98. A Regioselective Cyclohexannulation Procedure *via* Dienamine [4 + 2] Cycloaddition. Synthesis of Functionalised Decalins

by **Roger L. Snowden***, **Simon M. Linder**, and **Manfred Wüst**

Firmenich SA, Laboratoires de Recherche, CH-1211 Genève 8

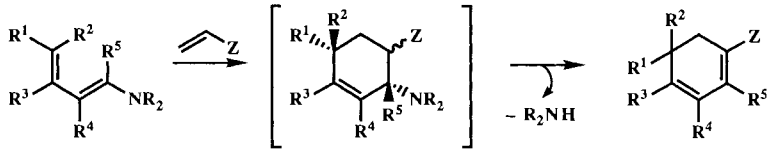
Dedicated to Dr. *G. Ohloff* on the occasion of his 65th birthday

(8.V.89)

A regioselective cyclohexannulation procedure, whose key step involves the [4 + 2] cycloaddition of dienamines **12**–**24** with methyl acrylate, allows the conversion of cycloalkanones **1**–**11** to bicyclic dienoates **25**–**37**. The chemistry of **26** is briefly examined and, in the context of organoleptic studies concerning functionalised 5,5,9-trimethyldecalins, the transformation of **37** to ketones **44** and **46** as well as to acetates **53**–**56** is described.

1. Introduction. – The synthetic application of dienamines **I** [1] as *Diels-Alder* dienes is well documented[1]). The main features of their reactions with dienophiles are high reactivity and the fact that the R_2N group controls the regiochemistry of the cycloaddition. For example, the use of electron-deficient ethylenic dienophiles leads to the selective forma-

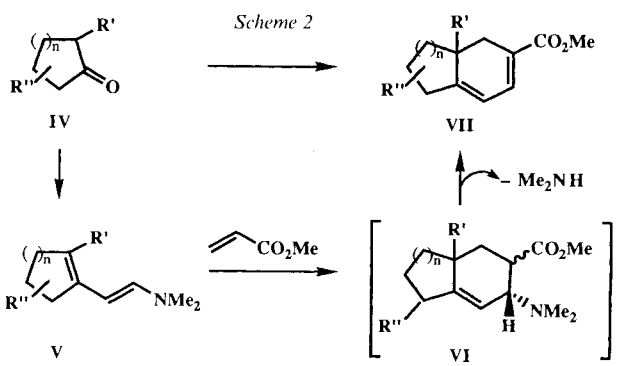
Scheme 1



I **II** **III**

Z = electron-withdrawing group

Scheme 2

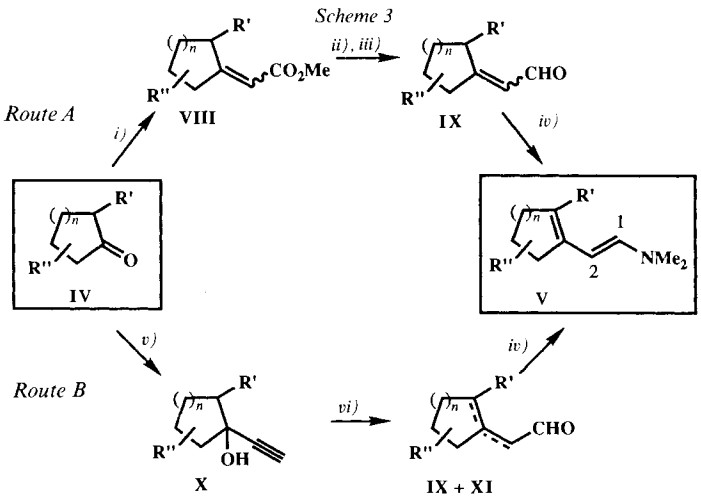


IV **V** **VI** **VII**

[1]) For a review, see [2]; for other examples, see [3].

tion of cycloadduct **II** which may then be readily converted to cyclohexadiene **III** *via* elimination of R_2NH *(Scheme 1)*. We now present full experimental details of an application of this reaction sequence to a cyclohexannulation procedure which allows the conversion of cycloalkanones **IV**, *via* **V** and **VI**, to bicyclic dienecarboxylates **VII** *(Scheme 2)*. In addition, we report on the chemistry of **VII**, particularly with respect to the construction of functionalised *trans*-decalins which are intermediates for the synthesis of potential ambra odorants [3][2]).

Results and Discussion. – *Dienamines* **12–24**. The dienamines employed in the present work were prepared from **IV** by using two synthetic routes (*Routes A* and *B* in *Scheme 3*).



i) $(MeO)_2P(O)CH_2CO_2Me$, NaH, THF. *ii)* $LiAlH_4$, Et_2O. *iii)* MnO_2, CH_2Cl_2. *iv)* 40% aq. Me_2NH, soln., 90° *v)* HC≡CNa, THF/toluene. *vi)* $[(Ph_3SiO)_2V(O)]$, xylene, reflux.

Route A involved the following procedure: treatment of **IV** with the sodium salt of methyl (dimethoxyphosphoryl)acetate gave the α,β-enoates **VIII** which were converted to the α,β-enals **IX** by reduction to the corresponding allylic alcohols followed by oxidation with MnO_2. In contrast, *Route B* entailed reaction of **IV** with sodium acetylide and isomerisation of the resulting acetylenic alcohols **X** to a mixture of the α,β- and β,γ-enals, **IX** and **XI**, using a silylvanadate catalyst [6]. *Routes A* and *B* are complementary as the *Wadsworth-Emmons* reaction, in comparison with the nucleophilic attack of sodium acetylide, is more sensitive to steric hindrance at the carbonyl group: in addition, the latter reagent is considerably basic and thus less suitable for non-sterically hindered ketones. Finally, treatment of **IX** or **XI** with 40% aq. Me_2NH solution directly afforded **V** in which the (*E*)-configuration of the C(1)=C(2) bond was confirmed by ^{1}H-NMR ($J(1,2) = 14$ Hz). Dienamines **12–24** were thus readily prepared from cycloalkanones **1–11**[3]) in 48–66% overall yield (*Table*).

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[2]) For preliminary communications, see [4].

[3]) Cycloalkanones **1–11** are either commercially available or readily prepared by standard literature procedures *(cf. Exper. Part)*.

Table. *Cyclohexannulation Procedure:* **IV**→**V**→**[VI]**→**VII**

Entry	Ketone **IV**	Dienamine **V** (*Route A* or *B*[a]), yield [%])	*Diels-Alder*-reaction conditions[b])	Products **VII**[c])[d])	Yield [%]
1	**1**	**12** ($n = 1$) (*A*, 48)	100°/3 h	**25** ($n = 1$)	81
2	**2**	**13** ($n = 2$) (*A*, 56)	100°/3 h	**26** ($n = 2$)	83
3	**3**	**14** ($n = 3$) (*A*, 60)	100°/3 h	**27** ($n = 3$)	86
4	**4**	**15**[e]) ($n = 8$) (*A*, 48)	100°/6 h	**28** ($n = 8$)	64
5	**5**	**16** (*A*, 59)	100°/3 h	**29**[f])	72
6	**6**	**17** (*A*, 57)	100°/3 h	**30**	84
7	**7**	**18** (*B*, 75)	100°/3 h	**31**	76
8	**8**	**19/20**[g]) (*A*, 54)	150°/24 h	**32/33** 57:43	82
9			100°/24 h	**32/33**[h]) 12:88	83
10	**9**	**21/22**[i]) (*B*, 53)	100°/24 h	**34/35** 20:80	80
11			100°/24 h	**34/35**[h]) 4:96	84
12	**10**	**23** (*B*, 58)	150°/24 h	**36**[h])	76
13	**11**	**24** (*B*, 66)	150°/24 h	**37**	84

[a]) *Cf. Scheme 3.*

[b]) CH_2=$CHCO_2Me$ (1.5 mol-equiv.), toluene.

[c]) Products isolated after treatment of cycloadduct **VI** with silica gel (80°, 3 h).

[d]) For characterisation purpose, dienoates **25**–**31** were converted to their corresponding carboxylic acids **25a**–**31a** *(Exper. Part)*.

[e]) *Ca.* 1:1 mixture of (*E*)- and (*Z*)-cyclododecenyl double-bond isomers.

[f]) Racemic mixture, only one enantiomer is shown.

[g]) *Ca.* 30:1 mixture of 1′- and 5′-cyclopentenyl double-bond isomers.

[h]) *Ca.* 1:1 diastereoisomeric mixture.

[i]) *Ca.* 4:1 mixture of 1′- and 6′-cyclohexenyl double-bond isomers.

Dienoates **25–37**. In order to complete the cyclohexannulation sequence (see **V**→**VII**, *Scheme 2*), **12–24** were heated with methyl acrylate (1.5 mol-equiv.) in toluene at 100 or 150°. Then, the resulting mixture of diastereoisomeric cycloadducts **VI** was treated with silica gel at 80°. This resulted in the smooth elimination of Me_2NH and allowed, in a one-pot procedure, the isolation of dienoates **25–37** in 64–86% yield (see the *Table*). *Entries 8–11* merit special comment as the use of different temperatures for the cycloaddition alters the composition of the final products. Thus, anticipating the lower reactivity of a more substituted dienamine, and in analogy with the cycloadditions of **23** and **24** (*Entries 12* and *13*), the isomeric mixtures **19**/**20** (*ca.* 30:1) as well as **21**/**22** (4:1) were treated with methyl acrylate at 150° (*Entries 8* and *10*). Subsequent elimination of Me_2NH from the intermediate cycloadducts afforded a 57:43 mixture **32**/**33** and a 20:80 mixture **34**/**35**, respectively. This result was initially surprising because the amount of **20** and **22** present in the substrate was insufficient to account for the relatively high proportions of **33** and **35**, respectively, in the final products. It is assumed that isomerisation of **19** to **20** and of **21** to **22** is occurring under the reaction conditions[4]). Indeed, in agreement with this hypothesis, performing the same experiments at 100° (*Entries 9* and *11*) afforded a 12:88 mixture **32**/**33** and a 4:96 mixture **34**/**35**. Apparently, the cycloadditions of **19** and **21** are effectively suppressed at 100°, whereas dienamine isomerisation is still taking place.

