63. Enantioselective Formation of Bicyclic Lactones by Rhodium-Catalyzed Intramolecular CH-Insertion Reactions

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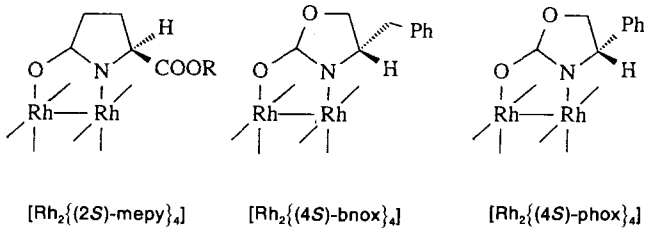
The decomposition of cyclohexyl diazoacetate (**5a**) in the presence of the chiral $[Rh_2\{(2S)\text{-mepy}\}_4]$ catalyst leads to a 3:1 *cis*/*trans* mixture of bicyclic lactone **6a** with an enantiomeric excess of 95–97% (*cis*) and 90% (*trans*). The conformationally rigid *tert*-butyl derivatives **5b** and **5c** afford, in the presence of the same catalyst, **6b** and **6c**, respectively, *via* insertion into the equatorial C–H bonds exclusively, with ee's of *ca.* 95%. A remarkable degree of induction (92–95%) results in the lactone **6g** upon decomposition of 1-isopropyl-2-methylpropyl diazoacetate (**5g**). The diazoacetates derived from 1-methylcyclohexanol, cyclopentanol and 1-methylcyclopentanol (**5d–f**) afford under similar conditions insertion products with higher diastereoselectivity, but significantly lower enantioselectivity. Other dirhodium catalysts are less efficient.

Introduction. – The use of transition-metal-catalyzed decomposition of diazo compounds in the presence of chiral catalysts, in particular based on Cu^I and Rh^{II}, for asymmetric synthesis is progressing very rapidly [1]. Both inter- and intramolecular carbene additions to alkenes leading to chiral cyclopropanes with high asymmetric induction were discovered. While the presently known Cu- [2–4] and Rh-catalysts [5–7] are competitive and/or complementary for cyclopropane formation, Rh^{II} is unique for carbenoid additions to triple bonds which lead to chiral cyclopropenes [8] [9]. Rh^{II}-Based catalysts are also efficient for intramolecular carbenoid insertion reactions into C–H bonds. Although this reaction is well established in synthetic chemistry [10] [11], only a few studies of the asymmetric version were reported so far. *Doyle et al.* [12] obtained enantiomeric excess as high as 91% in lactones formed upon intramolecular insertion of a series of simple diazoesters with $[Rh_2((2S)\text{-mepy})_4]$. In a related investigation, *Hashimoto et al.* achieved induction of up to 76% in intramolecular insertions of diazoketones using a Rh^{II} catalyst with *N*-phthaloyl-L-phenylalanine ligands [13]. A comparable degree of induction was found by *McKervey et al.* for insertion with a Rh^{II}-complexed-L-proline [14].

In the investigations of *Doyle*, *Hashimoto*, and *McKervey*, the enantiotopic C–H bonds in which the carbene is inserted, are located on the same C-atom. Obviously this is not a prerequisite for asymmetric synthesis, which may also be realized when the enantiotopic bonds are on different atoms. This situation occurs in *meso*-compounds, where the reacting bonds are interrelated by a plane of symmetry, which implies opposite configuration at the respective centers. This paper reports an investigation of some Rh^{II}-catalyzed C–H insertions with some representative diazoesters and diazoketones having enantiotopic C–H bonds at different atoms. Some of the results were published in preliminary form [15].

Results and Discussion. – The decomposition of diazoesters was carried out with the chiral Rh^{II}-catalysts $[Rh_2\{(2S)\text{-merphy}\}_4]$ (= tetrakis[μ-(*S*)-methyl 5-oxopyrrolidine-2-carboxylato-$\kappa N,\kappa O^5$]dirhodium(*Rh–Rh*)) and its (2*R*)-enantiomer, $[Rh_2\{(4S)\text{-bnox}\}_4]$ (= tetrakis[(4*S*)-4-benzyloxazolidin-2-onato-$\kappa N,\kappa O^2$]dirhodium(*Rh–Rh*)) [9], and $[Rh_2\{(4S)\text{-phox}\}_4]$ (= tetrakis[(4*S*)-4-phenyloxazolidin-2-onato-$\kappa N,\kappa O^2$]dirhodium-(*Rh–Rh*)) [16].

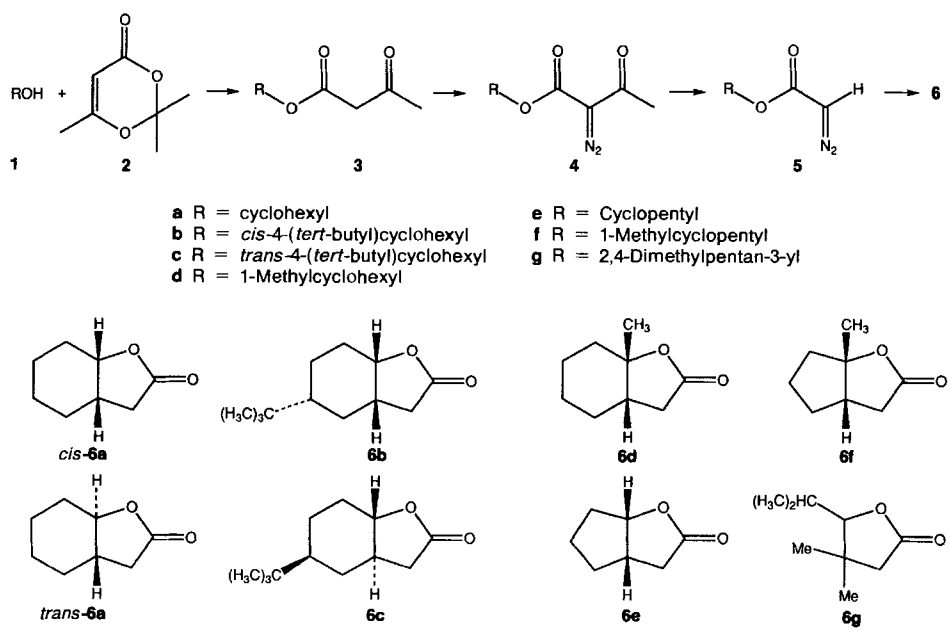


$[Rh_2\{(2S)\text{-mepy}\}_4]$ $[Rh_2\{(4S)\text{-bnox}\}_4]$ $[Rh_2\{(4S)\text{-phox}\}_4]$

The diazoesters were synthesized by reaction of the acetone adduct **2** of diketene (2,2,6-trimethyl-4*H*-1,3-dioxin-4-one) with the corresponding alcohol **1** in boiling *p*-xylene [17] (*Scheme 1*). The resulting acetoacetates **3** underwent diazo transfer with mesyl azide [18] in the presence of Et_3N to give diazoacetoacetates **4**. The latter were cleaved to the diazoacetates **5** with KOH in a two-phase system of H_2O and MeCN [19].

