169. Semicorrin Metal Complexes as Enantioselective Catalysts

Part 2

Enantioselective Cyclopropane Formation from Olefins with Diazo Compounds Catalyzed by Chiral (Semicorrinato)copper Complexes[1])

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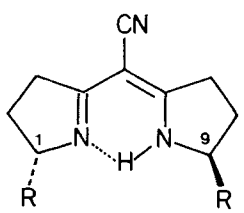
Copper complexes of chiral, C_2-symmetric semicorrin ligands were found to be efficient catalysts for the cyclopropane formation from olefins with diazo compounds. In the presence of 1 mol-% of catalyst, alkyl diazoacetates reacted smoothly with terminal olefins such as styrene, butadiene, and 1-heptene to give the corresponding optically active cyclopropanecarboxylic-acid derivatives *(Table 1, Scheme 2)*. With one of the catalysts, enantioselectivities up to 97% ee were obtained *(Table 2)*. Usually, the reactions were carried out using bis(semicorrinato)copper(II) complexes as precatalysts. In order to produce active catalysts, these complexes had to be activated first by heating in the presence of diazoacetate or by treatment with phenylhydrazine. Experiments with (semicorrinato)copper(I) complexes, prepared *in situ* from copper(I) *tert*-butoxide *(Scheme 4)*, suggest that the actual catalyst is a [mono(semicorrinato)]copper(I).

Introduction. – In the preceding communication [2], we have introduced chiral 1,9-disubstituted semicorrins **1** as ligands for enantioselective control of metal-catalyzed reactions. Here we report the first application for this class of ligands, the cyclopropane formation from olefins with diazo compounds, using (semicorrinato)copper complexes as enantioselective catalysts.



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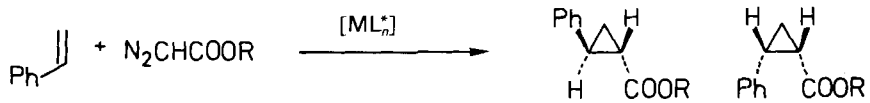
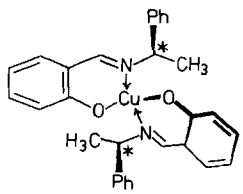
The first example of an enantioselective cyclopropane formation was reported by *Nozaki et al.* [3] more than 20 years ago *(cf. Scheme 1)*. Under the influence of the chiral (salicylaldiminato)copper complex **2**, achiral olefins and diazo compounds were converted to optically active cyclopropane derivatives. Although the optical yields were low,

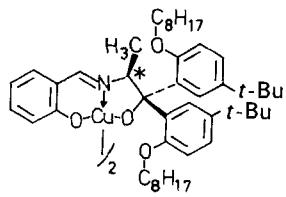
[1]) Taken in part from the Ph. D. thesis of *H.F.*, ETH-Zürich (in preparation); for a preliminary communication, see [1].

Scheme 1

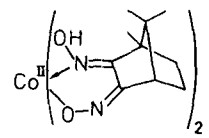




2 [3]



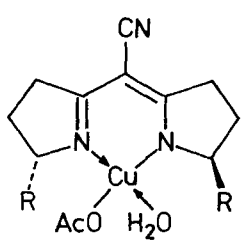
3 [4]



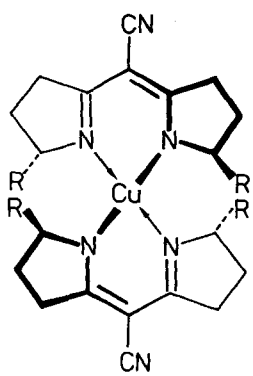
4 [5]

these findings were of considerable consequence to the development of enantioselective catalysis, as they demonstrated the general principle that a homogeneous metal catalyst can be rendered enantioselective by complexation with a chiral ligand. Subsequently, a number of research groups tried to improve the selectivity of this synthetically useful (C–C)-bond-forming reaction [4–6]. The most spectacular advances were reported by *Aratani et al.* [4]: with the Cu complex **3**, found by extensive evaluation of various ligands, they obtained enantioselectivities in the range of 80% for the cyclopropane formation from styrene, and even higher selectivities of up to 94% ee for the cyclopropane formation from trisubstituted olefins. Another group of highly enantioselective catalysts, Co(II) complexes of camphorquinone dioximes (see **4**), were developed by *Nakamura, Otsuka,* and coworkers [5]. The application of Co catalysts of this type, however, is limited to olefins with a terminal double bond conjugated to an aryl group or an additional C=C bond.

2. Cyclopropane Formation from Styrene. – As a first test of the semicorrin ligands **1**, we have investigated the properties of the Cu complexes **5**–**8** as catalysts for the cyclopropane formation from styrene with alkyl diazoacetates, a reaction which has been



5 R = CMe_2OH



6 R = COOMe

7 R = $CH_2OSiMe_2(t\text{-Bu})$

8 R = CMe_2OH

widely used as a standard for assessing the efficiency and selectivity of catalysts in cyclopropane formation [4–6]. The preparation and structural features of the complexes **5**–**8** have been discussed in the preceding communication [2]. All four complexes were found to be efficient catalysts, converting styrene and ethyl diazoacetate to optically active 2-phenylcyclopropane-1-carboxylates **9a** and **9b** in 60–80% yield *(cf. Table 1)*.

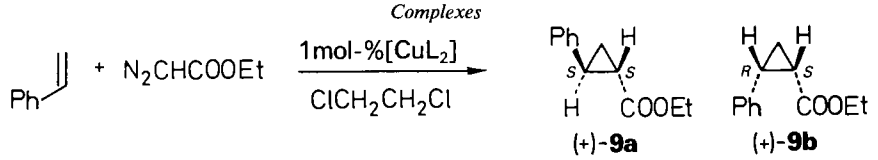
The reactions were carried out in 1,2-dichloroethane using 1 mol-% of catalyst. Increasing the relative amount of catalyst did not raise the enantioselectivity, whereas with lower catalyst/substrate ratios (< 0.5 mol-%), the optical yields decreased. To start the reaction, the Cu complexes had to be activated by heating in the presence of diazo compound (*cf. Section 4* and *Exper. Part*). After a short activation period, the reaction was then allowed to continue at the temperature indicated in *Table 1*. In order to suppress the formation of diethyl fumarate and maleate, the concentration of the diazo compound was kept at low levels by slow, continuous addition of ethyl diazoacetate to the reaction mixture by means of a syringe pump (*cf.* [7]). In this way, good yields of cyclopropane products were obtained.

The enantiomeric purity of the products **9a** and **9b** was determined by capillary GC of the diastereoisomeric mixture obtained by hydrolysis and reesterification with (+)- or (−)-menthol. Both, the derivative from (+)- and from (−)-menthol gave the same results, demonstrating that no kinetic discrimination effects in the esterification with menthol interfered with the analysis. The optical yields were determined independently from the specific rotation of the corresponding methyl esters [8]. For the methyl ester of the *trans*-isomer **9a**, the results were additionally confirmed by ^{1}H-NMR spectroscopy in the presence of tris(3-trifluoroacetyl-*d*-camphorato)europium(III) ([Eu(tfc)$_3$]) as a chiral shift reagent. All three methods provided identical results within experimental error. The *trans*- and the *cis*-product **9a** and **9b**, respectively, both had positive optical rotations; therefore, their configuration at C(1) is (*S*) [9].

