Monatshefte für Chemie 134, 1593–1606 (2003)
DOI 10.1007/s00706-003-0040-2

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Synthesis of Chiral Cyclohexenones from α-Campholenic, Fencholenic, and β-Campholenic Derivatives

Katrin Anhalt, Ines Sprung, and **Klaus Schulze***

Institut für Organische Chemie, Universität Leipzig, D-04103 Leipzig, Germany

Received February 10, 2003; accepted February 17, 2003
Published online October 9, 2003 © Springer-Verlag 2003

Summary. Optically active dimethylcyclohexenones, potential building blocks for enantioselective syntheses of various naturally active substances, were prepared. These compounds were obtained by oxidation with $KMnO_4/Pb(OAc)_4$ or ozonolysis of the corresponding cyclopentenic precursors, followed by aldol condensation. During the course of the preparation intermediate diols and chiral polyfunctional carbonyl derivatives were separated and identified analytically.

Keywords. Aldol condensation; Cyclohexenones; Oxidation; Ozonolysis; Terpenoids.

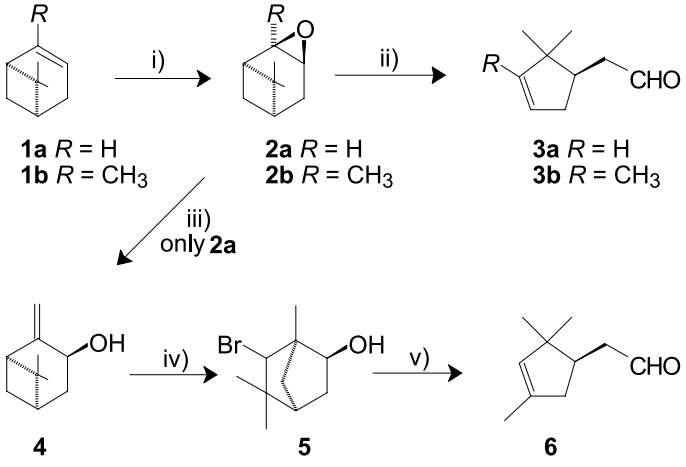
Introduction

α-Pinene (**1a**) and α-ethylapopinene (**1b**), which are both available in enantiomeric pure forms [1], are becoming more widely used in total syntheses of complex chiral, biologically active products [2]. Little is known about the use of α-campholenic and fencholenic derivatives, which are obtainable from α-pinene oxide (**2a**) by camphane-[3, 4] or fenchane-rearrangement [5] *via trans*-pinocarveol (**4**) and bromoisofenchol (**5**). The cyclopentenes of type **3** and **6** possess a stereogenic centre resulting from the C-5-centre of α-pinene.

The β-campholenic system **8** bears chiral information resulting from *trans*-epoxy-α-campholenic products of type **7** *via* the *Nametkin* rearrangement [6].

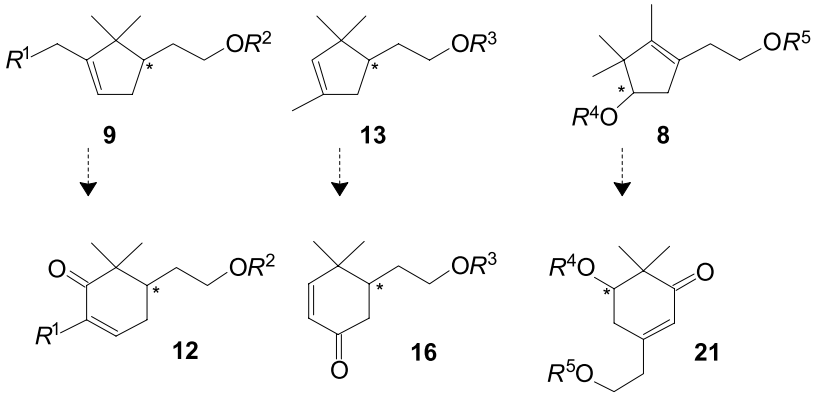
We herein report the preparation of chiral cyclohexenones **12**, **16**, and **21** from α-pinene. They may be suitable starting materials for natural compounds as, *e.g.* taxols [7], strigol [8], carotenoids [9], and fragrances [3, 10]. Enantiomeric excesses of the cyclohexenones correspond to the *ee* of the starting materials *a*-pinene or nopol.

* Corresponding author. E-mail: kschulze@organik.chemie.uni-leipzig.de



Scheme 1. i) *Ac*OOH, CH_2Cl_2, 40°C; ii) $ZnBr_2$, toluene, reflux; iii) Al(O*iPr*)$_3$, toluene, reflux; iv) HBr, pentane, −20°C; v) $AgNO_3$, *t-Bu*OH/H_2O

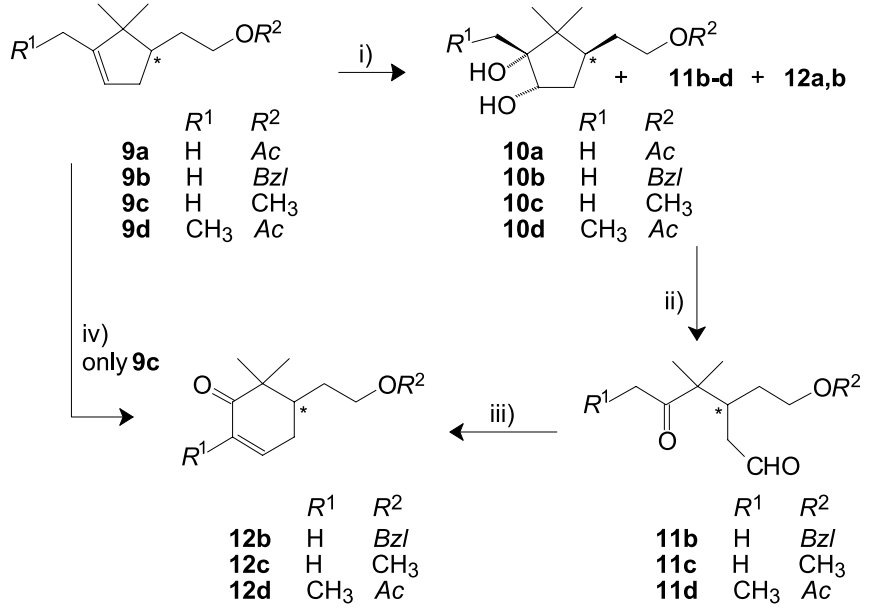
Scheme 2



Scheme 3

Results and Discussion

We first performed the oxidation of α-campholenic derivatives **9a**–**9d** with $KMnO_4$ and obtained mixtures of diols as well as other oxidized products. On treatment with Pb(O*Ac*)$_4$ the diol mixture led to either mixtures of **11** and **12** or pure cyclohexenone (in the case of **12a**). Refluxing with *p*-toluenesulfonic acid completed the aldol condensation to give **12b**–**12d**. An alternative route to cyclohexenone **12c** [3] involved ozonolysis followed by aldol cyclization. The overall yields, *e.g.* in the case of **12c**, were 53% *via* i)–iii) and 36% *via* iv).



	R^1	R^2
9a	H	*Ac*
9b	H	*Bzl*
9c	H	CH_3
9d	CH_3	*Ac*

	R^1	R^2
10a	H	*Ac*
10b	H	*Bzl*
10c	H	CH_3
10d	CH_3	*Ac*

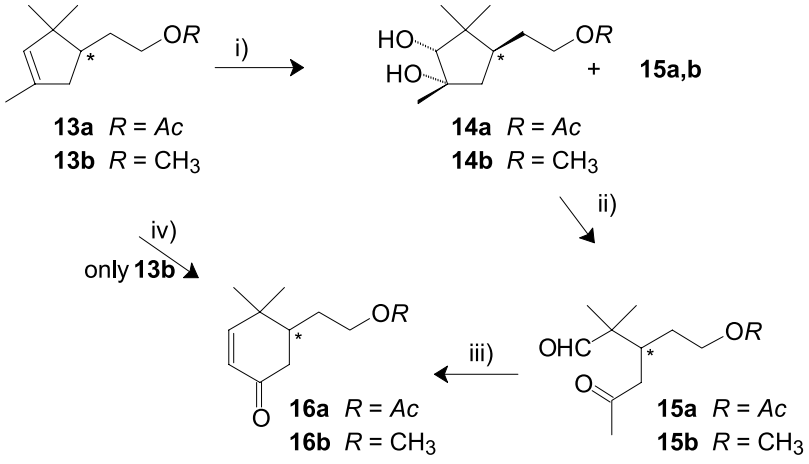
	R^1	R^2
12b	H	*Bzl*
12c	H	CH_3
12d	CH_3	*Ac*

	R^1	R^2
11b	H	*Bzl*
11c	H	CH_3
11d	CH_3	*Ac*

Scheme 4. i) $KMnO_4/MgSO_4$, $H_2O/EtOH$, 0–10°C; ii) $Pb(OAc)_4$, toluene, reflux; iii) *p-Ts*OH, toluene, reflux; iv) a) O_3, $CH_2Cl_2/MeOH$, −40°C; b) Zn/CH_3COOH, Et_2O, reflux; c) iii)

For preparation of dimethylcyclohexenones **16a** and **16b** from fencholenic derivatives we employed the methodology described above. Again, a mixture of diols **14a** and **14b** and aliphatic ketoaldehydes **15a** and **15b** was isolated after conversion with $KMnO_4$. This mixture could be transformed into the desired products **16a** and **16b** by oxidation and cyclization in 18 and 34% overall yields. Alternatively, **16b** was obtained after ozonolysis and aldol condensation in 44% overall yield.

