 1185*s*, 755*m*, 698*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.26 (*t*, *J* = 7.2, 3 H); 1.56–1.68 (*m*, 1 H); 1.86–1.92 (*m*, 1 H); 2.48–2.54 (*m*, 1 H); 4.16 (*q*, *J* = 7.2, 2 H); 7.07–7.30 (*m*, 5 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.3 (*q*); 17.0 (*t*); 24.1 (*d*); 26.1 (*d*); 60.6 (*t*); 126.1 (*d*); 126.4 (*d*); 128.4 (*d*); 140.1 (*s*); 173.4 (*s*). MS: 190 (33, M^+), 145 (23), 117 (100), 115 (50), 91 (21). HR-MS: 190.0981 ($C_{12}H_{14}O_2^+$; calc. 190.0994).

cis-**3**: Enantiomer separation by GC (see below). IR (film): 3009*w*, 1721*s*, 1186*s*, 1081*w*, 864*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.93 (*t*, *J* = 7.2, 3 H); 1.27–1.35 (*m*, 2 H); 1.70–1.76 (*m*, 1 H); 2.05–2.13 (*m*, 1 H); 2.59 (*m*, 1 H); 3.88 (*q*, *J* = 7.2, 2 H); 7.20–7.28 (*m*, 5 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 11.0 (*t*); 13.9 (*q*); 21.8 (*d*); 25.4 (*d*); 60.1 (*t*); 126.6 (*d*); 127.8 (*d*); 129.3 (*d*); 136.6 (*s*); 170.9 (*s*). MS: 190 (32, M^+), 145 (20), 117 (100), 115 (53), 91 (23). HR-MS: 190.1003 ($C_{12}H_{14}O_2^+$; calc. 190.0994).

2.5. *Cyclopropanation of Styrene with Ethyl Diazoacetate.* To the bis[dihydrooxazole] ligand **6** (1.3 mol-%), $[Cu(OTf)_2]$ (1.3 mol-%), and styrene (1.25 ml, 5.0 equiv.) in $CHCl_3$ (6.0 ml), ethyl diazoacetate (257 mg, 1.0 equiv.) in $CHCl_3$ (6.0 ml) was added dropwise. The mixture was stirred at r.t. for 1 h and then evaporated. The crude product was purified by FC: 129 mg (30%) of an 83:17 mixture of (1*R*,2*R*)-*trans*-**3** (83% ee) and (1*R*,2*S*)-*cis*-**3** (70% ee).

Ethyl trans-*(1*R,2R*)-2-Phenylcyclopropane-1-carboxylate* (*trans*-**3**). Enantiomer separation by GC (*β-Dex*, 5 min at 80°, then 1°/min, 10 min at 180°): t_R 55.3 ((1*R*,2*R*), major) and 55.5 ((1*S*,2*S*), minor).

Ethyl cis-*(1*R,2S*)-2-Phenylcyclopropane-1-carboxylate* (*cis*-**3**). Enantiomer separation by GC (*β-Dex*, 5 min at 80°, then 1°/min, 10 min at 180°): t_R 51.7 ((1*S*,2*R*), minor) and 52.2 ((1*R*,2*S*), major).

2.6. *Reduction of* **2a**: trans- *and* cis-*2-Phenyl-1-(triethylsilyl)cyclopropane-1-methanol* (**4**). To $LiAlH_4$ (2 equiv.) in THF (2.0 ml) under Ar, *trans*/*cis*-**2a** 3:1 (0.80 mmol) in THF (4.0 ml) was added. The mixture was stirred overnight at r.t. Excess $LiAlH_4$ was decomposed by addition of ethane-1,2-diamine (2 ml), followed by 8% NaOH soln. (2.0 ml) and H_2O. The crude product was extracted with Et_2O (10 ml), the extract dried (Na_2SO_4) and evaporated, and the resulting diasteroisomer mixture separated by FC (SiO_2, CH_2Cl_2/pentane 80:20).

