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Stereochemistry of the Rubottom Oxidation with Bicyclic Silyl Enol Ethers; Synthesis and Dimerization Reactions of Bicyclic α-Hydroxy Ketones

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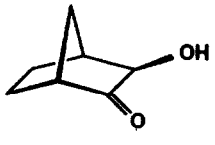
Key Words

Rubottom oxidation, stereochemistry, silyl enol ethers, α-hydroxy ketones, α-acyloxy ketones

Abstract: A modified and improved procedure for the Rubottom oxidation of bicyclic silyl enol ethers is described. The stereochemical outcome of this reaction is studied.

Recently we published an improved procedure[1] for the Lewis acid mediated reaction of α-hydroxy ketones with electron deficient acetylenes. For our studies towards the synthesis of model compounds for insect antifeedants related to the tricyclic hydroxy-dihydrofuran part of azadirachtin[2] we needed the bicyclic α-hydroxy ketones **1** (previously described in the literature[3]), **2** and **3**.



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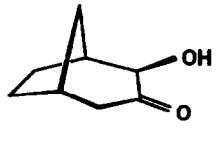

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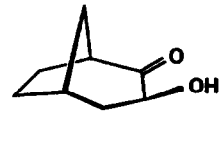


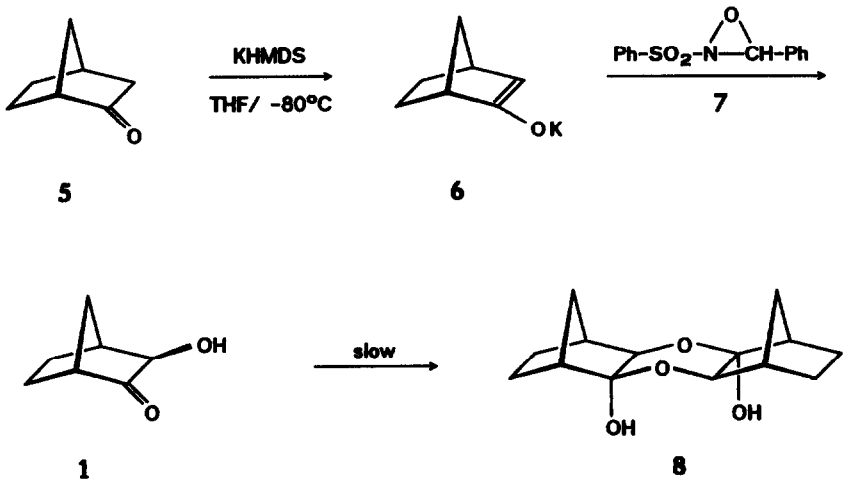
3

Several general procedures for the preparation of α-hydroxy ketones have been published: Davis oxidation[4] of enolates and silyl enol ethers with 2-sulphonyl

oxaziridines, Rubottom oxidation[5] of silyl enol ethers with mCPBA, Vedejs oxidation[6] of enolates with MoOPH or MoOPD, oxidation of silyl enol ethers with dimethyldioxirane[7] followed by hydrolysis, oxidation of silyl enol ethers with osmium tetroxide and N-methylmorpholine-N-oxide,[8] reaction of enolates with bis(trimethylsilyl) peroxide[9] and especially for α-hydroxy cyclohexanone, hydrolysis of α-bromo cyclohexanone[10] or oxidation of cyclohexanone with thallium(III)nitrate.[11]

Exo-3-hydroxy-bicyclo[2.2.1]heptan-2-one (**1**) has recently been synthesized by Creary[3] from 2-trimethylsilyloxy-bicyclo[2.2.1]hept-2-ene (**4**) according to the method of Rubottom[5] in 8% yield. Another approach has been reported by Jefford et al.[3], who used singlet oxygen to oxidize **4**, followed by deoxygenation with triphenylphosphine and hydrolysis in 68% yield.

