52. Stereoselective Conversion of Campholene- to Necrodane-Type Monoterpenes. Novel Access to (−)-(*R*,*R*)- and (*R*,*S*)-α-Necrodol and the Enantiomeric γ-Necrodols

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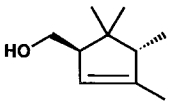
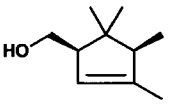
Naturally occurring (−)-(*R*,*R*)-α-necrodol ((−)-**1**) and its C(4)-epimer (−)-**2** are obtained in 84 and 44% yields, respectively, by lithium ethylenediamide (LEDA) treatment of the corresponding β-necrodols (−)-**3** and (−)-**4** (*Scheme 1, Table*), both readily available from (−)-campholenyl acetate ((−)-**i**) by an efficient stereoselective synthesis. The thermodynamically preferred (−)-(*R*)-γ-necrodol ((−)-**5**) becomes the major product (≥ 80% yield) after either prolonged treatment with LEDA or exposure of α- and β-necrodols to $BF_3 \cdot Et_2O$. In an alternative route, (+)-**5** is prepared starting from (+)-campholenal ((+)-**ii**) *via* Pd-catalysed decarbonylation to (−)-(*S*)-1,4,5,5-tetramethylcyclopent-1-ene ((−)-**6**) and subsequent application of an acid-catalysed CH_2O-addition/rearrangement sequence (*Scheme 2*).

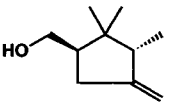
Introduction. – Belonging to a new group of monoterpenoid alcohols [1], the isomeric necrodols **1**–**5** have received much attention as preparatively challenging target molecules [2] due to their intriguing non-isoprenoid structures and their remarkable insect-repellant activities.



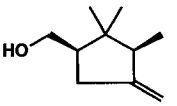
(−)-**1**
(−)-α-necrodol
(natural)



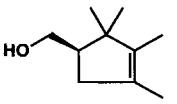
(−)-**2**
(−)-α-epi-necrodol



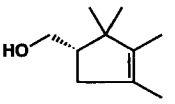
(−)-**3**
(−)-β-necrodol
(natural)



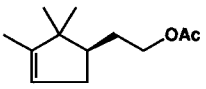
(−)-**4**
(−)-β-epi-necrodol



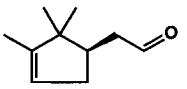
(−)-**5**
(−)-γ-necrodol



(+)-**5**
(+)-γ-necrodol



(−)-**i**[1])
(−)-campholenyl acetate



(+)-**ii**[1])
(+)-campholenal

[1]) Structural correlations of (−)-**i** and (+)-**ii** with (−)-α-pinene as well as their natural occurrence have been reported in [3].

The two naturally occurring isomers (−)-**1** and (−)-**3**[2]) have especially been the subject of intensive synthetic studies [2] [4]. Recently, we have disclosed an efficient synthesis of (−)-**3** by applying a stereoselective *Prins/retro-Prins*-rearrangement sequence [5] starting from (−)-campholenyl acetate ((−)-**i**). In contrast, the reported routes to the corresponding α- and γ-isomers (−)-**1**, (−)-**2**, (−)-**5**, and (+)-**5** are multistep, low-yielding processes [2]. As an improved approach to α- and γ-necrodols, we now report the C=C bond isomerisation of the epimeric β-isomers (−)-**3** and (−)-**4**. In addition, we describe a novel access to (+)-**5** by extension of the *Prins* methodology [5] to the cyclopentene (−)-**6**, itself readily available from (+)-campholenal ((+)-**ii**) by Pd/C-catalysed decarbonylation [6].