The expected regioselectivity of the cycloadditions is evident from the structures of the isolated products. However, the cycloaddition *endo*/*exo*-stereoselectivity is low and, in all the cases studied, results in the formation of a *ca.* 1.5:1 mixture of diastereoisomeric cycloadducts **VI**[5]), both of which afford **VII** after elimination of Me_2NH. In the four cases examined, the stereoselectivity induced by an asymmetric centre remote to the cycloaddition process varies from good (*viz.* **16**→**29**) to poor (*viz.* **20**→**33**, **22**→**35** and **23**→**36**). It appears that the *t*-Bu group at C(4′) in **16** effectively directs the approach of the dienophile from the less hindered opposite side, whereas the Me group at C(2′) in **20** and **22** and the Me group at C(6′) in **23** have little influence on the stereochemistry.

Chemistry of **26**. The synthetic utility of dienoates **VII** is illustrated by the transformations of **26** outlined in *Scheme 4*. Thus, catalytic hydrogenation of **26** selectively afforded α,β-enoate **38** (*trans*/*cis* 7:3) in 68% yield. Partial dehydrogenation of **26** with 4,5-dichloro-3,6-dioxo-1,4-cyclohexadiene-1,2-dicarbonitrile (DDQ) furnished tetrahydronaphthalenecarboxylate **39** in 72% yield, whereas total dehydrogenation to naphthalenecarboxylate **40** (76% yield) was effected by heating **26** in decalin in the presence of Pd/C. When **26** was reduced with $LiAlH_4$, the resulting primary allylic alcohol, when treated with a catalytic amount of acid, readily eliminated H_2O to give tetrahydronaphthalene **41** (65% yield). Similarly, reaction of **26** with MeMgI (2 mol-equiv.) resulted in the formation of a tertiary allylic alcohol which analogously afforded **42** (52% yield). These last two transformations are believed to proceed *via* acid-catalysed dehydration of the intermediate allylic alcohols (initiated by TsOH) followed by thermodynamically controlled isomerisation of the resulting triene.

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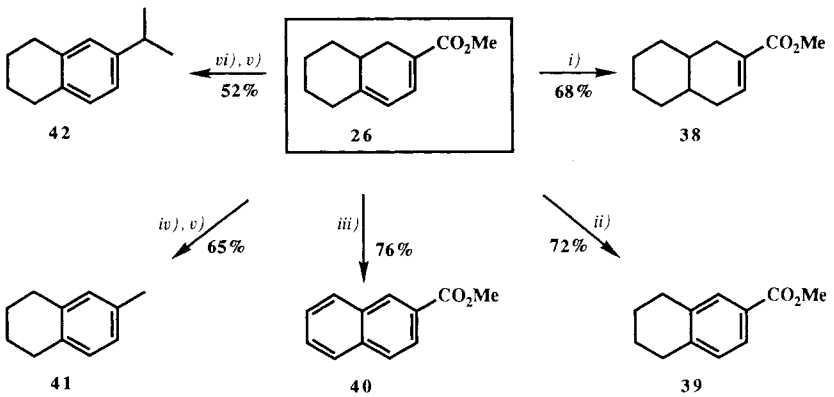
[4]) This isomerisation, possibly a consequence of traces of H_2O, presumably proceeds *via* **IX** and **XI**.

[5]) For each diastereoisomeric pair, the major diastereoisomer elutes more rapidly on silica gel (TLC), has a longer retention time on a non-polar chromatographic column (*SE-54;* GLC) and, in addition, its olefinic proton resonates further downfield (0.04–0.20 ppm; ^{1}H-NMR); it is tentatively proposed that this diastereoisomer is derived from the *endo*-cycloaddition transition state.

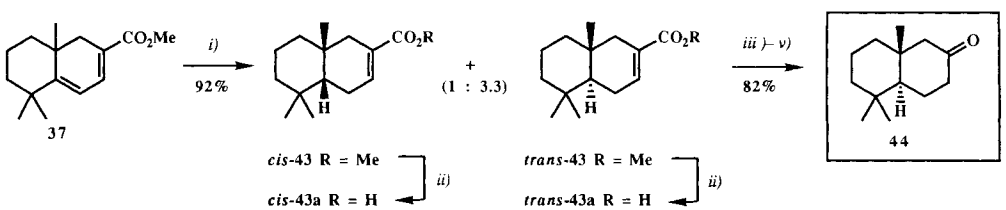
Scheme 4



i) H_2, 5% Pd/C, MeOH. *ii)* DDQ, toluene, r.t. *iii)* 5% Pd/C, decalin, reflux. *iv)* $LiAlH_4$, Et_2O. *v)* TsOH, toluene, reflux, *vi)* MeMgI, Et_2O.

Ketones **44** *and* **46**. In the context of our continued interest in the construction of specifically functionalised 5,5,9-trimethyl-*trans*-decalins [5], **37** was selectively converted to ketones **44** and **46**. Accordingly, catalytic hydrogenation of **37** selectively afforded α,β-enoates **43** (*trans*/*cis* 3.3:1) in 92% yield *(Scheme 5)*. Subsequent ester hydrolysis resulted in the formation of the α,β-enoic acid **43a** (*trans*/*cis* 3.3:1) from which *trans*-**43a** could be isolated by fractional recrystallisation (59% yield from **37**). Finally, *Curtius* degradation of *trans*-**43a** furnished **44** in 82% yield.

Scheme 5



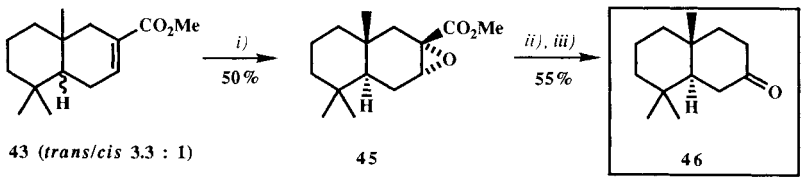
i) H_2, 10% Pd/C, MeOH. *ii)* KOH, MeOH then aq. HCl soln. *iii)* $SOCl_2$. *iv)* NaN_3, acetone/H_2O. *v)* Toluene, reflux then aq. HCl soln.

Alternatively, epoxidation of **43** (*trans*/*cis* 3.3:1) with permaleic acid followed by chromatographic purification afforded epoxyester **45** (50% yield) with high stereoselectivity *(Scheme 6)* [6]. Saponification of **45** followed by treatment of the resulting epoxyacid **45a** with aqueous acid produced **46** in 55% yield. This latter reaction represents an example of an 'abnormal' cleavage of a glycidic acid [7]. Thus, as shown in *Scheme 7*, protonation of **45a** results in selective epoxide cleavage to give, formally, carbocation **XII**[7]) which then affords **46** *via* proton loss and decarboxylation. No trace of **44**, the

[6]) The configuration of **45** is tentatively assigned from its ^{1}H-NMR spectrum in analogy with previous work [5].

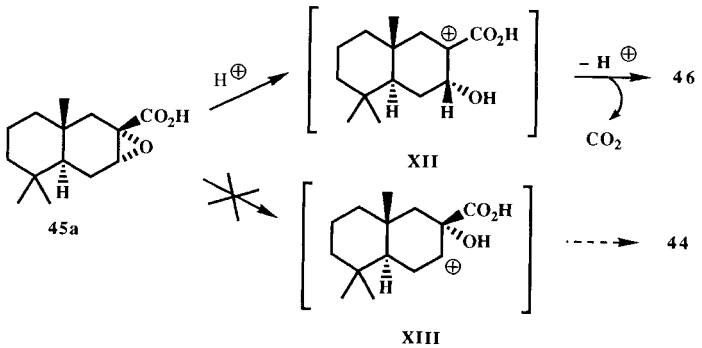
[7]) For a review concerning the involvement of α-carbonyl carbocations in preparative chemistry, see [8].

Scheme 6

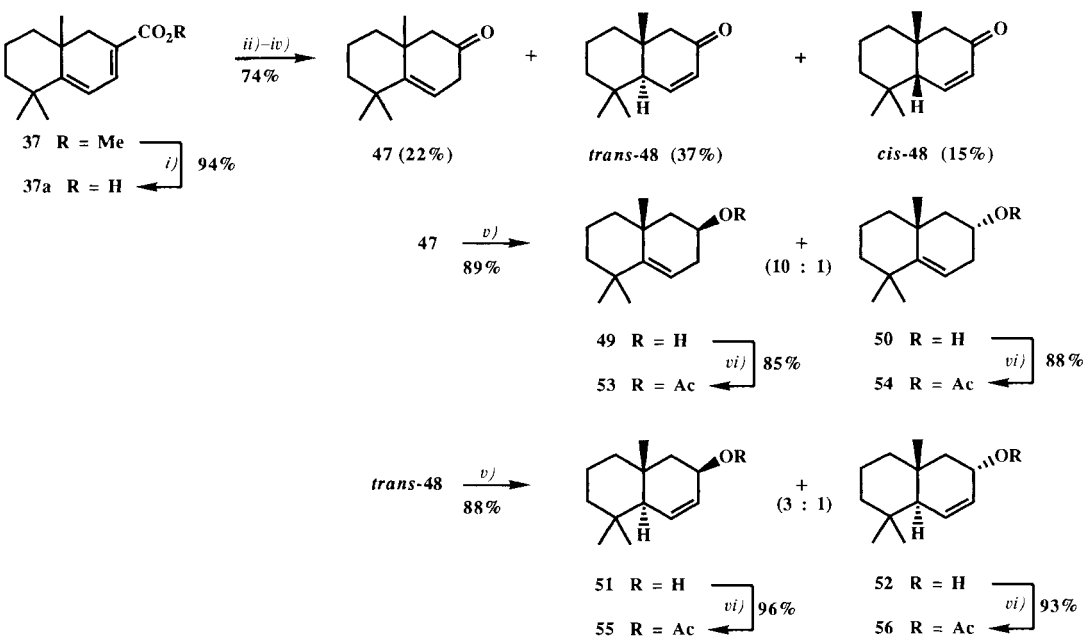


i) Maleic anhydride, 70% H_2O_2 soln., CH_2Cl_2, 40°. *ii)* KOH, MeOH/H_2O. *iii)* Aq. HCl soln.

Scheme 7



Scheme 8



i) KOH, MeOH, then aq. HCl soln. *ii)* $SOCl_2$. *iii)* NaN_3, acetone/H_2O. *iv)* Toluene, reflux, then aq. HCl, soln. reflux. *v)* $NaBH_4$, MeOH. *vi)* Ac_2O, pyridine.

product resulting from the alternative epoxide cleavage *via* carbocation **XIII**, was detected.