β-Campholenic derivatives **8** were accessible by *Nametkin* rearrangement of *trans*-epoxy-α-campholenic derivatives [6] and protection of the formed secondary



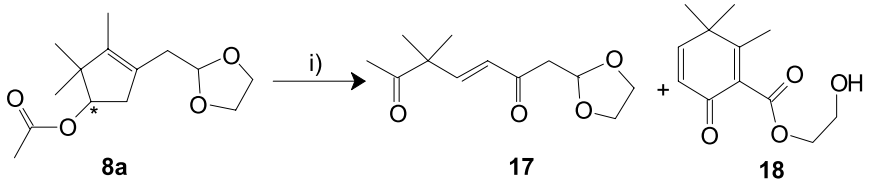
13a *R* = *Ac*
13b *R* = CH_3

14a *R* = *Ac*
14b *R* = CH_3

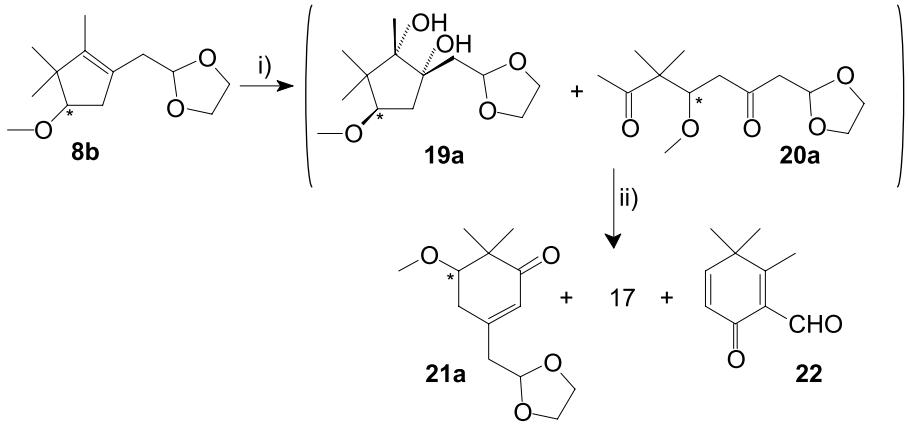
16a *R* = *Ac*
16b *R* = CH_3

15a *R* = *Ac*
15b *R* = CH_3

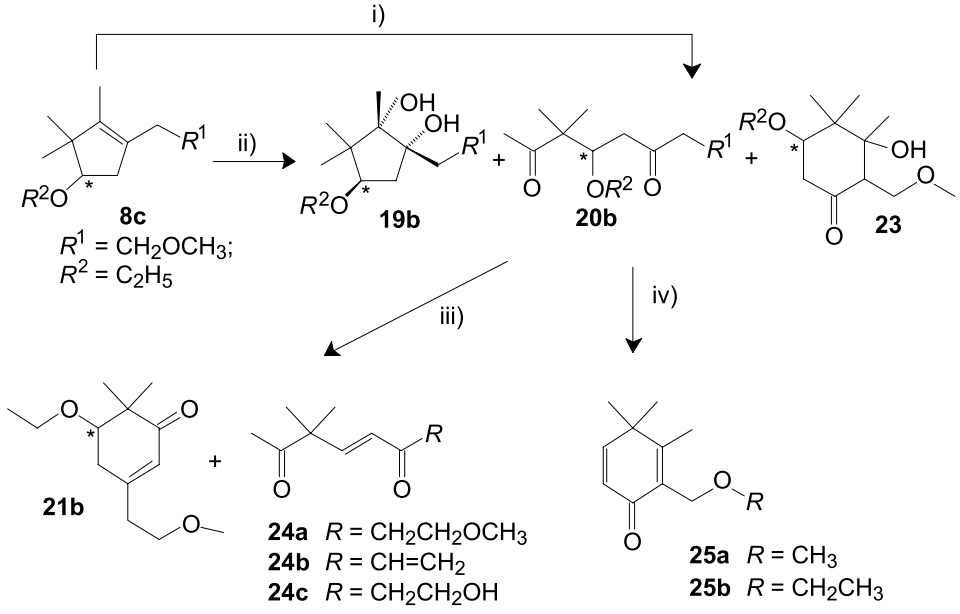
Scheme 5. i) $KMnO_4/MgSO_4$, $H_2O/EtOH$, 0–10°C; ii) $Pb(OAc)_4$, toluene, reflux; iii) *p-Ts*OH, toluene, reflux; iv) a) O_3, $CH_2Cl_2/MeOH$, −40°C; b) Zn/CH_3COOH, Et_2O, reflux; c) iii)



Scheme 6. i) $KMnO_4/MgSO_4$, $H_2O/EtOH$, reflux



Scheme 7. i) $KMnO_4/MgSO_4$, $H_2O/EtOH$, 0–10°C; ii) a) $Pb(OAc)_4$, toluene, reflux; b) *p-Ts*OH, toluene, reflux



Scheme 8. i) a) O_3, $CH_2Cl_2/MeOH$, −40°C; b) Zn/CH_3COOH, Et_2O, reflux; ii) $KMnO_4/MgSO_4$, $H_2O/EtOH$, 0–10°C; iii) *p-Ts*OH, toluene, reflux; iv) KOH, *Et*OH

alcohol. Oxidation of derivative **8a** gave exclusively α,β-unsaturated carbonyl compounds **17** and **18** lacking the desired asymmetric centre of the starting material. The oxidation of **8b** with $KMnO_4$ led to a mixture of diol **19a** and diketone **20a**. Major difficulties occured in the intramolecular cyclization of diketone **20a**. The main products were aliphatic α,β-unsaturated diketone **17** in addition to cyclohexanedienone **22**, but only 14% of the substituted cyclohexenone **21a** was obtained.

Oxidation of **8c** with $KMnO_4$ led also to a diol/diketone mixture. Ozonolysis gave exclusively **20b**. Cyclization of **20b** with *p*-toluenesulfonic acid gave 11% of the desired product **21b**. Treatment of **20b** with base yielded only the 3,4,4-trimethylcyclohexa-2,5-dienones **25a** and **25b**.

The stereochemistry of the diols **10**, **14**, and **19** was analysed by N*O*E-NMR experiments. We obtained diols in which both hydroxyl groups are in a *trans*-position with respect to the sidechain. The above-mentioned ozonolyses of **9c**, **13b**, and **8c** always gave exceptionally stable ozonides. It was not possible to completely reduce the obtained secondary ozonides, neither with Me_2S [3] nor with reagents like $P(Ph)_3$ or Na_2SO_3. We will discuss the isolated ozonide diastereomers as well as the influence of the methyl substituents on the reactivity of the ozonides in a forthcoming publication.

Experimental

NMR spectra were recorded on a Varian Gemini 200 or Gemini 2000 (^{1}H NMR: 200 MHz, ^{13}C NMR: 50.3 MHz), a Gemini 300 (^{1}H NMR: 300 MHz, ^{13}C NMR: 75.7 MHz) or Unity 400 (^{1}H NMR: 400 MHz, ^{13}C NMR: 100.6 MHz) spectrometer in $CDCl_3$. IR spectra of neat samples were obtained using a Carl-Zeiss-Jena Specord M 80 IR spectrophotometer or ATI Mattson, Genesis Series FT-IR spectrophotometer. Mass spectra were measured with a Masslab VG 12250 (column SGE 25QC2/BPX5 25 m × 0.22 mm × 0.25 μm) or a Hewlett-Packard HP 5890-II/5972 Series (column HP5 30 m × 0.32 mm × 0.25 μm). GLC were recorded on a Hewlett-Packard HP 5890-II (oven temperature is always written in brackets) equipped with a flame ionisation detector, capillary column: HP1 (25 m × 0.2 mm × 0.33 μm) and for determination of *ee*: Lipodex E, Macherey-Nagel (modified γ-cyclodextrin), 25 m × 0.25 mm). The silica gel used in column chromatography was from Merck KG 60 (230–400 mesh ASTM) and the pump from Optima (Model 10007). Distillations were done partially with a Büchi ball tube distillation instrument GKR 51, bp corresponds to air temperature. Ozone was produced with a Fischer ozone generator OZ 500 (output: 100 scale marks, O_2-stream: 40 dm^3/h). (1*S*)-(–)-α-Pinene (**1a**) (81% *ee*) was purchased from Merck and (1*R*)-(–)-nopol (91% *ee*) (**1b**) from Aldrich. Compound **3a** was prepared as reported [4a], **3b** [4c] and **6** were described [4b], **8a** was prepared as reported [5b].

General Procedures

I Oxidation with $KMnO_4$: To a well stirred ice-cooled soln. of 0.10 mol of the respective olefin in 200 cm^3 of ethanol was added dropwise a suspension of 0.10 mol of $KMnO_4$ and 0.08 mol of $MgSO_4$ in 250 cm^3 of H_2O so that the reaction temperature was about 5–10°C. After that the mixture was stirred at rt about 2 h and the conversion was monitored by GLC. If necessary, $KMnO_4$ and $MgSO_4$ were added again and the mixture was stirred until no educt was detected. Then MnO_2 was removed by filtration and the residue was washed with copious amounts of acetone. The combined filtrates were concentrated to about 100 cm^3, NaCl was added and the soln. was extracted with $CHCl_3$. The combined org. layers were dried (Na_2SO_4) and the solvent was removed in *vacuo*. The resulting crude oil was purified by column chromatography, distillation, or used immediately for the next reaction step.