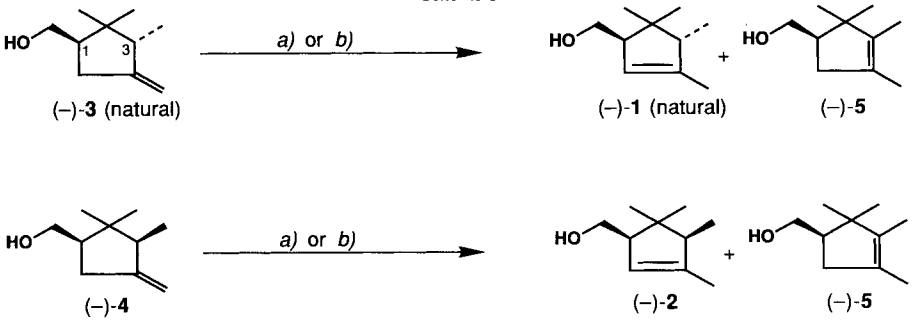
Results. – 1. *α- and γ-Necrodols by C=C Bond Isomerisation of β-Necrodols.* Previous attempts [2] to transform (−)-**3** and (−)-**4** into (−)-**1**, (−)-**2**, and (−)-**5** using transition metal catalysed C=C bond isomerisation have generally been unsuccessful. We, therefore, turned to more classical conditions and found that lithium ethylenediamide (LEDA) in ethylenediamine (*Condition a* [7]) and $BF_3 \cdot Et_2O$ in Et_2O (*Condition b*) were both highly efficient for this purpose. Thus, (−)-**3** and (−)-**4** were readily transformed into the

Table. *LEDA- and $BF_3 \cdot Et_2O$-Catalysed Isomerisation of (−)-β-Necrodol* ((−)-**3**) *and its Epimer (−)-***4** (see *Scheme 1*): *Formation of Natural (−)-α-Necrodol* ((−)-**1**), *its Epimer (−)-***2**, *and (−)-γ-Necrodol* ((−)-**5**)

Entry	Starting material	*Condition* [a])	Reaction time	Yield (dist.)	Product distributions [%]				
					starting material	(−)-**1**	(−)-**2**	(−)-**5**	unknown
1	(−)-**3**	*a*	8–10 min	92%	0.5	84	–	14	1.5
2	(−)-**3**	*a*	15 h	90%	0.1	8	–	90	1.9
3	(−)-**3**	*b*	15 h	80%	0.1	0.1	–	97	2.8
4	(−)-**4**	*a*	8–10 min	95%	2.5	–	44	52	1.5
5	(−)-**4**	*a*	15 h	90%	1	–	2	95	2
6	(−)-**4**	*b*	15 h	80%	0.8	–	0.2	97	2

[a]) *Condition a*: Li/$NH_2CH_2CH_2NH_2$ (*ca.* 1:20; *ca.* 6 mol-equiv. of $LiNHCH_2CH_2NH_2$); 70°. *Condition b*: $BF_3 \cdot Et_2O/Et_2O$ (*ca.* 1:20; *ca.* 0.1 mol-equiv. of $BF_3 \cdot Et_2O$); 20°.

Scheme 1



a) *b*) See *Footnote a* in the *Table*.

[2]) Both (−)-**1** and (−)-**3** have been isolated from the defence spray of the carrion beetle by *Meinwald* and coworkers [1] and characterised by enantiospecific syntheses [2]. They may be regarded as plant terpene metabolites originating from lavandulol structures [2].

corresponding endocyclic double-bond isomers, the final position of the C=C bond depending on whether basic or acidic conditions were employed (see *Table* and *Scheme 1*). Careful GC analysis of the isomerisation of (−)-**3** and (−)-**4** revealed that LEDA isomerises the C=C bond into both the α- and γ-positions, the product distributions being both substrate- and time-dependent; in contrast, $BF_3 \cdot Et_2O$ led to exclusive formation of (−)-**5** without the intermediate appearance of (−)-**1** and (−)-**2**.

Thus, treatment of (−)-**3** or (−)-**4** with a freshly prepared solution of lithium (6 mol-equiv.) in ethylenediamine at 70° (see *Table, Entries 1* and *4*) resulted in the complete disappearance of the starting material after 8–10 min and clean formation of mixtures of isomeric alcohols in over 90% yield. The mixture obtained from (−)-**3** contained (−)-**1** (84%) and (−)-**5** (14%), whilst that formed from (−)-**4** consisted of (−)-**2** (44%) and (−)-**5** (52%). Prolongation of the LEDA treatment resulted in further transformation of (−)-**1** and (−)-**2**, leading in both cases, after 15 h, to (−)-**5** as the final product (*Entries 2* and *5*). On the other hand, exposure of (−)-**3** or (−)-**4** to $BF_3 \cdot Et_2O$ (0.1 mol-equiv.) in Et_2O at 20° (*Entries 3* and *6*) resulted in almost complete conversion to (−)-**5** after 15 h. The final product (80–85% yield after distillation) contained less than 1–3% of starting materials and some unidentified by-products.