The enantioselectivity of the bis(semicorrinato) complexes increased in the order **6** < **7** < **8**. The mono(semicorrinato) complex **5** was less selective than the corresponding bis(semicorrinato) complex **8**. With **5** and **8**, the reaction was carried out at room temperature, whereas **6** and **7** required heating (40–60° for **7**, ⩾ 60° for **6**). Semicorrinato complexes of Ni(II), Co(II), and Rh(I) did not exhibit any significant catalytic activity towards ethyl diazoacetate under these conditions. Of the catalysts tested so far, the Cu complex **8** was clearly the most selective.

Analogous to the findings of *Aratani et al.* [4] and *Nakamura et al.* [5], the enantioselectivity of the reaction could substantially be improved by variation of the diazoacetate alkoxy group *(cf. Table 2)*. With the bulkier *tert*-butyl-ester group, the enantiomeric

Table 1. *Cyclopropane Formation from Styrene with Ethyl Diazoacetate Catalyzed by (Semicorrinato)copper Complexes*

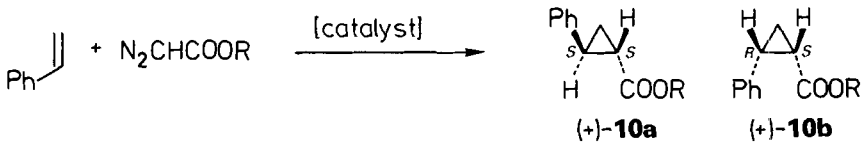


Catalyst	Temperature	Diastereoselectivity[a])	Enantiomeric excess[b])	
	[°C]	**9a**/**9b**	**9a** [%]	**9b** [%]
5	23	69:31	58	43
6	60	74:26	23	19
7	40	75:25	59	45
8	23	73:27	85	68

[a]) Determined by GC.

[b]) Determined by GC after hydrolysis and reesterification with (−)-menthol; estimated error ±1%.

Table 2. *Cyclopropane Formation from Styrene with Alkyl Diazoacetates and the (Semicorrinato)copper* **8**, *Comparison of* **8** *with the Catalysts* **3** [4] *and* **4** [5]



Entry	Catalyst	Diazo compound	Yield [%][a]) of	Diastereoselectivity[b])	Enantiomeric excess[c])	
		R	**10a** + **10b**	**10a**:**10b**	**10a** [%]	**10b** [%]
a	**8**	Ethyl	65	73:27	85	68
b	**8**	*t*-Butyl	60	81:19	93	92
c	**8**	(1*R*,3*R*,4*S*)-Menthyl[d])	65–75	85:15	91	90
d	**8**	(1*S*,3*S*,4*R*)-Menthyl[e])	60–70	82:18	97	95
e	**3**[f])	(1*S*,3*S*,4*R*)-Menthyl[e])		82:18	81	78
f	**4**[g])	Ethyl	92	46:54	75	67
g	**4**[g])	2,2-Dimethylpropyl	87	70:30	88	81

[a]) After column chromatography, based on styrene.
[b]) Determined by GC.
[c]) Determined by GC analysis of the (1*R*,3*R*,4*S*)- and (1*S*,3*S*,4*R*)-menthyl esters, estimated error ±1%.
[d]) (1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl, from (−)-menthol.
[e]) (1*S*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyl, from (+)-menthol.
[f]) Results taken from [4].
[g]) Results taken from [5]; reaction in neat styrene; yields based on diazoacetate.

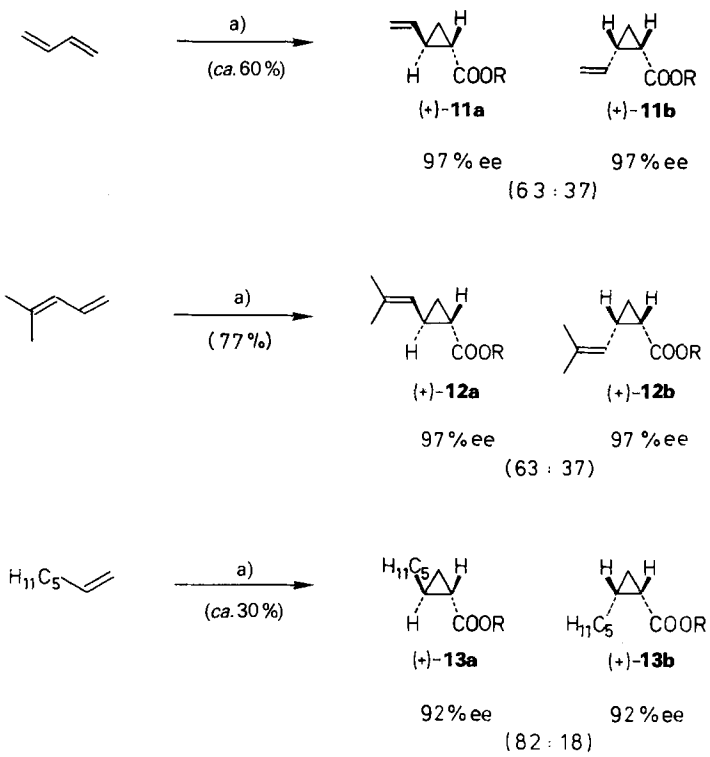
purity of both the *trans*- and the *cis*-product **10a** and **10b** exceeded 90% ee. Even better selectivities were obtained with (1*S*,3*S*,4*R*)-menthyl diazoacetate and **8**[2]). In a series of experiments, the enantiomeric purity of the *trans*-product **10a** consistently ranged between 96 and 98% ee. These values clearly exceed the selectivities previously observed in the cyclopropane formation from styrene with other catalysts (*cf. Entries e–g*).

The configuration of the menthyl group had a distinct effect on the enantioselectivity of the reaction. Although such an effect is negligible in the cyclopropane formation with achiral Cu catalysts [8], the interaction between the chiral menthyl group and the chiral semicorrin catalyst results in a marked selectivity difference between (1*S*,3*S*,4*R*)- and (1*R*,3*R*,4*S*)-menthyl diazoacetate. Analogous findings have been reported for cyclopropane formations with the catalyst **3** [4].

3. Further Examples. – The semicorrinato complex **8** was found to be an efficient, highly enantioselective catalyst for the cyclopropane formation from terminal olefins. Butadiene, 4-methyl-1,3-pentadiene, and 1-heptene all reacted with enantioselectivities in the range of 92–97% ee *(cf. Scheme 2)*. By this route, 2-vinylcyclopropanecarboxylic acid (**11a**, R=H) which has been used as a building block for the synthesis of the brown algae pheromones hormosirene and dictyopterene A [10] was readily prepared in high enantiomeric purity. Cyclopropane formation from 4-methyl-1,3-pentadiene occurred

[2]) Although cyclopropane formation with (1*S*,3*S*,4*R*)- or (1*R*,3*R*,4*S*)-menthyl diazoacetate is, strictly speaking, a diastereoselective rather than an enantioselective transformation, the terms 'enantioselectivity' and 'ee' are maintained for the sake of consistency.

Scheme 2



a) 1 mol-% **8**, $N_2CHCOOR$ (R = (1*S*,3*S*,4*R*)-menthyl), $ClCH_2CH_2Cl$, 23°.

exclusively at the less substituted double bond. The rather low *cis*/*trans* selectivities in the reactions of the dienes are somewhat disappointing, although this is a general problem of metal-catalyzed cyclopropane-generating reactions [11]. As an example of an olefin with an isolated, non-activated double bond, 1-heptene also reacted with high enantioselectivity. However, the reduced reactivity of the double bond compared to styrene or butadiene resulted in lower chemical yields due to competing formation of side products such as menthyl fumarate and maleate.