Acetates **53–56**. In order to investigate the organoleptic properties of unsaturated analogues of *Polywood*®[8]), acetates **53–56** were synthesised from **37** *(Scheme 8)*. Accordingly, saponification of **37** to **37a** (94% yield) was followed by a *Curtius* sequence to afford a chromatographically separable 2.5:1.5:1 mixture of enones **47**, *trans*-**48**, and *cis*-**48** in 74% yield[9]). Enones **47** and *trans*-**48** were then reduced with $NaBH_4$ in MeOH to afford a 10:1 mixture **49**/**50** and a 3:1 mixture **51**/**52**, respectively. Finally, separate acetylation of these four alcohols furnished pure samples of **53–56**. All four acetates possess a distinctive woody odour which is significantly accentuated for **53** and **55** in which the AcO group is in a pseudoaxial configuration. This result is thus in qualitative agreement with previous work [9].

Experimental Part

1. *General.* See [10].

2. *Dienamines* **12–24**. Starting from cycloalkanones **1–11**[10]), dienamines **12–24** were prepared using either *Route A* or *Route B* (*cf.* the *Table*).

General Procedure for Route A. A soln. of methyl (dimethoxyphosphoryl)acetate (38.2 g, 0.21 mol) in THF (50 ml) was added dropwise within 30 min to a stirred slurry of NaH (55% dispersion in oil *(Fluka)*; 9.6 g, 0.22 mol) in THF (400 ml) at r.t. under N_2. After a further 45 min, a soln. of the cycloalkanone (*viz.* **1–6**, **8**; 0.2 mol) in THF (100 ml) was added dropwise within 30 min. The mixture was then refluxed during 24 h, cooled to 5°, and sat. aq. NH_4Cl soln. (200 ml) added dropwise. The aq. phase was extracted with Et_2O (100 ml) and the combined org. phase washed with sat. aq. NaCl soln. (2 × 100 ml), dried (Na_2SO_4), and concentrated. Distillation *i.v.* afforded α,β-enoate **VIII** as a colourless oil.

A soln. of **VIII** (0.1 mol) in Et_2O (50 ml) was added dropwise within 15 min to a stirred slurry of $LiAlH_4$ (3.8 g, 0.1 mol) in Et_2O (220 ml) at 0° under N_2. The mixture was allowed to attain r.t. and stirred at r.t. during 1 h. To the cooled mixture was now added successively, dropwise, H_2O (3.8 ml), 15% aq. NaOH soln. (3.8 ml), and H_2O (11.4 ml). Filtration *(Hyflo)* and concentration of the filtrate afforded the crude allylic alcohol which, without further purification, was dissolved in CH_2Cl_2 (500 ml) and vigorously stirred with MnO_2 (*Merck*; 122 g, 1.4 mol) at r.t. during 3 h. Filtration *(Hyflo)* and concentration of the filtrate afforded a residual oil which was distilled *i.v.* to furnish the α,β-enal **IX**.

Treatment of a soln. of **IX** in toluene (120 ml) with 40% aq. Me_2NH soln. (*Fluka*; 26.8 g, 0.21 mol) at 90° during 1 h, followed by an extractive workup (Et_2O) and distillation *i.v.* afforded dienamines **12–17** and **19**/**20** (*ca.* 30:1) as pale yellow oils.

(1E)-2-(Cyclopent-1'-enyl)-N,N-*dimethylethen-1-ylamine* [13] (**12**). Yield from **1**, 48%. B.p. 44–45°/0.05 Torr. IR: 1630, 1600, 1340, 1280, 1198, 1130, 1080, 950, 920, 812, 712, 690. ^{1}H-NMR: 1.87 (*m*, 2 H); 2.36 (4 H); 2.66 (*s*, 6 H); 5.20 (*d*, J = 14, 1 H); 5.32 (*m*, 1 H); 6.14 (*d*, J = 14, 1 H). MS: 137 (100, M^+), 122 (21), 108 (27), 94 (57), 91 (38), 77 (16).

(1E)-2-(Cyclohex-1'-enyl)-N,N-*dimethylethen-1-ylamine* [13] (**13**). Yield from **2**, 56%. B.p. 54–56°/0.05 Torr. IR: 1620, 1440, 1340, 1130, 1080, 1062, 1040, 920, 840, 800, 680. ^{1}H-NMR: 1.67 (4 H); 2.10 (4 H); 2.63 (*s*, 6 H); 5.01 (*d*, J = 14, 1 H); 5.41 (*m*, 1 H); 6.15 (*d*, J = 14, 1 H). MS: 151 (100, M^+), 136 (32), 122 (27), 108 (80), 94 (27), 79 (30).

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[8]) *Polywood*® (= (2*RS*,4a*RS*,8a*SR*)-decahydro-5,5,8a-trimethylnaphthalen-2-yl acetate) is a fragrance chemical possessing a woody-like ambergris-type odour.

[9]) Equilibration of this kinetically controlled mixture of enones using either acid (aq. HCl soln. or TsOH in toluene) or base (MeONa, MeOH) led to a mixture of *cis*-**48** (69%), *trans*-**48** (26%), and **47** (6%).

[10]) Ketones **1–5** and **9–11** are commercially available from either *Fluka* or *Aldrich*: **6** and **7** were obtained by catalytic hydrogenation of 4,4-dimethylcyclohex-2-en-1-one *(Aldrich)* and 6,6-dimethylcyclohex-2-en-1-one [11], resp., whereas **8** was prepared from ethyl 2-oxocyclopentane-1-carboxylate [12].

(1E)-2-(Cyclohept-1'-enyl)-N,N-*dimethylethen-1-ylamine* (**14**). Yield from **3**, 60%. B.p. 59–61°/0.01 Torr. IR: 1630, 1440, 1340, 1204, 1130, 1080, 960, 920, 830. ^{1}H-NMR: 1.20–2.00 (6 H); 2.00–2.40 (4 H); 2.67 (*s*, 6 H); 4.98 (*d*, *J* = 14, 1 H); 5.54 (*t*, *J* = 7, 1 H); 6.17 (*d*, *J* = 14, 1 H). MS: 165 (100, M^+), 150 (25), 137 (50), 121 (34), 108 (29), 94 (40), 79 (39).

(1E)-2-(Cyclododec-1'-enyl)-N,N-*dimethylethen-1-ylamine* (**15**; *(1'E)*/*(1'Z)* *ca.* 1:1). Yield from **4**, 48%. B.p. (bulb-to-bulb dist.) 180–200° (bath)/0.05 Torr. IR: 2900, 1630, 1440, 1350, 1132, 1084, 922. ^{1}H-NMR: 1.10–1.80 (16 H); 2.00–2.50 (4 H); 2.65, 2.71 (2 *s*, 6 H); 4.92, 5.12 (2 *d*, *J* = 14, 1 H); 5.06, 5.16 (2 *t*, *J* = 7, 1 H); 6.17, 6.28 (2 *d*, *J* = 14, 1 H). MS: 235 (100, M^+), 136 (49), 124 (34), 111 (100), 96 (47), 71 (51), 42 (40).

*(1E)-2-[4'-(*tert*-Butyl)cyclohex-1'-enyl]*-N,N-*dimethylethen-1-ylamine* (**16**). Yield from **5**, 59%. B.p. 93–96°/0.02 Torr. IR: 1636, 1618, 1462, 1340, 1200, 1180, 1080, 960, 920, 832, 810. ^{1}H-NMR: 0.85 (*s*, 9 H); 1.00–2.50 (7 H); 2.64 (*s*, 6 H); 5.01 (*d*, *J* = 14, 1 H); 5.39 (*m*, 1 H); 6.11 (*d*, *J* = 14, 1 H). MS: 207 (48, M^+), 192 (24), 150 (40), 123 (60), 108 (100), 95 (22).

(1E)-2-(4',4'-Dimethylcyclohex-1'-enyl)-N,N-*dimethylethen-1-ylamine* (**17**). Yield from **6**, 57%. B.p. 42–44°/0.03 Torr. IR: 1640, 1620, 1340, 1200, 1080, 1040, 920, 820, 720, 690. ^{1}H-NMR: 0.90 (*s*, 6 H); 1.42 (*t*, *J* = 6, 2 H); 2.63 (*s*, 6 H); 5.01 (*d*, *J* = 14, 1 H); 5.29 (*m*, 1 H); 6.12 (*d*, *J* = 14, 1 H). MS: 179 (48, M^+), 164 (8), 123 (77), 108 (100), 95 (18), 80 (13).

(1E)-2-(2'-Methylcyclopent-1'-enyl)-N,N-*dimethylethen-1-ylamine* (**19**) *and (1E)-2-(5'-Methylcyclopent-1'-enyl)*-N,N-*dimethylethen-1-ylamine* (**20**; *ca.* 30:1 mixture[11])). Yield from **8**, 54%. B.p. 38–40°/0.02 Torr. IR: 1610, 1420, 1340, 1130, 1080, 1030, 920, 790. ^{1}H-NMR (**19**): 1.72 (*s*, 3 H); 1.50–2.60 (6 H); 2.63 (*s*, 6 H); 5.01 (*d*, *J* = 14, 1 H); 5.98 (*d*, *J* = 14, 1 H). ^{1}H-NMR (**20**): 1.02 (*d*, *J* = 7, 3 H); 4.77 (*d*, *J* = 14, 1 H); 5.32 (*t*, *J* = 6, 1 H); 6.77 (*d*, *J* = 14, 1 H). MS: 151 (100, M^+), 136 (50), 122 (11), 108 (27), 105 (19), 91 (24), 79 (25).

General Procedure for Route B. Acetylene was bubbled through a mechanically stirred slurry of Na (30% dispersion in toluene *(Fluka)*; 16 g, 0.7 mol) in THF (300 ml) under N_2 whilst maintaining the reaction temp. at 20–25°. After 1 h, the mixture was cooled to 0° and the cycloalkanone (*viz.* **7**, **9**–**11**; 0.35 mol) added dropwise within 30 min. The mixture was allowed to attain r.t., stirred during 3 h, and re-cooled to 5°, and H_2O (100 ml) was cautiously added dropwise. Separation of the phases was followed by extraction (Et_2O) of the aq. phase. The combined org. phase was washed with sat. aq. NaCl soln., dried (Na_2SO_4), and concentrated. Distillation *i.v.* afforded the corresponding acetylenic alcohol **X** as a colourless oil.