For structural characterisation, the individual necrodols were isolated by chromatography. The identities of (−)-**1**, (−)-**2**, and (−)-**5** were confirmed by spectral comparison with authentic samples [2]. Because no racemisation is expected during their formation, these products are thus assumed to have the same optical purity as (−)-**3** and (−)-**4** (*ca.* 94% ee)[3]).

Mechanistically, the markedly different pathways of the C=C bond isomerisations of (−)-**3** and (−)-**4** are rationalised by the inherently different reaction behaviours of the two catalysts utilised. The fact that LEDA initiates C=C bond isomerisation by allylic deprotonation [7] indicates that the small amount of (−)-**5** (14%) formed from (−)-**3** (*Entry 1*) may have its origin in the low steric accessibility of H–C(3) due to the *cis*-oriented CH_2OH–C(1). In contrast, for (−)-**4**, in which H–C(3) is as readily accessible as H–C(5), both isomerisation products (−)-**2** and (−)-**5** are formed in comparable amounts. These steric arguments may be used to explain the distinctly slower reaction rate for the transformations (−)-**3** → (−)-**1** → (−)-**5** in comparison with (−)-**4** → (−)-**2** → (−)-**5** (see *Table*).

On the other hand, $BF_3 \cdot Et_2O$, which effects isomerisation by prior electrophilic interaction with the C=C bond, is less sensitive to steric constraints. The exclusive and direct formation of (−)-**5** from both (−)-**3** and (−)-**4** (*Entries 3* and *6*) may be, therefore, due to the thermodynamically preferred tetrasubstituted position of the C=C bond. In agreement with this hypothesis is the fact that these C=C bond isomerisations were found to be irreversible under these conditions.

2. *(+)-γ-Necrodol ((+)-**5**) from Campholenal ((+)-**ii**).* With the aim of synthesizing the enantiomer (+)-**5** of γ-necrodol[4]) for comparative organoleptic experiments, the approach depicted in *Scheme 2* was adopted. On Pd-catalysed decarbonylation of the

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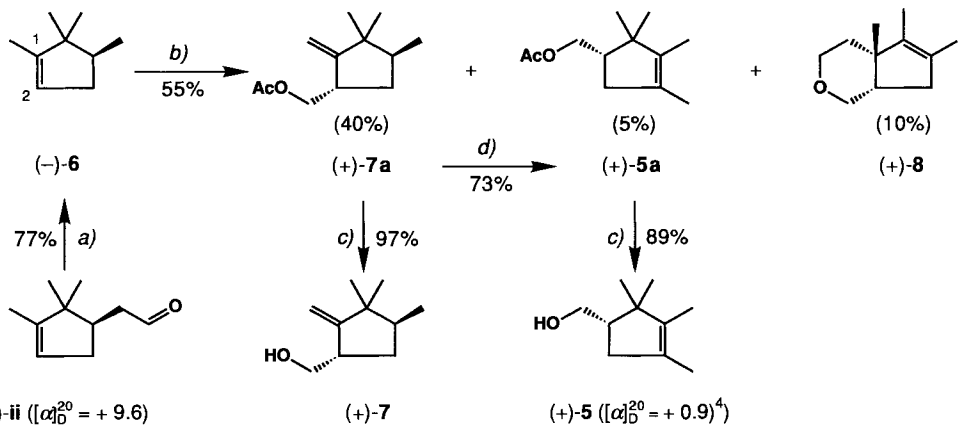
[3]) We found the following optical rotations in $CHCl_3$: (−)-**1**, $[\alpha]_D^{20} = -129.7$; (−)-**2**, $[\alpha]_D^{20} = -49.9$; (−)-**5**, $[\alpha]_D^{20} = -21.2$. Previously reported values [2]: (−)-(*R,R*)-**1**, $[\alpha]_D^{20} = -76.5$; (+)-(*S,R*)-**2**, $[\alpha]_D^{20} = +24.5$, (+)-(*S*)-**5**, $[\alpha]_D^{20} = +15.1$ ($CHCl_3$).