trans-**4**: Yield 45%. Colorless oil. Enantiomer separation by GC (*β-Dex*, 5 min at 140°, then 0.5°/min to 180°, 10 min at 180°): t_R 48.6 ((1*S*,2*S*), minor) and 49.1 ((1*R*,2*R*), major); absolute configuration assigned from that of *trans*-**2a**. IR (film): 2945*m*, 2871*m*, 1458*w*, 1239*w*, 1003*s*, 726*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.68 (*q*, *J* = 7.9, 6 H); 0.87–0.99 (*m*, 2 H); 1.05 (*t*, *J* = 7.9, 9 H); 2.24 (*t*, *J* = 6.7, 1 H); 3.22 (*d*, *J* = 11.8, 1 H); 3.53 (*d*, *J* = 11.8, 1 H); 7.24–7.30 (*m*, 5 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 2.6 (*t*); 7.6 (*q*); 11.7 (*t*); 15.9 (*s*); 24.3 (*d*); 65.7 (*t*); 126.2

(*d*); 128.3 (*d*); 128.9 (*d*); 138.4 (*s*). MS: 233 (12, $[M - C_2H_5]^+$), 215 (27), 130 (36), 115 (43), 103 (100), 87 (65), 75 (80). HR-MS: 233.1386 ($C_{14}H_{21}OSi^+$; calc 233.1362).

cis-**4**: Yield 13%. Colorless oil. Enantiomer separation by GC (*β-Dex*, 5 min 120°, then 1°/min to 180°, 10 min 180°): t_R 57.0 ((1*R*,2*R*), major) and 57.3 ((1*S*,2*S*), minor); absolute configuration assigned based on that of *cis*-**2a**. IR (film): 2951*m*, 2874*m*, 1455*w*, 1238*w*, 1005*s*, 726*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.24–0.40 (*m*, 6 H); 0.85 (*t*, *J* = 7.7, 9 H); 1.20 (*t*, *J* = 5.6, 1 H); 1.47 (*s*, 1 H); 2.10–2.20 (*m*, 2 H); 3.27 (*d*, *J* = 11.0, 1 H); 3.87 (*d*, *J* = 11.0, 1 H); 7.20–7.30 (*m*, 5 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 3.3 (*t*); 7.6 (*q*); 12.0 (*t*); 17,6 (*s*); 27.0 (*d*); 71.5 (*t*); 126.2 (*d*); 127.9 (*d*); 129.7 (*d*); 139.7 (*s*). MS: 233 (8, $[M - C_2H_5]^+$), 215 (21), 171 (12), 130 (39), 115 (39), 103 (100), 87 (60), 75 (85). HR-MS: 233.1372 ($C_{14}H_{21}OSi^+$; calc. 233.1361).

2.7. *Oxydative Desilylation of* trans/cis-**2b**: *Ethyl* trans-*1-Hydroxy-2-phenylcyclopropane-1-carboxylate* (*trans*-**5**). Peracetic acid (6.0 ml; 35% in AcOH) was added to *trans*/*cis*-**2b** 78:23 (204 mg, 0.61 mmol) and $Hg(OAc)_2$ (233 mg, 0.73 mmol). After stirring overnight at r.t., the mixture was diluted with Et_2O (100 ml). After slow addition of sat. thiosulfate, the org. layer was washed with H_2O (2 × 100 ml) and 5% $NaHCO_3$ soln. (50 ml) and evaporated. Purification by FC (SiO_2, pentane/AcOEt 80:20) afforded *trans*-**5** (31 mg, 24%). IR (film): 3451*w*, 2978*w*, 1722*m*, 1180*m*, 1015*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.76 (*t*, *J* = 7.1, 3 H); 1.66 (*dd*, *J* = 10.3, 6.0, 1 H); 1.97 (*dd*, *J* = 8.6, 6.0, 1 H); 2.77 (*t*, *J* = 9.6, 1 H); 3.77–3.87 (*m*, 2 H); 7.17–7.27 (*m*, 5 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 13.5 (*q*); 18.6 (*t*); 34.5 (*d*); 60.8 (*s*); 61.1 (*t*); 126.6 (*d*); 127.9 (*d*); 128.9 (*d*); 135.9 (*s*); 172.5 (*s*).