II Reaction of diols with Pb(OAc)$_4$: To a stirred soln. of 10 mmol of Pb(OAc)$_4$ in 5 cm^3 of dry toluene was added at rt 10 mmol of the diol and the mixture was refluxed (0.5–15 h) until no educt was detected by GLC. Then it was filtered and the residue was thoroughly washed with toluene. After that the combined org. layers were evaporated. The crude oil was purified by column chromatography, distillation, or used immediately for the next reaction step.

III Reaction of dicarbonyl compounds with p-toluenesulfonic acid: To a soln. of 10 mmol of the dicarbonyl compound in 20 cm^3 of dry toluene a spatula tip of *p*-toluenesulfonic acid was added and refluxed (*ca.* 0.5–3 h) until no educt was monitored by GLC. The cooled reaction mixture was washed with H_2O, dried (Na_2SO_4), and concentrated. The crude oil was purified by distillation or column chromatography.

IV Ozonolysis of cyclopentenic double bonds: 1 mmol of olefin was diluted in 21 cm^3 of dry CH_2Cl_2 and 25 cm^3 of methanol and cooled to −40°C. A flow of O_3 was passed through until the soln. became blue and no starting material was detected by TLC. The apparatus was purged with O_2 and N_2. The solvent was evaporated and the residue either purified by column chromatography or used without purification for the next reaction.

V Decomposition of ozonides with Zn/acetic acid: To a stirred soln. of 1 mmol of the crude product from ozonolysis in 15 cm^3 of diethyl ether was added at rt 3 g of Zn-powder and 2 cm^3 of acetic acid. The reaction mixture was refluxed until no ozonide was detected by TLC. The precipitate was filtered off and washed with diethyl ether. The combined org. layers were washed with H_2O and saturated $NaHCO_3$ solution, dried (Na_2SO_4), and concentrated. The crude product was purified by distillation or column chromatography.

2-[(4-Methoxy-2,3,3-trimethylcyclopent-1-enyl)methyl]-1,3-dioxolane (**8b**, $C_{13}H_{22}O_3$)

To a well stirred suspension of 28 mmol of NaH in 10 cm^3 of dry *n*-hexane at rt 4.30 g of 2-[(4-hydroxy-2,3,3-trimethylcyclopent-l-enyl)methyl]-1,3-dioxolane [5b] (20.3 mmol) in 10 cm^3 of dry *n*-hexane were added dropwise. After that the mixture was refluxed for 3 h and to the cooled reaction mixture 3.3 cm^3 of MeI (52 mmol) were added at rt. After one night at rt the mixture was stirred at 40°C (*ca.* 10 h) until no educt was detected by GLC. The reaction mixture was cooled to 0°C and ice H_2O was added. The aqueous layer was further extracted with *n*-hexane and the combined org. layers were washed with H_2O and brine, dried (Na_2SO_4), and then concentrated to give 79% of crude **8b**. Ball tube distillation gave 1.90 g (41%) of a colourless liquid. $Bp_{0.9}$ 110°C; GLC (180°C): 88%; IR: $\bar{\nu} = 2822$ (CH_3–O), 1648 (>C=C<), 1127, 1099, 1038 (C–O–C) cm^{-1}; MS: $m/z = 227$ (<1, $M^+ + H$), 226 (<1, M^+), 225 (<1, $M^+ - H$), 194 (4, M^+-CH_4O), 182 (<1, M^+-C_2H_4O), 107 (2), 91 (5), 73 (100); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.89$ (s, 3′-$CH_{3'}$), 1.00 (s, 3′-CH_3) 1.50 (t, $J = 2.0$ Hz, 2′-CH_3), 2.21 (m, 1H, 5′-CH_2), 2.37 (d, $J = 4.8$ Hz, CH_2), 2.52 (ddm, $J = 15.3$, 6.8 Hz, 1H, 5′-CH_2), 3.44 (s, CH_3–O), 3.46 (t, $J = 6.8$ Hz, 4′-CH), 3.81 (m, 4-CH_2), 3.94 (m, 5-CH_2) 4.85 (t, $J = 4.8$ Hz, 2-CH) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 10.13$ (2′-CH_3), 19.33/25.95 (3′-CH_3), 34.21 (CH_2), 39.26 (5′-CH_2), 49.11 (3′-C), 58.14 (CH_3–O), 65.28 (4-CH_2, 5-CH_2), 89.20 (4′-CH), 104.36 (2-CH), 125.29 (1′-C), 141.46 (2′-C) ppm.

Methyl[2-(4-ethoxy-2,3,3-trimethylcyclopent-1-enyl)ethyl]ether (**8c**, $C_{13}H_{24}O_2$)

Methyl[2-(4-hydroxy-2,3,3-trimethylcyclopent-1-enyl)ethyl]ether: 13.76 g of *trans*-Epoxy-α-campholene methylether (0.075 mol) gave as reported in Ref. [5b] 17.3 g of the trimethylcyclopentanol derivative. 2.00 g of this crude product were purified for analytical identification by ball tube distillation to give 1.40 g (88%) of a colourless liquid. $Bp_{2.5}$ 105°C; GLC (120°C): 92%; IR: $\bar{\nu} = 3426$ (–OH), 1646 (>C=C<), 1116 (C–O–C) cm^{-1}; MS: $m/z = 184$ (<1, M^+), 166 (25, M^+-H_2O), 151 (2, M^+-H_2O, –CH_3), 137 (20), 121 (93), 108 (72), 95 (21), 79 (23), 45 (100); ^{1}H NMR (200 MHz, $CDCl_3$):

$\delta = 0.92$ (s, 3′-CH_3), 0.94 (s, 3′-CH_3), 1.51 (t, $J = 2.0$ Hz, 2′-CH_3), 1.82 (bs, OH), 2.13 (dm, $J = 15.7$ Hz, 1H, 5′-CH_2), 2.30 (dt, $J = 3.2$, 7.1 Hz, 2-CH_2), 2.53 (ddm, $J = 15.7$, 6.6 Hz, 1H, 5′-CH_2), 3.31 (s, CH_3–O), 3.67 (t, $J = 7.1$ Hz, 1-CH_2), 3.84 (t, $J = 6.0$ Hz, 4′-CH) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 10.13$ (2′-CH_3), 19.15/25.00 (3′-CH_3), 29.40 (2-CH_2), 42.16 (5′-CH_2), 49.79 (3′-C), 58.93 (CH_3–O), 71.59 (1-CH_2), 80.12 (4′-CH), 127.68 (1′-C), 139.64 (2′-C) ppm.

Methyl[2-(4-ethoxy-2,3,3-trimethylcyclopent-1-enyl)ethyl]ether (**8c**): To a well stirred suspension of 166 mmol of NaH in 50 cm^3 of dry cyclohexane at rt 12.90 g of methyl[2-(4-hydroxy-2,3,3-trimethylcyclopent-l-enyl)ethyl]ether (70 mmol) were dropped. After that the mixture was stirred at rt for 3 h and 13.2 cm^3 of *Et*I (164 mmol) in 30 cm^3 of dry cyclohexane were added. After 2 h at rt the mixture was refluxed (about 7 h) until only 2% of educt was detected by GLC. The reaction mixture was cooled to 0°C and ice H_2O was added. The aqueous layer was extracted with cyclohexane and the combined org. layers were washed with H_2O and brine, dried (Na_2SO_4), and then concentrated. The crude product contained 87% **8c**. Distillation gave 8.1 g (55%) of a colourless liquid. $Bp_{2.2}$ 75–77°C; n_{20}^D: 1.4556; GLC (120°C): 95%; IR: $\bar{\nu} = 2807$ (CH_3–O), 1648 (>C=C<), 1119, 1104 (C–O–C) cm^{-1}; MS: $m/z = 212$ (4, M^+), 211 (3, $M^+ - H$), 197 (18, M^+-CH_3), 166 (52, M^+-C_2H_6O), 151 (8), 137 (20), 121 (100), 108 (75); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.88$ (s, 3′-CH_3), 0.98 (s, 3′-CH_3), 1.17 (t, $J = 6.8$ Hz, $\underline{CH_3}$–CH_2–O), 1.48 (t, $J = 2.0$ Hz, 2′-CH_3), 2.16 (ddm, $J = 15.3$, 6.5 Hz, 1H, 5′-CH_2), 2.28 (t, $J = 7.2$ Hz, 2-CH_2), 2.40 (ddm, $J = 15.3$, 7.0 Hz, 1H, 5′-CH_2), 3.30 (s, CH_3–O), 3.34 (t, $J = 7.2$ Hz, 1-CH_2), 3.49 (q, $J = 6.8$ Hz, CH_3–$\underline{CH_2}$–O), 3.52 (m, 4′-CH) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 9.85$ (2′-CH_3), 15.94 ($\underline{CH_3}$–CH_2–O), 19.41/26.00 (3′-CH_3), 29.50 (2-CH_2), 39.21 (5′-CH_2), 49.10 (3′-C), 58.89 (CH_3–O), 65.84 (CH_3–$\underline{CH_2}$–O), 71.66 (1-CH_2), 87.31 (4′-CH), 127.30 (1′-C), 140.05 (2′-C) ppm.