[4]) Enantiomer (+)-**5** was first obtained by *Meinwald* and coworkers [2b] in connection with synthetic work directed towards (+)-**1** and (+)-**3** starting from (−)-bornyl acetate.

Scheme 2

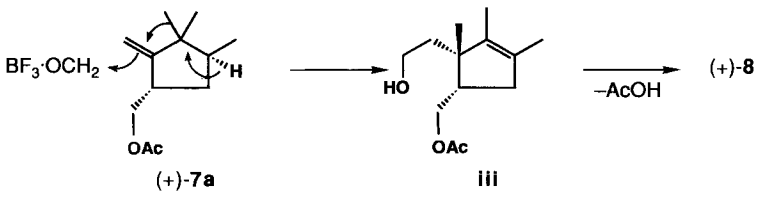


a) 5% Pd/C, 180–200°. *b*) Paraformaldehyde, $BF_3 \cdot Et_2O$, Ac_2O, CH_2Cl_2, 0°. *c*) $LiAlH_4$, Et_2O. *d*) $BF_3 \cdot Et_2O$, toluene, 15 h.

readily available (+)-campholenal ((+)-**ii**; ee *ca.* 94%)[1]), (–)-1,4,5,5-tetramethylcyclopent-1-ene ((–)-**6**) was obtained in 77% yield [6]. *Prins-Blomquist* conditions (CH_2O, Ac_2O, $BF_3 \cdot Et_2O$ [8]) then led stereoselectively to the formation of *trans*-acetate (+)-**7a** as the sole primary reaction product without detectable traces of its *cis*-stereoisomer (GC limits $\leq 1\%$)[5]). If equimolar quantities of starting materials were used and the reaction was then quenched by hydrolysis after *ca.* 90% conversion of (–)-**6** (GC control), the isolated yield of (+)-**7a** was 40%. Under these conditions, only (+)-**5a** (*ca.* 5%) and bicyclic ether (+)-**8** (10%) were formed as detectable by-products. Prolongation of the reaction time caused further rearrangement of (+)-**7a** to (+)-**5a**, but also led to increased formation of unidentified by-products. Best yields of (+)-**5a** (*ca.* 73%) were obtained by separate treatment of (+)-**7a** with $BF_3 \cdot Et_2O$ in toluene at 20°.

As expected, increased formation of ether (+)-**8** was observed by using an excess of paraformaldehyde and may become, if desired, the major product. A plausible mechanism is presented in *Scheme 3*. Thus, a $BF_3 \cdot OCH_2$ complex initially adds to the C=C bond in (+)-**7a** with concomitant 1,2-Me-shift and proton loss to give intermediate **iii**, which then eliminates AcOH to form ether (+)-**8**.

Scheme 3



Organoleptic Properties. – Sensory evaluation of the isomeric α- and γ-necrodols **1**–**5** revealed in all cases weak odour profiles with predominant camphoraceous-herbal-like

[5]) This reaction behaviour of (–)-**6** is identical to that previously observed for (–)-**i** [5].

notes. In addition, no significant odour difference was discerned between optical antipodes.

Experimental Part

General. See [5].

Starting Materials. Preparation of the isomeric β-necrodols (−)-**3** ($[\alpha]_D^{20} = -17.85$ ($c = 1.68$, $CHCl_3$)) and (−)-**4** ($[\alpha]_D^{20} = -81.7$ ($c = 1.2$, $CHCl_3$)) and of (+)-campholenal ((+)-**ii**; $[\alpha]_D^{20} = +9.6$ (neat); enantiomeric excess *ca.* 94%) as described previously [5].