A soln. of **X** (0.3 mol) in xylene (500 ml) containing a polymeric silylvanadate catalyst[12]) (10 g) was refluxed during 18 h under N_2. Evaporation and distillation *i.v.* afforded a mixture **IX**/**XI** which, after treatment with 40% aq. Me_2NH soln. *(vide supra)*, furnished dienamines **18**, **21**/**22** (4:1), **23**, and **24** as pale yellow oils.

(1E)-2-(6',6'-Dimethylcyclohex-1'-enyl)-N,N-*dimethylethen-1-ylamine* (**18**). Yield from **7**, 57%. B.p. 50–53°/0.05 Torr. IR: 1640, 1460, 1360, 1220, 1148, 1092, 1010, 940, 890, 820, 720. ^{1}H-NMR: 1.03 (*s*, 6 H); 1.53 (4 H); 2.00 (2 H); 2.63 (*s*, 6 H); 4.74 (*d*, *J* = 14, 1 H); 5.42 (*m*, 1 H); 6.26 (*d*, *J* = 14, 1 H). MS: 179 (100, M^+), 164 (86), 135 (30), 122 (29), 108 (44), 94 (63), 91 (30), 79 (38).

(1E)-2-(2'-Methylcyclohex-1'-enyl)-N,N-*dimethylethen-1-ylamine* (**21**) *and (1E)-2-(6'-Methylcyclohex-1'-enyl)*-N,N-*dimethylethen-1-ylamine* (**22**; 4:1 mixture[11])). Yield from **9**, 53%. B.p. 55–61°/0.04 Torr. IR: 1640, 1618, 1340, 1202, 1100, 1070, 920, 790, 720. ^{1}H-NMR (**21**): 1.60 (4 H); 1.72 (*s*, 3 H); 2.03 (2 H); 2.10 (2 H); 2.67 (*s*, 6 H); 5.29 (*d*, *J* = 14, 1 H); 6.19 (*d*, *J* = 14, 1 H). ^{1}H-NMR (**22**): 1.13 (*d*, *J* = 7, 3 H); 2.65 (*s*, 6 H); 4.86 (*d*, *J* = 14, 1 H); 5.34 (*t*, *J* = 6, 1 H); 6.19 (*d*, *J* = 14, 1 H). MS (**21**): 165 (100, M^+), 150 (53), 136 (16), 122 (43), 108 (15), 94 (17). MS (**22**): 165 (100, M^+), 150 (51), 136 (16), 122 (35), 108 (28), 94 (25).

(1E)-2-(2',6'-Dimethylcyclohex-1'-enyl)-N,N-*dimethylethen-1-ylamine* (**23**). Yield from **10**, 58%. B.p. 56–58°/0.02 Torr. IR: 1630, 1610, 1440, 1330, 1202, 1130, 1066, 922. ^{1}H-NMR: 1.10 (*d*, *J* = 7, 3 H); 1.70 (*s*, 3 H); 1.40–2.30 (7 H); 2.65 (*s*, 6 H); 5.08 (*d*, *J* = 14, 1 H); 6.18 (*d*, *J* = 14, 1 H). MS: 179 (100, M^+), 164 (62), 136 (35), 122 (32), 108 (35), 93 (31), 79 (22), 71 (27).

(1E)-2-(2',6',6'-Trimethylcyclohex-1'-enyl)-N,N-*dimethylethen-1-ylamine* (**24**). Yield from **11**, 66%. B.p. 66–69°/0.02 Torr. IR: 1640, 1450, 1350, 1140, 1080, 940, 780, 718. ^{1}H-NMR: 0.99 (*s*, 6 H); 1.30–2.20 (9 H); 2.61 (*s*, 6 H); 4.58 (*d*, *J* = 14, 1 H); 5.82 (*d*, *J* = 14, 1 H). MS: 193 (100, M^+), 178 (71), 133 (17), 122 (29), 108 (26).

3. *General Procedure for the Preparation of Dienoates* **25**–**37**. A soln. of the dienamine (*viz.* **12**–**24**; 0.01 mol) and methyl acrylate (1.3 g, 0.015 mol) in toluene (20 ml) was heated at 100 or 150° *(cf. Table)* under N_2 in an *Inox* autoclave until reaction was complete (GLC analysis). An aliquot of the product mixture was analysed by GLC and ^{1}H-NMR and, without further purification, silica gel (0.06–0.2 mm *(Merck)*; 5 g) was added and the mixture

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[11]) *Estimated by* ^{1}H-NMR analysis.

[12]) Prepared from dichlorodiphenylsilane and sodium vanadate in acetone/H_2O [6b].

stirred at 80° during 2–6 h (GLC analysis). Filtration *(Hyflo)* of the cooled mixture, evaporation of the filtrate, and purification by CC (silica gel, cyclohexane/AcOEt 4:1) afforded **25**–**37** as colourless oils (R_f 0.50–0.54; b.p. (bulb-to-bulb dist.) 180–200° (bath)/0.1 Torr). The mixtures **32**/**33** and **34**/**35** *(cf. Entries 8–11)* were separated by prep. GLC *(Carbowax)*: in each case, the former isomer has the lower retention time (t_R).

For characterisation purposes, **25**–**31** (0.5-g aliquot) were saponified with a soln. of NaOH (2 mol-equiv.) in MeOH (10 ml) at reflux. Evaporation, acidification (aq. HCl soln.), and extractive workup afforded crystalline samples of carboxylic acids **25a**–**31a**.

*Methyl 2,3,3a,4-Tetrahydro-1*H*-indene-5-carboxylate* (**25**). Yield from **12**, 81%. IR: 1700, 1578, 1426, 1270, 1240, 1184, 1094, 1056, 840, 740. ^{1}H-NMR: 1.29 (*m*, 1 H); 1.58 (*m*, 1 H); 1.85–2.00 (2 H); 2.11 (*m*, 1 H); 2.30–2.60 (3 H); 2.85 (*dd*, *J* = 16, 9, 1 H); 3.74 (*s*, 3 H); 5.88 (*m*, 1 H); 7.07 (*m*, 1 H). ^{13}C-NMR: 168.4 (*s*); 156.9 (*s*); 135.8 (*d*); 124.8 (*s*); 115.0 (*d*); 51.5 (*q*); 41.0 (*d*); 33.4 (*t*); 30.7 (*t*); 27.8 (*t*); 24.7 (*t*). MS: 178 (59, M^+), 150 (61), 135 (9), 119 (52), 105 (19), 91 (100).

*2,3,3a,4-Tetrahydro-1*H*-indene-5-carboxylic Acid* (**25a**). M.p. 174–176°. IR ($CDCl_3$): 3000 (br.), 1675, 1640, 1570, 1420, 1280, 1260, 1190. ^{1}H-NMR (+D_2O): 0.80–3.20 (9 H); 5.92 (*m*, 1 H); 7.24 (*m*, 1 H). MS: 164 (23, M^+), 135 (28), 119 (48), 105 (11), 91 (100), 77 (13).

Methyl 1,5,6,7,8,8a-Hexahydronaphthalene-2-carboxylate (**26**). Yield from **13**, 83%. IR: 1700, 1580, 1426, 1272, 1258, 880, 840, 828, 740, 620. ^{1}H-NMR: 1.20–1.45 (3 H); 1.81 (2 H); 1.97 (*m*, 1 H); 2.02 (br. *d*, *J* = 16, 1 H); 2.07 (br. *d*, *J* = 14, 1 H); 2.38 (*m*, 1 H); 2.40 (br. *d*, *J* = 14, 1 H); 2.76 (*dd*, *J* = 16, 9, 1 H); 3.74 (*s*, 3 H); 5.73 (*m*, 1 H); 6.91 (*m*, 1 H). ^{13}C-NMR: 168.1 (*s*); 150.9 (*s*); 133.6 (*d*); 123.9 (*s*); 117.3 (*d*); 51.4 (*q*); 36.6 (*d*); 35.7 (*t*); 34.5 (*t*); 29.5 (*t*); 27.2 (*t*); 26.0 (*t*). MS: 192 (35, M^+), 161 (18), 149 (38), 133 (23), 105 (28), 91 (100), 77 (17).

1,5,6,7,8,8a-Hexahydronaphthalene-2-carboxylic Acid (**26a**). M.p. 137–139°. IR ($CDCl_3$): 3000 (br.), 1675, 1570, 1420, 1280. ^{1}H-NMR (+D_2O): 1.00–3.00 (11 H); 5.74 (*m*, 1 H); 7.04 (*m*, 1 H). MS: 178 (22, M^+), 149 (10), 135 (32), 105 (23), 91 (100), 77 (20).

*Methyl 5,6,7,8,9,9a-Hexahydro-1*H*-benzocycloheptene-2-carboxylate* (**27**). Yield from **14**, 86%. IR: 1700, 1570, 1426, 1378, 1240, 1080, 960, 840, 820, 760, 740. ^{1}H-NMR: 1.20–1.90 (8 H); 2.25–2.55 (5 H); 3.74 (*s*, 3 H); 5.80 (*d*, *J* = 5.5, 1 H); 6.95 (*d*, *J* = 5.5, 1 H). ^{13}C-NMR: 168.2 (*s*); 154.2 (*s*); 134.1 (*d*); 124.8 (*s*); 119.7 (*d*); 51.4 (*q*); 37.9 (*d*); 36.8 (*t*); 32.8 (*t*); 29.9 (*t*); 29.4 (*t*); 28.8 (*t*); 27.9 (*t*). MS: 206 (32, M^+), 175 (15), 163 (29), 150 (39), 105 (34), 91 (100), 77 (19).

*5,6,7,8,9,9a-Hexahydro-1*H*-benzocycloheptene-2-carboxylic Acid* (**27a**). M.p. 152–154°. IR ($CDCl_3$): 3000 (br.), 1670, 1626, 1570, 1420, 1260, 820. ^{1}H-NMR ((D_6)DMSO): 1.00–2.00 (8 H); 2.00–2.70 (5 H); 5.85 (*d*, *J* = 5.5, 1 H); 6.87 (*d*, *J* = 5.5, 1 H). MS: 192 (17, M^+), 149 (17), 136 (46), 105 (32), 91 (100), 79 (20).