5-(2-Acetoxyethyl)-6,6-dimethylcyclohex-2-enone (**12a**, $C_{12}H_{18}O_3$)

a) Reaction of α-campholene acetate (**9a**) *with $KMnO_4$:* According to procedure I 15.5 g of α-campholene acetate [3] (0.079 mol) gave 23.0 g (74%) of a crude product which contained 59% **10a** and 27% **12a**. For analytical use, ball tube distillation of a small amount was performed. *t-4-(2-Acetoxyethyl)-1,5,5-trimethylcyclopentane-R-1,c-2-diol* (**10a**): Bp 185°C; GLC (180°C): 84%; IR: $\bar{\nu} = 3450$ (–OH), 1740 (C=O), 1240, 1040 (C–O–C) cm^{-1}; MS: $m/z = 188$ (1, M^+-C_2H_2O), 170 (80, M^+-C_2H_2O, $-H_2O$), 152 (1), 143 (1), 137 (5), 127 (5), 109 (55), 83 (45), 44 (100); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.66$ (s, 5-CH_3), 0.89 (s, 5-CH_3), 1.07 (s, 1-CH_3), 1.10–2.50 (m, 4-CH, 3-CH_2, 1′-CH_2), 2.00 (s, C(O)–CH_3), 3.95 (m, 2-CH, 2′-CH_2) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 19.48/20.40$ (5-CH_3), 20.10 (1-CH_3), 21.45 (C(O)–CH_3), 30.03 (1′-CH_2), 37.87 (3-CH_2), 42.03 (4-CH), 46.61 (5-C), 64.72 (2′-CH_2), 76.90 (2-CH), 82.14 (1-C), 171.72 (C=O) ppm.

b) Reaction of the crude product of a) with $Pb(OAc)_4$: According to procedure II 23.00 g of the mixture of **10a** and **12a** gave after distillation 6.43 g (39% *via a*) and *b*)) of the colourless oil **12a**; analytical data see Ref. [3].

5-(2-Benzyloxyethyl)-6,6-dimethylcyclohex-2-enone (**12b**, $C_{17}H_{22}O_2$)

a) Reaction of α-campholene benzylether (**9b**) *with $KMnO_4$:* According to procedure I 5.19 g of α-campholene benzylether [11] (**9b**) (21 mmol) and 5.11 g of $KMnO_4$ gave after distillation 2.15 g (31%) of a mixture which contained 57% **10b** and 30% secondary products.

t-4-(2-Benzyloxyethyl)-1,5,5-trimethylcyclopentane-R-1,c-2-diol (**10b**): $Bp_{0.7}$ 135°C; GLC (180°C): 96%; MS: $m/z = 278$ (<1, M^+), 260 (<1, M^+-H_2O), 259 (<1), 246 (M^+-CH_4O), 205 (<1), 185 (3), 170 (23), 152 (8), 123 (15), 105 (46), 91 (100); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.68$ (s, 5-CH_3), 0.95 (s, 5-CH_3), 1.13 (bs, 1-CH_3), 1.20–2.50 (m, 4-CH, 3-CH_2, 1′-CH_2), 3.36 (m, 2′-CH_2), 4.05 (m, 2-CH), 4.50 (s, $\underline{CH_2}$–C_{arom}), 7.26–7.35 (m, 5H, CH_{arom}) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 19.61/20.21/20.62$ (1-CH_3, 5-CH_3), 31.19 (1′-CH_2), 38.21 (3-CH_2), 42.13 (4-CH), 47.95 (5-C), 70.60 (2′-CH_2), 73.50 ($\underline{CH_2}$–C_{arom}), 77.20 (2-CH), 82.43 (1-C), 128.02/128.16/128.85 (CH_{arom}), 138.97 (C_{arom}) ppm.

b) Reaction of the mixture from a) with $Pb(OAc)_4$: According to procedure II 2.1 g of the mixture of **10b** and secondary oxidized products gave 2.1 g of a liquid, which contained 55% **11b** and 40% **12b**. It was not possible to separate the products neither by distillation nor by column chromatography. GLC (200°C): 94% **11b** and **12b**, GLC (Chrompack CP-Chiral-Dex CB, 200°C): 55% **11b** and 40% **12b**. *3-(2-Benzyloxyethyl)-4,4-dimethyl-5-oxohexanal* (**11b**): MS: $m/z = 276$ (< 1, M^+), 261 (< 1, M^+-CH_3), 243 (4, M^+-CH_3, $-H_2O$), 169 (6), 127 (4), 107 (10), 91 (100); ^{1}H NMR (200 MHz, $CDCl_3$) (simultaneously with **12b**): $\delta = 1.04$ (s, 4-CH_3), 1.07 (s, 4-CH_3), 1.30–2.60 (m, 3-CH, 1′-CH_2, 2-CH_2), 2.15 (s, 6-CH_3), 3.43 (m, 2′-CH_2), 4.40 (s, $\underline{CH_2}$–C_{arom}), 7.28–7.33 (m, 5H, CH_{arom}), 9.67 (bs, CHO) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$) (simultaneously with **12b**): $\delta = 21.03/21.63$ (4-CH_3), 25.40 (6-CH_3), 31.59 (1′-CH_2), 35.29 (3-CH), 45.78 (2-CH_2), 51.17 (4-C), 68.62 (2′-CH_2), 73.01 ($\underline{CH_2}$–C_{arom}), 127.65/128.12/128.25 (CH_{arom}), 138.14 (C_{arom}), 201.56 (CHO), 213.59 (5-C=O) ppm.

c) Reaction of the mixture from b) with p-toluenesulfonic acid: According to procedure III 1.80 g of the **11b**/**12b** mixture yielded after ball tube distillation 1.11 g (67%) of the liquid oil **12b**. $Bp_{1.2}$ 195°C; GLC (Chrompack CP-Chiral-Dex CB, 200°C): 94%; IR: $\bar{\nu} = 3063$ (–C=CH), 3031 (–CH_{arom}), 1672 (C=O), 1104 (s, C–O–C), 739, 698 (m, –CH_{arom}) cm^{-1}; MS: $m/z = 258$ (< 1, M^+), 167 (2, M^+-C_7H_7), 152 (20, M^+-C_7H_7, –CH_3), 149 (5), 123 (2), 107 (15), 91 (100); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.98$ (s, 6-CH_3), 1.16 (s, 6-CH_3), 1.47 (m, 1H, 1′-CH_2), 1.91 (m, 1H, 1′-CH_2), 1.98 (m, 5-CH), 2.00 (m, 1H, 4-CH_2), 2.43 (m, 1H, 4-CH_2), 3.51 (m, 2′-CH_2), 4.49 (d, $J = 2.6$ Hz, $\underline{CH_2}$–C_{arom}), 5.93 (td, $J = 10.2$, 1.8 Hz, 2-CH), 6.80 (m, 3-CH), 7.30–7.35 (m, 5H, CH_{arom}) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 19.31/22.68$ (6-CH_3), 29.17 (4-CH_2), 29.70 (1′-CH_2), 41.00 (5-CH), 45.64 (6-C), 68.99 (2′-CH_2), 73.42 ($\underline{CH_2}$–C_{arom}), 128.14/128.93/ 138.82 (CH_{arom}, C_{arom}), 128.57 (2-CH), 147.94 (3-CH), 205.34 (1-C=O) ppm.

5-(2-Methoxyethyl)-6,6-dimethylcyclohex-2-enone (**12c**, $C_{11}H_{18}O_2$)

a) Reaction of α-campholene methylether (**9c**) *with $KMnO_4$:* According to procedure I 7.72 g of α-campholene methylether (46 mmol) yielded a crude oil which contained 23% **9c**, 40% **10c**, and 24% **11c**. Ball tube distillation yielded for analytical identification pure diol. *t-4-(2-Methoxyethyl)-1,5,5-trimethylcyclopentane-R-1,c-2-diol* (**10c**): $Bp_{0.36}$ 125°C; GLC (150°C): 92%; IR: $\bar{\nu} = 3418$ (–OH), 2829 (CH_3–O), 1116, 1089, 1065 (C–O–C) cm^{-1}; MS: $m/z = 202$ (1, M^+), 170 (100, M^+-CH_4O), 152 (1), 137 (5), 127 (8), 109 (30), 83 (25); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.66$ (s, 5-CH_3), 0.93 (s, 5-CH_3), 1.12 (s, 1-CH_3), 1.26 (m, 1H, 1′-CH_2), 1.62 (m, 1H, 1′-CH_2), 1.69 (m, 1H, 3-CH_2), 1.72 (m, 1H, 3-CH_2), 2.12 (m, 4-CH), 2.32 (bs, OH), 2.63 (bs, OH), 3.31 (s, CH_3–O), 3.36 (m, 2′-CH_2), 4.00 (m, 2-CH) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 19.54/20.43$ (5-CH_3), 20.18 (1-CH_3), 30.98 (1′-CH_2), 38.11 (3-CH_2), 41.93 (4-CH), 46.61 (5-C), 59.03 (CH_3–O), 72.87 (2′-CH_2), 77.10 (2-CH), 82.37 (1-C) ppm.

b) Reaction of the mixture from a) with $Pb(OAc)_4$ and p-toluenesulfonic acid: According to procedure II 3.20 g of a mixture of **10c** and **11c** (16 mmol) gave a crude product (13% **11c** and 63% **12c**), which was used without further purification for procedure III. Ball tube distillation yielded 2.69 g (92%) of the colourless oil **12c**. $Bp_{0.4}$ 85°C; GLC (150°C): 92%; IR: $\bar{\nu} = 3033$, 821 (–C=CH), 2829 (CH_3–O), 1677 (C=O), 1117 (C–O–C) cm^{-1}; MS: $m/z = 183$ (1, $M^+ + H$), 182 (8, M^+), 167 (2, M^+-CH_3), 154 (2), 150 (16), 135 (18), 123 (15), 82 (35), 68 (100); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.96$ (s, 6-CH_3), 1.13 (s, 6-CH_3), 1.40 (m, 1H, 1′-CH_2), 1.83 (m, 1H, 1′-CH_2), 1.93 (m, 5-CH), 2.11 (m, 1H, 4-CH_2), 2.48 (m, 1H, 4-CH_2), 3.29 (s, CH_3–O), 3.37 (d, $J = 5.6$ Hz, 1H, 2′-CH_2), 3.41 (d, $J = 5.6$ Hz , 1H, 2′-CH_2), 5.90 (td, $J = 10.9$, 1.9 Hz, 2-CH), 6.80 (m, 3-CH) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 19.37/22.76$ (6-CH_3), 29.24 (4-CH_2), 29.64 (1′-CH_2), 41.05 (5-CH), 45.65 (2-C), 59.03 (CH_3–O), 71.49 (2′-CH_2), 128.54 (2-CH), 147.71 (3-CH), 205.01 (1-C=O) ppm.