1. *LEDA-Catalysed Isomerisation of (−)-***3** *and (−)-***4**. 1.1. *(−)-***1** *and (−)-***5** *from (−)-***3**. Alcohol (−)-**3** (1.8 g, 11.7 mmol) was added to a freshly prepared soln. of Li (0.485 g, 69 mmol) in ethylenediamine (10.8 ml) [7] heated at 70° until the disappearance of (−)-**3** (*i.e.* 8–10 min (GC control); *Condition a*), then poured onto ice, extracted with Et_2O, washed with sat. aq. NH_4Cl soln. and with brine to neutrality, dried (Na_2SO_4), evaporated, and purified by bulb-to-bulb distillation (oven temp. 130°/3 Torr): 1.65 g (92%) of colourless oil, consisting of (−)-**3** (0.5%), (−)-**1** (84%), (−)-**5** (14%), and unknown products (1.5%; GC). LEDA treatment of (−)-**3** for 15 h led to a mixture (90% yield) of (−)-**3** (0.1%), (−)-**1** (8%), (−)-**5** (90%), and unknown components (1.9% GC). Separation by prep. GC (5-m *Carbowax* column) gave pure (−)-**1** followed by pure (−)-**5**.

*(−)-(1*R*,4*R*)-3,4,5,5-Tetramethylcyclopent-2-ene-1-methanol* ((−)-**1**). $[\alpha]_D^{20} = -129.7$ ($c = 1.1$, $CHCl_3$). IR: 3600, 2900, 1460, 1370, 1060, 1000, 850. ^{1}H-NMR: 0.88 (*d*, $J = 7.2$, 3 H); 0.92 (*s*, 3 H); 1.00 (*s*, 3 H); 1.64 (*d*, $J = 1.5$, 3 H); 2.19 (*q*, $J = 7.2$, 1 H); 2.30 (*m*, 1 H); 3.59 (*ABX*, $J = 5.4$, 10.5, $\Delta = 21$, 2 H); 5.25 (br. *s*, 1 H). ^{13}C-NMR: 145.8 (*s*); 123.3 (*d*); 63.2 (*t*); 56.5 (*d*); 52.3 (*d*); 43.0 (*s*); 25.0 (*q*); 23.6 (*q*); 15.2 (*q*); 12.0 (*q*). MS: 154 (7, M^+), 139 (43), 123 (97), 105 (15), 95 (21), 91 (23), 81 (100), 79 (25), 77 (18), 67 (29), 55 (24), 41 (27).

*(−)-(1*R*)-2,2,3,4-Tetramethylcyclopent-3-ene-1-methanol* ((−)-**5**). $[\alpha]_D^{20} = -21.2$ ($c = 1.14$, $CHCl_3$). IR: 3270, 2900, 1480, 1360, 1000. ^{1}H-NMR: 0.82 (*s*, 3 H); 1.05 (*s*, 3 H); 1.48 (*s*, 3 H); 1.59 (*s*, 3 H); 1.99 (*m*, 2 H); 2.30 (*m*, 1 H); 3.62 (*dd*, $J = 7.2$, 10.8, 1 H); 3.78 (*dd*, $J = 6.2$, 10.8, 1 H). ^{13}C-NMR: 138.7 (*s*); 128.1 (*s*); 64.3 (*t*); 50.5 (*d*); 47.6 (*s*); 39.3 (*t*); 27.2 (*q*); 19.9 (*q*); 14.1 (*q*); 9.1 (*q*). MS: 154 (25, M^+), 139 (100), 121 (97), 109 (29), 105 (32), 93 (33), 91 (22), 79 (21), 67 (23), 55 (18), 41 (36).