3. *Intramolecular Cyclopropanation of Allyl Diazo(triethylsilyl)acetates* **7**. 3.1. *Allyl Diazoacetates* **7a–d**. The diazo precursors **7a–d** were synthesized according to literature procedures from the appropriate allylic alcohols and 2,2,4-trimethyl-1,3-dioxacyclohex-4-en-6-one (=2,2,6-trimethyl-4*H*-1,3-dioxin-4-one) in refluxing xylene. The resulting acetoacetate esters underwent diazo transfer to afford diazoacetoacetates, which were subjected to cleavage with base to yield the diazo esters **7a–d** [18][19].

3.2. *Silylation of Allyl Diazoacetates* **7a–d**: *Allyl Diazo(triethysilyl)acetates* **8a–d**, *General Procedure.* ^{i}Pr$_2$NEt (290 µl, 1.66 mmol) followed by $TfOSiEt_3$ (380 µl, 1.66 mmol) in Et_2O (2.5 ml) was added, at −78°, to the diazo acetate **7a–d** (1.50 mmol) in Et_2O (5.0 ml). After stirring overnight at r.t., the mixture was neutralized with Na_2CO_3, filtered, and evaporated. The residue was purified by FC.

Prop-2-enyl Diazo(triethylsilyl)acetate (**8a**) [19]. From allyl diazoacetate [32] after FC (SiO_2, pentane/AcOEt 97:3): yield 81%. IR (film): 2955*m*, 2090*s*, 1687*s*, 1254*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.75–0.83 (*m*, 6 H); 1.01 (*t*, *J* = 7.4, 9 H); 4.66 (*td*, *J* = 1.5, 5.6, 2 H); 5.24–5.37 (*m*, 2 H); 5.89–6.02 (*m*, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 3.1 (*t*); 7.1 (*q*); 65.3 (*t*); 117.9 (*t*); 132.5 (*d*); 169.1 (*s*). MS: 240 (< 1, M^+), 217 (1), 183 (20), 143 (21), 115 (80), 87 (100), 59 (70). HR-MS: 240.1306 ($C_{11}H_{20}O_2N_2Si^+$; calc. 240.1294).

*(2*E*)-3-Phenylprop-2-enyl Diazo(triethylsilyl)acetate* (**8b**). From *trans*-cinnamyl diazoacetate [17][19][33] after FC (SiO_2, pentane/AcOEt 90:10): yield 72%. Yellow oil. IR (film): 2955*w*, 2876*w*, 2084*s*, 1683*s*, 1255*s*, 736*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.81 (*q*, *J* = 7.9, 6 H); 1.04 (*t*, *J* = 7.9, 9 H); 4.83 (*d*, *J* = 6.4, 2 H); 6.29 (*td*, *J* = 6.2, 15.8, 1 H); 6.66 (*d*, *J* = 15.8, 1 H); 7.27–7.42 (*m*, 5 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 3.1 (*t*); 7.0 (*q*); 65.1 (*t*); 123.5 (*d*); 126.6 (*d*); 128.0 (*d*); 128.6 (*d*); 133.8 (*d*); 136.3 (*s*); 169.2 (*s*). MS: 316 (2, M^+), 259 (11), 217 (6), 117 (100), 115 (32), 87 (22), 59 (13). HR-MS: 316.1609 ($C_{17}H_{24}O_2N_2Si^+$; calc. 316.1607).

2-Methylprop-2-enyl Diazo(triethylsilyl)acetate (**8c**) [17][19]. From methallyl diazoacetate after FC (SiO_2, pentane/AcOEt 96:4): yield 85%. Yellow oil. IR (film): 2953*w*, 2874*w*, 2114*s*, 2084*s*, 1684*s*, 1259*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.76 (*q*, *J* = 7.4, 6 H); 0.99 (*t*, *J* = 7.4, 9 H); 1.77 (*s*, 3 H); 4.56 (*s*, 2 H); 4.95 (*d*, *J* = 23.0, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 3.0 (*t*); 7.0 (*q*); 19.4 (*q*); 67.9 (*t*); 112.7 (*t*); 140.1 (*s*); 169.2 (*s*). MS: 254 (3, M^+), 217 (68), 189 (49), 157 (48), 115 (55), 87 (100), 55 (62). HR-MS: 254.1471 ($C_{12}H_{22}O_2N_2Si^+$; calc. 254.1450).