We decided to prepare the desired α-hydroxy ketones according to the procedure of Davis and coworkers.[4] Bicyclo[2.2.1]heptan-2-one (**5**) was readily prepared according to Schleyer et al.[12] and transformed into its potassium enolate **6** by potassium-hexamethyldisilazide KHMDS at dry ice temperature. The reaction with (±)-trans-2-(phenylsulfonyl)-3-phenyloxaziridine (**7**) proceeded without difficulties (Scheme 1). The enolate was consumed within one hour and transformed into **1**. This was easily shown by GC analysis of the reaction mixture (yield determined by GC: 100%).



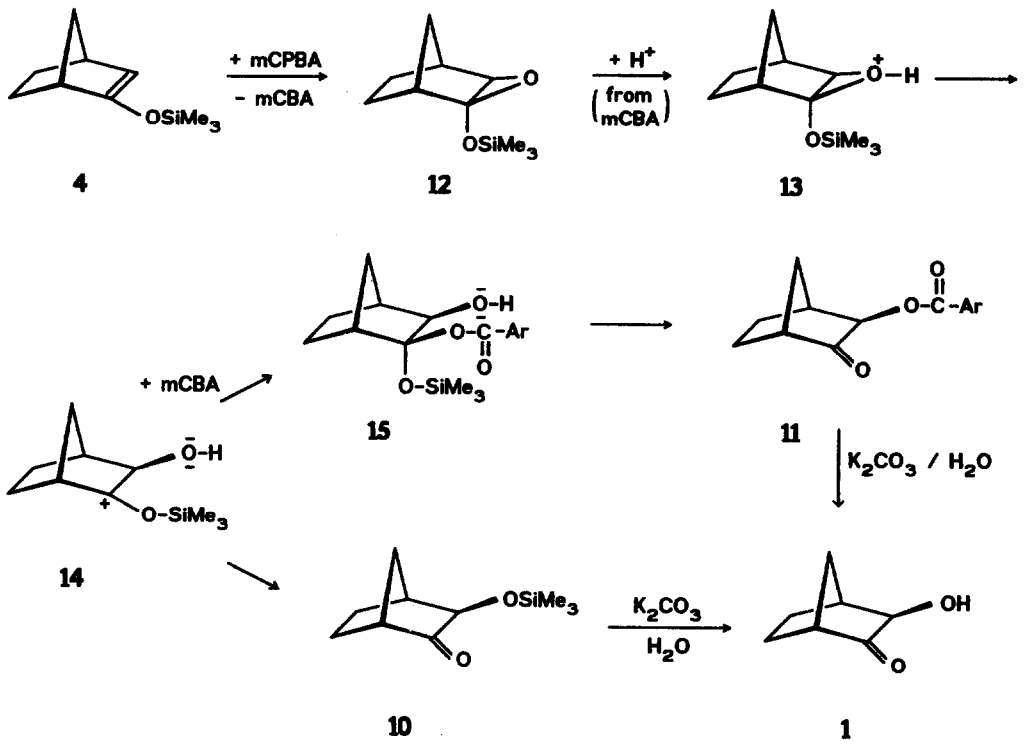
Scheme 1. Davis oxidation of bicyclo[2.2.1]heptan-2-one (**5**).

Unfortunately, work up and isolation of the pure compound proved to be not as straightforward as the reaction itself. Usually, Davis and coworkers isolate their α-hydroxy ketones by chromatography on silica gel, which is the method of choice in the case of such complex reaction mixtures (one product and at least three side products from the oxidizing reagent) However, in this case the chromatographic purification is not recommended for two reasons: firstly, **1** readily dimerizes, and secondly, **1** and **8** have approximately the same retention factor as phenylsulfonylamide (**9**) in all solvents and solvent mixtures tested. Separation of **8** and **9** by crystallization was similarly unsuccessful.

Finally, the reaction mixture was distilled. By this method, it was possible to isolate pure **1** in 30-35% yield. Unfortunately, large amounts of **1** remained in the distillation residue, even at temperatures of 200°C and pressures as low as 0,01 Torr. For this reason, the described method was abandoned.