c) Ozonolyses of α-campholene methylether (**9c**), *decomposition of the ozonide, and cyclisation with p-toluenesulfonic acid:* According to procedures I, II, and III 2.76 g of α-campholene methylether [12]

(16.4 mmol) yielded without purification of the intermediate products after final ball tube distillation 1.06 g (36%) of cyclohexenone **12c**.

d) Ozonolyses of α-campholene methylether (**9c**) *and decomposition of the ozonide:* According to procedures I and II 1.84 g of α-campholene methylether [12] (10.9 mmol) yielded after ball tube distillation 0.76 g (35%) of the colourless oil *3-(2-methoxyethyl)-4,4-dimethyl-5-oxohexanal* (**11c**): $Bp_{0.95}$ 100°C; GLC (180°C): 86%; IR: $\bar{\nu} = 2833$ (CH_3–O), 1726, 1704 (C=O), 1118 (C–O–C) cm^{-1}; MS: $m/z = 200$ (< 1, M^+), 167 (1, M^+-CH_3, –H_2O), 157 (5, M^+-CH_3CO), 139 (1), 125 (15), 107 (30), 86 (42), 43 (100); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.02$ (s, 4-CH_3), 1.05 (s, 4-CH_3), 1.34 (m, 1H, 2′-CH_2), 1.60 (m, 1H, 2′-CH_2), 2.13 (s, 6-CH_3), 2.31 (m, 1H, 2-CH_2), 2.61 (m, 1H, 2-CH_2), 2.34 (m, 3-CH), 3.21 (s, CH_3–O), 3.29 (t, $J = 6.1$ Hz, 1′-CH_2), 9.69 (t, $J = 1.8$ Hz, 1-CHO) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 21.49/21.99$ (4-CH_3), 25.80 (6-CH_3), 31.81 (2′-CH_2), 35.75 (3-CH), 46.19 (2-CH_2), 51.55 (4-C), 58.89 (CH_3–O), 71.30 (1′-CH_2), 201.95 (1-CHO), 213.89 (5-C=O) ppm.

5-(2-Acetoxyethyl)-2,6,6-trimethylcyclohex-2-enone (**12d**, $C_{13}H_{20}O_3$)

*a) Reaction of ethyl-α-campholene acetate (**9d**) with $KMnO_4$:* According to procedure I (but rt during $KMnO_4$ addition) 1.84 g of ethyl-α-campholene acetate [3] (**9d**) (8.7 mmol) yielded 1.44 g (62% relating to **10d**) of a liquid which contained 74% **10d** and 13% **11d**. *t-4-(2-Acetoxyethyl)-1-ethyl-5,5-dimethylcyclopentane-R-1,c-2-diol* (**10d**): GLC (180°C): 74%; MS: $m/z = 244$ (3, M^+), 226 (2, M^+-H_2O), 207 (2), 184 (20, M^+-CH_3COOH), 166 (8), 151 (5), 141 (17), 123 (42), 82 (62), 43 (100); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.66$ (s, 5-CH_3), 0.95 (s, 5-CH_3), 0.98 (t, $\underline{CH_3}$–CH_2), 1.00–2.60 (m, 4-CH, 3-CH_2, 1′-CH_2), 1.54 (t, $J = 7.5$ Hz, $\underline{CH_2}$–CH_3), 2.04 (s, C(O)–CH_3), 4.40 (m, 2-CH, 2′-CH_2) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 8.51$ ($\underline{CH_3}$–CH_2), 18.84/20.90 (5-CH_3), 21.52 (C(O)–CH_3), 27.71 ($\underline{CH_2}$–CH_3), 29.66 (1′-CH_2), 39.03 (3-CH_2), 42.38 (4-CH), 47.70 (5-C), 64.71 (2′-CH_2), 76.82 (2-CH), 83.07 (1-C), 171.74 (C=O) ppm.

b) Reaction of the mixture from a) with $Pb(OAc)_4$: According to procedure II 1.20 g (3.64 mmol of **10d** and 0.65 mmol of **11d**) yielded after ball tube distillation 0.30 g (29%) of the colourless oil *3-(2-acetoxyethyl)-4,4-dimethyl-5-oxoheptanal* (**11d**). $Bp_{0.85}$ 175°C; GLC (80°C): 72%; MS: $m/z = 242$ (4, M^+), 224 (5, M^+-H_2O), 198 (3, M^+-C_2H_4O), 182 (4, M^+-CH_3COOH), 164 (2), 138 (30), 121 (20), 95 (43), 83 (100); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.98$ (t, 7-CH_3), 0.99 (s, 4-CH_3), 1.05 (s, 4-CH_3), 1.20–1.80 (m, 1′-CH_2), 2.00 (s, CH_3–C(O)), 2.00–2.70 (m, 3-CH, 6-CH_2, 2-CH_2), 3.99 (m, 2′-CH_2), 9.71 (bs, 1-CHO) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 8.48$ (7-CH_3), 21.32/21.76/22.10 (4-CH_3, CH_3–C(O)–), 30.87/30.95 (1′-CH_2, 6-CH_2), 35.16 (3-CH), 46.29 (2-CH_2), 51.17 (4-C), 63.32 (2′-CH_2), 171.41 (C=O), 213.89 (5-C=O), 201.71 (1-CHO) ppm.

c) Reaction of **11d** *with p-toluenesulfonic acid:* According to procedure III 144 mg of **11d** (5.95 mmol) yielded after ball tube distillation 54 mg (41%) of the colourless liquid **12d** (analytical data see Ref. [3]).

5-(2-Acetoxyethyl)-4,4-dimethylcyclohex-2-enone (**16a**, $C_{12}H_{18}O_3$)

a) Reaction of fencholene acetate (**13a**) *with $KMnO_4$:* According to general procedure I 5.7 g of fencholene acetate [13] (28.6 mmol) gave with 10 g of $KMnO_4$ a crude product (8.0 g, 46% relating to **14a** and 37% to **15a**) which contained 38% **14a** and 31% **15a**. Column chromatography (cyclohexane:petroleum ether = 1:1) was performed for analytical identification. *t-4-(2-Acetoxyethyl)-1,3,3-trimethylcyclopentane-R-1,c-2-diol* (**14a**): GLC (180°C): 83%; IR: $\bar{\nu} = 3440$ (br, –OH), 1740 (C=O), 1240, 1060, 1040 (C–O–C=) cm^{-1}; MS: $m/z = 157$ (18, M^+-CH_2COOCH_3), 137 (1), 111 (3), 109 (3), 97 (100), 82 (15), 69 (25); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.84$ (s, 3-CH_3), 0.95 (s, 3-CH_3), 1.29 (s, 1-CH_3), 1.30–2.10 (m, 4-CH, 5-CH_2, 1′-CH_2), 2.02 (s, CH_3–C(O)–), 2.50–2.90 (bs, 1-OH, 2-OH),

3.26 (s, 2-CH), 4.02 (m, 2′-CH_2) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 21.50$ (CH_3–C(O)–), 24.27/24.50/27.94 (1-CH_3, 3-CH_3), 29.50 (1′-CH_2), 43.11 (4-CH), 43.58 (5-CH_2), 45.16 (3-C), 64.51 (2′-CH_2), 77.35 (1-C), 86.67 (2-CH), 171.74 (C=O) ppm; *3-(2-Acetoxyethyl)-2,2-dimethyl-5-oxohexanal* (**15a**): GLC (180°C): 78%; MS: $m/z = 212$ (< 1), 175 (7, M^+-$C(CH_3)_2$-CHO), 137 (3), 110 (4), 97 (100), 82 (10), 69 (10); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.93$ (s, 2-CH_3), 0.99 (s, 2-CH_3), 1.10–2.50 (m, 1′-CH_2, 3-CH, 4-CH_2), 1.99 (s, CH_3–C(O)–), 2.11 (s, 6-CH_3), 3.95 (t, $J = 7.2$ Hz, 2′-CH_2), 9.37 (s, 1-CHO) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 19.06/19.48$ (2-CH_3), 21.40 (CH_3–C(O)–), 30.44 (1′-CH_2), 34.13 (6-CH_3), 40.63 (3-CH), 45.12 (4-CH_2), 49.51 (2-C), 63.31 (2′-CH_2), 171.41 (C=O), 206.03 (1-CHO), 207.39 (5-C=O) ppm.

b) Reaction of the mixture from a) with $Pb(OAc)_4$ and p-toluenesulfonic acid: According to procedures II and III 8.0 g of the mixture of 13.2 mmol of **14a** and 10.5 mmol of **15a** yielded without cleaning of the intermediate product after ball tube distillation 2.0 g (41%) of the colourless liquid **16a**. Bp_1 165°C; GLC (180°C): 83%; IR: $\bar{\nu} = 3040$, 740 (–C=CH), 1740, 1680 (C=O), 1240, 1050 (C–O–C) cm^{-1}; MS: $m/z = 210$ (5, M^+), 168 (10, M^+-C_2H_2O), 150 (90, M^+-CH_3COOH), 135 (60), 123 (65), 107 (40), 95 (100), 81 (50); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.97$ (s, 4-CH_3), 1.11 (s, 4-CH_3), 1.20–2.60 (m, 5-CH, 6-CH_2, 1′-CH_2), 1.99 (s, CH_3C(O)–), 4.06 (m, 2′-CH_2), 5.80 (d, $J = 10.0$ Hz, 2-CH), 6.60 (d, $J = 10.0$ Hz, 3-CH) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 20.64/27.98$ (4-CH_3), 21.37 (CH_3–C(O)), 29.53 (1′-CH_2), 36.32 (4-C), 39.63 (6-CH_2), 40.77 (5-CH), 62.85 (2′-CH_2), 126.89 (2-CH), 161.13 (3-CH), 171.34 (C=O), 199.63 (1-C=O) ppm.