Methyl Bicyclo[10.4.0]hexadeca-14,16-diene-14-carboxylate (**28**). Yield, 64% from **15**. IR: 1695, 1580, 1465, 1435, 1270, 1090. ^{1}H-NMR: 1.00–2.55 (22 H); 2.63 (*d*, *J* = 17, 1 H); 3.73 (*s*, 3 H); 5.85 (br. *d*, *J* = 5.5, 1 H); 6.92 (*dd*, *J* = 5.5, 3, 1 H). MS: 276 (12, M^+), 245 (8), 163 (42), 150 (100), 105 (36), 91 (60).

Bicyclo[10.4.0]hexadeca-14,16-diene-14-carboxylic Acid (**28a**). M.p. 186–188°. IR ($CDCl_3$): 3000 (br.), 1670, 1580, 1420, 1280. ^{1}H-NMR ((D_6)DMSO): 1.00–1.80 (18 H); 1.90–2.70 (5 H); 5.90 (*m*, 1 H); 6.84 (*m*, 1 H). MS: 262 (5, M^+), 149 (21), 136 (100), 123 (18), 105 (26), 91 (82), 79 (21).

*Methyl 7-(*tert*-Butyl)-1,5,6,7,8,8a-hexahydronaphthalene-2-carboxylate* (**29**). Yield from **16**, 72%. IR: 1700, 1580, 1430, 1360, 1266, 1236, 1080, 1058, 836, 740. ^{1}H-NMR: 0.84 (*s*, 9 H); 1.30–1.70 (5 H); 2.00–2.65 (5 H); 3.74 (*s*, 3 H); 5.78 (*m*, 1 H); 6.97 (*m*, 1 H). ^{13}C-NMR: 168.3 (*s*); 151.5 (*s*); 134.7 (*d*); 124.8 (*s*); 117.5 (*d*); 51.5 (*q*); 41.6 (*d*); 33.4 (*d*); 30.0 (*t*); 28.5 (*t*); 28.0 (*t*); 27.2 (3 *q*); 22.5 (*t*). MS: 248 (38, M^+), 191 (36), 163 (32), 150 (74), 131 (63), 105 (59), 91 (85), 57 (100).

*7-(*tert*-Butyl)-1,5,6,7,8,8a-hexahydronaphthalene-2-carboxylic Acid* (**29a**). M.p. 144–146°. IR ($CDCl_3$): 3000 (br.), 1670, 1570, 1420, 1360, 1270, 1250. ^{1}H-NMR (+D_2O): 0.84 (*s*, 9 H); 0.90–3.00 (10 H); 5.82 (*m*, 1 H); 7.15 (*m*, 1 H). MS: 234 (10, M^+), 149 (14), 136 (31), 105 (23), 91 (74), 57 (100).

Methyl 1,5,6,7,8,8a-Hexahydro-7,7-dimethylnaphthalene-2-carboxylate (**30**). Yield from **17**, 84%. IR: 1700, 1578, 1425, 1380, 1360, 1260, 1230, 1100, 1066, 840, 740. ^{1}H-NMR: 0.95 (*s*, 3 H); 0.97 (*s*, 3 H); 1.15 (*t*, *J* = 12.5, 1 H); 1.30 (*ddd*, *J* = 12.5, 5.5, 5.5, 1 H); 1.47 (*m*, 1 H); 1.64 (*m*, 1 H); 1.97 (br. *dd*, *J* = 16, 16, 1 H); 2.29 (*m*, 1 H); 2.31 (*m*, 1 H); 2.51 (*m*, 1 H); 2.71 (*dd*, *J* = 16, 9, 1 H); 3.74 (*s*, 3 H); 5.77 (*m*, 1 H); 6.92 (*m*, 1 H). ^{13}C-NMR: 168.0 (*s*); 150.4 (*s*); 133.8 (*d*); 124.1 (*s*); 117.6 (*d*); 51.4 (*q*); 47.9 (*t*); 38.9 (*t*); 32.9 (*d*); 32.4 (*q*); 30.8 (*s*); 30.2 (*t*); 29.5 (*t*); 24.0 (*q*). MS: 220 (48, M^+), 163 (30), 150 (40), 119 (25), 105 (83), 91 (100).

1,5,6,7,8,8a-Hexahydro-7,7-dimethylnaphthalene-2-carboxylic Acid (**30a**). M.p. 129–131°. IR ($CDCl_3$): 3000 (br.), 1670, 1630, 1562, 1420, 1270, 1240, 840. ^{1}H-NMR (+D_2O): 0.99 (2 *s*, 6 H); 0.80–3.20 (9 H); 5.79 (*m*, 1 H); 7.07 (*m*, 1 H). MS: 206 (21, M^+), 150 (16), 136 (29), 105 (58), 91 (100), 77 (25), 70 (27).

Methyl 1,5,6,7,8,8a-Hexahydro-5,5-dimethylnaphthalene-2-carboxylate (**31**). Yield from **18**, 76%. UV (EtOH): 306 (11700). IR: 1708, 1580, 1440, 1280, 1250, 1100, 1080, 860, 750. ^{1}H-NMR: 1.06 (*s*, 3 H); 1.15 (*s*, 3 H);

1.25 (*m*, 1 H); 1.36 (*m*, 1 H); 1.51 (*m*, 1 H); 1.55–1.70 (2 H); 1.93 (*m*, 1 H); 2.02 (*m*, 1 H); 2.53 (*m*, 1 H); 2.73 (*dd*, *J* = 16, 9, 1 H); 3.74 (*s*, 3 H); 5.90 (*m*, 1 H); 6.94 (*m*, 1 H). ^{13}C-NMR: 166.0 (*s*); 158.3 (*s*); 134.0 (*s*); 123.8 (*s*); 115.0 (*d*); 51.4 (*q*); 41.0 (*t*); 36.5 (*s*); 35.9 (*t*); 33.6 (*d*); 29.9 (*t*); 28.8 (*q*); 28.2 (*q*); 21.5 (*t*). MS: 220 (34, M^+), 189 (18), 163 (30), 150 (100), 145 (29), 119 (26), 105 (50), 91 (77).

1,5,6,7,8,8a-Hexahydro-5,5-dimethylnaphthalene-2-carboxylic Acid (**31a**). M.p. 136–138°. IR ($CDCl_3$): 3000 (br.), 1670, 1560, 1420, 1270, 850, 830. ^{1}H-NMR (+D_2O): 1.05 (*s*, 3 H); 1.16 (*s*, 3 H); 1.00–3.00 (9 H); 5.92 (br. *d*, *J* = 6, 1 H); 7.07 (*dd*, *J* = 6, 2, 1 H). MS: 206 (22, M^+), 145 (20), 136 (93), 105 (43), 91 (100), 77 (25).

*Methyl 2,3,3a,4-Tetrahydro-3a-methyl-1*H*-indene-5-carboxylate* (**32**) *and Methyl 2,3,3a,4-Tetrahydro-1-methyl-1*H*-indene-5-carboxylate* (**33**; *ca.* 1:1 diastereoisomeric mixture). Ratio **32**/**33**, 57:43 or 12:88. Yield from **19**/**20** (*ca.* 30:1), 82 or 83%.

Data of **32**. IR: 1690, 1580, 1430, 1360, 1260, 1060, 900. ^{1}H-NMR: 0.92 (*s*, 3 H); 1.52 (*m*, 1 H); 1.75–1.90 (4 H); 2.22 (br. *d*, *J* = 17, 1 H); 2.39 (*m*, 1 H); 2.56 (*m*, 1 H); 2.94 (*d*, *J* = 17, 1 H); 3.75 (*s*, 3 H); 5.79 (*m*, 1 H); 7.03 (*m*, 1 H). ^{13}C-NMR: 168.6 (*s*); 161.0 (*s*); 134.4 (*d*); 123.8 (*s*); 114.0 (*d*); 51.5 (*q*); 41.1 (*t*); 35.9 (*t*); 33.8 (*s*); 29.6 (*t*); 22.5 (*t*); 21.5 (*q*). MS: 192 (21, M^+), 177 (32), 133 (53), 117 (30), 105 (100), 91 (40).

Data of **33**. ^{1}H-NMR: 1.10, 1.15 (2 *d*, *J* = 7, 3 H); 1.10–1.60 (2 H); 1.80–2.10 (3 H); 2.45–2.75 (2 H); 2.83, 2.85 (*dd*, *J* = 17, 10, 1 H); 3.75 (*s*, 3 H); 5.83 (*m*, 1 H); 7.10 (*m*, 1 H). MS (isomer **A**[13]): 192 (17, M^+), 161 (10), 150 (40), 133 (28), 117 (21), 105 (40), 91 (100). MS (isomer **B**[13]): 192 (20, M^+), 16 (14), 150 (45), 133 (30), 117 (28), 105 (49), 91 (100).

Methyl 1,5,6,7,8,8a-Hexahydro-8a-methylnaphthalene-2-carboxylate (**34**) *and Methyl 1,5,6,7,8,8a-Hexahydro-5-methylnaphthalene-2-carboxylate* (**35**; *ca.* 1:1 diastereoisomeric mixture). Ratio **34**/**35**, 20:80 or 4:96; yield from **21**/**22** (4:1), 80 or 84%.

Data of **34**. IR ($CDCl_3$): 1690, 1570, 1434, 1276, 1240, 1095, 1060, 900, 850. ^{1}H-NMR: 0.95 (*s*, 3 H); 1.20–1.90 (6 H); 2.16 (br. *d*, *J* = 17, 1 H); 2.27 (*m*, 2 H); 2.51 (*d*, *J* = 17, 1 H); 3.75 (*s*, 3 H); 5.70 (*d*, *J* = 5, 1 H); 6.93 (*m*, 1 H). ^{13}C-NMR: 168.4 (*s*); 160.1 (*s*); 133.2 (*d*); 124.0 (*s*); 117.6 (*d*); 51.4 (*q*); 42.0 (*t*); 38.3 (*t*); 34.1 (*s*); 31.5 (*t*); 26.2 (*t*); 22.3 (*t*); 21.6 (*q*). MS: 206 (40, M^+), 191 (38), 175 (20), 163 (55), 147 (41), 105 (100), 91 (25).