Although Creary[3] reported low yields for the Rubottom oxidation of 2-trimethylsilyloxy-bicyclo[2.2.1]hept-2-ene (**4**) we decided to carefully study this reaction. **4** was easily prepared according to the excellent procedure published by Cazeau[13]. Rubottom oxidation using standard conditions (CH_2Cl_2, mCPBA, -15°C) indeed gave only small amounts of **1**, together with large quantities of **5** due to cleavage of **4** by m-chlorobenzoic acid (mCBA). We now succeeded in minimizing this side reaction by using a completely non polar solvent (e.g. pentane), adding sodium bicarbonate as buffer and running the reaction at lower temperature (-25°C). Only traces of **5** could be detected in the reaction mixture by TLC and GC. After 6 h at -25°C all the starting material was consumed and transformed into two products. The first product was the expected exo-3-trimethylsilyloxy-bicyclo[2.2.1]heptan-2-one **10** (R_f = 0.73; diethyl ether:pentane 1:1 (v/v)). The second one was exo-3-(3'-chlorobenzoyloxy)-bicyclo[2.2.1]heptan-2-one **11** (R_f = 0.55; diethyl ether:pentane 1:1 (v/v)). A possible reaction path explaining all the observed products is given in scheme 2.

Since we were interested in **1**, we tried several methods for the conversion of the reaction mixture into a single product: HCl/H_2O/MeOH, AMBERLYST®15/H_2O/MeOH, NaOH/H_2O/MeOH, DOWEX®/MeOH[14], TBAF/THF and NEt_3HF/THF[15], but all these were unsatisfactory. We found that a mild method for the conversion of **10** and **11** into **1** or **8** respectively, is stirring the crude product mixture with half saturated K_2CO_3 solution overnight. Furthermore, residual mCBA is also completely removed. In order to obtain good yields of **1** or **8** respectively, it is important to carefully extract the aqueous phase (for details see experimental part).



Scheme 2. Reaction pathway leading from **4** to **10**, **11** and **1**.

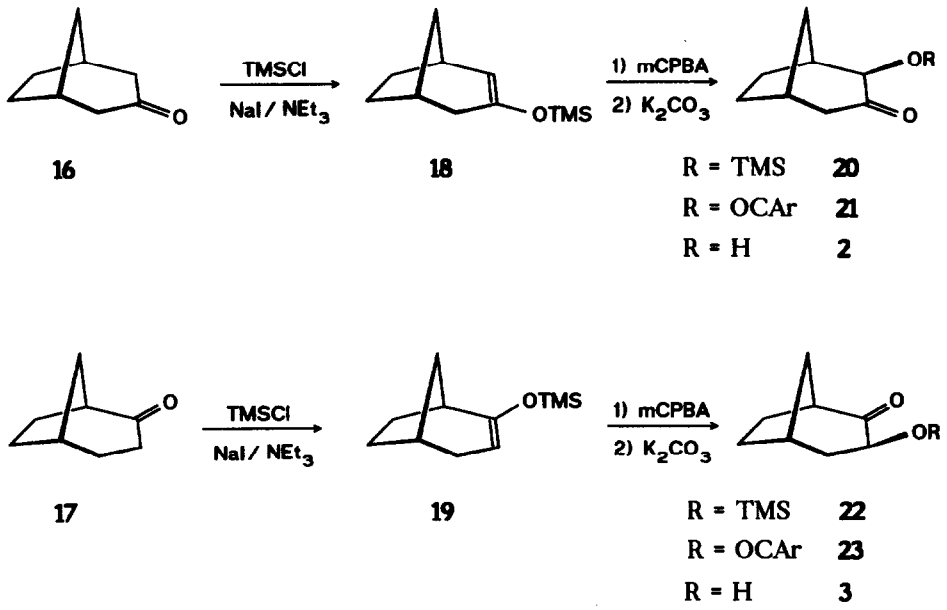
1 readily dimerizes to give **8**. The exo orientation of the hydroxy group in **1** results from the exo attack of mCPBA on **4** which is sterically favored over the endo attack. An additional proof for the stereochemistry depicted in scheme 2 is the X-ray structure of **8**.[16] The endo-H at C3 (3.40 ppm, d) couples with the bridgehead proton at C4. The coupling constant is 2.7 Hz which is in the range for vicinal coupling in the norbornane skeleton[3a].