Initially, experiments for decomposition of diazoacetates **5** with $[Rh_2(OAc)_4]$ failed and afforded none of the expected bicyclic lactones **6**. However, the situation changed, when $[Rh_2(OAc)_4]$ was replaced with $[Rh_2\{(2S)\text{-mepy}\}_4]$ or its (2*R*)-enantiomer. *E.g.*,

Scheme 1



reaction of **5a** in CH_2Cl_2 at room temperature afforded lactone **6a** in 30% yield as a 3:1 mixture of *cis*- and *trans*-isomers (*Table 1*). This result is surprising, since cyclohexyl diazomalonate is known to react with Cu- [20] and Rh-catalysts [21] preferentially to β-lactones and not to γ-lactones. The change in products upon changing the catalyst in our experiments has a simple explanation: the principal product formed in the presence of $[Rh_2(OAc)_4]$ is due to reaction of the intermediate metallocarbene with trace impurities of H_2O. These products are very difficult to suppress, but the reactions catalyzed with carboxamido- or oxazolidinonato-rhodium catalysts are less affected by it, so that the desired C–H insertion predominates. No β-lactones nor decomposition products thereof were observed in our reactions.

The stereoisomers of **6a** were identified by comparison of their spectral data with published values [22]. They were separable on a chiral GC column (*Lipodex E*) and showed ee's for *cis*-**6a** of 95% (with $[Rh_4\{(2S)\text{-mepy}\}_4]$) and of 97% (with $[Rh_4\{(2R)\text{mepy}\}_4]$). The ee of *trans*-**6a** was 91% with both catalysts. The absolute configuration of *cis*-**6a**, obtained from reaction with the $[Rh_2((2S)\text{-mepy})_4]$, was (3a*S*, 7a*S*) and that of *trans*-**6a** (3a*S*, 7a*R*) (see *Table 1* and *Exper. Part*). Since *cis*- and *trans*-**6a** have the same configuration at C(3a), it follows that C–H insertion takes place into the diastereotopic bonds at the same center. In other words, the orientation of the cyclohexane ring of the Rh-complexed carbene must be approximately the same for

Table 1. *Decomposition of Alkyl Diazoacetates with Chiral Rhodium(II) Catalysts*

Diazoacetate	Catalyst	Product	Yield [%]	*cis*/*trans*	ee [%]	Comment
5a R = Cyclohexyl	$[Rh_2(OAc)_4]$	**6a**	46	40:60	–	ref. [15]
	$[Rh_2\{(2S)\text{-mepy}\}_4]$		30	75:25	95 (*cis*)	(3a*S*,7a*S*), *cis*
					90 (*trans*)	(3a*S*,7a*R*), *trans*
	$[Rh_2\{(2R)\text{-mepy}\}_4]$		30	75:25	97 (*cis*)	(3a*R*,7a*R*), *cis*
						(3a*R*,7a*S*), *trans*
	$[Rh_2\{(4S)\text{-bnox}\}_4]$		30	33:67	60	(3a*R*,7a*R*), *cis*
						(3a*R*,7a*S*), *trans*
	$[Rh_2\{(4S)\text{-phox}\}_4]$		5	–	–	(3a*R*,7a*S*), *trans*
5b R = *cis*-4-(*tert*-Butyl)-cyclohexyl	$[Rh_2\{(2S)\text{-mepy}\}_4]$	**6b**	40	–	95	
	$[Rh_2\{(2R)\text{-mepy}\}_4]$		40	–	96	
5c R = *trans*-4-(*tert*-Butyl)-cyclohexyl	$[Rh_2\{(2S)\text{-mepy}\}_4]$	**6c**	30	–	94	
	$[Rh_2\{(2R)\text{-mepy}\}_4]$		30	–	95	
5d R = 1-Methylcyclohexyl	$[Rh_2\{(2S)\text{-mepy}\}_4]$	**6d**	30	–	74	
	$[Rh_2\{(2R)\text{-mepy}\}_4]$		30	–	66	
	$[Rh_2\{(4S)\text{-bnox}\}_4]$		30	–	44	
5e R = Cyclopentyl	$[Rh_2\{(2S)\text{-mepy}\}_4]$	**6e**	25	–	38	(3a*S*,6a*S*)
	$[Rh_2\{(2R)\text{-mepy}\}_4]$		25	–	38	(3a*R*,6a*R*)
	$[Rh_2\{(4S)\text{-bnox}\}_4]$		15	–	3	
5f R = 1-Methylcyclopentyl	$[Rh_2\{(2S)\text{-mepy}\}_4]$	**6f**	30	–	31	
	$[Rh_2\{(2R)\text{-mepy}\}_4]$		30	–	36	
	$[Rh_2\{(4S)\text{-bnox}\}_4]$		17	–	1	
5g R = 2,4-Dimethyl-pentan-3-yl	$[Rh_2\{(2S)\text{-mepy}\}_4]$	**6g**	42	–	92	
	$[Rh_2\{(2R)\text{-mepy}\}_4]$		42	–	95	

formation of both diastereoisomers. With [Rh_2((4*R*)-bnox)$_4$], the ratio of *cis*/*trans*-**6a** changed to 1:2; the ee's of both isomers were, however, significantly lower. The [Rh_2((4*R*)-phox)$_4$] catalyst, in turn, produced mainly secondary reaction products. The isomer *cis*-**6a** was isolated in low yield, and its ee was not determined.

Cyclohexyl diazoacetate (**5a**) occurs in two equilibrating conformations, one with an equatorial, the other with an axial diazoacetate group. For geometric reasons, the axial conformer may only lead to *cis*-**6a**, while reaction of the equatorial conformer can lead to *cis*- and *trans*-**6a**. The ratio of *cis*/*trans*-**6a** could either be determined by the preference of the metallocarbene for insertion into one of the diastereotopic bonds or, at least in part, by the position of the conformational equilibrium of the axial and equatorial conformers. We have, therefore, investigated the decomposition of the conformationally blocked *cis*- and *trans*-4-(*tert*-butyl)cyclohexyl diazoacetates **5b** and **5e** with [Rh_2(mepy)$_4$]. Both gave only one lactone, namely **6a** and **6c**, respectively, which originate from insertion of the carbene into the equatorial C–H bonds. The induction was almost identical to that observed with **6a**. Preferential insertion into equatorial C–H bonds was observed in the [Rh_2(OAc)$_4$]-catalyzed decomposition of cyclohexyl diazomalonate and was attributed to the better accessibility of the equatorial H-atoms [21]. The validity of this interpretation is currently under investigation.