Data of **35**. ^{1}H-NMR: 1.10 (2 *d*, *J* = 7, 3 H); 1.00–2.65 (9 H); 2.74 (2 *dd*, *J* = 17, 10, 1 H); 3.74, 3.75 (2 *s*, 3 H); 5.75, 5.79 (2 br. *d*, *J* = 6, 1 H); 5.92, 5.95 (2 br. *d*, *J* = 6, 1 H). MS (isomer **A**[13]): 206 (63, M^+), 175 (38), 163 (43), 150 (100), 131 (29), 105 (48), 91 (99). MS (isomer **B**[13]): 206 (56, M^+), 175 (31), 163 (43), 150 (100), 131 (27), 105 (47), 91 (89).

Methyl 1,5,6,7,8,8a-Hexahydro-5,8a-dimethylnaphthalene-2-carboxylate (**36**; *ca.* 1:1 diastereoisomeric mixture). Yield from **23**, 76%. IR: 1700, 1566, 1430, 1278, 1240, 1220, 1182, 1120, 1080, 842, 820, 760, 704. ^{1}H-NMR: 0.95, 0.99 (2 *s*, 3 H); 1.11, 1.18 (2 *d*, *J* = 7, 3 H); 1.25–1.85 (6 H); 2.15, 2.17 (2 br. *d*, *J* = 17, 1 H); 2.46, 2.50 (2 *d*, *J* = 17, 1 H); 3.75, 3.76 (2 *s*, 3 H); 5.80 (*m*, 1 H); 6.98 (*m*, 1 H). MS (isomer **A**[13]): 220 (44, M^+), 205 (25), 189 (16), 163 (64), 149 (45), 145 (29), 119 (35), 105 (100), 91 (41). MS (isomer **B**[13]): 220 (42, M^+), 205 (23), 189 (15), 163 (51), 149 (38), 145 (29), 119 (35), 105 (100), 91 (40).

Methyl 1,5,6,7,8,8a-Hexahydro-5,5,8a-trimethylnaphthalene-2-carboxylate (**37**). Yield from **24**, 84%. M.p. 41–42°. IR: 1705, 1570, 1460, 1440, 1260, 1225, 1100, 850, 740, 670. ^{1}H-NMR: 0.80 (*s*, 3 H); 1.14 (*s*, 3 H); 1.16 (*s*, 3 H); 1.20–1.80 (6 H); 2.12 (*dd*, *J* = 16, 3, 1 H); 2.43 (*d*, *J* = 16, 1 H); 3.74 (*s*, 3 H); 5.98 (*d*, *J* = 5.5, 1 H); 6.99 (*dd*, *J* = 5.5, 3, 1 H). ^{13}C-NMR: 168.1 (*s*); 162.2 (*s*); 133.8 (*s*); 124.5 (*s*); 117.1 (*d*); 51.4 (*q*); 41.5 (*t*); 40.2 (*t*); 40.0 (*t*); 35.7 (*s*); 35.0 (*s*); 31.6 (*q*); 31.2 (*q*); 23.8 (*q*); 18.4 (*t*). MS: 234 (50, M^+), 219 (31), 164 (100), 149 (67), 119 (50), 105 (86), 91 (54).

4. *Methyl 1,4,4a,5,6,7,8,8a-Octahydronaphthalene-2-carboxylate* (**38**; *trans*/*cis* 7:3). A soln. of **26** (0.38 g, 2 mmol) in cyclohexane (10 ml) containing 5% Pd/C (50 mg) was hydrogenated at r.t. After the absorption of 46 ml of H_2 (20 min), the mixture was filtered (*Hyflo*) and the filtrate concentrated. Distillation *i.v.* of the residual oil afforded crude **38** as a colourless oil (0.31 g, 68% (GLC analysis)). B.p. (bulb-to-bulb dist.) 160–180°/0.1 Torr. IR: 1710, 1644, 1430, 1240, 1066, 720. ^{1}H-NMR: 0.80–3.00 (14 H); 3.67 (*cis*-**38**), 3.70 (*trans*-**38**) (2 *s*, 3 H); 6.90 (*m*, 1 H). MS (*trans*-**38**): 194 (38, M^+), 162 (21), 134 (100), 119 (20), 113 (41), 105 (23), 91 (55), 81 (60). MS (*cis*-**38**): 194 (43, M^+), 162 (22), 134 (100), 119 (18), 105 (20), 95 (50), 91 (60), 67 (38).

5. *Methyl 5,6,7,8-Tetrahydronaphthalene-2-carboxylate* (**39**). DDQ (0.45 g, 2 mmol) was added portionwise during 30 min to a stirred soln. of **26** (0.38 g, 2 mmol) in toluene (10 ml) at r.t. After 16 h, the mixture was poured into sat. aq. $NaHCO_3$ soln. (20 ml) and extracted with Et_2O. Workup and distillation *i.v.* afforded crude **39** as a

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[13]) On GLC analysis, isomers **A** and **B** have the lower and higher t_R, resp., on a non-polar capillary column (*SE 54*, 30 m).

colourless oil (0.32 g, 72% (GLC analysis)). B.p. (bulb-to-bulb dist.) 150–170°/0.1 Torr ([14]: 149–150°/4 Torr). IR: 1720, 1608, 1570, 1430, 1270, 1220, 1180, 1095, 990, 780, 760. ^{1}H-NMR: 1.82 (4 H); 2.82 (4 H); 3.90 (*s*, 3 H); 7.13 (*d*, *J* = 8, 1 H); 7.75 (*d*, *J* = 8, 1 H); 7.76 (*s*, 1 H). MS: 190 (47, M^+), 175 (4), 159 (52), 131 (100), 115 (10), 91 (14).

6. *Methyl Naphthalene-2-carboxylate* (**40**). A soln. of **26** (1.5 g, 7.8 mmol) in decalin (20 ml) containing 5% Pd/C (0.2 g) was refluxed during 24 h under N_2. The cooled mixture was filtered *(Hyflo)* and the filtrate concentrated. CC (silica gel, cyclohexane/AcOEt 4:1) and recrystallisation (petroleum ether 30/50) afforded **40** as white crystals (1.12 g, 76%). M.p. 70–72°. IR: 1706, 1430, 1280, 1220, 1196, 1122, 820, 776. ^{1}H-NMR: 3.96 (*s*, 3 H); 7.40–8.20 (6 H); 8.60 (br. *s*, 1 H). MS: 186 (56, M^+), 155 (100), 127 (96), 101 (8), 77 (14).

7. *1,2,3,4-Tetrahydro-6-methylnaphthalene* (**41**). A soln. of **26** (1.3 g, 6.8 mmol) in Et_2O (10 ml) was added dropwise within 10 min to a stirred slurry of $LiAlH_4$ (0.5 g, 0.013 mol) in Et_2O (20 ml) at 0° under N_2. The mixture was allowed to attain r.t. and stirred at r.t. during 1 h. To the cooled mixture was now added successively, dropwise, H_2O (0.5 ml), 15% aq. NaOH soln. (0.5 ml), and H_2O (1.5 ml). Filtration *(Hyflo)* and concentration of the filtrate afforded a colourless oil (1.3 g) which was dissolved in toluene (20 ml). TsOH (0.1 g) was added, the mixture refluxed during 1 h with continual azeotropic removal of H_2O (*Dean-Stark* apparatus) under N_2, cooled to r.t., and washed with sat. aq. $NaHCO_3$ and sat. aq. NaCl soln., and the org. phase dried (Na_2SO_4) and evaporated. Distillation *i.v.* of the residual oil gave **41** as a colourless oil (0.6 g, 65%). B.p. (bulb-to-bulb dist.) 100–110°/10 Torr. IR: 1616, 1500, 1444, 1434, 820, 800, 722, 690. ^{1}H-NMR: 1.75 (4 H); 2.24 (*s*, 3 H); 2.70 (4 H); 6.88 (3 H). MS: 146 (58, M^+), 131 (100), 128 (16), 118 (83), 105 (38), 91 (26).

8. *1,2,3,4-Tetrahydro-6-isopropylnaphthalene* (**42**). A soln. of **26** (1 g, 5.2 mmol) in Et_2O (10 ml) was added dropwise within 10 min to a stirred soln. of MeMgI (0.017 mol; freshly prepared from Mg (0.4 g, 0.017 mol) and MeI (2.5 g, 0.018 mol)) in Et_2O (20 ml) at reflux under N_2. After 1 h at reflux, the cooled mixture was poured into sat. aq. NH_4Cl soln. (50 ml). Extractive workup (Et_2O) afforded a colourless oil (1 g) which was submitted to the same dehydration procedure and product isolation used in *Exper. 7:* **42** as a colourless oil (0.47 g, 52%). B.p. (bulb-to-bulb dist.) 90–120°/2 Torr. IR: 1500, 1452, 1430, 1042, 900, 872, 820, 800, 704. ^{1}H-NMR: 1.25 (*d*, *J* = 7, 6 H); 1.80 (4 H); 2.76 (4 H); 2.84 (*m*, 1 H); 6.94 (br. *s*, 1 H); 6.99 (*AB*, *J* = 8, 2 H). MS: 174 (25, M^+), 159 (100), 131 (44), 117 (39), 91 (19).

9. *Methyl 1,4,4a,5,6,7,8,8a-Octahydro-5,5,8a-trimethylnaphthalene-2-carboxylate* (**43**; *trans*/*cis* 3.3:1). A soln. of **37** (16.5 g, 0.07 mol) in MeOH (300 ml) containing 10% Pd/C (0.2 g) was hydrogenated at r.t. After the absorption of 1.6 l of H_2 (20 min), the mixture was filtered *(Hyflo)* and the filtrate concentrated and fractionally distilled *i.v.* to afford **43** as a colourless oil (15.3 g, 92%). B.p. 108–110°/0.2 Torr. Separation of *trans*- from *cis*-**43** was effected by prep. GLC *(Carbowax)* of an aliquot (1 g).

Data of trans-**43**. IR: 1700, 1650, 1430, 1240, 1060, 1020, 730, 680. ^{1}H-NMR: 0.85 (*s*, 3 H); 0.88 (*s*, 3 H); 0.89 (*s*, 3 H); 1.10–1.70 (7 H); 1.90–2.35 (4 H); 3.72 (*s*, 3 H); 6.97 (*m*, 1 H). ^{13}C-NMR: 168.1 (*s*); 139.4 (*d*); 128.5 (*s*); 51.5 (*q*); 47.8 (*d*); 44.3 (*t*); 42.6 (*t*); 41.7 (*t*); 32.8 (*q*); 32.7 (*s*); 32.6 (*s*); 24.6 (*t*); 21.3 (*q*); 19.0 (*q*); 18.8 (*t*). MS: 236 (27, M^+), 221 (14), 161 (12), 137 (22), 124 (56), 109 (100), 91 (32).