Monomer **1** could be obtained from **8** by melting **8** at 170-175°C and subsequent sublimation of the monomer at ≈100°C and ≈15 Torr. For larger quantities, a Kugelrohr apparatus was found convenient.

By this method we prepared the hydroxy ketones **2** and **3**. The starting ketone **16** was prepared according to Kraus et al.,[17] ketone **17** according to Nedenskov et al..[18]

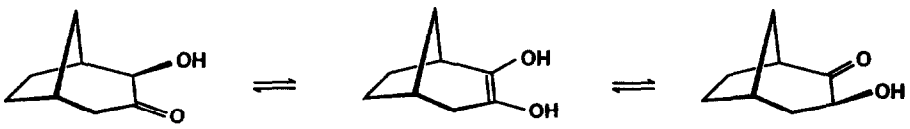
The corresponding trimethylsilyl enol ethers **18** and **19** were synthesized following the procedure of Cazeau et al.[13] (**19** has recently been described by Stothers et al.[19]).

Rubottom oxidation of both, **18** and **19** led in both cases to a mixture of the corresponding α-trimethylsilyloxy ketone and α-(3'chlorobenzoyloxy) ketone, which were not isolated but hydrolyzed directly after reaction with mCPBA (Scheme 3.).



Scheme 3. Synthesis of α-hydroxy ketones **2** and **3**.

Hydrolysis has to be carried out at 0°C due to decomposition and base catalyzed rearrangement (via the ene diol) of **2** and **3** (Scheme 4.). The pure compounds were isolated by flash chromatography. (**2** still contains very small amounts of the corresponding endo isomer after chromatography).



2 3

Scheme 4. Base catalyzed rearrangement of **2** and **3**.

The exo or axial orientation of the hydroxy group in **2** and **3** was established by ^{1}H-NMR spectroscopy. In **2** the endo or equatorial H at C2 (3.63 ppm, d) couples with the bridgehead proton at C1 with ^3J = 3.6 Hz. These values, especially the chemical shift of the equatorial proton, are in accordance with published data[20]. In **3** the endo proton at C3 (4.10 ppm, dd) couples with the two protons at C4 to give a doublet of doublets with the coupling constants $^3J_{ax,ax}$ = 8.61 Hz and $^3J_{ax,eq}$ = 7.82 Hz.

For sterical reasons the hydroxy ketones **2** and **3** do not dimerize.

Experimental

All reactions were carried out in oven dried glassware (140°C, 8h) which was assembled when still hot and immediately flushed with dry N_2. Pentane was dried by refluxing over Na dispersion and distillation under N_2. THF was dried and freed from peroxides by filtering through a column of basic Al_2O_3, refluxing over Na dispersion and distillation under N_2. Triethylamine was refluxed over CaH_2 and distilled under N_2. Acetonitrile was dried with molecular sieves (4 Å) and flushed with N_2. Trimethylsilylchloride was purchased from Fluka, Neu-Ulm, Germany, and distilled under N_2. mCPBA (technical product containing mCPBA, mCBA and water) was purchased from Janssen Chimica, Brüggen, Germany, and was dried by dissolving in CH_2Cl_2, drying with $MgSO_4$ and evaporating the solvent. It was stored in an exsiccator under N_2 at 4°C. The peroxide content was established iodometrically (NaI, H_2O, HOAc, $CHCl_3$, then titration with 0.1 n $Na_2S_2O_3$ solution). TLC was performed with TLC plates SIL G 25 UV_{254} from Macherey-Nagel, Düren, Germany. The spots were visualized with I_2 vapours or by spraying with a mixture of 0.5 ml 4-methoxy-benzaldehyde, 50 ml HOAc and 1 ml H_2SO_4 conc. and heating a few minutes to 100-120°C. For flash chromatography, silica gel (32-63μm) from Merck, Darmstadt, Germany, was used. ^{1}H-NMR spectra were recorded on a Bruker AC 250 spectrometer (250 MHz), ^{13}C-NMR spectra

on the same machine (62.896 MHz). IR spectra were recorded on a Perkin Elmer 281 B spectrometer and mass spectra were recorded on a Finnigan MAT TSQ 70 under EI conditions.