5-(2-Methoxyethyl)-4,4-dimethylcyclohex-2-enone (**16b**, $C_{11}H_{18}O_2$)

a) Reaction of fencholene methylether (**13b**) *with $KMnO_4$:* According to procedure I 2.61 g of fencholene methylether [14] (**13b**) (15.5 mmol) and 3.35 g of $KMnO_4$ yielded 2.66 g (28% relating to **14b** and 34% to **15b**) of a liquid which contained 33% **14b** and 39% **15b**. Compounds were separated by column chromatography (petroleum ether:ethyl acetate = 1:1). *t-4-(2-Methoxyethyl)-1,3,3-trimethylcyclopentane-R-1,c-2-diol* (**14b**): GLC (180°C): 87%; IR: $\bar{\nu} = 3426$ (–OH), 2831 (CH_3–O), 1113, 1070 (C–O–C) cm^{-1}; MS: $m/z = 202$ (< 1, M^+), 184 (2, M^+-H_2O), 169 (1, M^+-CH_3), 152 (2), 129 (100), 97 (90), 43 (94); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.83$ (s, 3-CH_3), 0.94 (s, 3-CH_3), 1.20–2.00 (m, 4-CH, 5-CH_2, 1′-CH_2), 1.28 (s, 1-CH_3), 2.63 (bs, 1-OH), 2.83 (d, $J = 7.3$ Hz, 2-OH), 3.29 (m, 2′-CH_2), 3.30 (s, CH_3–O), 3.33 (s, 2-CH) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 24.25/24.49$ (3-CH_3), 28.02 (1-CH_3), 30.35 (1′-CH_2), 43.14 (4-CH), 43.76 (3-C, 5-CH_2), 58.97 (CH_3–O), 72.73 (2′-CH_2), 76.36 (1-C), 86.74 (2-CH) ppm.

b) Reaction of the crude product of a) with $Pb(OAc)_4$: According to procedure II 2.00 g of the mixture of 6.5 mmol of **14b** and 3.9 mmol of **15b** yielded after ball tube distillation 0.98 g (47%) of the colourless liquid *3-(2-methoxyethyl)-2,2-dimethyl-5-oxohexanal* (**15b**). $Bp_{0.98}$ 100°C; GLC (180°C): 81%; IR: $\bar{\nu} = 2831$ (CH_3–O), 1720 (C=O), 1117 (C–O–C) cm^{-1}; MS: $m/z = 201$ (< 1, $M^+ + H$), 200 (< 1, M^+), 199 (< 1, $M^+ - H$), 186 (1, M^+-CH_3), 167 (7, M^+-CH_3, –H_2O), 111 (10), 97 (18), 82 (35), 43 (100); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.92$ (s, 2-CH_3), 0.97 (s, 2-CH_3), 1.34 (m, 1H, 1′-CH_2), 1.60 (m, 1H, 1′-CH_2), 2.09 (s, 6-CH_3), 2.36 (m, 4-CH_2), 2.45 (m, 3-CH), 3.18 (s, CH_3–O), 3.28 (m, 2′-CH_2), 9.38 (s, 1-CHO) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 19.16/19.29$ (2-CH_3), 30.48 (6-CH_3), 31.48 (1′-CH_3), 35.27 (3-CH), 45.49 (4-CH_2), 49.55 (2-C), 58.73 (CH_3–O), 71.89 (2′-CH_2), 206.35 (1-CHO), 207.56 (5-C=O) ppm.

c) Reaction of **15b** *with p-toluenesulfonic acid:* According to procedure III 729 mg of **15b** (3.64 mmol) yielded after ball tube distillation 402 mg (61%) of the colourless liquid **16b**. $Bp_{1.3}$ 120°C; GLC (180°C): 88%; IR: $\bar{\nu} = 3022$, 780 (–C=CH), 2830 (CH_3–O), 1680 (C=O), 1117 (C–O–C) cm^{-1}; MS: $m/z = 182$ (5, M^+), 167 (7, M^+-CH_3), 150 (23, M^+-CH_4O), 135 (42), 123 (90), 108 (30), 96 (92), 81 (72), 45 (100); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.97$ (s, 4-CH_3), 1.12 (s, 4-CH_3), 1.32 (m, 1H, 1′-CH_2), 1.84 (m, 1H, 1′-CH_2), 1.99 (m, 5-CH), 2.12 (m, 1H, 6-CH_2), 2.47 (dd, $J = 16.3$, 3.7 Hz, 1H,

6-CH_2), 3.27 (s, CH_3–O), 3.33 (m, 2′-CH_2), 5.80 (d, $J = 10.2$ Hz, 2-CH), 6.60 (d, $J = 10.2$ Hz, 3-CH) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 20.71/28.00$ (4-CH_3), 30.42 (1′-CH_2), 36.35 (4-C), 39.67 (6-CH_2), 40.65 (5-CH), 59.10 (CH_3–O), 70.93 (2′-CH_2), 126.84 (2-CH), 161.48 (3-CH), 200.26 (1-C=O) ppm.

d) Ozonolyses of fencholene methylether (**13b**), *decomposition of the ozonide, and cyclisation with p-toluenesulfonic acid:* According to procedures IV, V, and III 1.62 g of fencholene methylether (**13b**) (9.64 mmol) yielded without purification of the intermediate products after final ball tube distillation 0.76 g (44%) of cyclohexenone **16b**.

Reaction of 2-[(4-Acetoxy-2,3,3-trimethylcyclopent-1-enyl)methyl]-1,3-dioxolane (**8a**) *with $KMnO_4$*

According to procedure I 10.00 g of **8a** [5b] (39 mmol) yielded 14.9 g of crude product, which contained 32% **8a**, 34% **17**, and 15% **18**. Compounds were separated by column chromatography (petroleum ether:ethyl acetate = 1:3). *1-(1,3-Dioxolan-2-yl)-5,5-dimethylhept-3-en-2,6-dione* (**17**): GLC (180°C): 94%, IR: $\bar{\nu} = 1711$, 1670 (C=O), 1621 (>C=C<), 1127 (C–O–C) cm^{-1}; MS: $m/z = 225$ (<1, M^+-H), 211 (<1, M^+-CH_3), 184 (20, M^+-C_2H_2O), 141 (3), 111 (10), 96 (45), 73 (100); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.26$ (s, 6H, 5-CH_3), 2.10 (s, 7-CH_3), 2.91 (d, $J = 5.0$ Hz, 1-CH_2), 3.85–3.92 (m, 4′-CH_2, 5′-CH_2), 5.23 (t, $J = 5.0$ Hz, 2′-CH), 6.15 (d, $J = 16.3$ Hz, 3-CH), 6.90 (d, $J = 16.3$ Hz, 4-CH) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 23.96$ (5-CH_3), 26.38 (7-CH_3), 45.49 (1-CH_2), 51.26 (5-C), 65.41 (4′-CH_2, 5′-CH_2), 101.52 (2′-CH), 129.47 (3-CH), 150.99 (4-CH), 196.69 (2-C=O), 209.36 (6-C=O) ppm; *2,3,3-Trimethyl-6-oxocyclohexa-1,4-dienecarboxylic acid (2-hydroxyethyl)ester* (**18**): GLC (120°C): 96%; IR: $\bar{\nu} = 3452$ (–OH), 1733, 1659 (C=O), 1625 (>C=C<), 1247, 1058 (C–O–C=) cm^{-1}; MS: $m/z = 226$ (<1, M^+), 223 (<1), 211 (<1, M^+-CH_3), 194 (50, M^+-CH_4O), 179 (20), 163 (100), 149 (80); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.28$ (s, 6H, 3-CH_3), 2.04 (s, 2-CH_3), 3.82 (t, $J = 4.6$ Hz, 2′-CH_2), 4.41 (t, $J = 4.6$ Hz, 1′-CH_2), 6.21 (d, $J = 10.0$ Hz, 4-CH), 6.84 (d, $J = 10.0$ Hz, 5-CH ppm); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 17.16$ (2-CH_3), 25.99 (3-CH_3), 40.80 (3-C), 60.99 (2′-CH_2), 67.15 (1′-CH_2), 126.43 (5-CH), 132.95 (1-C), 158.68 (4-CH), 163.93 (2-C), 167.38 (O–C=O), 183.53 (6-C=O) ppm.