The enantiomeric purity of the cyclopropane derivatives depicted in *Scheme 2* was determined by GC analysis after hydrolysis and reesterification with (+)- and (−)-menthol or (+)- and (−)-2-octanol. The absolute configuration was assigned based on the known sign of rotation of *cis*- and *trans*-2-vinyl- and 2-methylcyclopropane-1-carboxylates [10] [12]. In all cases, the measured optical rotation was positive, implying that the *cis*- as well as the *trans*-products all had (*S*)-configuration at C(1).

4. Mechanistic Aspects. – The stereochemical characteristics of the cyclopropane-forming reactions catalyzed by (semicorrinato)copper complexes showed some remarkable parallels to the corresponding reactions with the (salicylaldiminato)copper **3** [4]: (1) In all examples studied so far, the absolute configuration of the products at the asymmetric C-atom derived from diazoacetate was the same, for the *cis*- as well as for the *trans*-isomers (*cf. Table 2* and *Scheme 2*). (2) Although the chiral ligand efficiently

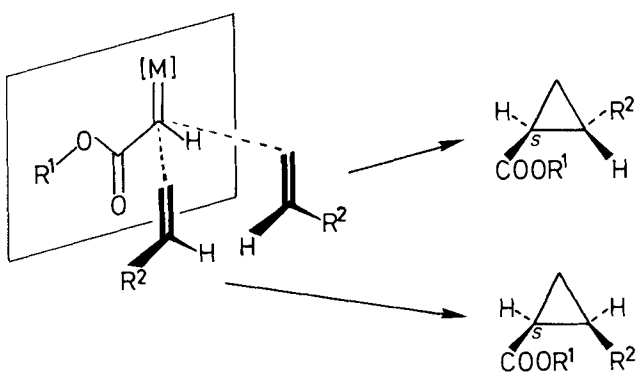
controlled the enantioselectivity of the reaction, its influence on the *cis/trans* selectivity in the reactions of styrene and other terminal olefins was negligible.

The second point is illustrated by the examples given in *Table 1*. Despite the marked structural differences of the semicorrin ligands of the complexes **6–8**, the *cis/trans* selectivities (but not the enantioselectivites!) of the three catalysts are almost identical. Moreover, the *cis/trans* ratios are very similar to the ratios obtained with ethyl diazoacetate and (acetylacetonato)copper (28:72 [11a]) or with the salicylaldiminato complex **2** (30:70 [3]; *cf. Scheme 1*). Both, *Aratani*'s catalyst **3** [4] and the semicorrinato complex **8** produce a *cis/trans* ratio of 18:82 in the cyclopropane formation from styrene with menthyl diazoacetate *(cf. Table 2)*. Hence, the *cis/trans* selectivity in the reactions of styrene and other terminal olefins appears to be determined almost exclusively by the structure of the diazo compound and the olefinic substrate, irrespective of the catalyst structure.

The selectivity of the catalyst **3** has been interpreted by *Aratani* [4b] (*cf.* also [5]) with the occurrence of a metal-carbene intermediate in which one of the two enantiotopic faces of the trigonal carbene C-atom is shielded by the chiral ligand such that the olefin preferentially approaches from the less hindered side. This would imply that the enantioselectivity of the reaction is determined primarily by the different accessibility of the two faces of the metal-carbene. Depending on which of the two enantiotopic faces of the olefin is attacked by the carbenoid, either the *cis*- or the *trans*-isomer is formed, both having the same absolute configuration at the carboxyl-bearing C-atom *(cf. Scheme 3)*.

The oxidation state of the Cu catalyst in cyclopropane-forming reactions of this type has been the subject of extensive debate [11]. Although this point has not been conclusively settled for the various Cu(I) and Cu(II) complexes investigated so far, at least for the reactions described in this work, we have good evidence that the catalytically active species is a (semicorrinato)copper(I) complex. As mentioned above (*cf. Section 2*), the bis(semicorrinato)copper(II) complexes **6–8** showed no apparent reactivity towards alkyl diazoacetates unless they were activated by heating in the presence of the diazo compound. The complex **8**, *e.g.*, had to be treated with alkyl diazoacetate at 60° for a few min until its violet color changed to yellowish-brown. This produced a catalyst which after cooling to 23° under N_2 remained active. An active catalyst was also obtained by reacting

Scheme 3

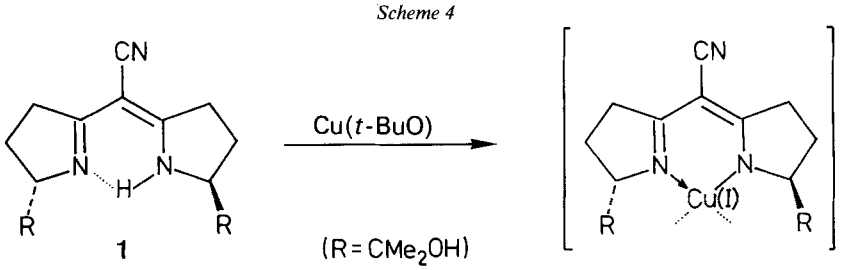


8 with 1–2 mol-equiv. of phenylhydrazine at room temperature (*cf.* [4b]). Upon addition of diazoacetate to the resulting yellowish-white suspension, N_2 evolution was observed, and the mixture gradually turned homogeneous. The Cu species formed under these conditions had the same catalytic properties as the species produced by heat activation in the presence of diazoacetate. When a solution of the activated Cu complex was flushed with O_2, catalytic activity was lost, and the original violet bis(semicorrinato)copper(II) **8** could be recovered in high yield. These observations which point to a Cu(I) species as the active catalyst are in line with the findings of *Aratani* [4d]: the (salicylaldiminato)copper **3** also had to be activated first either by heating in the presence of diazoacetate or by treatment with an alkylhydrazine.

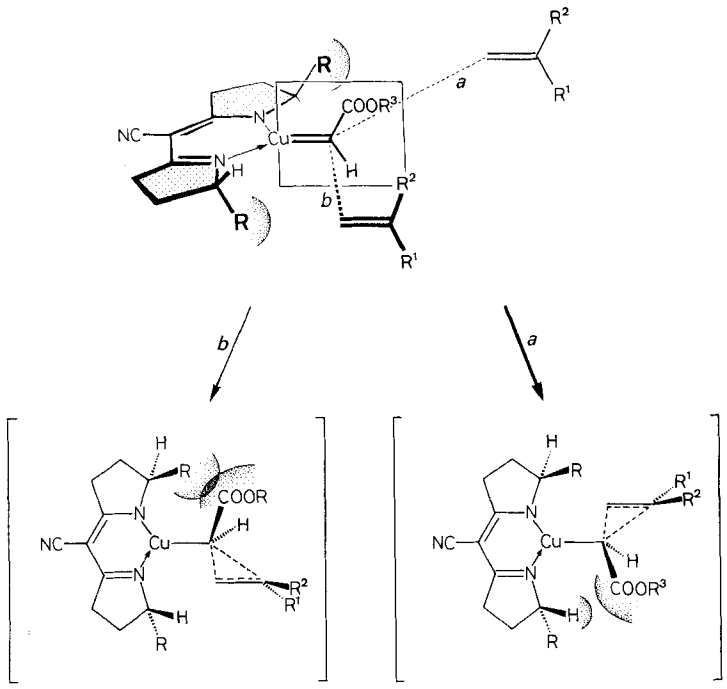
In our case, the most convincing evidence for a Cu(I) complex as the active species came from experiments with (semicorrinato)copper(I) complexes prepared *in situ* from semicorrin ligands and copper(I) *tert*-butoxide [13], a very reactive metalating agent which is soluble in apolar solvents and readily obtained in high purity by sublimation. The reaction of Cu(*t*-BuO) with 1.2 mol-equiv. of the ligand **1** (R = CMe_2OH) in a glove box under N_2 produced a white suspension, similar to that obtained by treatment of the bis(semicorrinato) complex **8** with phenylhydrazine *(cf. Scheme 4)*. The Cu(I) complex formed *in situ* from Cu(*t*-BuO) showed the same catalytic activity towards diazo compounds as the active catalysts prepared from **8** by heat treatment with diazoacetate or by reduction with phenylhydrazine. In the cyclopropane formation from styrene with menthyl diazoacetate, the enantioselectivity, the *cis/trans* selectivity, and the chemical yields obtained with these three differently prepared catalysts were identical within experimental error. We, therefore, conclude that the bis(semicorrinato)copper(II) **8** which we used as a pre-catalyst, upon activation with diazoacetate or phenylhydrazine, is reduced with concomitant loss of one of the two semicorrin ligands, to form a mono(semicorrinato)copper(I) complex which is the actual catalyst in the cyclopropane-forming reactions described in *Sections 2* and *3*.