2-Trimethylsilyloxy-bicyclo[2.2.1]hept-2-ene (4), 3-Trimethylsilyloxy-bicyclo[3.2.1] oct-2-ene (18) and 2-Trimethylsilyloxy-bicyclo[3.2.1]oct-2-ene (19).

In a 1 l three necked round bottom flask with magnetic stirrer, reflux condenser, dropping funnel and N_2-inlet, 0.2 mol of the appropriate ketone was dissolved in 200 ml pentane. A solution of 0.25 mol NaI (dried in a drying pistol at 140°C over KOH for 8-12h) in 250 ml acetonitrile was added. Then 0.25 mol triethylamine was added and finally 0.25 mol trimethylsilyl chloride was added dropwise. During stirring overnight at room temperature a white precipitate ($HNEt_3I$) was formed. The pentane phase was separated and the acetonitrile phase was extracted three times with 200 ml pentane. The combined pentane phases were evaporated in vacuo and distilled through a Vigreux column at reduced pressure.

4: boiling point: 86°C/25 Torr; yield: 87%; ^{1}H-NMR ($CDCl_3$, 250 MHz): 4.65 (1H, d, J 3.24 Hz, H3); 2.73 (1H, m, H4); 2.52 (1H, m, H1); 1.68-0.99 (6H, m, CH-C$\underline{H}_2$-C$\underline{H}_2$-CH and CH-C$\underline{H}_2$-CH); 0.16 (9H, s, $(CH_3)_3Si$); ^{13}C-NMR ($CDCl_3$, 62.896 MHz): 161.0 (s, C2); 105.3 (d, C3); 46.9 (t, C7); 45.4 (d, C1); 40.9 (d, C4); 27.6 (t, C5); 24.6 (t, C6); -0.1 (q, $(CH_3)_3Si$); IR (film): 3080 (m); 2960-2870 (s); 1610 (s); MS: 182 (M^+, 12%); 167 (M^+-CH_3, 12%); 154 (M^+-C_2H_4, 92%); 73 (Me_3Si^+,100%); $C_{10}H_{18}OSi$: calc.: 182.1127; found: 182.1102.

18: boiling point: 82-84°C/9 Torr; yield: 91-92%; ^{1}H-NMR ($CDCl_3$, 250 MHz): 4.9 (1H, d, J 7.1 Hz, H2); 2.27-2.19 (3H, m, H4 and $H8_{syn}$); 1.75-1.18 (7H, m) 0.0 (9H, s, $(CH_3)_3Si$); ^{13}C-NMR ($CDCl_3$, 62.896 MHz): 148.7 (s, C3); 111.7 (d, C2); 41.7 (t, C4); 36.0 (t, C8 and d, C1); 33.9 (t, C6); 33.5 (t, C7); 30.2 (d, C5); IR (film): 3050 (w); 2950-2830 (s); 1655 (m); MS: 196 (M^+, 18%); 181 (M^+-CH_3, 10%); 167 (M^+-CH_3-CH_2, 100%); 151 (M-3CH_3, 50%); 73 ($SiMe_3^+$, 43%); $C_{11}H_{20}OSi$: calc.: 196.1283; found: 196.1318.