3-(1,3-Dioxolan-2-yl)methyl-5-methoxy-6,6-dimethylcyclohex-2-enone (**21a**, $C_{13}H_{20}O_4$)

a) Reaction of **8b** *with $KMnO_4$:* According to procedure I 1.30 g of **8b** (5.8 mmol) and 1.45 g of $KMnO_4$ yielded 1.74 g (37% relating to **19a** and 51% to **20a**) of a mixture which contained 32% **19a** and 44% **20a**. The products were separated by column chromatography (petroleum ether: ethyl acetate = 1:3). *2-[(R-1,c-2-Dihydroxy-t-4-methoxy-2,3,3-trimethylcyclopentyl)methyl]-1,3-dioxolane* (**19a**): GLC (180°C): 80%; IR: $\bar{\nu} = 3478$ (–OH), 2824 (CH_3–O), 1096 (C–O–C) cm^{-1}; MS: $m/z = 259$ (<1, M^+-H), 245 (<1, M^+-CH_3), 243 (1), 242 (4, M^+-H_2O), 185 (20), 173 (15), 160 (8), 143 (10), 73 (100); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.88$ (s, 3′-CH_3), 1.09 (s, 2′-CH_3), 1.13 (s, 3′-CH_3), 1.78 (dd, $J = 14.0$, 7.6 Hz, 1H, 5′-CH_2), 1.89 (dd, $J = 14.4$, 7.2 Hz, 1H, CH_2), 2.02 (dd, $J = 14.4$, 3.2 Hz, 1H, 5′-CH_2), 2.25 (dd, $J = 14.0$, 7.6 Hz, 1H, 5′-CH_2), 3.33 (s, CH_3–O), 3.67 (t, $J = 7.6$ Hz, 4′-CH), 3.86 (m, 5-CH_2), 3.96 (m, 4-CH_2), 5.18 (dd, $J = 7.2$, 3.2 Hz, 2-CH) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 19.09$ (3′-CH_3), 19.70 (2′-CH_3), 23.55 (3′-CH_3), 41.82 (CH_2), 42.44 (5′-CH_2), 47.39 (3′-C), 58.06 (CH_3–O), 64.92 (5-CH_2), 64.96 (4-CH_2), 78.60 (1′-C), 81.91 (2′-C), 86.53 (4′-CH), 102.86 (2-CH) ppm; *1-(1,3-Dioxolan-2-yl)-5,5-dimethyl-4-methoxyheptane-2,6-dione* (**20a**): GLC (180°C): 84%; IR: $\bar{\nu} = 2831$ (CH_3–O), 1708 (C=O), 1132, 1097 (C–O–C) cm^{-1}; MS: $m/z = 259$ (<1, $M^+ + H$), 258 (<1, M^+), 257 (<1, M^+-H), 226 (1, M^+-CH_4O), 184 (1), 173 (18), 139 (4), 129 (6), 85 (12), 73 (100); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.05$ (s, 5-CH_3), 1.09 (s, 5-CH_3), 2.14 (s, 7-CH_3), 2.55 (dd, $J = 8.5$, 3.7 Hz, 3-CH_2), 2.80 (d, $J = 5.0$ Hz, 1-CH_2), 3.29 (s, CH_3–O), 3.87–3.96 (m, 4-CH, 4′-CH_2, 5′-CH_2), 5.21 (t, $J = 5.0$ Hz, 2′-CH) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$):

$\delta = 20.78/21.42$ (5-CH_3), 26.98 (7-CH_3), 46.07 (3-CH_2), 48.51 (1-CH_2), 52.61 (5-C), 59.85 (CH_3–O), 65.41 (4′-CH_2, 5′-CH_2), 81.12 (4-CH), 101.21 (2′-CH), 205.9 (2-C=O), 213.10 (6-C=O) ppm.

b) Reaction of the crude product of a) with $Pb(OAc)_4$ and p-toluenesulfonic acid: According to procedures II and III 1.30 g of the mixture of **19a** and **20a** (1.6 mmol relating to **19a** and 2.2 mmol to **20a**) yielded as crude product 73% compound **20a** which reacted with *p*-toluenesulfonic acid according to procedure III to 0.94 g (14% relating to **21a**) of a mixture which contained 41% **17**, 12% **22**, and 14% **21a**. The compounds were separated by column chromatography (petroleum ether:ethyl acetate = 1:1). **21a**: GLC (180°C): 63%; MS: $m/z = 240$ (2, M^+), 226 (< 1), 225 (< 1, M^+-CH_3), 195 (< 1, M^+-C_2H_5O), 153 (2), 135 (2), 86 (18), 73 (100); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.05$ (s, 6-CH_3), 1.12 (s, 6-CH_3), 2.00–3.00 (m, CH_2), 2.53 (d, $J = 6.1$ Hz, 4-CH_2), 3.36 (s, CH_3–O), 2.83–3.97 (m, 5-CH), 4.99 (t, $J = 4.7$ Hz, 2′-CH), 5.88 (s, 2-CH) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 19.16/22.31$ (6-CH_3), 32.74 (4-CH_2), 42.62 (CH_2), 47.12 (6-C), 58.34 (CH_3–O), 65.45 (4′-CH_2, 5′-CH_2), 83.98 (5-CH), 103.16 (2′-CH), 127.41 (2-CH), 154.09 (3-C), 203.55 (1-C=O) ppm; *2,3,3-Trimethyl-6-oxocyclohexa-1,4-dienecarbaldehyde* (**22**): GLC (120°C): 74%; IR: $\bar{\nu} = 1734$, 1659 (C=O), 1624 (>C=C<) cm^{-1}; MS: $m/z = 164$ (1, M^+), 151 (10), 149 (100, M^+-CH_3), 136 (18, M^+-CO), 121 (43, M^+-CH_3CO), 91 (31); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.32$ (s, 6H, 3-CH_3), 2.35 (s, 2-CH_3), 6.23 (d, $J = 9.9$ Hz, 5-CH), 6.80 (d, $J = 9.9$ Hz, 4-CH), 10.40 (s, CHO) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 17.35$ (2-CH_3), 26.25 (3-CH_3), 41.91 (3-C), 127.08 (5-CH), 130.35 (1-C), 157.61 (4-CH), 173.82 (2-C), 186.02 (6-C=O), 194.74 (CHO) ppm.

5-Ethoxy-3-(2-methoxyethyl)-6,6-dimethylcyclohex-2-enone (**21b**, $C_{13}H_{22}O_2$)

a) Reaction of **8c** *with $KMnO_4$:* According to procedure I 2.85 g of **8c** (13.4 mmol) and 4.20 g of $KMnO_4$ yielded 2.67 g of a crude product which contained 11% **19b**, 66% **20b**, and 10% **23**. Compounds were separated partially by column chromatography (petroleum ether:ethyl acetate = 1.5:1). *t-4-Ethoxy-1-(2-methoxyethyl)-2,3,3-trimethylcyclopentane-R-1,c-2-diol* (**19b**): GLC (180°C): 37% **19b** beside 56% **20b**; MS: $m/z = 231$ (< 1, M^+-CH_3), 228 (6, M^+-H_2O), 213 (5, M^+-CH_3, –H_2O), 167 (15), 157 (65), 132 (12), 115 (10), 99 (100); ^{1}H NMR (200 MHz, $CDCl_3$) (simultaneously with **20b**): $\delta = 0.80$ (s, 3-CH_3), 1.07 (s, 3-CH_3), 1.13 (s, 2-CH_3), 1.78 (bs, 1-OH), 2.14 (bs, 2-OH), 3.37 (s, CH_3–O) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$) (simultaneously with **20b**): $\delta = 15.99$ ($\underline{CH_3}$–CH_2–O), 19.46/19.86/27.70 (2-CH_3, 3-CH_3), 37.83 (1′-CH_2), 43.27 (5-CH_2), 47.95 (3-C), 59.43 (CH_3–O), 66.24 (CH_3–$\underline{CH_2}$–O), 70.79 (2′-CH_2), 80.89 (1-C), 82.02 (2-C), 84.81 (4-CH) ppm; *4-Ethoxy-8-methoxy-3,3-dimethyloctane-2,6-dione* (**20b**): GLC (180°C): 90%; IR: $\bar{\nu} = 2830$ (CH_3–O), 2360, 1708 (C=O), 1116, 1093 (C–O–C) cm^{-1}; MS: $m/z = 244$ (1, M^+), 229 (2, M^+-CH_3), 226 (1, M^+-H_2O), 212 (5, M^+-CH_4O), 198 (7, M^+-C_2H_6O), 159 (68), 143 (5), 129 (5), 100 (10), 87 (100); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.05$ (s, 3-CH_3), 1.08 (s, 3-CH_3), 1.05 (t, $J = 6.8$ Hz, $\underline{CH_3}$–CH_2–O), 2.14 (s, 1-CH_3), 2.50 (2d, $J = 7.3$, 3.6 Hz, 5-CH_2), 2.66 (t, $J = 6.2$ Hz, 7-CH_2), 3.30 (s, CH_3–O), 3.40 (m, CH_3–$\underline{CH_2}$–O), 3.60 (t, $J = 6.2$ Hz, 8-CH_2), 4.04 (dd, $J = 7.3$, 3.6 Hz, 4-CH) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 15.94$ ($\underline{CH_3}$–CH_2–O), 20.98/21.98 (3-CH_3), 27.18 (1-CH_3), 44.18 (7-CH_2), 45.77 (5-CH_2), 52.60 (3-C), 59.25 (CH_3–O), 67.57 (CH_3–$\underline{CH_2}$–O), 67.86 (8-CH_2), 79.90 (4-CH), 208.08 (6-C=O), 213.41 (2-C=O) ppm; *5-Ethoxy-3-hydroxy-2-methoxymethyl-3,4,4-trimethylcyclohexanone* (**23**): GLC (180°C): 74%; IR: $\bar{\nu} = 3480$ (–OH), 2817 (CH_3–O), 1711 (C=O), 1102 (C–O–C) cm^{-1}; MS: $m/z = 229$ (< 1, M^+-CH_3), 226 (< 1, M^+-H_2O), 211 (< 1, M^+-CH_3, –H_2O), 198 (2), 175 (1), 166 (1), 151 (8), 143 (10), 127 (15), 100 (100); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.03$ (s, 4-CH_3), 1.21 (s, 4-CH_3), 1.11 (s, 3-CH_3), 1.16 (t, $J = 7.0$ Hz, $\underline{CH_3}$–CH_2–O), 2.51–2.67 (m, 6-CH_2), 3.16 (m, 2-CH), 3.19 (m, 5-CH), 3.37 (s, CH_3–O), 3.56 (m, CH_3–$\underline{CH_2}$–O), 3.77–3.85 (m, 2-CH–$\underline{CH_2}$–O) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 15.94$ ($\underline{CH_3}$–CH_2–O), 16.31/20.16 (4-CH_3), 21.11 (3-CH_3), 44.70 (4-C), 45.09 (6-CH_2), 55.27 (2-CH), 59.82 (CH_3–O), 66.31 (CH_3–$\underline{CH_2}$–O), 70.50 (2-CH–$\underline{CH_2}$–O), 77.14 (3-C) 80.50 (5-CH), 206.77 (1-C=O) ppm.