The yields of the reactions with **5b** were higher than those obtained with **5a** or with the other diazoacetates owing to a change in the experimental procedure. Since the major side reaction is due to the presence of H_2O, the diazo compound was distilled prior to use or, when this was not possible, dried over molecular sieves. For the same reason, the solvent, CH_2Cl_2, was distilled from CaH_2 immediately prior to use. In addition, it was observed that reactions in refluxing CH_2Cl_2 led to slightly higher yields than reactions at room temperature. Under the optimized reaction conditions, a satisfactory yield of lactone **6a** may even be obtained with [Rh_2(OAc)$_4$], although the carboxamido-rhodium catalysts are clearly more efficient for the transformation of **5a** [15].

The 1-methylcyclohexyl diazoacetate (**5d**) gave lactone **6d** as a single stereoisomer with *cis*-configuration, but the asymmetric induction (*ca.* 70%) was significantly lower than that obtained with **6a–c**. Considering the preference of cyclohexyl diazoacetates to insert into equatorial C–H bonds mentioned above, it would be expected that the lactones with *cis*-configuration are derived from that conformation of **5d** that has the diazoacetate group in the axial orientation. The difference of 1.1 kcal/mol of the *A*-values of the acetoxy (0.71) and Me (1.80) groups [23] suggests that the diazoacetate should predominantly be in the axial orientation, which is the one favorable for equatorial insertion.

The cyclopentyl and 1-methylcyclopentyl diazoacetates (**5a, f**) afforded lactones **6e, f**. Only the stereoisomers with the *cis*-configuration were observed. The ee's of the lactones were unsatisfactory, only 38 and *ca.* 34% for **6e** and **6f**, respectively, with [Rh_2(mepy)$_4$]. With [Rh_2(bnox)$_4$], there was practically no asymmetric induction. It is noteworthy, however, that the absolute configuration of the 6- and 5-ring-fused *cis*-lactones obtained with [Rh_2((2*S*)-mepy)$_4$] was identical, *i.e.* (3a*S*,7a*S*) for **6a** and (3a*S*,6a*S*) for **6e**. Owing to the low level of induction, no efforts was made to improve the yields of **6e, f**.

It is tempting to ascribe the enhanced enantioselectivity in the decomposition of **5a** leading to bicyclic lactones over that leading to monocyclic ones to the higher skeletal rigidity of the intermediate metallocarbene. However, the decomposition of 2,4-

dimethylpentan-3-yl diazoacetate (= 1-isopropyl-2-methylpropyl diazoacetate; **5g**) showed that this interpretation is not valid, since here the monocyclic lactone was obtained with a comparable ee (92–95%). Although the insertion into the tertiary C–H bond of **5g** does not lead to a quaternary chiral center, the lactone as a whole is chiral. Further extension of this methodology toward generation of quaternary chiral centers is in progress.

At present, it is premature to interpret the experimental variations of the enantioselectivities within this series of compounds. There must be some subtle geometrical effects which we cannot yet rationalize, owing to the limited amount of data. However, the presence of an O-atom adjacent to the reacting diazocarbonyl function seems to be important. Diazoketones which are structurally related to the diazoesters **5a** and **5d** behave differently and undergo intramolecular C–H insertion with practically no asymmetric induction in the presence of carboxamido-rhodium(II) catalysts.

The diazoketones **9a, b** were synthesized by known procedures as shown in *Scheme 2*: Ethyl cyano(cyclohexylidene)acetate (**7**) [24] was converted to (1-methylcyclohexyl)acetic acid (**8a**) *via* addition of methylmagnesium iodide [25], followed by hydrolysis of the ester and cyano functions and subsequent decarboxylation [26]. The diazoketone **9a** was obtained *via* conversion of **8a** to the acyl chloride which was reacted with an excess of diazomethane [27]. The synthesis of **9b** by the same route was not attempted, since the cyano(cyclopentylidene)acetate corresponding to **7** is inert towards methylmagnesium iodide or dimethyl copper lithium [25]. Thus, **8b** was synthesized from 1-methylcyclopentanol by addition of the tertiary methylcyclopentyl cation to 1,1-dichlorothene [28] and transformed to **9b** in analogy to **9a**. Reaction of **9a** with $[Rh_2(OAc)_4]$ in CH_2Cl_2 at room temperature afforded a 92:8 mixture of *cis*/*trans*-**10a** in 70% yield. Under the same conditions, **9b** afforded *cis*-**10b** exclusively (80% yield). The ketones were converted to the mixture of diastereoisomeric ketals **11a, b** by reaction with (2*R*,3*R*)-butane-2,3-diol [29]. The diastereoisomers of **11a** and those of **11b** were separable by capillary GC. In addition, most of the ^{13}C-NMR resonance signals of both ketals appeared as two lines of

Scheme 2

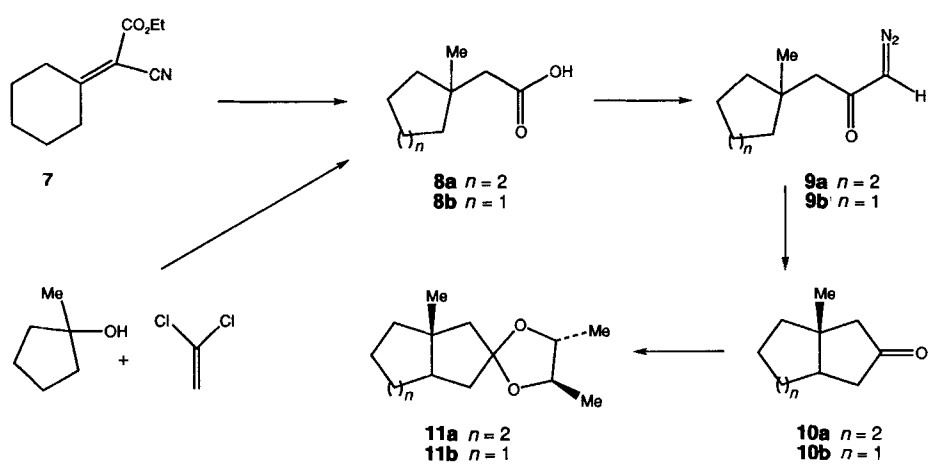


Table 2. *Decomposition of Diazoketones with Chiral Rhodium(II) Catalysts*

Diazoketone	Catalyst	Product	Yield [%]	ee [%][a]	Comment
9a	$[Rh_2(OAc)_4]$	**10a**	77	–	*cis*/*trans* 92:8
	$[Rh_2\{(2S)\text{-mepy}\}_4]$		33	0	*cis*/*trans* 98:2
9b	$[Rh_2(OAc)_4]$	**10b**	80	–	*cis*
	$[Rh_2\{(2S)\text{-mepy}\}_4]$		58	0	*cis*
	$[Rh_2\{(4S)\text{-bnox}\}_4]$		78	0	*cis*
9b	$[Rh_2\{(4S)\text{-phox}\}_4]$		58	7	*cis*

[a]) From diastereoisomeric ketal **11**.

equal intensities, which allowed independent determination of the asymmetric induction. As shown in *Table 2*, the asymmetric inductions obtained in these reactions with chiral catalysts were practically zero or so low that they are of no practical interest. It appears, from these data, that the carboxamido- and oxazolidinonato-rhodium(II) catalysts are much less suited for intramolecular C–H insertion reactions of diazoketones than of diazoesters.