Data of cis-**43**. IR: 1700, 1650, 1430, 1260, 1240, 1210, 1060, 720. ^{1}H-NMR: 0.72 (*s*, 3 H); 0.87 (*s*, 3 H); 0.88 (*s*, 3 H); 1.10–1.70 (7 H); 1.81 (*d*, *J* = 18, 1 H); 2.20–2.50 (3 H); 3.73 (*s*, 3 H); 6.97 (*m*, 1 H). ^{13}C-NMR: 168.1 (*s*); 139.1 (*d*); 128.8 (*s*); 51.4 (*q*); 47.0 (*d*); 42.4 (*t*); 40.6 (*t*); 33.9 (*s*); 33.2 (*q*); 32.6 (*t*); 32.2 (*s*); 31.5 (*q*); 24.6 (*t*); 21.1 (*q*); 18.7 (*t*). MS: 236 (38, M^+), 221 (7), 205 (9), 161 (9), 124 (63), 109 (100), 91 (34).

10. *(4a*RS,*8a*SR*)-1,4,4a,5,6,7,8,8a-Octahydro-5,5,8a-trimethylnaphthalene-2-carboxylic Acid* (*trans*-**43a**). A soln. of **43** (*trans*/*cis* 3.3:1; 6.75 g, 0.029 mol) and KOH (5 g, 0.09 mol) in MeOH (25 ml) was refluxed during 4 h, cooled to r.t., and concentrated. Acidification (10% aq. HCl soln.) of the residue and recrystallisation (AcOEt) of the precipitate afforded *trans*-**43a** as white crystals (3.8 g). M.p. 192–193°. IR ($CDCl_3$): 3100 (br.), 1680, 1640, 1420, 1280, 880, 740, 700, 640. ^{1}H-NMR (+D_2O): 0.93 (3 *s*, 9 H); 0.80–2.50 (11 H); 7.13 (*m*, 1 H). MS: 222 (4, M^+), 207 (3), 137 (15), 124 (76), 109 (100), 91 (20), 81 (25).

11. *(4a*RS,*8a*SR*)-3,4,4a,5,6,7,8,8a-Octahydro-5,5,8a-trimethylnaphthalen-2(1*H*)-one* (**44**). A mixture of *trans*-**43a** (3.7 g, 0.017 mol) and $SOCl_2$ (4 g, 0.034 mol) was stirred at reflux during 3 h. Evaporation and distillation *i.v.* afforded the crude acyl chloride of *trans*-**43a** as a pale green solid (3.8 g; b.p. 102–104°/0.1 Torr; ^{1}H-NMR: 0.85 (*s*, 3 H); 0.87 (2 *s*, 6 H); 7.43 (*m*, 1 H)) which, without further purification, was dissolved in acctone (20 ml) and added dropwise within 15 min to a stirred soln. of NaN_3 (1.5 g, 0.023 mol) in H_2O (15 ml) at 5°; the mixture was then stirred at r.t. during 3 h. Extraction (toluene, 3 × 20 ml) and workup gave the crude acyl azide of *trans*-**43a** as a yellow oil (^{1}H-NMR: 0.85 (*s*, 3 H); 0.87 (2 *s*, 6 H); 7.07 (*m*, 1 H)) which was dissolved in toluene (15 ml) and added dropwise within 10 min to toluene (20 ml) at 100° (evolution of N_2). After addition, the soln. was refluxed during 30

min, and then, 10N HCl soln. (1.8 ml) was cautiously added dropwise within 10 min (evolution of CO_2). The mixture was heated under reflux for a further 10 min, cooled, and neutralised with sat. aq. $NaHCO_3$ soln. The org. phase was dried (Na_2SO_4) and concentrated; recrystallisation of the residual solid afforded **44** as white crystals (2.65 g, 82%). M.p. 58–59° ([5]: 59–60°). Spectra: identical with those of an authentic sample.

12. *(2*RS*,3*SR*,4a*RS*,8a*SR*)-Methyl 2,3-Epoxy-1,2,3,4,4a,5,6,7,8,8a-decahydro-5,5,8a-trimethylnaphthalene-2-carboxylate* (**45**). At 30°, 70% aq. H_2O_2 soln. (6 g) was added dropwise within 10 min to a stirred soln. of **43** (*trans*/*cis* 3.3:1; 9.5 g, 0.04 mol) and maleic anhydride (6.7 g, 0.068 mol) in CH_2Cl_2 (30 ml). After 64 h, 70% aq. H_2O_2 soln. (6 g) was re-added and after a further 20 h, the mixture was poured into cold sat. aq. $NaHCO_3$ soln. Separation of the org. phase, workup, CC (silica gel (50 g), cyclohexane/AcOEt 9:1), and recrystallisation (petroleum ether 30/50, –50°) afforded **45** as white crystals (5 g, 65% from *trans*-**43**). M.p. 51–53°. IR: 1720, 1430, 1280, 1220, 1190, 1050, 900, 720. ^{1}H-NMR: 0.86 (2 *s*, 6 H); 0.93 (*s*, 3 H); 0.90–1.20 (3 H); 1.35–1.60 (5 H); 1.70 (*m*, 1 H); 2.15 (*dd*, *J* = 14, 4, 1 H); 2.38 (*d*, *J* = 14, 1 H); 3.50 (br. *s*, 1 H); 3.75 (*s*, 3 H). ^{13}C-NMR: 172.0 (*s*); 59.3 (*d*); 55.8 (*s*); 52.6 (*q*); 43.2 (*t*); 43.1 (*d*); 42.4 (*t*); 41.5 (*t*); 32.5 (*q*); 31.4 (*s*); 22.4 (*t*); 21.9 (*q*); 19.8 (*q*); 18.6 (*t*). MS: 252 (3, M^+), 236 (10), 159 (10), 137 (18) 124 (52), 109 (100), 91 (26), 81 (26).

13. *(4a*RS*,8a*SR*)-3,4,4a,5,6,7,8,8a-Octahydro-4a,8,8-trimethylnaphthalen-2(1*H*)-one* (**46**). A mixture of **45** (3.5 g, 0.014 mol) and NaOH (1.2 g, 0.03 mol) in MeOH/H_2O 1:1 (80 ml) was refluxed during 5 h, cooled, and 10N HCl soln. (3.5 ml) in MeOH/H_2O 1:1 (30 ml) was added dropwise. The mixture was then refluxed during 1 h, cooled to r.t., and poured into cold sat. aq. $NaHCO_3$ soln. (200 ml). Extraction (Et_2O), workup, CC (silica gel (30 g), cyclohexane/AcOEt 9:1), and distillation *i.v.* afforded **46** as a white solid (1.5 g, 55%). M.p. 34–36° ([5]: 37–38°). Spectra: identical with those of an authentic sample.

14. *1,5,6,7,8,8a-Hexahydro-5,5,8a-trimethylnaphthalene-2-carboxylic Acid* (**37a**). A soln. of **37** (2.34 g, 0.01 mol) and KOH (1.7 g, 0.03 mol) in MeOH (15 ml) was refluxed during 5 h, cooled to r.t., and concentrated. Acidification (10% aq. HCl soln.) of the residue and recrystallisation (AcOEt) of the precipitate afforded **37a** as white crystals (2.06 g, 94%). M.p. 153–154°. IR ($CDCl_3$): 3050 (br.), 1670, 1630, 1420, 1280, 1230, 854, 820. ^{1}H-NMR (+D_2O): 1.03 (*s*, 3 H); 1.16 (2 *s*, 6 H); 1.20–2.00 (6 H); 2.20 (*AB*, *J* = 16, 2 H); 6.05 (*d*, *J* = 6, 1 H); 7.16 (*dd*, *J* = 6, 2, 1 H). MS: 220 (35, M^+), 205 (18), 150 (100), 135 (60), 119 (30), 105 (75), 91 (88).

15. *3,5,6,7,8,8a-Hexahydro-5,5,8a-trimethylnaphthalen-2(1*H*)-one* (**47**), *(4a*RS*,8a*RS*)- and (4a*RS*,8a*SR*)-4a,5,6,7,8,8a-Hexahydro-5,5,8a-trimethylnaphthalen-2(1*H*)-one* (*cis*- and *trans*-**48**, resp.). A mixture of **37a** (11 g, 0.05 mol) and $SOCl_2$ (8.9 g, 0.075 mol) was stirred at reflux during 3 h. Evaporation and distillation *i.v.* afforded the crude acyl chloride of **37a** as a pale yellow oil (11.3 g; b.p. 120–122°/0.2 Torr; ^{1}H-NMR: 1.03 (*s*, 3 H); 1.16 (2 *s*, 6 H); 2.35 (*AB*, *J* = 16, 2 H); 6.11 (*d*, *J* = 6, 1 H); 7.36 (*dd*, *J* = 6, 2, 1 H)) which, without further purification, was dissolved in acetone (30 ml) and added dropwise within 20 min to a stirred soln. of NaN_3 (4.3 g, 0.066 mol) in H_2O (20 ml) at 5°; the mixture was then stirred at r.t. during 3 h. Extraction (toluene, 3 × 30 ml) and workup gave the crude acyl azide of **37a** as a pale yellow solid (^{1}H-NMR: 1.00 (*s*, 3 H); 1.16 (2 *s*, 6 H); 2.30 (*AB*, *J* = 16, 2 H); 6.00 (*d*, *J* = 6, 1 H); 7.05 (*dd*, *J* = 6, 2, 1 H)) which was dissolved in toluene (40 ml) and added dropwise within 20 min to toluene (60 ml) at 100° (evolution of N_2). After addition, the soln. was refluxed during 30 min, and the 10N HCl soln. (5 ml) was cautiously added dropwise during 10 min (evolution of CO_2). The mixture was heated under reflux for 75 min, cooled, and neutralised with sat. aq. $NaHCO_3$ soln. The org. phase was separated, dried (Na_2SO_4), and concentrated. Distillation *i.v.* of the residual oil gave a 1.5:2.5:1 mixture **47**/*trans*-**48**/*cis*-**48** (GLC analysis) as a colourless oil (7.1 g, 74%; b.p. 82–92°/0.1 Torr). Separation was effected by CC (silica gel (100 g), cyclohexane/AcOEt 9:1) of an aliquot (1 g).