*(2*Z*)-Pent-2-enyl Diazo(triethylsilyl)acetate* (**8d**) [19]. From (2*Z*)-pent-2-enyl diazoacetate (**7d**) after FC (SiO_2, pentane/AcOEt 95:5): yield 80%. Yellow oil. IR (film): 2954*w*, 2085*s*, 1687*s*, 1257*s*, 1074*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.75 (*q*, *J* = 7.8, 6 H); 0.98 (*t*, *J* = 7.7, 9 H); 0.97–1.01 (*m*, 3 H); 2.12 (*dquint.*, *J* = 7.4, 1.4, 2 H); 4.68 (*td*, *J* = 0.6, 6.9, 2 H); 5.48–5.53 (*m*, 1 H); 5.61–5.67 (*m*, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 3.1 (*t*); 7.0 (*q*); 14.0 (*q*); 20.9 (*t*); 60.4 (t); 122.9 (*d*); 136.8 (*d*); 169.5 (*s*). MS: 268 (1, M^+), 211 (17), 171 (66), 143 (15), 115 (86), 103 (70), 87 (100), 75 (33), 69 (51), 59 (37). HR-MS: 268.1623 ($C_{13}H_{24}O_2N_2Si^+$; calc. 268.1607).

3.3. *Intramolecular Cyclopropanation of Allyl Diazo(triethylsilyl)acetates* **8a–d**. *General Procedure*. To the Rh^{II} catalyst (2% with respect to **8**) was added the diazosilylacetate **8a–d** (0.40 mmol) under Ar in 5 min. The mixture was stirred during 2 h at r.t. The soln. was evaporated and the residue purified by FC.

*(1*S*,5*R*)-1-(Triethylsilyl)-3-oxabicyclo[3.1.0]hexan-2-one* (**9a**). FC (SiO_2, pentane/AcOEt 97:3) afforded **9a**. For yields, see *Table 2*. Colorless oil. Enantiomer separation by GC (*Lipodex E*, 5 min at 120°, then 1°/min to 160°, 10 min at 160°): t_R 17.3 ((1*S*,5*R*), major) and 18.4 ((1*R*,5*S*), minor); for abs. configuration, see below. $[\alpha]_D^{20} = +7.2$ (*c* = 1.00, EtOH; for 30% ee). IR (film): 2954*m*, 2876*m*, 1753*s*, 1248*m*, 994*s*. ^{1}H-NMR (300 MHz,

$CDCl_3$): 0.59–0.67 (*m*, 6 H); 0.96 (*t*, *J* = 8.1, 9 H); 1.17 (*dd*, *J* = 7.0, 4.5, 1 H); 2.04–2.06 (*m*, 1 H); 4.24 (*m*, 2 H). ^{13}C-NMR (MHz, $CDCl_3$): 2.0 (*t*); 7.2 (*q*); 13.3 (*s*); 15.6 (*t*); 21.9 (*t*); 68.2 (*t*); 178.8 (*s*). MS: 183 (85, $[M - C_2H_5]^+$), 139 (30), 111 (100), 83 (42), 59 (27), 53 (36). HR-MS: 183.0850 ($C_9H_{15}O_2Si^+$; calc. 183.0841).

rel-(*1*R,*5*S,*6*R)*-6-Phenyl-1-(triethylsilyl)-3-oxabicyclo[3.1.0]hexan-2-one* (**9b**). After FC (SiO_2, pentane/AcOEt 97:3), yield 9% with $[Rh_2\{(S)\text{-nttl}\}_4]$ and 10% with $[Rh_2\{(S)\text{-bpttl}\}_4]$ (*Table 3*). Colorless oil. IR (film): 2953*m*, 2874*m*, 1713*s*, 1189*s*, 1051*s*, 966*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.31–0.52 (*m*, 6 H); 0.88 (*t*, *J* = 7.9, 9 H); 2.56 (*d*, *J* = 4.5, 1 H); 2.75 (*t*, *J* = 4.0, 1 H); 4.40–4.50 (*m*, 2 H); 7.30–7.40 (*m*, 5 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 2.9 (*t*); 7.3 (*q*); 23.6 (*s*); 25.7 (*d*); 33.3 (*d*); 68.3 (*t*); 127.7 (*d*); 128.4 (*d*); 129.2 (*d*); 135.2 (*s*); 178.4 (*s*). MS: 259 (100, $[M - C_2H_5]^+$), 157 (43), 129 (48), 115 (14), 87 (41), 59 (26). HR-MS: 259.1143 ($C_9H_{15}O_2Si^+$; calc. 259.1154).