1.2. *(−)-***2** *and (−)-***5** *from (−)-***4**. Alcohol (−)-**4** (1 g, 6.5 mmol) was treated with LEDA as described in *1.1* for 8–10 min to afford a mixture (0.95 g, 95% yield) of (−)-**4** (2.5%), (−)-**2** (44%), (−)-**5** (52%), and unknown components (1.5%; GC). After 15 h, the product distribution was (−)-**4** (1%), (−)-**2**) (2%), (−)-**5** (95%), and unknown components (2%; GC). Separation by prep. GC (5-m *Carbowax* column) gave pure (−)-**2** followed by (−)-**5**. *(−)-(1*R*,4*S*)-3,4,5,5-Tetramethylcyclopent-2-ene-1-methanol* ((−)-**2**). $[\alpha]_D^{20} = -49.9$ ($c = 1.2$, $CHCl_3$). IR: 3600, 3040, 1360, 1040. ^{1}H-NMR: 0.82 (*s*, 3 H); 0.90 (*d*, $J = 7.2$, 3 H); 1.08 (*s*, 3 H); 1.68 (*d*, $J = 1.4$, 3 H); 2.11 (*q*, $J = 7.2$, 1 H); 2.36 (*m*, 1 H); 3.56 (*ABX*, $J = 6$, 11, $\Delta = 38$, 2 H); 5.24 (br. *s*, 1 H). ^{13}C-NMR: 145.3 (*s*); 123.3 (*d*); 63.8 (*t*); 57.8 (*d*); 53.3 (*d*); 43.3 (*s*); 30.6 (*q*); 18.3 (*q*); 15.2 (*q*); 13.6 (*q*). MS: 154 (5, M^+), 139 (7), 123 (100), 105 (8), 95 (11), 91 (13), 81 (67).

1.3 *LEDA Treatment of (−)-***5**. Pure (−)-**5** (0.3 g, 1.95 mmol) was heated in a mixture of Li (0.3 g, 42.8 mmol) in ethylenediamine (5 ml) at 70° for 15 h (*Condition a*). GC: no formation of (−)-**1**, (−)-**2**, (−)-**3**, or (−)-**4** (GC limits *ca.* 0.5%).

2. *$BF_3 \cdot Et_2O$-Catalysed Isomerisation of (−)-***3** *and (−)-***4** *to (−)-***5**. A 35:65 mixture (−)-**3**/(−)-**4** (1 g, 6.5 mmol) in Et_2O (10 ml) was stirred with $BF_3 \cdot Et_2O$ (0.15 ml) overnight at r.t. (*Condition b*). The soln. was washed with brine until neutral, dried (Na_2SO_4), evaporated, and purified by bulb-to-bulb distillation (oven temp. 130°/4 Torr) to yield a mixture (0.8 g, 80%) of (−)-**3** (0.1%), (−)-**4** (0.8%), (−)-**1** (1%), (−)-**2** (1%), (−)-**5** (95%), and known components (*ca.* 2.1%; GC) as a colourless oil. Purified (−)-**5** ($[\alpha]_D^{20} = -21$ ($c = 1.95$, $CHCl_3$)) was spectrally identical with an authentic sample (*vide supra*).

3. *Decarbonylation of (+)-Campholenal* ((+)-**ii**) *to (−)-(4*S*)-1,4,5,5-Tetramethylcyclopent-1-ene* ((−)-**6**). Heating of (+)-**ii** (500 g, 3.29 mol) together with 5% Pd/C (2.5 g) at 180–200° (oil bath) in a *Vigreux* distillation apparatus under stirring resulted in the continuous formation and distillation of (−)-**6** (313 g, 77%). Colourless oil. $[\alpha]_D^{20} = -0.9$ (neat). B.p. 126°/760 Torr. GC purity: *ca.* 90%. IR: 3030, 2950, 1450, 1010, 790. ^{1}H-NMR: 0.75 (*s*, 3 H); 0.93 (*d*, $J = 7.2$, 3 H); 0.95 (*s*, 3 H); 1.61 (br. *s*, 3 H); 1.84 (*m*, 2 H); 2.25 (*m*, 1 H); 5.22 (br. *s*, 1 H). ^{13}C-NMR: 148.5 (*s*); 122.1 (*d*); 46.8 (*s*); 44.8 (*d*); 37.8 (*t*); 25.7 (*q*); 19.5 (*q*); 14.4 (*q*); 12.8 (*q*). MS: 124 (15, M^+), 109 (100), 91 (14), 79 (19), 67 (30), 55 (6).