Data of **47**. R_f (cyclohexane/AcOEt 4:1) 0.49. IR: 1725, 1460, 1380, 1320, 1265, 1230, 990, 850, 670. ^{1}H-NMR: 1.10 (2 *s*, 6 H); 1.16 (*s*, 3 H); 1.00–2.00 (6 H); 2.30 (*AB*, *J* = 13, 2 H); 2.87 (*m*, 2 H); 5.57 (*dd*, *J* = 4, 4, 1 H). MS: 192 (37, M^+), 177 (17), 150 (30), 135 (100), 122 (14), 107 (29), 93 (31), 79 (25).

Data of cis-**48**. R_f (cyclohexane/AcOEt 4:1) 0.37. IR: 1682, 1460, 1380, 878. ^{1}H-NMR: 0.88 (*s*, 3 H); 1.00 (*s*, 3 H); 1.07 (*s*, 3 H); 1.20–1.60 (7 H); 1.89 (*d*, *J* = 18, 1 H); 2.74 (*d*, *J* = 18, 1 H); 6.11 (*d*, *J* = 10, 1 H); 6.98 (*dd*, *J* = 10, 6, 1 H). ^{13}C-NMR: 200.6 (*s*); 150.6 (*d*); 129.6 (*d*); 53.0 (*d*); 46.4 (*t*); 40.2 (*t*); 35.0 (*s*); 32.8 (*q*); 31.7 (*q*); 23.1 (*q*); 18.8 (*t*). MS: 192 (8, M^+), 177 (4), 149 (19), 121 (13), 109 (100), 91 (9), 79 (18).

Data of trans-**48**. R_f (cyclohexane/AcOEt 4:1) 0.33. IR: 1680, 1460, 1380, 1250, 1170, 880, 820, 720. ^{1}H-NMR: 0.91 (*s*, 3 H); 1.00 (*s*, 3 H); 1.03 (*s*, 3 H); 1.20–1.80 (7 H); 2.21 (*m*, 2 H); 6.07 (*dd*, *J* = 10, 3, 1 H); 6.98 (*dd*, *J* = 10, 2, 1 H). ^{13}C-NMR: 199.7 (*s*); 150.5 (*d*); 130.2 (*d*); 58.0 (*t*); 54.6 (*d*); 41.5 (*t*); 40.4 (*t*); 39.8 (*s*); 32.5 (*q*); 22.0 (*q*); 18.8 (*q*); 18.5 (*t*). MS: 192 (25, M^+), 177 (7), 149 (14), 135 (15), 122 (70), 109 (100), 81 (45).

16. *(2*RS*,8a*SR*)- and (2*RS*,8a*RS*)-1,2,3,5,6,7,8,8a-Octahydro-5,5,8a-trimethylnaphthalen-2-ol* (**49** and **50**, resp.). A soln. of **47** (0.73 g, 3.8 mmol) in MeOH (5 ml) was added dropwise to a stirred suspension of $NaBH_4$

(0.14 g, 3.8 mmol) in MeOH (15 ml) at r.t. After 2 h, the mixture was acidified with 10% aq. HCl soln. (10 ml). Extraction (Et_2O) and workup afforded a 10:1 mixture **49**/**50** (0.65 g, 89%) which was separated by CC (silica gel (80 g), cyclohexane/AcOEt 4:1).

Data of **49**. White crystals. R_f (cyclohexane/AcOEt 4:1) 0.29. M.p. 80–81°. IR ($CDCl_3$): 3650, 3450 (br.), 1480, 1380, 1060, 1044, 840, 680. ^{1}H-NMR (+D_2O): 1.06 (*s*, 3 H); 1.13 (*s*, 3 H); 1.30 (*s*, 3 H); 0.80–1.70 (7 H); 1.84 (*m*, 1 H); 2.05 (*m*, 1 H); 2.40 (*m*, 1 H); 3.97 (*m*, 1 H); 5.40 (*m*, 1 H). MS: 194 (32, $M^{+\cdot}$), 179 (14), 161 (100), 150 (14), 135 (78), 119 (40), 109 (76), 91 (58), 79 (44).

Data of **50**. White crystals. R_f (cyclohexane/AcOEt 4:1) 0.24. M.p. 75–77°. IR ($CDCl_3$): 3630, 3430 (br.), 1475, 1385, 1060, 1030. 660. ^{1}H-NMR (+D_2O): 1.06 (2 *s*, 6 H); 1.22 (*s*, 3 H); 1.20–1.80 (8 H); 2.40 (*m*, 2 H); 4.08 (*m*, 1 H); 5.33 (*m*, 1 H). MS: 194 (27, $M^{+\cdot}$), 179 (17), 161 (100), 150 (14), 135 (73), 119 (39), 107 (57), 91 (54), 79 (39).

17. *(2*RS*,4a*SR*,8a*RS*)- and (2*RS*,4a*RS*,8a*SR*)-1,2,4a,5,6,7,8,8a-Octahydro-5,5,8a-trimethylnaphthalen-2-ol* (**51** and **52**, resp.). A soln. of *trans*-**48** (2 g, 0.0104 mol) in MeOH (20 ml) was added dropwise within 15 min to a stirred suspension of $NaBH_4$ (0.4 g, 0.0105 mol) in MeOH (20 ml) at r.t. After 2 h, the mixture was acidified with 10% aq. HCl soln. (20 ml). Extraction (Et_2O) and workup afforded a 3:1 mixture **51**/**52** (1.8 g, 88%) which was separated by CC (silica gel (200 g), cyclohexane/AcOEt 4:1).

Data of **51**. Viscous, colourless oil. R_f (cyclohexane/AcOEt) 0.24. B.p. (bulb-to-bulb dist.) 180°/0.1 Torr. IR: 3350 (br.), 1460, 1380, 1370, 1120, 1040, 994, 960, 918, 892, 818, 770, 690. ^{1}H-NMR (+D_2O): 0.85 (*s*, 3 H); 0.91 (*s*, 3 H); 1.03 (*s*, 3 H); 1.00–2.20 (9 H); 4.20 (*m*, 1 H); 5.82 (*m*, 2 H). MS: 194 (12, $M^{+\cdot}$), 179 (11), 161 (24), 109 (100), 105 (23), 91 (33), 81 (34).

Data of **52**. Viscous, colourless oil. R_f (cyclohexane/AcOEt 4:1) 0.17. B.p. (bulb-to-bulb dist.) 180°/0.1 Torr. IR: 3300 (br.), 1460, 1380, 1030, 944, 800, 720. ^{1}H-NMR (+D_2O): 0.85 (*s*, 3 H); 0.91 (2 *s*, 6 H); 0.80–2.40 (9 H); 4.33 (*m*, 1 H); 5.75 (*m*, 2 H). MS: 194 (15, $M^{+\cdot}$), 179 (12), 161 (35), 109 (100), 105 (41), 91 (54), 81 (39).

18. *Preparation of Acetates* **53**–**56**. In four separate experiments, a soln. of **49**, **50**, **51**, or **52** (0.194 g, 1 mmol) and Ac_2O (0.15 g, 1.2 mmol) in pyridine (2 ml) was refluxed during 6 h, cooled to r.t., and then poured into cold 10% aq. HCl soln. (40 ml). Extraction (Et_2O), workup, and CC (silica gel (5 g), cyclohexane/AcOEt 4:1) afforded **53**–**56** as colourless oils. B.p. (bulb-to-bulb dist.) 180–200°/0.1 Torr. R_f (cyclohexane/AcOEt 4:1) 0.53.

*(2*RS*,8a*SR*)-1,2,3,5,6,7,8,8a-Octahydro-5,5,8a-trimethylnaphthalen-2-yl Acetate* (**53**). Yield from **49**, 85%. IR: 1730, 1460, 1374, 1360, 1250, 1230, 1210, 1030, 960, 866, 820, 660, 600. ^{1}H-NMR: 1.07 (*s*, 3 H); 1.13 (*s*, 3 H); 1.25 (*s*, 3 H); 1.00–2.50 (10 H); 2.02 (*s*, 3 H); 5.03 (*m*, 1 H); 5.37 (*m*, 1 H). MS: 236 (0, $M^{+\cdot}$), 176 (58), 161 (42), 133 (18), 119 (39), 105 (94), 91 (100).

*(2*RS*,8a*RS*)-1,2,3,5,6,7,8,8a-Octahydro-5,5,8a-trimethylnaphthalen-2-yl Acetate* (**54**). Yield from **50**, 88%. IR ($CDCl_3$): 1725, 1460, 1368, 1260, 1030, 650. ^{1}H-NMR: 1.07 (2 *s*, 6 H); 1.27 (*s*, 3 H); 1.00–2.50 (10 H); 2.03 (*s*, 3 H); 5.05 (*m*, 1 H); 5.30 (*m*, 1 H). MS: 236 (0, $M^{+\cdot}$), 176 (50), 161 (41), 133 (18), 119 (35), 105 (95), 91 (100).

*(2*RS*,4a*SR*,8a*RS*)-1,2,4a,5,6,7,8,8a-Octahydro-5,5,8a-trimethylnaphthalen-2-yl Acetate* (**55**). Yield from **51**, 96%. IR: 1730, 1460, 1370, 1240, 1120, 1030, 960, 910, 810. ^{1}H-NMR: 0.87 (*s*, 3 H); 0.93 (*s*, 3 H); 1.00 (*s*, 3 H); 1.00–2.20 (9 H); 2.01 (*s*, 3 H); 5.23 (*m*, 1 H); 5.83 (*m*, 2 H). MS: 236 (0, $M^{+\cdot}$), 194 (16), 176 (74), 161 (52), 133 (30), 119 (35), 105 (85), 91 (100).

*(2*RS*,4a*RS*,8a*SR*)-1,2,4a,5,6,7,8,8a-Octahydro-5,5,8a-trimethylnaphthalen-2-yl Acetate* (**56**). Yield from **52**, 93%. IR: 1740, 1460, 1375, 1240, 1024, 982, 950, 924, 806. ^{1}H-NMR: 0.83 (*s*, 3 H); 0.93 (*s*, 3 H); 1.01 (*s*, 3 H); 1.00–2.20 (9 H); 2.03 (*s*, 3 H); 5.50 (*m*, 1 H); 5.76 (*m*, 2 H). MS: 236 (0, $M^{+\cdot}$), 194 (12), 176 (75), 161 (52), 133 (32), 119 (34), 105 (91), 91 (100).

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