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Experimental Part

1. *General.* See [16] [30]. *Carboxamido- and Oxazolidinonato-rhodium(II) Catalysts.* See [9] [16].

2. *Alkyl 3-Oxobutanoates: General Procedure* [17]. Alcohol **1** (50 mmol) was heated with freshly distilled **2** (7.10 g, 50 mmol) in xylene (10 ml) in an oil-bath (150°) during 30 min. After cooling to r.t., the xylene was evaporated and **3** purified by distillation under reduced pressure.

Cyclohexyl 3-Oxobutanoate [31] (**3a**): Yield 80%. B.p. 59°/0.005 Torr. IR (CH_2Cl_2): 3057*w*, 2941*s*, 2861*m*, 1736*s*, 1714*s*, 1649*w*, 1450*w*. ^{1}H-NMR ($CDCl_3$): 4.80 (*m*, 1 H); 3.42 (*s*, 2 H); 2.26 (*s*, 3 H); 2.00–1.10 (*m*, 10 H).

cis-4-(tert-*Buthyl*)*cyclohexyl 3-Oxobutanoate* (**3b**): Yield 72%. B.p. 92°/0.001 Torr. ^{1}H-NMR ($CDCl_3$): 5.07 (*m*, 1 H); 3.44 (*q*, ^4J = 0.5, 2 H); 2.27 (*t*, ^4J = 0.5, 3 H); 1.95 (*m*, 2 H); 1.50–0.95 (*m*, 5 H); 0.84 (*s*, 9 H). ^{13}C-NMR: 200.7 (*s*); 166.5 (*s*); 70.8 (*d*); 50.4 (*t*); 47.3 (*q*); 32.4 (*s*); 30.4 (*t*); 30.1 (*d*); 27.3 (*q*); 21.5 (*t*). MS: 240 (0.2, M^+), 184 (1), 155 (0.1), 138 (3), 123 (7), 103 (58), 57 (100).

trans-*4-(*tert-*Butyl)cyclohexyl 3-Oxobutanoate* (**3c**): Yield 85%. B.p. 90–92°/0.001 Torr. IR ($CHCl_2$): 3061*w*, 2955*s*, 2866*s*, 1736*s*, 1714*s*, 1649*w*. ^{1}H-NMR ($CDCl_3$): 4.70 (*m*, 1 H); 3.42 (*s*, 2 H); 2.17 (*s*, 3 H); 2.05 (*m*, 2 H); 1.80 (*m*, 2 H); 1.32 (*m*, 2 H); 1.15–0.95 (*m*, 3 H); 0.85 (*s*, 9 H). ^{13}C NMR: 200.7 (*s*); 166.7 (*s*); 74.9 (*q*); 32.3 (*s*); 31.9 (*t*); 30.9 (*d*); 27.6 (*q*); 25.4 (*t*). MS: 240 (1, M^+), 183 (1), 155 (0.5), 139 (13), 123 (12), 103 (78), 57 (100). HR-MS: 240.1718 ($C_{14}H_{24}O_3^+$, calc. 240.1725).

1-Methylcyclohexyl 3-Oxobutanoate [17] (**3d**): Yield 82%. B.p. 57°/0.01 Torr ([17]: 74–75°/0.3 Torr). IR (CH_2Cl_2): 3025*m*, 2938*s*, 2863*m*, 1735*s*, 1712*s*, 1647*w*, 1448*m*. ^{1}H-NMR ($CDCl_3$): 3.38 (*s*, 2 H); 2.26 (*s*, 3 H); 2.20–2.00 (*m*, 2 H); 1.60–1.20 (*m*, 1 H).

Cyclopentyl 3-Oxobutanoate [32] (**3e**): Yield 78%. B.p. 65°/0.005 Torr. IR (CH_2Cl_2): 3061*w*, 2968*m*, 2875*w*, 1737*s*, 1715*s*, 1649*m*, 1408*m*. ^{1}H-NMR ($CDCl_3$): 5.22 (*m*, 1 H); 3.41 (*s*, 2 H); 2.26 (*s*, 3 H); 2.00–1.50 (*m*, 8 H). MS: 170 (0.5, M^+), 116 (10), 103 (20), 85 (38), 68 (29), 57 (100).

1-Methylcyclopentyl 3-Oxobutanoate [33] (**3f**): Yield 70%. B.p. 52°/0.005 Torr. IR (CH_2Cl_2): 3061*w*, 2968*m*, 1737*s*, 1714*s*, 1647*w*. ^{1}H-NMR ($CDCl_3$): 3.36 (*s*, 2 H); 2.25 (*s*, 3 H); 1.75–1.55 (*m*, 11 H).

1-Isopropyl-2-methylpropyl 3-Oxobutanoate (**3g**): Yield 76%. B.p. 51°/0.01 Torr. IR (CH_2Cl_2): 2968*s*, 2877*w*, 1736*s*, 1714*s*, 1649*w*. ^{1}H-NMR ($CDCl_3$): 4.64 (*t*, ^3J = 6, 1 H); 3.49 (*s*, 2 H); 2.29 (*s*, 3 H); 1.91 (*m*, 2 H); 0.90 (*d*, ^3J = 6.6, 6 H); 0.87 (*d*, ^3J = 6.6, 6 H). ^{13}C-NMR: 200.5 (*s*); 167.0 (*s*); 84.1 (*d*); 50.1 (*t*); 30.2 (*d*); 29.3 (*q*); 19.4 (*q*); 17.1 (*q*). MS: 200 (34, M^+), 157 (4), 115 (11), 103 (100), 85 (52), 57 (55). HR-MS: 200.1406 ($C_{11}H_{20}O_3^+$, calc. 200.1412).

3. *Alkyl 2-Diazo-3-oxobutanoates* [11] **4**: *General Procedure.* To **3** (30 mmol) in MeCN (48 ml) in a flame-dried flask was added methane sulfonyl azide [18] (4.00 g, 33 mmol) and Et_3N (6.07 g, 60 mmol) under N_2. After 3 h at r.t., the soln. was diluted with 8% NaOH soln. and extracted with 3 × 50 ml of CH_2Cl_2. The org. phase was dried ($MgSO_4$) and evaporated. The residue was purified by CC (silica gel, 4% AcOEt/petroleum ether): **4** as a yellow oil.