4. Prins-Blomquist *Reaction of (−)-***6**: *(+)-***5a**, *(+)-***7a**, *and (+)-***8**. $BF_3 \cdot Et_2O$ (5 ml) was added dropwise at 0° to a stirred mixture of (−)-**6** (250 g, 2.02 mol), paraformaldehyde (72 g, 2.4 mol), Ac_2O (280 ml), and 2,6-di(*tert*-butyl)-4-methylphenol (0.5 g) in CH_2Cl_2 (1.5 l). The mixture was stirred overnight at r.t. and then

poured onto brine, and the org. phase was washed with sat. aq. $NaHCO_3$ and NaCl soln., dried (Na_2SO_4), and evaporated. GC: < 10% of (−)-**6**, 14% of (+)-**8**, 60% of (+)-**7a**, 9% of (+)-**5**, and 7–10% unknown. Distillation of the crude oil (32–100°/7 Torr) afforded a colourless oil (245 g). Fractional distillation using a 20-cm column packed with stainless steel helices at 0.5 Torr gave 50 g of a head fraction ((−)-**6** and (+)-**8**; b.p. ≤ 50°) and 178 g of (+)-**7a**/(+)-**5a** 9:1 (b.p. 50°–57°; 45% yield). Separation by prep. GC (5-m *Carbowax* column) afforded pure samples of (+)-**5a**, (+)-**7a**, and (+)-**8**.

(+)-(1S)-(2,2,3,4-Tetramethylcyclopent-3-enyl)methyl Acetate ((+)-**5a**). $[\alpha]_D^{20} = +0.82$ (neat.). IR: 2900, 1730, 1440, 1360, 1230, 1020. ^{1}H-NMR: 0.82 (*s*, 3 H); 1.05 (*s*, 3 H); 1.49 (*s*, 3 H); 1.59 (*s*, 3 H); 1.98 (*m*, 1 H); 2.06 (*s*, 3 H); 1.92 (*m*, 1 H); 2.25 (*m*, 1 H); 4.13 (*m*, 2 H). ^{13}C-NMR: 171.3 (*s*); 138.5 (*s*); 127.9 (*s*); 65.9 (*t*); 47.7 (*s*); 46.8 (*d*); 39.2 (*t*); 27.0 (*q*); 21.0 (*q*); 19.9 (*q*); 14.1 (*q*); 9.2 (*q*). MS: 196 (2, M^+), 136 (17), 121 (100), 105 (15), 93 (17), 79 (8), 67 (3), 55 (4), 43 (23).

(+)-(1S,4S)-(3,3,4-Trimethyl-2-methylidenecyclopentyl)methyl Acetate ((+)-**7a**). $[\alpha]_D^{20} = +5.8$ ($c = 3.42$, $CHCl_3$). IR: 2900, 1720, 1450, 1360, 1210, 1020, 880. ^{1}H-NMR: 0.84 (*s*, 3 H); 0.87 (*d*, $J = 6.8$, 3 H); 1.03 (*s*, 3 H); 1.52 (*m*, 1 H); 1.70 (*m*, 2 H); 2.06 (*s*, 3 H); 2.88 (*m*, 1 H); 3.91 (*dd*, $J = 9$, 10.8, 1 H); 4.05 (*dd*, $J = 5.4$, 10.8, 1 H); 4.90 (*m*, 2 H). ^{13}C-NMR: 171.0 (*s*); 162.1 (*s*); 105.5 (*t*); 68.0 (*t*); 44.9 (*s*); 42.1 (*d*); 40.8 (*d*); 34.2 (*t*); 27.0 (*q*); 23.3 (*q*); 21.0 (*q*); 14.1 (*q*). MS: 196 (0, M^+), 151 (1), 136 (23), 121 (100), 107 (45), 93 (37), 79 (17), 43 (47).