b) Reaction of **20b** *with p-toluenesulfonic acid:* According to procedure III 234 mg of **20b** (0.96 mmol) yielded a mixture (270 mg) which contained 25% **4a**, 40% **24b**, 13% **24c**, and 11% **21b**. Compounds were separated partially by column chromatography (petroleum ether:ethyl acetate = 1:1). *8-Methoxy-3,3-dimethyloct-4-ene-2,6-dione* (**24a**): GLC (180°C): 92%; IR: $\bar{\nu} = 2829$, 2815 (CH_3–O), 1711, 1674 (C=O), 1624 (>C=C<), 1119 (C–O–C) cm^{-1}; MS: $m/z = 199$ (<1, $M^+ + H$), 183 (<1, M^+-CH_3), 167 (<1, M^+-CH_3–O), 156 (85, M^+-C_2H_2O), 139 (1), 128 (18), 111 (20), 96 (65), 87 (43), 43 (100); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.28$ (s, 6H, 3-CH_3), 2.12 (s, 1-CH_3), 2.81 (t, $J = 6.3$ Hz, 7-CH_2), 3.31 (s, CH_3–O), 3.67 (t, $J = 6.3$ Hz, 8-CH_2), 6.15 (d, $J = 16.2$ Hz, 5-CH), 6.91 (d, $J = 16.2$ Hz, 4-CH) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 24.00$ (3-CH_3), 26.37 (1-CH_3), 41.04 (7-CH_2), 51.22 (3-C), 59.31 (CH_3–O), 68.08 (8-CH_2), 129.31 (5-CH), 150.34 (4-CH), 198.60 (6-C=O), 209.46 (2-C=O) ppm; *3,3-Dimethylocta-4,7-diene-2,6-dione* (**24b**): GLC (180°C): 91%; IR: $\bar{\nu} = 1712$, 1667 (C=O), 1625, 1612 (>C=C<) cm^{-1}; MS: $m/z = 167$ (<1, $M^+ + H$), 151 (<1, M^+-CH_3), 124 (45, M^+-C_2H_2O), 109 (100), 107 (5), 95 (8), 81 (12); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.31$ (s, 6H, 3-CH_3), 2.14 (s, 1-CH_3), 5.86 (dd, $J = 10.5$, 1.3 Hz, 1H, 8-CH_2), 6.29 (dd, $J = 17.5$, 1.3 Hz, 1H, 8-CH_2), 6.40 (d, $J = 16.1$ Hz, 5-CH), 6.60 (dd, $J = 17.5$, 10.5 Hz, 7-CH), 7.00 (d, $J = 16.1$ Hz, 4-CH) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 23.97$ (3-CH_3), 26.40 (1-CH_3), 51.37 (3-C), 126.97 (5-CH), 129.67 (8-CH_2), 135.50 (7-CH), 151.22 (4-CH), 189.93 (6-C=O), 209.31 (2-C=O) ppm; *8-Hydroxy-3,3-dimethyloct-4-ene-2,6-dione* (**24c**): GLC (180°C): 62% **24b** and 29% **21b**; MS: $m/z = 170$ (85), 139 (1, M^+-C_2H_5O), 124 (20), 101 (32), 97 (72), 81 (25), 43 (100); ^{1}H NMR (200 MHz, $CDCl_3$) (simultaneously with **21b**): $\delta = 1.28$ (s, 6H, 3-CH_3), 2.12 (s, 1-CH_3), 2.82 (t, $J = 6.4$ Hz, 7-CH_2), 3.70 (t, $J = 6.4$ Hz, 8-CH_2) 6.15 (d, $J = 16.3$ Hz, 5-CH), 6.91 (d, $J = 16.3$ Hz, 4-CH) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$) (simultaneously with **21b**): $\delta = 23.90$ (3-CH_3), 26.31 (1-CH_3), 41.13 (7-CH_2), 51.17 (3-C), 65.94 (8-CH_2), 129.46 (5-CH), 150.34 (4-CH), 199.00 (6-C=O), 209.66 (2-C=O) ppm; **21b**: MS: $m/z = 226$ (<1, M^+), 211 (<1, M^+-CH_3), 194 (39, M^+-CH_4O), 180 (25), 167 (15), 149 (15), 135 (17), 121 (18), 107 (24), 100 (100); ^{1}H NMR (200 MHz, $CDCl_3$) (simultaneously with **24c**): $\delta = 1.04$ (s, 6-CH_3), 1.12 (s, 6-CH_3), 1.15 (t, $J = 6.9$ Hz, $\underline{CH_3}$–CH_2–O), 2.44 (t, $J = 6.4$ Hz, 1′-CH_2), 2.53–2.62 (m, 4-CH_2), 3.32 (s, CH_3–O), 3.47 (m, CH_3–$\underline{CH_2}$–O), 3.53 (t, $J = 6.4$ Hz, 2′-CH_2), 5.82 (bs, 2-CH) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$) (simultaneously with **24c**): $\delta = 15.47$ ($\underline{CH_3}$–CH_2–O), 19.04/22.10 (6-CH_3), 33.13/38.02 (4-CH_2, 1′-CH_2), 47.13 (6-C), 59.15 (CH_3–O), 67.97 (CH_3–$\underline{CH_2}$–O), 70.41 (2′-CH_2), 81.89 (5-CH), 125.77 (2-CH), 157.49 (3-C), 204.17 (1-C=O) ppm.

c) Ozonolyses of **8c** *and decomposition of the ozonide to* **20b***:* According to procedures IV and V 1.90 g of **8c** (8.96 mmol) yielded without purification of the intermediate products after final ball tube distillation 1.11 g (51%) of the liquid **20b**.

d) Reaction of **20b** *with NaOH/EtOH:* To a stirred soln. of 234 mg of **20b** (0.96 mmol) in 10 cm^3 of ethanol at rt 100 mg of KOH in 3 cm^3 of ethanol were added and refluxed about 15 min. After that 100 cm^3 of diethyl ether were added and the organic layer was washed with H_2O, sat. NH_4Cl-soln., brine, dried (Na_2SO_4), and concentrated. Purification by column chromatography (petroleum ether: ethyl acetate = 2:1) yielded 64 mg (39%) of **25a** and 25 mg (16%) of **25b**. *2-Methoxymethyl-3,4,4-trimethylcyclohexa-2,5-dienone* (**25a**): GLC (180°C): 96%; IR: $\bar{\nu} = 2813$ (CH_3–O), 1662, 1628 (C=O), 1624 (>C=C<), 1105, 1086 (C–O–C) cm^{-1}; MS: $m/z = 180$ (<1, M^+), 179 (<1, M^+-H), 165 (100, M^+-CH_3), 150 (30), 135 (20), 122 (12), 105 (10); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.25$ (s, 6H, 4-CH_3), 2.08 (s, 3-CH_3), 3.34 (s, CH_3–O), 4.29 (s, CH_2–O), 6.20 (d, $J = 9.9$ Hz, 6-CH), 6.74 (d, $J = 9.9$ Hz, 5-CH) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 16.10$ (3-CH_3), 26.47 (4-CH_3), 40.84 (4-C), 58.74 (CH_3–O), 64.84 (CH_2–O), 126.73 (6-CH), 132.20 (2-C), 157.14 (5-CH), 164.88 (3-C), 185.24 (1-C=O) ppm; *2-Ethoxymethyl-3,4,4-trimethylcyclohexa-2,5-dienone* (**25b**): GLC (120°C): 82%; IR: $\bar{\nu} = 2809$ (CH_3–O), 1664, 1629 (C=O), 1097 (C–O–C) cm^{-1}; MS: $m/z = 195$ (<1, $M^+ + H$), 194 (<1, M^+), 179 (100, M^+-CH_3), 151 (80, M^+-CH_3, –CO), 135 (20), 123 (25), 105 (18), 91 (20); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.18$ (t, $J = 7.2$ Hz, $\underline{CH_3}$–CH_2–O), 1.24 (s, 6H, 4-CH_3), 2.08 (s, 3-CH_3), 3.50 (t, $J = 7.2$ Hz, CH_3–$\underline{CH_2}$–O), 4.32 (s, 2-C–$\underline{CH_2}$–O), 6.18

(d, $J = 9.9$ Hz, 6-CH), 6.68 (d, $J = 9.9$ Hz, 5-CH) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 15.63$ ($\underline{CH_3}$–CH_2–O), 16.03 (3-CH_3), 26.36 (4-CH_3), 40.77 (4-C), 62.78 (CH_3–$\underline{CH_2}$–O), 66.27 (2-C–$\underline{CH_2}$–O), 126.81 (6-CH), 132.40 (2-C), 157.15 (5-CH), 164.89 (3-C), 185.40 (1-C=O) ppm.

Acknowledgements

We would like to thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and DRAGOCO Gerberding & Co. GmbH for financial support.

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