rel-*(1*S,*5*R)*-5-Methyl-1-(triethylsilyl)-3-oxabicyclo[3.1.0]hexan-2-one* (**9c**). After FC (SiO_2, pentane/AcOEt 97:3), yield 20% with $[Rh_2\{(S)\text{-nttl}\}_4]$ (*Table 3*). Colorless oil. Enantiomer separation by GC (*β-Dex*, 5 min at 120°, then 1°/min to 180°, 10 min at 180°): t_R 27.5 (minor) and 27.7 (major). IR: 2954*m*, 2879*m*, 1750*s*, 1188*s*, 1056*s*, 1006*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.68–0.76 (*m*, 6 H); 0.99 (*t*, *J* = 7.5, 9 H); 1.09 (*d*, *J* = 4.2, 1 H); 1.16 (*d*, *J* = 3.9, 1 H); 1.36 (*s*, 3 H); 3.94 (*d*, *J* = 8.8, 1 H); 4.20 (*d*, *J* = 8.8, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 2.5 (*t*); 7.3 (*q*); 16.8 (*q*); 22.9 (*t*); 30.0 (*s*); 72.2 (*t*); 113.9 (*s*); 179.4 (*s*). MS: 197 (100, $[M - C_2H_5]^+$), 125 (92), 115 (36), 103 (24), 97 (54), 87 (52). HR-MS: 197.1004 ($C_{12}H_{22}O_2Si^+$; calc. 197.0998).

cis-*4-(1-Methylethenyl)-3-(triethylsilyl)oxetan-2-one* (**11**). After FC (SiO_2, pentane/AcOEt 97:3), yield 18% with $[Rh_2\{(S)\text{-nttl}\}_4]$. IR (film): 2956*m*, 2874*m*, 1807*s*, 1255*w*, 1111*s*, 1008*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.67–0.76 (*m*, 6 H); 0.98 (*t*, *J* = 8.1, 9 H); 1.79 (*s*, 3 H); 3.55 (*dd*, *J* = 6.4, 2.5, 1 H); 4.88 (*d*, *J* = 6.4, 1 H); 5.08 (*s*, 1 H); 5.26 (*s*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 3.5 (*t*); 7.2 (*q*); 19.1 (*d*); 44.6 (*q*); 73.3 (*d*); 113.0 (*t*); 140.2 (*s*); 170.0 (*s*). MS: 226 (3, M^+), 198 (17), 197 (100), 125 (54), 103 (38), 75 (54). HR-MS: 226.138750 ($C_{12}H_{22}O_2Si^+$; calc. 226.1389).

*(1*S,*5*R,*6*R)*-6-Ethyl-1-(triethylsilyl)-3-oxabicyclo[3.1.0]hexan-2-one* (**9d**). After FC (SiO_2, pentane/AcOEt 97:3), yield 76% with $[Rh_2\{(S)\text{-nttl}\}_4]$, 38% ee (determined after desilylation to **10d**). For abs. configuration, see below. Colorless oil. IR (film): 2952*m*, 2873*m*, 1745*s*, 1197*w*, 1070*m*, 1000*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.64 (*q*, *J* = 7.7, 6 H); 0.96 (*t*, *J* = 7.7, 9 H); 1.04 (*t*, *J* = 7.2, 3 H); 1.26–1.55 (*m*, 3 H); 2.08 (*t*, *J* = 5.6, 1 H); 4.13 (*d*, *J* = 9.6, 1 H); 4.29 (*dd*, *J* = 9.6, 5.5, 1 H). ^{13}C-NMR (MHz, $CDCl_3$): 2.1 (*t*); 7.2 (*q*); 13.3 (*q*); 17.0 (*t*); 19.4 (*s*); 27.1 (*d*); 27.3 (*d*); 65.1 (*t*); 177.1 (*s*). MS: 211 (100, $[M - C_2H_5]^+$), 115 (16), 109 (15), 103 (69), 81 (25), 75 (46). HR-MS: 211.1158 ($C_{11}H_{19}O_2Si^+$; calc. 211.1154).