Cyclohexyl 2-Diazo-3-oxobutanoate (**4a**): Yield 77%. IR (CH_2Cl_2): 3025*w*, 2941*m*, 2862*w*, 2143*s*, 1710*s*, 1652*s*, 1450*w*, 1307*s*. ^{1}H-NMR ($CDCl_3$); 4.90 (*m*, 1 H); 2.46 (*s*, 3 H); 2.00–1.20 (*m*, 10 H).

cis-*4-(*tert-*Butyl)cyclohexyl 2-Diazo-3-oxobutanoate* (**4b**): Yield 76%. IR (CH_2Cl_2): 3060*w*, 2952*s*, 2867*m*, 2141*s*, 1712*s*, 1652*s*. ^{1}H-NMR ($CDCl_3$): 5.19 (*m*, 3 H); 2.47 (*s*, 3 H); 1.98 (*m*, 2 H); 1.57 (*m*, 2 H); 1.35–1.00 (*m*, 5 H); 0,84 (*s*, 9 H).

trans-*4-(*tert-*Butyl)cyclohexyl 2-Diazo-3-oxobutanoate* (**4c**): Yield 88%. IR (CH_2Cl_2): 3054*w*, 2956*m*, 2143*s*, 1711*s*, 1652*s*. ^{1}H-NMR ($CDCl_3$): 4.76 (*m*, 1 H); 2.47 (*s*, 3 H); 2.05 (*m*, 2 H); 1.80 (*m*, 2 H); 1.50–1.00 (*m*, 5 H); 0.85 (*s*, 9 H).

1-Methylcyclohexyl 2-Diazo-3-oxobutanoate (**4d**): Yield 79%. IR (CH_2Cl_2): 3023*m*, 2938*s*, 2141*s*, 1709*s*, 1649*s*, 1448*m*, 1325*s*. ^{1}H-NMR ($CDCl_3$): 2.44 (*s*, 3 H); 2.20–2.10 (*m*, 2 H); 1.60–1.40 (*m*, 8 H); 1.55 (*s*, 3 H).

Cyclopentyl 2-Diazo-3-oxobutanoate (**4e**): Yield 76%. IR (CH_2Cl_2): 3059*w*, 2969*m*, 2876*w*, 2143*s*, 1711*s*, 1653*s*, 1327*s*, 1308*s*. ^{1}H-NMR ($CDCl_3$): 5.30 (*m*, 1 H); 2.47 (*s*, 3 H); 2.00–1.50 (*m*, 8 H).

1-Methylcyclopentyl 2-Diazo-3-oxobutanoate (**4f**): Yield 75%. IR (CH_2Cl_2): 2971*m*, 2140*s*, 1711*s*, 1651*s*, 1366*s*, 1330*s*. ^{1}H-NMR ($CDCl_3$): 2.43 (*s*, 3 H); 2.12 (*m*, 2 H); 1.67 (*m*, 9 H).

1-Isopropyl-2-methylpropyl 2-Diazo-3-oxobutanoate (**4g**): Yield 88%. IR (CH_2Cl_2): 3060*w*, 2969*s*, 2878*w*, 2142*s*, 1713*s*, 1652*s*, 1465*w*. ^{1}H-NMR ($CDCl_3$): 4.71 (*t*, ^3J = 6.4, 1 H); 2.49 (*s*, 3 H); 1.97 (*m*, 2 H); 0.93 (*d*, ^3J = 6.8, 6 H); 0.89 (*d*, ^3J = 6.8, 6 H).

4. *Alkyl Diazoacetates* (**5**): *General Procedure* [19]. To **4** (23.6 mmol) in MeCN (20 ml) was added with vigorous stirring 8% KOH soln. (100 ml) at r.t. within 10 min. Stirring was continued for 14 h at r.t. After addition of H_2O (20 ml), the mixture was extracted with Et_2O (2 × 100 ml), the extract dried ($MgSO_4$) and evaporated, and the crude **5** purified by CC (silica gel, 4% AcOEt/petroleum ether).

Cyclohexyl Diazoacetate (**5a**): Yield 65%. IR (CH_2Cl_2): 2938*m*, 2860*w*, 2112*s*, 1683*s*, 1387*m*. ^{1}H-NMR ($CDCl_3$): 4.85 (*m*, 1 H); 4.70 (*s*, 1 H); 2.00–1.10 (*m*, 10 H). ^{13}C-NMR: 166.3 (*s*); 73.1 (*d*); 46.2 (*d*); 31.7 (*t*); 25.3 (*t*); 23.6 (*t*). MS: 168 (2, M^+), 140 (1), 122 (4), 98 (7), 87 (57), 83 (61), 69 (40), 76 (32), 55 (100). HR-MS: 168.0946 ($C_8H_{12}N_2O_2^+$, calc. 168.0898).

cis-*4-(*tert-*Butyl)cyclohexyl Diazoacetate* (**5b**): Yield 63%. IR (CH_2Cl_2): 3055*w*, 2954*s*, 2868*m*, 2111*s*, 1693*s*, 1388*s*. ^{1}H-NMR ($CDCl_3$): 5.10 (*m*, 1 H); 4.72 (br. *s*, 1 H); 1.98 (*m*, 2 H); 1.60 (*m*, 2 H); 1.48 (*m*, 2 H); 1.25 (*m*, 2 H); 1.03 (*m*, 1 H); 0.86 (*s*, 9 H). ^{13}C-NMR: 167.0 (*s*); 70.0 (*d*); 47.4 (*d*); 46.3 (*d*); 32.5 (*s*); 30.7 (*t*); 27.4 (*q*); 21.5 (*t*). MS: 225 (1.2, $[M + 1]^+$), 224 (0.1), 139 (8), 138 (11), 123 (9), 95 (6), 87 (63), 81 (25), 69 (28), 67 (26), 57 (100). HR-MS: 224.152 ($C_{12}H_{20}N_2O_2^+$, calc. 224.1524).

trans-*4-(*tert-*Butyl)cyclohexyl Diazoacetate* (**5c**): Yield 80%. IR (CH_2Cl_2): 3055*w*, 2954*s*, 2866*s*, 2112*s*, 1685*s*, 1389*s*. ^{1}H-NMR ($CDCl_3$): 4.80–4.60 (*m*, 1 H); 4.68 (*s*, 1 H); 2.03 (*m*, 2 H); 1.80 (*m*, 2 H); 1.40–1.00 (*m*, 5 H); 0.83 (*s*, 9 H). ^{13}C-NMR: 166.5 (*s*); 74.2 (*d*); 47.0 (*d*); 46.2 (*d*); 32.2 (*t*); 27.5 (*q*); 25.4 (*t*). MS: 224 (0.4, M^+), 181 (0.6), 167 (0.8), 154 (1), 138 (12), 123 (13), 98 (8), 87 (37), 67 (21), 57 (100). HR-MS: 196.1473 ($C_{12}H_{20}O_2^+$, calc. 196.1463).