A tentative rationale for the observed stereoselectivity of the (semicorrinato)copper catalysts is given in *Scheme 5*. In line with the available data on metal-catalyzed reactions of diazo compounds [3–6] [11], we assume that the (semicorrinato)copper(I) first reacts with the alkyl diazoacetate to form a metal carbene complex. The metal carbenoid then attacks the olefin as shown in *Scheme 5*. An approach of this type which resembles the mode of addition of free carbenes to olefins [14] has been proposed for cyclopropane formation from metal carbene complexes by various authors [11]. The principal bonding interaction during the first stage of the reaction develops between the electrophilic

Scheme 4



Scheme 5



carbenoid C-atom and the more nucleophilic of the two olefinic C-atoms with concomitant pyramidalization of the involved centers. Depending on the direction of attack, the carboxy group at the carbenoid center either moves forward or backward relative to the plane bisecting the semicorrin ligand (*cf. Scheme 5, Pathways a* and *b*, resp.). In the latter case (*b*), a repulsive steric interaction builds up between the carboxy group and the substituent R of the semicorrin ligand. Therefore, pathway *a*, which either leads to the *cis*-(1*S*)- or to the *trans*-(1*S*)-cyclopropanecarboxylate, is expected to be favored over *b*, in accord with our experimental findings. This model also accounts for the fact that the *cis*/*trans* selectivity almost exclusively depends on the structures of the olefin and the diazo compound whereas the effect of the semicorrin ligand is negligible. In a transition structure of the type shown in *Scheme 5*, the olefinic substituents R^1 and R^2 are too remote to experience any significant interaction with the semicorrin ligand. Therefore, the *cis*/*trans* selectivity is expected to be dominated by the interactions between the substituents at the olefinic double bond and the carbenoid moiety.

5. Conclusion. – The remarkable enantioselectivities obtained with the (semicorrinato)copper complex **8** point to a considerable potential of cyclopropane-generating catalysts of this type. Although further work will be necessary in order to assess the scope and limitations of (semicorrinato)copper catalysts, many possible applications in synthesis can be foreseen. The three-membered ring compounds, which are readily available in high enantiomeric purity by the metal-catalyzed cyclopropane formation from olefins, are versatile synthetic building blocks that can be transformed regio- and stereoselectively

in a variety of ways [15]. Besides, there are numerous natural as well as artificial compounds of biological importance that contain a cyclopropane ring as a chiral structural unit [4] [10] [16].

In summary, we have shown that the stereochemical course of a metal-catalyzed reaction can be efficiently controled by semicorrin ligands. Considering the almost unlimited and continuously growing number of synthetically useful metal-catalyzed processes, many further applications of semicorrin ligands can be envisaged. Among the reactions we are currently investigating are metal-catalyzed conjugate reductions of α,β-unsaturated carbonyl compounds. As we have found, (semicorrinato)cobalt complexes can act as efficient, highly enantioselective catalysts for reductions of this type. The results of this study will be reported in a forthcoming paper [17].

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Experimental Part

1. General. – See [2]. 1,3-Butadiene: *Fluka, purum*, freshly dist.; chloroacetyl chloride, ethyl diazoacetate: *Fluka, purum*; 1-heptene: *Fluka, pract.*, redist.; 4-methyl-1,3-pentadiene: *Fluka, purum;* pyridine: *Fluka, puriss.*, dist. over CaH_2; styrene: *Fluka, purum*, freshly dist. (+)-Menthol (98.1% ee), (−)-menthol (99.4% ee), (+)-(*S*)-2-octanol (92.7% ee), and (−)-(*R*)-2-octanol (97.8% ee): *Fluka puriss.*; their enantiomeric purity was determined by GC analysis (see below) of the corresponding esters with (−)-camphanic acid [19], *i.e.* ester from (+)-menthol (t_R 27.7) and ester from (−)-menthol (t_R 29.4; column *C*; 140→190°, 5°/min), ester from (+)-2-octanol (t_R 46.7) and ester from (−)-2-octanol (t_R 47.5; column *C*; 90→170°, 3°/min). GC: *Carlo Erba Fractovap 2150* and *4160* fitted with a flame-ionization detector; carrier gas H_2, 0.5 ml/s, injection, split mode; injector temp. 225°; retention times t_R[min] and integrals from a *Hewlett-Packard-3380-A* integrator; capillary colums prepared and operated as described in [18]; column *A*: *SE-52* on $BaCO_3$, 0.3 mm × 42 m, 0.15 μm; column *B*: *SE-54*, 0.3 mm × 18 m, 0.175 μm; column *C*: *Pluronic 64* on $BaCO_3$, 0.3 mm × 34 m, 0.14 μm. MPLC (medium-pressure liquid chromatography): *Merck* silica gel *60*, 0.040–0.063 mm; 4.8 × 46-cm column; pressure *ca.* 20 kg/cm^2.

2. (1*S*,3*S*,4*R*)- and (1*R*,3*R*,4*S*)-Menthyl Diazoacetate (*cf.* [4][8]). – *(1*S*,3*S*,4*R*)-Menthyl Chloroacetate* (= *(1*S*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyl Chloroacetate*). A soln. of chloroacetyl chloride (6.4 ml, 80 mmol) in 40 ml of anh. Et_2O was continuously added within 2 h to a mixture of (+)-menthol (12.5 g, 80 mmol) and pyridine (6.5 ml, 80 mmol) in 160 ml of anh. Et_2O at 0°. After warming to 23°, the yellow suspension was stirred for 4 h. The precipitate was removed by filtration. The soln. was extracted with 2N HCl, followed by sat. $NaHCO_3$ and sat. NaCl soln. Removal of the solvent and drying at 15 Torr afforded crude (1*S*,3*S*,4*R*)-menthyl chloroacetate (19.9 g, *ca.* 100%) which was used without further purification. TLC (hexane/AcOEt 6:1): R_f 0.62. ^{1}H-NMR (80 MHz, $CDCl_3$): 0.77 (*d*, *J* = 7, CH_3); 0.90 (*d*, *J* = 7, CH_3); 0.91 (*d*, *J* = 6.5, CH_3); 0.9–2.2 (*m*, 9 H); 4.02 (*s*, $ClCH_2CO$); 4.78 (*td*, *J* = 11, 4, CHOCO).