3.4. *Desilylation of 1-(Triethylsilyl)-3-oxabicyclo[3.1.0]hexan-2-ones* **9a**,**d**: *General Procedure.* At r.t., 1M Bu_4NF in THF (1 ml) was added dropwise to the appropriate oxabicyclohexanone (0.56 mmol). After stirring for 2–4 h, H_2O (2.0 ml) was added, the mixture extracted with CH_2Cl_2, the org. layer dried ($MgSO_4$) and evaporated, and the residue purified by FC.

*(1*R,*5*S*)-3-Oxabicyclo[3.1.0]hexan-2-one* (**10a**). FC (SiO_2, pentane/AcOEt 96:4) afforded 12 mg (36%) of **10a**. Colorless oil. Enantiomer separation by GC (*Lipodex E*, 10 min at 100°, then 1°/min to 150°, 10 min at 150°). t_R 27.6 ((1*R*,5*S*), major) and 29.8 ((1*S*,5*R*), minor); for abs. configuration, see *3.4*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.85–0.88 (*m*, 1 H); 1.22–1.30 (*m*, 1 H); 2.03–2.10 (*m*, 1 H); 2.20–2.27 (*m*, 1 H); 4.22 (*d*, *J* = 9.2 Hz, 1 H); 4.32–4.37 (*m*, 1 H).

*(1*R,*5*S,*6*R)*-6-Ethyl-3-oxabicyclo[3.1.0]hexan-2-one* (**10d**). FC (SiO_2, pentane/AcOEt 96:4) afforded 12 mg (37%) of **10d**. Colorless oil. Enantiomer separation by GC (*Lipodex E*, 5 min 120°, 1°/min to 160°, 10 min 160°): t_R 17.4 ((1*S*,5*R*,6*S*), minor) and 18.1 ((1*R*,5*S*,6*R*), major); for abs. configuration, see *3.4*. $[\alpha]_D^{20} = 26.3$ (*c* = 0.24, EtOH, for 28% ee). IR (film): 2965*m*, 2876*w*, 1756*s*, 1173*w*, 1058*s*, 979*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.07 (*t*, *J* = 6.8, 3 H); 1.40–1.43 (*m*, 3 H); 2.18–2.29 (*m*, 2 H); 4.15 (*d*, *J* = 9.9, 1 H); 4.41 (*dd*, *J* = 9.8, 5.3, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 13.3 (*q*); 16.3 (*t*); 22.5 (*d*); 22.7 (*d*); 23.9 (*d*); 66.0 (*t*); 175.1 (*s*). MS: 126 (3, M^+), 111 (9), 97 (15), 85 (100), 67 (84), 55 (46). HR-MS: 126.0688 ($C_7H_{10}O_2^+$; calc. 126.0680).

3.4. *Absolute Configuration of* **10a**,**d**. Optically active 3-oxabicyclo[3.1.0]hexan-2-ones **10a**,**d** of known absolute configuration were synthesized *via* intramolecular cyclopropanation of **7a** and **7d**, respectively, in the presence of $[Rh_2\{(S)\text{-mepy}\}_4]$ according to the *General Procedure* described in *3.3*.

*(1*R,*5*S*)-3-Oxabicyclo[3.1.0]hexan-2-one* (**10a**). FC (SiO_2, pentane/AcOEt 95:5) afforded 61 mg (37%) of **10a** with 89% ee. Enantiomer separation by GC (*Lipodex E*, 10 min at 100°, then 1°/min to 150°, 10 min at 150°): t_R 27.0 ((1*R*,5*S*), major) and 29.9 ((1*S*,5*R*), minor).

*(1*R,*5*S,*6*R)*-6-Ethyl-3-oxabicyclo[3.1.0]hexan-2-one* (**10d**). FC (SiO_2, pentane/AcOEt 95:5) gave 46 mg (38%) of **10d** with 97% ee. Enantiomer separation by GC (*Lipodex E*, 5 min at 120°, then 1°/min to 160°, 10 min at 160°): t_R 17.3 ((1*S*,5*R*,6*S*), minor) and 17.9 ((1*R*,5*S*,6*R*), major).

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