1-Methylcyclohexyl Diazoacetate (**5d**): Yield 82%. IR (CH_2Cl_2): 3018*w*, 2937*m*, 2863*w*, 2111*s*, 1679*s*, 1448*w*, 1372*s*. ^{1}H-NMR ($CDCl_3$): 4.64 (*s*, 1 H); 2.12 (*m*, 2 H); 1.60–1.20 (*m*, 11 H). ^{13}C-NMR: 82.9 (*s*); 46.5 (*d*); 36.8 (*t*); 25.9 (*q*); 22.0 (*t*). MS: 181 (1), 154 (119), 139 (34), 121 (10), 111 (44), 96 (38), 81 (100), 67 (77), 55 (68). HR-MS: 182.1102 ($C_9H_{14}O_2N_2^+$, calc. 182.1055).

Cyclopentyl Diazoacetate (**5e**): Yield 74%. IR (CH_2Cl_2): 3122*w*, 2965*m*, 2875*w*, 2112*s*, 1686*s*, 1387*s*, 1347*m*. ^{1}H-NMR ($CDCl_3$): 5.23 (*m*, 1 H); 4.68 (*s*, 1 H); 2.00–1.60 (*m*, 8 H). ^{13}C-NMR: 166.6 (*s*); 77.7 (*d*); 46.2 (*d*); 32.7 (*t*); 23.6 (*t*). MS: 154 (4, M^+), 87 (85), 69 (100). HR-MS: 154.0742 ($C_7H_{10}O_2N_2^+$, calc. 154.0742).

1-Methylcyclopentyl Diazoacetate (**5f**): Yield 86%. IR (CH_2Cl_2): 3122*w*, 2969*m*, 2875*w*, 2109*s*, 1686*s*, 1372*s*. ^{1}H-NMR ($CDCl_3$): 4.65 (*s*, 1 H); 2.12 (*m*, 2 H); 1.76–1.50 (*m*, 9 H). ^{13}C-NMR: 90.9 (*s*); 46.7 (*d*); 39.3 (*t*); 24.7 (*q*); 23.8 (*t*). MS: 167 (1), 140 (4), 125 (4), 111 (12), 97 (48), 81 (42), 67 (100), 59 (28). HR-MS: 140.0912 ($C_8H_{12}O_2^+$, calc. 140.0837).

1-Isopropyl-2-methylpropyl Diazoacetate (**5g**): Yield 78%. IR (CH_2Cl_2): 3055*w*, 2968*s*, 2877*w*, 2111*s*, 1687*s*, 1465*m*, 1379*s*. ^{1}H-NMR ($CDCl_3$): 4.75 (br. *s*, 1 H); 4.64 (*t*, ^3J = 6.2, 1 H); 1.90 (*m*, 2 H); 0.90 (*d*, ^3J = 7, 6 H); 0.87 (*d*, ^3J = 7, 6 H). ^{13}C-NMR: 167.0 (*s*); 83.2 (*d*); 45.7 (*d*); 29.4 (*d*); 19.5 (*q*); 17.1 (*q*). MS: 185 (13, $[M + 1]^+$), 155 (5), 141 (29), 99 (73), 87 (24), 69 (100), 57 (66). HR-MS: 184.1216 ($C_9H_{16}O_2N_2^+$, calc. 184.1211).

5. *Intramolecular C–H Insertion of* **5** *in the Presence of [Rh_2{(2S)-mepy}$_4$]: General Procedure.* Alkyl diazoacetate **6** (1 mmol) in dry CH_2Cl_2 (5.0 ml) was added under N_2 in 20 h, by means of a syringe pump, to

$[Rh_2\{(2S)\text{-mepy}\}_4]$ (20 mg, 0.02 mmol) and 3.0 g of molecular sieves in CH_2Cl_2 (20 ml, freshly distilled from CaH_2) in a flame-dried flask. After the addition, the catalyst was removed by filtration throug a plug of silica gel. The solvent was evaporated and the residue purified by bulb-to-bulb distillation under reduced pressure, then by flash chromatography (silica gel, Et_2O/hexane 10:1).

Hexahydrobenzofuran-2(3H)-one [22] [34–36]: (*cis*- and *trans*-**6a**): Yield 30%; *cis*/*trans* 7:3 ($[Rh_2(mepy)_4]$) or 7:13 ($[Rh_2(bnox)_4]$), determined by capillary GC (cross-linked methylsilicone column) with electronic integration. B.p. 70°/0.005 Torr (bulb-to-bulb dist.). IR (CH_2Cl_2): 2989*w*, 2940*s*, 1775*s*, 1448*w*. ^{1}H-NMR ($CDCl_3$): *cis*-**6a**: 4.60 (*m*, 1 H); 2.80–1.00 (*m*, 11 H); *trans*-**6a**: 3.97 (*m*, 1 H); 2.80–1.00 (*m*, 11 H). MS: 140 (5), 111 (8), 96 (40), 81 (70), 67 (100), 55 (62).

Abs. configuration of *cis*-**6a** from reaction with $[Rh_2\{(2S)\text{-mepy}\}_4]$: (3a*S*,7a*S*), from $[\alpha]_D^{20} = -47.9$ ($CHCl_3$, $c = 1.22$) of a sample containing 91% *cis*- and 8% *trans*-**6a** ([35]: $[\alpha]_D^{24.3} = -40.3$). Abs. configuration of *trans*-**6a** from reaction with $[Rh_2\{(4S)\text{-bnox}\}_4]$: (3a*R*,7a*S*), from $[\alpha]_D^{20} = +35.78$ ($CHCl_3$, $c = 0.40$) of a sample composed of 40.7% of (3a*R*,7a*R*) ([35]: $[\alpha]_D^{20} = +41.9$), 9.8% of (3a*S*,7a*S*) ([35]: $[\alpha]_D^{24.3} = -40.3$), 38.9 and 10.6% of (3a*R*,7a*S*) or (3a*S*,7a*R*) ([35]: $[\alpha]_D^{23} = +78.5$ and $[\alpha]_D^{22.8} = -77.6$, resp.).

(3aR,5S*,7aR*)-5-(*tert*-Butyl)hexahydrobenzofuran-2(3H)-one* (**6b**): Yield 40%. M.p. 46°. $[\alpha]_D^{20} = +27$ ($CHCl_3$, $c = 0.957$), with $[Rh_2\{(2S)\text{-mepy}\}_4]$. IR ($CH_2Cl_2$): 3055*w*, 2956*s*, 2868*m*, 1774*s*, 1468*w*. ^{1}H-NMR ($CDCl_3$): 4.46 (*m*, $^3J = 3.45$, 1 H); 2.72–2.66 (*dd*, $^2J = 16.5$, $^3J = 6.6$, 1 H); 2.32 (*m*, 2 H); 2.19 (*d*, $^2J = 16.5$, 1 H); 1.74 (*m*, 1 H); 1.60 (*m*, 2 H); 1.25–1.10 (*m*, 1 H); 0.98 (*m*, 1 H); 0.86 (*m*, 1 H); 0.83 (*s*, 9 H). ^{13}C-NMR: 177.0 (*s*); 78.9 (*d*); 45.6 (*d*); 38.9 (*t*); 36.2 (*d*); 32.8 (*s*); 29.0 (*t*); 28.4 (*t*); 27.3 (*q*); 20.7 (*t*). MS: 181 (4, $[M - Me]^+$), 141 (9), 140 (1), 122 (16), 94 (11), 80 (100), 57 (59). HR-MS: 181.1239 ($C_{11}H_{17}O_2^+$, calc. 181.1228).