*(1*S*,3*S*,4*R*)-Menthyl Glycinate* (= *(1*S*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyl Glycinate*). Crude (1*S*,3*S*,4*R*)-menthyl chloroacetate (19.9 g, *ca.* 80 mmol) in a mixture of DMF (360 ml) and 25% aq. NH_3 (150 ml) was stirred for 24 h at 23°. Then, the mixture was extracted with Et_2O and the org. layer washed with sat. Na_2CO_3 soln., dried (Na_2SO_4) and concentrated to give 15.0 g (*ca.* 88%) of (1*S*,3*S*,4*R*)-menthyl glycinate as a yellowish oil. TLC (AcOEt/hexane 3:1): R_f 0.18. ^{1}H-NMR (80 MHz, $CDCl_3$): 0.76 (*d*, *J* = 7, CH_3); 0.89 (*d*, *J* = 7, 2 CH_3); 0.9–2.2 (*m*, 11 H); 3.40 (*s*, NCH_2CO); 4.74 (*td*, *J* = 11, 4, CHOCO).

*(1*S*,3*S*,4*R*)-Menthyl Diazoacetate* (= *(1*S*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyl Diazoacetate*) [4c]. A mixture of crude (1*S*,3*S*,4*R*)-menthyl glycinate (15.0 g, *ca.* 70 mmol), isopentyl nitrite (11.3 ml, 84 mmol), and AcOH (1.2 ml, 21 mmol) in 140 ml of $CHCl_3$ was heated to reflux for 3.5 h until the ninhydrin test was no longer positive. The mixture was diluted with CH_2Cl_2 and extracted in sequence with 1N H_2SO_4, H_2O, sat. $NaHCO_3$ soln., and again with H_2O. It was then filtered through cotton, evaporated and purified by chromatography in two batches (8 × 20-cm column, hexane/AcOEt 20:1) to give 9.7 g (62%) of (1*S*,3*S*,4*R*)-menthyl diazoacetate as a

crystalline, yellow solid. M.p. 48–49°. TLC (hexane/AcOEt 15:1): R_f 0.37. $[\alpha]_D$ = +88.0 (c = 1.0, $CHCl_3$). UV: 248 (16200), 373 (20). IR: 2120*s*, 1680*s*, 1470*w*, 1455*w*, 1390*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.79 (*d*, J = 7.0, CH_3); 0.90 (*d*, J = 7.0, CH_3); 0.91 (*d*, J = 6.5, CH_3); 0.83–1.15 (*m*, 3 H); 1.31–1.58 (*m*, 2 H); 1.63–1.73 (*m*, 2 H); 1.82–1.92 (*m*, 1 H); 2.00–2.08 (*m*, 1 H); 4.70 (*s*, CHN_2); 4.76 (*td*, J = 10.9, 4.4, CHOCO). ^{13}C-NMR (75 MHz, $CDCl_3$): 16.5 (CH_3); 20.7 (CH_3); 22.0 (CH_3); 23.7 (CH_2); 26.4 (CH); 31.4 (CH); 34.2 (CH_2); 41.3 (CH_2); 46.2 (CH); 47.2 (CH); 74.8 (CH); 166.5 (CO). MS: 224 (0.4, M^+), 83 (100).

(1R,3R,4S)-Menthyl Diazoacetate (= *(1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl Diazoacetate*). Prepared by the same route starting from (–)-menthol. M.p. 48–49°. $[\alpha]_D$ = –89.2 (c = 1.0, $CHCl_3$). The anal. data of (1*S*,3*S*,4*R*)- and (1*R*,3*R*,4*S*)-diazoacetate are in accordance with the data given in [4c] and [8].

3. Cyclopropanes from Styrene (*Tables 1* and *2*). – All reactions were carried out as described for the reaction of styrene with (1*S*,3*S*,4*R*)-menthyl diazoacetate.

3.1. *With (1S,3S,4R)-Menthyl Diazoacetate. General Procedure.* To a mixture of 64 mg (0.1 mmol) of **8** [2], 5 ml of 1,2-dichloroethane, and 2.3 ml (20 mmol) of styrene under N_2, 10 drops of a soln. of (1*S*,3*S*,4*R*)-menthyl diazoacetate (see below) were added with stirring and heated in an oil bath to 85° (*ca.* 10 min) until **8** had completely dissolved (violet→reddish-brown). The mixture was cooled to 23° under a slow stream of N_2 (→homogeneous violet soln.). The N_2 inlet was disconnected, and a soln. of (1*S*,3*S*,4*R*)-menthyl diazoacetate (2.24 g, 10 mmol) in 1,2-dichloroethane (3 ml) was continuously added within 16 h by means of a syringe pump (→ gradually yellowish-brown). After addition, stirring was continued for *ca.* 4 h until N_2 evolution ceased and the diazo compound could no longer be detected by TLC (hexane/AcOEt 15:1, R_f 0.36). A small sample of the crude mixture (5%) was filtered through a silica-gel column with hexane/AcOEt 15:1 and analyzed by GC (column *A*; 100→200°, 1°/min): t_R 80.2 (0.60%, (1*R*,2*S*)-**10b**), 80.56 (17.64%, (1*S*,2*R*)-**10b**), 85.08 (79.71%, (1*S*,2*S*)-**10a**), 86.56 (2.05%, (1*R*,2*R*)-**10a**); **10a**/**10b** = 82:18; **10a**: 96.8% ee, **10b**: 95.2% ee (corrected for the enantiomeric purity of (+)-menthol (98.1% ee); *cf. Section 1*). The remaining 95% of the crude product was purified by column chromatography (5 × 15 cm; 1.2 l of pentane/Et_2O 40:1 followed by 0.8 l of pentane/Et_2O 30:1) to give 1.95 g (63% based on diazoacetate) of *(1S,3S,4R)-menthyl (1S)-2-phenylcyclopropane-1-carboxylates* (82:18 mixture, **10a**/**10b**, R = (1*S*,3*S*,4*R*)-menthyl), contaminated by 6 mol-% of dimenthyl fumarate (^{1}H-NMR). TLC (hexane/AcOEt 15:1): R_f 0.52 (**10a**), 0.46 (**10b**), 0.38 (fumarate), 0.34 (maleate). ^{1}H-NMR (300 MHz, CD_2Cl_2): 0.47 (*d*, J = 6.9, 0.45 H, CH_3 (**10b**)); 0.57–2.09 (*m*, 22 H); 2.44–2.62 (*m*, 0.94 H, PhC*H*); 4.38 (*td*, J = 10.9, 4.4, 0.15 H, COOCH of **10b**); 4.69 (*td*, J = 10.9, 4.4, 0.79 H, COOCH of **10a**); 7.07–7.30 (*m*, 4.68 H, Ph); signals of dimenthyl fumarate (6 mol-% by integration): 4.78 (*td*, J = 10.9, 4.4, HCOOC); 6.78 (*s*, CH=CH).

Analogous experiments using 1 mol-equiv. of styrene and 1.2 mol-equiv. of (1*S*,3*S*,4*R*)-menthyl diazoacetate also gave a 82:18 mixture **10a**/**10b** (R = (1*S*,3*S*,4*R*)-menthyl) in 65–70% yield based on styrene with enantioselectivities in the range of 96–98% ee for **10a** and 95–96% ee for **10b**.