(+)-(1S,6S)-6,7,8-Trimethyl-3-oxabicyclo[4.3.0]non-7-ene ((+)-**8**). $[\alpha]_D^{20} = +3.7$ ($c = 2.27$, $CHCl_3$). IR: 2800, 1440, 1110. ^{1}H-NMR: 0.96 (*t*, $J = 3.6$, 1 H); 0.98 (*s*, 3 H); 1.48 (*s*, 3 H); 1.56 (*m*, 1 H); 1.61 (*s*, 3 H); 1.80 (*m*, 2 H); 2.69 (*m*, 1 H); 3.28 (*dd*, $J = 7.2$, 16.2, 1 H); 3.38 (*m*, 1 H); 3.59 (*m*, 1 H); 3.69 (*dd*, $J = 3.6$, 10.8, 1 H). ^{13}C-NMR: 136.9 (*s*); 129.7 (*s*); 68.6 (*t*); 64.7 (*t*); 45.9 (*s*); 43 (*d*); 38.2 (*t*); 33.6 (*t*); 24.6 (*q*); 14.3 (*q*); 9.4 (*q*). MS: 166 (47, M^+), 151 (45), 133 (15), 121 (88), 107 (100), 96 (22), 93 (69), 79 (30), 67 (17), 53 (13), 41 (35).

5. *$BF_3 \cdot Et_2O$-Treatment of (+)-***7a**. $BF_3 \cdot Et_2O$ (10 ml) was added dropwise at r.t. to a stirred soln. of (+)-**7a** (120 g, 0.61 mol) in toluene (1 l) and then stirred overnight at r.t. The black mixture was poured onto brine, washed with sat. aq. $NaHCO_3$ and NaCl soln., dried (Na_2SO_4), and evaporated. Distillation afforded (+)-**5a** as a colourless oil (87.7 g, 73%). B.p. 53–57°/0.3 Torr.

6. *$LiAlH_4$ Reduction of (+)-***5a** *and (+)-***7a** *to (+)-***5** *and (+)-***7**, *resp.* A soln. of (+)-**5a** or (+)-**7a** (5 g, 25 mmol) in dry Et_2O (30 ml) was added dropwise to a stirred suspension of $LiAlH_4$ (0.722 g, 19 mmol) in dry Et_2O (30 ml). During the addition, the temp. rose to 35°. The mixture was stirred for 30 min and then cooled to 0° (ice-bath). H_2O (0.722 ml), NaOH (15%, 0.722 ml), and H_2O (2.17 ml) were successively added under vigourous stirring. The mixture was stirred for further 30 min and filtered and the filtrate evaporated. Bulb-to-bulb distillation (oven temp. 130°/3 Torr) afforded (+)-**5** (3.34 g, 85%) or (+)-**7** (3.8 g, 97%) as colourless oils.

(+)-(1S)-2,2,3,4-Tetramethylcyclopent-3-ene-1-methanol ((+)-**5**). $[\alpha]_D^{20} = +3.5$ ($c = 1.4$, $CHCl_3$). IR: 3300, 2900, 1440, 1020. ^{1}H-NMR: 0.83 (*s*, 3 H); 1.05 (*s*, 3 H); 4.90 (*s*, 3 H); 1.60 (*s*, 3 H); 1.99 (*m*, 2 H); 2.31 (*m*, 1 H); 3.62 (*dd*, $J = 7.2$, 10.8, 1 H); 3.78 (*dd*, $J = 5.4$, 10.8, 1 H). MS: 154 (25, M^+), 139 (100), 12 (97), 109 (30), 105 (34), 93 (33).

(+)-(1S,4S)-3,3,4-Trimethyl-2-methylidenecyclopentane-1-methanol ((+)-**7**). $[\alpha]_D^{20} = +5.9$ ($c = 3.2$, $CHCl_3$). IR: 3300, 2900, 1640, 1450, 1020, 880. ^{1}H-NMR: 0.85 (*s*, 3 H); 0.89 (*d*, $J = 3.6$, 3 H); 1.04 (*s*, 3 H); 1.54 (*m*, 1 H); 1.72 (*m*, 2 H); 2.75 (*m*, 1 H); 3.56 (*d*, $J = 6.3$, 2 H); 4.87 (*d*, $J = 2.2$, 1 H); 4.93 (*d*, $J = 2.2$, 1 H). ^{13}C-NMR: 163.0 (*s*); 104.8 (*t*); 66.1 (*s*); 44.9 (*d*); 42.5 (*d*); 34.1 (*t*); 26.9 (*q*); 23.4 (*q*); 14.2 (*q*). MS: 154 (3, M^+), 136 (17), 121 (100), 107 (35), 93 (37), 81 (80), 67 (43), 55 (32), 41 (24).

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