(3aR,5S*,7aS*)-5-(*tert*-Butyl)hexahydrobenzofuran-2(3H)-one* (**6c**): Yield 30%. M.p. 48°. $[\alpha]_D^{20} = +62.2$ ($CHCl_3$, $c = 1.5$), with $[Rh_2\{(2R)\text{-mepy}\}_4]$. IR ($CH_2Cl_2$): 3064*w*, 2956*s*, 2866*m*, 1774*s*. ^{1}H-NMR: 3.75 (*m*, $^3J = 10.8$, 1 H); 2.50 (*dd*, $^2J = 16.2$, $^3J = 6.6$, 1 H); 2.25 (*m*, 2 H); 2.07–1.87 (*m*, 3 H); 1.60–1.50 (*m*, 1 H); 1.25 (*m*, 2 H); 1.08 (*m*, 1 H); 0.85 (*s*, 9 H). ^{13}C-NMR: 176.8 (*s*); 85.3 (*d*); 47.5 (*d*); 44.7 (*d*); 36.1 (*t*); 32.5 (*s*); 29.9 (*t*); 29.0 (*t*); 27.7 (*q*); 25.0 (*t*). MS: 197 (21, $[M + 1]^+$), 181 (4), 141 (9), 122 (6), 95 (7), 80 (22), 57 (100). HR-MS: 197.1536 ($C_{12}H_{20}O_2^+$, calc. 197.1541).

cis-*Hexahydro-7a-methylbenzofuran-2(3H)-one* [37] (**6d**): Yield 30%. B.p. 75°/0.005 Torr (bulb-to-bulb dist.). $[\alpha]_D^{20} = +7.8$ ($CHCl_3$, $c = 1.9$), with $[Rh_2\{(2S)\text{-mepy}\}_4]$. IR ($CH_2Cl_2$): 2979*w*, 2940*w*, 2863*w*, 1773*s*. ^{1}H-NMR ($CDCl_3$): 2.80–2.10 (*m*, 3 H); 2.00–1.10 (*m*, 8 H); 1.40 (*s*, 3 H). MS: 154 (33), 139 (96), 131 (15), 121 (19), 111 (100), 98 (17), 84 (24), 77 (11), 68 (35), 55 (38), 49 (23).

cis-*Hexahydro-2*H*-cyclopenta[*b*]furan-2-one* [22] [37] (**6e**): Yield 25%. B.p. 65°/0.005 Torr (bulb-to-bulb dist.). $[\alpha]_D^{20} = -18.3$ (MeCN, $c = 0.191$) for ee = 38%, with $[Rh_2\{(2S)\text{-mepy}\}_4]$; $[\alpha]_D^{20} = +12.8$ (MeOH, $c = 0.218$) for ee = 38% with $[Rh_2\{(2R)\text{-mepy}\}_4]$ ([22]: $[\alpha]_D^{27} = -36$). IR (CH_2Cl_2): 2936*s*, 1765*s*. ^{1}H-NMR ($CDCl_3$): 5.10–4.92 (*m*, 1 H); 3.00–1.45 (*m*, 9 H). MS: 126 (7), 98 (33), 97 (39), 80 (36), 68 (63), 67 (85), 54 (100).

cis-*Hexahydro-6a-methyl-2*H*-cyclopenta[*b*]furan-2-one* (**6f**): Yield 30%. B.p. 65°/0.001 Torr (bulb-to-bulb dist.). $[\alpha]_D^{20} = -13.4$ ($CHCl_3$, $c = 0.973$) forr ee = 31%, with $[Rh_2\{(2S)\text{-mepy}\}_4]$. IR ($CH_2Cl_2$): 3057*w*, 2968*s*, 2875*w*, 1763*s*, 1454*w*, 1195*m*, 1150*m*. ^{1}H-NMR ($CDCl_3$): 2.95–2.89 (*m*, 1 H); 2.60–1.52 (*m*, 8 H); 1.50 (*s*, 3 H). MS: 140 (13, M^+), 125 (8), 112 (13), 111 (18), 97 (100), 81 (22), 69 (19), 58 (36).

4,5-Dihydro-5-isopropyl-4,4-dimethylfuran-2(3H)-one (**6g**): Yield 42%. $[\alpha]_D^{20} = +66.9$ ($CHCl_3$, $c = 1.44$) for ee = 92%, with $[Rh_2\{(2S)\text{-mepy}\}_4]$. IR ($CH_2Cl_2$): 3058*w*, 2966*s*, 2878*m*, 1772*s*, 1467*m*, 1232*s*. ^{1}H-NMR ($CDCl_3$): 3.73 (*d*, $^3J = 8.8$, 1 H); 2.46–2.26 (*m*, *AB*, 2 H); 1.95 (*m*, 1 H); 1.23 (*s*, 1 H); 1.10 (*s*, 3 H); 1.07 (*d*, $^3J = 6.6$, 3 H); 0.98 (*d*, $^3J = 6.6$, 3 H). ^{13}C-NMR: 176.0 (*s*); 93.8 (*d*); 46.2 (*t*); 39.4 (*s*); 29.3 (*d*); 26.8 (*q*); 21.1 (*q*); 20.5 (*q*); 19.4 (*q*). MS: 157 (39, $[M + 1]^+$), 128 (9), 113 (84), 85 (24), 71 (25), 56 (100). HR-MS: 156.1159 ($C_9H_{16}O_2^+$, calc. 156.1150).

6. *Diazoketones* **9**. *(1-Methylcyclohexyl)acetic Acid* (**8a**). Prepared from **7** according to [25] [26]. B.p. 72°/0.04 Torr. IR (CH_2Cl_2): 3600–2500 *s* (br.), 1704*s*, 1447*m*. ^{1}H-NMR ($CDCl_3$): 11.0–10.0 (*s*, 1 H); 2.27 (*s*, 2 H); 1.50–1.30 (*m*, 10 H); 1.05 (*s*, 3 H).

(1-Methylcyclopentyl)acetic Acid (**8b**). Prepared from 1,1-dichloroethene according to [28]. B.p. 131–132°/20 Torr. IR (CH_2Cl_2): 3400–3000*s* (br.), 2958*s*, 2873*m*, 1707*s*. ^{1}H-NMR ($CDCl_3$): 11.5 (*s*, 1 H); 2.35 (*s*, 2 H); 1.68–1.48 (*m*, 8 H); 1.08 (*s*, 3 H).