19: boiling point: 84-85°C/10 Torr (Lit[19]: 90-95°C/4 Torr); yield: 81%; ^{1}H-NMR ($CDCl_3$, 250 MHz): 4.25 (1H, m, H3); 2.14-2.08 (2H, m); 2.00-1.97 (1H, m); 1.76-1.47 (4H, m); 1.32-1.24 (3H, m); 0.0 (9H, s, $(CH_3)_3Si$); ^{13}C-NMR ($CDCl_3$, 62.896 MHz): 156.8 (s, C2); 98.1 (d, C3); 41.3 (d, C1); 35.3 (t, C4); 34.5 (t, C8); 33.9 (d, C6); 32.9 (t, C6); 30.3 (t, C7); 0.3 (q, $(CH_3)_3Si$); IR (film): 3050-3020 (w); 2950-2840 (s); 1660 (s); MS: 196 (M^+, 48%); 181 (M^+-CH_3, 20%); 168 (M^+-C_2H_4, 41%); 167 (M^+-CH_3-CH_2, 50%); 73 ($(CH_3)_3Si$, 100%); $C_{11}H_{20}OSi$: calc.: 196.1283; found: 196.1314.

exo-3-Hydroxy-bicyclo[2.2.1]heptan-2-one (1). In a 1 l three necked round bottom flask with cooling jacketed dropping funnel, N_2-inlet, magnetic stirrer and bubbler, 11.3 g mCPBA (55 mmol, 85%) and 18.5 g $NaHCO_3$ (0.22 mol) were suspended in 300 ml pentane. This mixture was stirred for 10 min. at room temperature and then cooled to -25°C. A solution of 9.1 g (50 mmol) 2-trimethylsilyloxy-bicyclo [2.2.1]hept-2-ene (**4**) in 50 ml pentane was rapidly added after cooling to -25°C and stirring was continued for 6 h. Then the precipitate was filtered off and the residue was carefully washed with cold diethyl ether. **Testing the filtrate with KI for peroxides is highly recommended. If there is still some mCPBA present, the combined filtrates have to be treated with a few ml of saturated Na_2SO_3-solution to reduce the peracid.** Then the organic solvent was evaporated under reduced pressure and the residue was stirred vigorously with 500 ml half saturated K_2CO_3 solution for 10-12 h at room temperature. A white precipitate **8** was formed. The reaction mixture was carefully extracted with 10 portions of 100 ml methylene chloride. The white precipitate **8** was combined with the organic phases. After extraction THF was added to the combined organic phases until all **8** has been dissolved. Drying with $MgSO_4$ and evaporating the solvent yielded a white slurry of **1** and **8** which solidified upon standing at room temperature for 3-5 days. The dimer was crystallized from small amounts of dry CH_3OH or large amounts of dry $CHCl_3$. yield: 6.3 g (quant.). Melting **8** at 170-175°C (melting point 168-170°C) under an atmosphere of N_2, cooling down to 100-120°C and sublimation at 15 Torr gives **1**.

1: ^{1}H-NMR ($CDCl_3$, 250 MHz): 3.84 (1H, s, OH); 3.40 (1H, d, $H3_{endo}$, J 2.7 Hz); 2.45 (1H, br. s.); 2.42 (1H, br. s.); 2.05-1.22 (6H, m); ^{13}C-NMR ($CDCl_3$, 62.896 MHz); 217.9 (s, C2); 75.3 (d, C3); 47.8 (d, C4); 41.5 (d, C1); 34.0 (t, C7); 23.9 (t, C5); 23.5 (t, C6); IR (film): 3380 (s); 2940-2850 (s); 1730 (s); IR ($CHCl_3$, 40 mg/ml): 3540 (m, free OH); 3460 (m, OH with hydrogen bonding); MS: 126 (M^+, 10); 98 (M^+-CO, 10%); 57 ($C_2HO_2^+$, 100%); $C_7H_{10}O_2$: calc.: 126.0681; found: 126.0697.