The products **10a** and **10b** were further characterized by conversion to the corresponding methyl esters; the ee values were checked by GC of the (1*R*,3*R*,4*S*)-menthyl esters, by polarimetry, and NMR with chiral shift reagents (*cf. 3.4* and *3.5*).

3.2. *Modified Procedure A (Catalyst Activation with Phenylhydrazine).* To a suspension of **8** (20 mg, 0.03 mmol) in 1.5 ml of 1,2-dichloroethane under N_2 were added 0.20 ml (0.03 mmol) of 0.15M phenylhydrazine in 1,2-dichloroethane. Upon stirring at 23° for 5 min, the violet color of **8** disappeared and a white precipitate formed. After addition of the olefin, menthyl diazoacetate was slowly added at 23°, as described in *3.1*. The reaction immediately started when the first drop of the diazo compound was added. The mixture gradually became homogeneous during the first 2–3 h while the color changed to yellowish-brown.

3.3. *Modified Procedure B (Using (Semicorrinato)copper(I) Complexes).* In a glove box under N_2 (< 20 ppm O_2), 0.3 ml (0.03 mmol) of 0.1M Cu(*t*-BuO) [13] in cyclohexane was added to a soln. of **1** [2] (R = CMe_2OH; 12 mg, 0.04 mmol) in 1 ml of 1,2-dichloroethane (→white, gel-like precipitate, supernatant soln. of very faint violet color). After addition of the olefin in 0.5 ml of 1,2-dichloroethane, the flask was sealed with a rubber septum and taken out of the glove box. Cyclopropane formation was then carried out at 23°, as described above. N_2-Evolution started immediately after the first drop of diazo compound had been added. During the first 30–60 min, the precipitate dissolved and the soln. turned yellowish-brown.

3.4. *Hydrolysis of the Menthyl Esters and Conversion to the Methyl Esters.* The mixture **10a**/**10b** (82:18; R = (1*S*,3*S*,4*R*)-menthyl; see *3.1*) was hydrolyzed, as described in [4c] (1 mmol of ester, 3.6 ml of MeOH, 2.2 ml of 25% aq. NaOH soln., 4 h, reflux) to give the *(1S)-2-phenylcyclopropane-1-carboxylic acids* (**10a**/**10b**; *ca.* 8:2; R = H) as a yellowish oil (98% yield). ^{1}H-NMR of crude **10a**/**10b** (R = H): in accordance with [5b,c] [8]; no signals of fumaric acid.

The acids **10a/10b** (R = H) in CH_2Cl_2/Et_2O 1:1 were treated with 0.3M diazomethane in Et_2O. The resulting *methyl (1S)-2-phenylcyclopropane-1-carboxylates* (**10a/10b**; R = CH_3) were separated by column chromatography (hexane/AcOEt 20:1) to give pure **10a** (*trans*, R = CH_3) and **10b** (*cis*, R = CH_3), total yield *ca.* 85%. TLC (hexane/AcOEt 15:1): R_f 0.31 (**10a**), 0.26 (**10b**). GC (column *B*; 50→200°, 3°/min): t_R 19.8 (**10a**), 17.5 (**10b**). ^{1}H-NMR: in accordance with [8] (*cf.* also *Fig. 4* in [5c]). $[\alpha]_D$: positive for **10a** and **10b**; optical purity from measured $[\alpha]_D$'s and $[\alpha]_D$'s of optically pure **10a** and **10b** (R = CH_3) [8] agreeing within ±3% with ee's determined by GC of **10a** and **10b** (R = (1*S*,3*S*,4*R*)- or (1*R*,3*R*,4*S*)-menthyl; *cf. 3.1* and *3.5*).

^{1}H-NMR Analysis with [Eu(tfc)$_3$]. A sample of (+)-**10a** (R = CH_3; 91.5% ee by GC; 18 mg, 0.10 mmol) and 66 mg (0.074 mmol) of [(Eu(tfc)$_3$)] were dissolved in 0.4 ml of CD_2Cl_2 and filtered. ^{1}H-NMR: 5.12, 5.05 (2*s*, 96:4 rel. int., CH_3O of the 2 enantiomers); 92% ee.

3.5. *Esterification with (−)-Menthol* (*cf.* [20]). To a soln. of **10a/10b** (R = H; 12 mg, 74 µmol; *cf. 3.4*) in 0.4 ml 0.25M pyridine (0.10 mmol) in toluene, $SOCl_2$ (0.4 ml of 0.7M soln. in toluene; 0.28 mmol) and (−)-menthol (0.4 ml of 1.4M soln. in toluene; 0.56 mmol) were added. The mixture was stirred at 100° for 1 h, diluted with Et_2O and extracted with 0.1N phospate buffer pH 3 (3 ×), followed by sat. $NaHCO_3$ soln. The crude **10a/10b** (R = (1*R*,3*R*,4*S*)-menthyl) was taken up in pentane and analyzed by GC (*cf. 3.1*): after correction for the enantiomeric purity of (+)- and (−)-menthol (*cf. Section 1*), agreement within 1% of the ee's from (1*R*,3*R*,4*S*)-menthyl esters **10a** and **10b** and that from the corresponding (1*S*,3*S*,4*R*)-menthyl esters.

3.6. *With Ethyl Diazoacetate.* Styrene (5 mmol) was treated with ethyl diazoacetate (6.5 mmol) in the presence of **8** (0.065 mmol) as described in *3.1*. Column chromatography (hexane/AcOEt 9:1) gave a 73:27 mixture **10a/10b** (R = Et; total yield 65%), contaminated by 14 mol-% (^{1}H-NMR) of diethyl fumarate[3]). TLC (hexane/AcOEt 9:1) R_f 0.39 (**10a**), 0.31 (**10b**+fumarate). ^{1}H-NMR (300 MHz, CD_2Cl_2): 0.99 (*t*, *J* = 7.1, 0.66 H, CH_3(**10b**)); 1.22–1.36 (*m*, H–C(3)), 1.25 (*t*, *J* = 7.1, CH_3(**10a**)), 1.30 (*t*, *J* = 7.1, 3.62 H, CH_3 (fumarate)); 1.51–1.68 (*m*, 0.86 H, H–C(3)); 1.83–1.91 (*m*, 0.64 H, H–C(1) (**10a**)); 2.01–2.10 (*m*, 0.22 H, H–C(1) (**10b**)); 2.43–2.51, 2.51–2.61 (2 *m*, 0.86 H, H–C(1) (**10a/10b**)); 3.86 (*q*, *J* = 7.1, 0.44 H, CH_2O (**10b**)); 4.13 (*q*, *J* = 7.1, 1.28 H, CH_2O (**10a**)); 4.23 (*q*, *J* = 7.1, 0.56 H, CH_2O (fumarate)); 6.80 (*s*, 0.28 H, CH=CH (fumarate)); 7.07–7.30 (*m*, 4.30 H, Ph); for the ^{1}H-NMR data of **10a** and **10b** (R = Et), *cf.* [5c].

The ee's of **10a** and **10b** (R = Et, see *Table 1*) were determined by GC of the (1*R*,3*R*,4*S*)-menthyl esters, as described in *3.5*.