1-Diazo-3-(1-methylcyclohexyl)propan-2-one (**9a**). To **8a** (3.75 g, 24 mmol) in CH_2Cl_2 (25 ml) containing 3 drops of DMF was added slowly, at 0°, oxalyl chloride (3.5 ml, 1.7 equiv.) by means of a syringe. Then the temp. was raised to r.t. and the mixture stirred for 3 additional h. After evaporation, the residue was reacted with *ca.* 5 equiv. of CH_2N_2 in Et_2O [27]. After 12 h, excess CH_2N_2 was removed by passing a stream of N_2 through the soln. Usual workup and CC (silica gel, AcOEt/hexane 1:3) gave **9a**. Yield 53%. IR (CH_2Cl_2): 3118*w*, 3015*m*, 2929*s*, 2856*m*, 2105*s*, 1732*m*, 1631*s*, 1452*m*, 1364*s*. ^{1}H-NMR ($CDCl_3$): 5.20 (*s*, 1 H); 2.20 (*s*, 2 H); 1.43–1.24 (*m*, 10 H);

1.01 (*s*, 3 H). MS: 180 (1), 152 (5), 109 (5), 97 (20), 84 (100), 67 (17), 55 (59). HR-MS: 180.1254 ($C_{10}H_{16}ON_2^+$, calc. 180.1262).

1-Diazo-3-(1-methylcyclopentyl)propan-2-one (**9b**). The procedure described for **9a** afforded **9b** from **8a** in 48% yield. IR (CH_2Cl_2): 3017*w*, 2957*m*, 2872*w*, 2106*s*, 1632*s*, 1361*s*. ^{1}H-NMR ($CDCl_3$): 5.19 (*s*, 1 H); 2.28 (*s*, 2 H); 1.70–1.20 (*m*, 8 H); 1.05 (*s*, 3 H). MS: 138 (10, $[M - N_2]^+$), 120 (7), 95 (8), 83 (100), 67 (29), 55 (93). HR-MS: 138.1022 ($C_9H_{14}O^+$, calc. 138.1044).

7. *Intramolecular C–H Insertions of Diazoketones* **9**. cis-*Octahydro-3a-methy-2*H-*inden-2-one* (**10a**). According to the procedure described for **6** (*Exper. 5*). Yields: *Table 2*. IR (CH_2Cl_2): 3017*w*, 2929*s*, 2861*w*, 1737*s*, 1449*w*, 1403*w*. ^{1}H-NMR ($CDCl_3$): 2.24–1.34 (*m*, 13 H); 1.13 (*s*, 3 H). ^{13}C-NMR: 218.9 (*s*); 51.6 (*t*); 42.6 (*t*); 41.3 (*d*); 37.8 (*s*); 34.1 (*t*); 26.6 (*q*); 26.4 (*t*); 22.0 (*t*); 21.8 (*t*). MS: 152 (100, M^+), 109 (45), 81 (25), 67 (25), 55 (13). A sample prepared according to [11] had identical spectral data.

cis-*Hexahydro-3a-methylpentalen-2(1*H*)-one* (**10b**). As described for **10a**. IR (CH_2Cl_2): 3016*m*, 2955*s*, 2869*m*, 1732*s*, 1452*w*, 1402*w*. ^{1}H-NMR ($CDCl_3$): 2.50–1.00 (*m*, 11 H); 1.14 (*s*, 3 H). ^{13}C-NMR: 220.4 (*s*); 51.6 (*t*); 46.9 (*s*); 46.8 (*d*); 44.9 (*t*); 39.8 (*t*); 32.8 (*t*); 27.4 (*q*); 24.3 (*t*). MS: 138 (60, M^+), 125 (8), 95 (100), 82 (68), 67 (59), 54 (32). HR-MS: 138.1035 ($C_9H_{14}O^+$, calc. 138.1044).

*(4*R*,5*R*)*-cis-*3'a,7'a-Octahydro-3'a,4,5-trimethylspiro[1,3-dioxolane-2,2'-[2*H*]indene]* (**11a**). To **10a** (70 mg, 0.46 mmol) in benzene (20 ml) was added (*R,R*)-butan-2,3-diol (1.0 mmol) and toluene-4-sulfonic acid (5.0 mg). The mixture was heated to reflux for 16 h and H_2O separated by a *Dean-Stark* apparatus. After cooling, CH_2Cl_2 and H_2O were added. The org. layer was washed ($NaHCO_3$) and dried ($MgSO_4$). Yield 87% after CC (silica gel, 15% AcOEt/petroleum ether). IR (CH_2Cl_2): 2929*s*, 1261*w*, 1092*s*. ^{1}H-NMR ($CDCl_3$): 3.50–3.40 (*m*, 2 H); 2.01–1.10 (*m*, 19 H); 0.96 (*s*, 3 H). ^{13}C-NMR: 116.4, 116.0 (2*s*); 78.3, 78.2 (2*d*); 77.9, 77.8 (2*d*); 53.9, 52.0 (2*t*); 43.5, 43.6 (2*t*); 43.2, 42.9 (2*d*); 39.0, 28.7 (2*s*); 34.1, 33.2 (2*t*); 26.7, 25.6 (2*q*); 25.9, 24.5 (2*t*); 22.3, 21.0 (2*t*); 22.2, 22.1 (2*t*); 17.3, 17.2 (2*q*); 17.1, 16.9 (2*q*). MS: 224 (45, M^+), 209 (5), 180 (10), 167 (38), 153 (57), 141 (24), 127 (37), 95 (36), 81 (41), 67 (44), 55 (100). HR-MS: 224.1758 ($C_{14}H_{24}O_2^+$, calc. 224.1776).

*(4*R*,5*R*)*-cis-*3'a,6'a-Octahydro-3'a,4,5-trimethylspiro[1,3-dioxolane-2,2'(2'*H*)-pentalene]* (**11b**). As described for **11a**. Yield 90%. IR (CH_2Cl_2): 3009*m*, 2960*s*, 2865*m*, 1454*w*, 1377*w*, 1262*s*, 1095*s*, 1015*s*. ^{1}H-NMR ($CDCl_3$): 3.60–3.50 (*m*, 2 H); 2.10–1.95 (*m*, 2 H); 1.78–1.18 (*m*, 15 H); 1.13 (*s*, 3 H). ^{13}C-NMR: 117.4 (*s*); 78.2, 78.1 (2*d*); 78.0, 77.8 (2*d*); 50.8, 50.6 (2*t*); 47.9, 47.8 (2*d*); 47.1 (*s*); 44.5, 44.4 (2*t*); 42.1, 42.0 (2*t*); 33.3, 33.2 (2*t*); 29.5, 29.3 (2*q*); 25.2 (*t*); 17.3, 17.2 (2*q*); 17.1, 17.0 (2*q*). MS: 210 (100, M^+), 195 (36), 181 (7), 167 (92), 153 (92), 141 (35), 127 (57), 114 (28), 95 (48), 81 (31). HR-MS: 210.1605 ($C_{13}H_{22}O_2^+$, calc. 210.1619).

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