3.7. *With* tert-*Butyl Diazoacetate.* Reaction of styrene (1.7 mmol) with *tert*-butyl diazoacetate [22] (2.2 mmol) in the presence of **8** (0.028 mmol) gave, after column chromatography with hexane/AcOEt 20:1, **10a/10b** (R = *t*-Bu; 60% yield), contaminated by 20 mol-% (^{1}H-NMR) of di(*tert*-butyl) fumarate and 5 mol-% of di(*tert*-butyl)-maleate[3]). TLC (hexane/AcOEt 15:1): R_f 0.49 (**10a**), 0.45 (fumarate), 0.37 (**10b**), 0.28 (maleate). GC (column *C*; 50→180°, 1.5°/min): t_R 32.4 (19.5%, fumarate), 32.6 (3.8%, maleate), 47.4 (14.3%, **10b**), 52.1 (62.5%, **10a**). ^{1}H-NMR (80 MHz): 1.05–2.65 (*m*), 1.13 (*s*, *t*-Bu (**10b**)), 1.46 (*s*, *t*-Bu, (**10a**)), 1.50 (*s*, 14.2 H, *t*-Bu (fumarate, maleate)); 6.05 (*s*, 0.1 H, CH=CH (maleate)); 6.67 (*s*, 0.38 H, C=CH (fumarate)); 7.03–7.50 (*m*, 3.8 H, Ph).

A sample of the *tert*-butyl-ester mixture (containing 0.4 mmol of **10a/10b** (R = *t*-Bu)) was dissolved in neat CF_3COOH (2 ml) and stirred at 23° for 10 min. After removal of CF_3COOH under vacuum, the residue was repeatedly taken up in benzene and evaporated (3 ×). The crude product was dissolved in CH_2Cl_2 and separated from fumaric and maleic acid by filtration to afford a sample of acids **10a/10b** (R = H; *ca.* 100% yield; pure according to ^{1}H-NMR). The ee's of **10a** and **10b** (R = H) were determined by GC after conversion to the (1*R*,3*R*,4*S*)-menthyl esters (*cf. 3.5*).

4. Cyclopropanes from 1,3-Butadiene, 4-Methyl-1,3-pentadiene, and 1-Heptene *(Scheme 2).* – 4.1. *(1S,3S,4R)-Menthyl* trans-*(1S)- and* cis-*(1S)-2-Vinylcyclopropane-1-carboxylates* ((+)-**11a** and (+)-**11b**, resp.). After addition of 1,3-butadiene (2.9 ml, 50 mmol) through a cannula, to **8** (65 mg, 0.1 mmol) in 4 ml of 1,2-dichloroethane, the reaction was carried out as described in *3.1*. The temp. was kept at *ca.* 25° with an oil bath (30–35°). After activation of the catalyst, and after addition of 50% of the (1*S*,3*S*,4*R*)-menthyl-diazoacetate soln. (2.24 g (10 mmol) dissolved in 0.9 ml of 1,2-dichloroethane), additional portions of butadiene (4 g each) were added. MPLC (pentane/Et_2O 90:1, 12 ml/min) afforded 1.57 g of a colorless oil. ^{1}H-NMR and GC: 0.91 g of **11a** (R = (1*S*,3*S*,4*R*)-menthyl), 0.54 g of **11b** (R = (1*S*,3*S*,4*R*)-menthyl), and 0.12 g of dimenthyl fumarate. Total yield 58%, based on diazoacetate; **11a/11b** 63:37. TLC (hexane/AcOEt 15:1): R_f 0.66 (**11b**), 0.52 (**11a**), 0.40 (fumarate). GC (column *A*; 70→200°, 0.5°/min): t_R 104.1 ((1*R*,2*S*)-**11a**), 106.6 ((1*S*,2*R*)-**11a**), 107.7 ((1*R*,2*R*)-**11b**), 108.6

[3]) The *cis*/*trans* isomers **10a/10b** could be separated by column chromatography. However, in order to exclude the possibility of enantiomer differentiation during chromatography ('EE effect' [21]), the mixture was hydrolyzed without further purification.

((1*S*,2*S*)-**11b**; R = (1*S*,3*S*,4*R*)-menthyl); the assignments of the peaks and the ee's of **11a** (97 ± 1%) and **11b** (97 ± 2%) which were calculated from the peak intensities, were confirmed by GC of the corresponding (1*R*,3*R*,4*S*)-menthyl esters *(cf. 3.5)*.

By MPLC (pentane/Et_2O 90:1, 12 ml/min) of the product mixture, enriched samples of **11a** (R = (1*S*,3*S*,4*R*)-mentyl; *trans*/*cis* 9:1) and of **11b** (*cis*/*trans* 9:1) were obtained. The two samples were hydrolyzed to the corresponding **11a** (R = H) and **11b** (R = H), resp., as described in *3.4* (*ca.* 100% yield; reaction time for **11a**, 22 h; for **11b**, 44 h).

Data of **11a** (R = H; containing 9 mol-% of the *cis* isomer): TLC (hexane/AcOEt 2:1): R_f 0.38. $[\alpha]_D$ = +165 (*c* = 2.1, EtOH; *cf.* [10a] [23]). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.06 (*ddd*, *J*(1,3) = 8.3, *J*(2,3) = 6.4, J_{gem} = 4.4, H_{Re}–C(3)); 1.43 (*ddd*, *J*(2,3) = 9.0, *J*(1,3) = 5.1, J_{gem} = 4.4, H_{Si}–C(3)); 1.64 (*ddd*, *J*(1,3; *cis*) = 8.3, *J*(1,3; *trans*) = 5.1, *J*(1,2) = 3.9, H–C(1)); 2.04–2.14 (*m*, H–C(2)); 5.02 (*ddd*, *J* = 10.1, 1.5, 0.4), 5.18 (*ddd*, *J* = 17.0, 1.5, 0.5; CH_2=CH); 5.40 (*ddd*, *J* = 17.0, 10.1, 8.3, CH_2=C*H*); 8.1 (br., COOH); additional weak signals due to the *cis*-isomer.

Data of **11b** (R = H; containing 13 mol-% of the *trans* isomer): TLC (hexane/AcOEt 2:1): R_f 0.34. $[\alpha]_D$ = +136 (*c* = 1.0, EtOH). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.26–1.32 (*m*, CH_2(3)); 1.89–2.08 (*m*, H–C(1), H–C(2)); 5.08 (*dd*, *J* = 10.3, 1.7), 5.26 (*dd*, *J* = 17.1, 1.7; CH_2=CH); 5.79 (*ddd*, *J* = 17.1, 10.3, 9.0, CH_2=C*H*); additional weak signals due to the *trans* isomer.

4.2. *(1S,3S,4R)-Menthyl* trans-*(1S)- and* cis-*(1S)-2-(2-Methyl-1-propenyl)cyclopropane-1-carboxylates* ((+)-**12a** and (+)-**12b**, resp.). As described in *3.1*, 4-methyl-1,3-pentadiene (0.69 ml, 6 mmol) was reacted with 20 mg (0.03 mmol) of **8** and 675 mg (3 mmol) of (1*S*,3*S*,4*R*)-menthyl diazoacetate. After column chromatography with pentane/Et_2O 20:1, 677 mg of a colorless oil was obtained. ^{1}H-NMR: 65:35 mixture **12a**/**12b** (R=(1*S*,3*S*,4*R*)-menthyl) and 3 mol-% of dimenthyl fumarate. Total yield 77% (based on diazoacetate). GC (column *A*; 50→200°, 0.9°/min): t_R 106.9 ((1*R*,2*R*)-**12b**; R = (1*S*,3*S*,4*R*)-menthyl), 107.4 ((1*S*,2*S*)-**12b**), 107.9 ((1*S*,2*R*)-**12a**), 109.3 ((1*R*,2*S*)-**12a**); *trans*/*cis* 63:37; **12a** and **12b**: 97 ± 1% ee; these values were confirmed by GC after hydrolysis and reesterification with (–)-menthol (see *3.4* and *3.5*). TLC (hexane/AcOEt 15:1): R_f 0.48 (**12a**/**12b**). ^{1}H-NMR (300 MHz, $CDCl_3$): 0.70–2.08 (*m*, superimposed: 4 *d* (*J* = 7.0) at 0.72, 0.76, 0.86, and 0.89, *d* (*J* = 6.5) at 0.90, *d* (*J* = 1.3) at 1.69, *d* (*J* = 1.2) at 1.71, *d*(*J* = 1.1) at 1.73; 28.3 H); 4.59–4.85 (*m* consisting of 4.64 (br. *d*, *J* = 8.7, CH=C of **12a**) and 4.68, 4.70, 4.79 (3 *td*, *J* = 10.8, 4.4, 1.66 H, CHOCO of **12a**/**12b** and dimenthyl fumarate); 5.01 (br. *d*, *J* = 8.6, 0.34 H, CH=C of **12b**); 6.82 (*s*, 0.07 H, CH=CH of dimenthyl fumarate).

Hydrolysis and esterification with diazomethane, as described in *3.4*, gave a 64:36 mixture **12a**/**12b** (R = CH_3) in 95% yield after chromatography. Anal. samples of **12a** and **12b** (R = CH_3) were obtained by column chromatography of **12a**/**12b** acids (R = H) with petroleum ether/Et_2O 10:1→3:1 and a 2nd chromatography using pentane/Et_2O 4:1. TLC (hexane/AcOH 3:1): R_f 0.19 (**12a**, R = H), 0.24 (**12b**, R = H). Esterification with diazomenthane and column chromatography with pentane/Et_2O provided pure samples of **12a** and **12b** (R = CH_3).

Data of **12a** (R = CH_3): TLC (pentane/Et_2O 25:1): R_f 0.32. $[\alpha]_D$ = +161 (*c* = 1.1, CH_2Cl_2). IR: 1725*s*, 1440*m*, 1400*m*, 1380*m*, 1355*m*, 1300*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.86 (*ddd*, *J*(1,3) = 8.2, *J*(2,3) = 6.3, J_{gem} = 4.1, H_{Re}–C(3)); 1.36 (*ddd*, *J*(2,3) = 9.0, *J*(1,3) = 5.0, J_{gem} = 4.1, H_{Si}–C(3)); 1.54 (*ddd*, *J*(1,3; *cis*) = 8.2, *J*(1,3; *trans*) = 5.0, *J*(1,2) = 3.9, H–C(1)); 1.68 (*d*, *J* = 1.3, CH_3); 1.73 (*d*, *J* = 1.2, CH_3); 2.07 (*dddd*, *J* = 9.0, 9.0, 6.3, 3.9, H–C(2)); 3.68 (*s*, CH_3O); 4.59 (br. *d*, *J* = 9.0, CH=C). ^{13}C-NMR (75 MHz, $CDCl_3$): 16.1 (C(3)); 18.3 (CH_3); 21.6, 22.0 (C(1), (C(2)); 25.5 (CH_3); 51.7 (CH_3O); 124.5 (C=*C*H); 134.0 (*C*=CH); 174.4 (COO). MS: 154 (28, M^+), 111 (28), 95 (100).

Data of **12b** (R = CH_3): TLC (pentane/Et_2O 25:1): R_f 0.32. $[\alpha]_D$ = +231 (*c* = 0.75, CH_2Cl_2). IR: 1725*s*, 1440*m*, 1385*m*, 1355*m*, 1315*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.16 (*ddd*, *J*(2,3) = 7.1, *J*(1,3) = 5.9, J_{gem} = 4.6, H_{Si}–C(3)); 1.20 (*ddd*, *J*(2,3) = 8,5, *J*(1,3) = 7.9, J_{gem} = 4.6, H_{Re}–C(3)); 1.71 (*d*, *J* = 1.2, CH_3); 1.72 (*d*, *J* = 1.3, CH_3); 1.89 (*ddd*, *J*(1,2) = 8.7, *J*(1,3; *cis*) = 7.9, *J*(1,3; *trans*) = 5.9, H–C(1)); 2.01 (*dddd*, *J* = 8.8, 8.7, 8.5, 7.1, H–C(2)); 3.67 (*s*, CH_3O); 5.08 (br. *d*, *J* = 8.8, CH=C). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.3 (C(3)); 18.2 (CH_3); 20.2, 20.5 (C(1), C(2)); 25.8 (CH_3); 51.5 (CH_3O); 120.9 (C=*C*H); 134.5 (*C*=CH); 172.7 (COO). MS: 154 (25, M^+), 111 (27), 95 (100).

4.3. *(1S,3S,4R)-Menthyl* trans-*(1S)- and* cis-*(1S)-2-Pentylcyclopropane-1-carboxylates* ((+)-**13a** and (+)-**13b**, resp.). A soln. of 1-heptene (2.12 ml, 15 mmol) in 1.5 ml of 1,2-dichloroethane was reacted with (1*S*,3*S*,4*R*)-menthyl diazoacetate (675 mg, 3 mmol) using 39 mg (0.06 mmol) of **8**, as described in *3.1*.

Hydrolysis of **13a**/**13b** (R = (1*S*,3*S*,4*R*)-menthyl) (40 h, reflux, *cf. 3.4*) followed by esterification with diazomethane and column chromatography (pentane/Et_2O 90:1→50:1) afforded 91 mg of **13a** (R = CH_3) and 21 mg of **13b** (R = CH_3). Total yield 22% (based on diazoacetate). TLC (pentane/Et_2O 50:1): R_f 0.21 (**13a**), 0.26 (**13b**).

Data of **13a** (R = CH_3): $[\alpha]_D$ = +71 (*c* = 2.6, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): 0.65–0.72 (*m*, 1 H); 0.88 (*t*, *J* = 6.8, 3 H); 1.11–1.19 (*m*, 1 H); 1.23–1.45 (*m*, 10 H); 3.66 (*s*, CH_3O). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.0 (CH_3);

15.6 (C(3)); 20.0, 23.0 (C(1), C(2)); 22.6, 28.8, 31.5, 33.0 ($(CH_2)_4$); 51.6 (CH_3O); 175.0 (COO). MS: 170 (3, M^+), 139 (21), 138 (18), 115 (11), 114 (29), 113 (37), 97 (19), 96 (44), 87 (100).

Data of **13b** (R = CH_3): $[\alpha]_D$ = +51 (*c* = 0.2, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): 0.83–1.05 (*m*, 5 H); 1.15–1.62 (*m*, 9 H); 1.64–1.72 (*m*, 1 H); 3.67 (*s*, CH_3O).

For determining the enantiomeric purity, the acids **13a** (R = H) and **13b** (R = H) were esterified with (+)-(*S*)-2-octanol and (−)-(*R*)-2-octanol, as described in *3.5*. The ee's of **13a** (92 ± 1%) and **13b** (93 ± 2%) were determined by GC of the octyl esters prepared from non-chromatographed **13a**/**13b** (R = H) and from chromatographed, isomerically pure **13a** (R = H) and **13b** (R = H). GC (column *A*; 100→200°, 1°/min; R = (+)-(*S*)-2-octyl): t_R 48.8 ((1*S*,2*R*)-**13b**), 50.0 ((1*S*,2*S*)-**13a**), 51.3 ((1*R*,2*S*)-**13b**/(1*R*,2*R*)-**13a**).

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