8: ^{1}H-NMR (DMSO-d_6, 250 MHz): 5.51 (2H, s, OH); 3.40 (2H, d, J 1.8 Hz, H3); 2.09 (2H, br. d, $H7_{syn}$); 2.01 (2H, br. s); 1.99 (2H, br. s); 1.81-1.73 (2H, m); 1.58-1.49 (2H, m); 1.31-1.16 (6H, m); ^{13}C-NMR (Aceton-d_6, 100 MHz): 102.5 (s, C2); 77.6 (d, C3); 48.0 (d, C4); 43.4 (d, C1); 36.3 (t, C7); 25.0 (t, C5); 23.7 (t, C6); IR (KBr): 3450 (s); 2980-2880 (s); MS: 234 (M^+-H_2O, 3%); 126 (M^+/2, 20%); 82 (M^+/2-CO_2, 56%); 57 ($C_2HO_2^+$, 100%).

exo-2-Hydroxy-bicyclo[3.2.1]octan-3-one (2) and exo-3-hydroxy-bicyclo[3.2.1]octan-2-one (3): In a 1 l three necked round bottom flask with cooling jacketed dropping funnel, N_2-inlet, magnetic stirrer and bubbler, 11.3 g mCPBA (55 mmol, 85%) and 18.5 g $NaHCO_3$ (0.22 mol) were suspended in 300 ml pentane. This mixture was stirred for 10 min. at room temperature and then cooled to 0°C. A solution of 9.8 g (50 mmol)

3-trimethylsilyloxy-bicyclo[3.2.1]oct-2-ene (**18**) [2-trimethylsilyloxy-bicyclo[3.2.1]oct-2-ene (**19**)] in 50 ml pentane was rapidly added after cooling to 0°C and stirring was continued for 12 h. Then the precipitate was filtered off and the residue was carefully washed with cold diethyl ether. **Testing the filtrate with KI for peroxides is highly recommended. If there is still some mCPBA present, the combined filtrates have to be treated with a few ml of saturated Na_2SO_3-solution to reduce the peracid.** Then the organic solvent was evaporated under reduced pressure and the residue was stirred vigurously with 500 ml half saturated K_2CO_3 solution for 16-20 h at 0°C. The reaction mixture was carefully extracted with 10 portions of 100 ml methylene chloride. Drying with $MgSO_4$ and evaporating the solvent yielded the crude product, which was purified by flash chromatography (pentane : diethyl ether 1:1 v/v). yield:(**2**): 5.6 g (80%); melting point 177-179°C [(**3**): 5.0 g (71%), colorless oil].

2: ^{1}H-NMR ($CDCl_3$, 250 MHz): 3.63 ppm (1H, d, H2, J 3.6 Hz); 3.61 (1H, s, OH); 2.63 (1H, ddd, $H8_{syn}$, J 14.0 Hz, 4.2 Hz, 1.6 Hz); 2.53-2.35, 2.20-2.07, 1.41-1.09 (9H, m); ^{13}C-NMR ($CDCl_3$, 62.896 MHz): 212.8 (s, C3); 78.7 (d, C2); 46.7 (t, C4); 41.0 (t, C8); 34.7 (d, C1); 31.3 (t, C5); 28.4 (t, C6); 24.6 (t, C7); IR (KBr): 3390 (s); 2960-2780 (s); 1705 (s); MS: 140 (M^+, 53%); 111 (M^+-C_2H_4, 49%); 94 (M^+-C_2H_4-H_2O, 76%); 79 (M^+-C_2H_4-H_2O-CH_2, 100%); $C_8H_{12}O_2$: calc.: 140.0837; found: 140.0837.

3: ^{1}H-NMR ($CDCl_3$, 250 MHz): 4.10 (1H, dd, H3, J 8.61 Hz, 7.82 Hz); 4.11 (1H, s, OH); 2.80 (1H, t, J 5.5 Hz, $H4_{endo}$); 2.35 (2H, m); 1.86-1.72 (4H, m); 1.68-1.54 (4H, m); ^{13}C-NMR ($CDCl_3$, 62.896 MHz); 213.7 (s, C2); 71 (d, C3); 49.2 (d, C1); 43.2 (t, C4); 40.0 (t, C8); 34.2 (d, C5); 28.2 (t, C6); 27.0 (t, C7); IR (film): 3440 (s); 2930-2850 (s); 1695 (s); MS: 140 (M^+, 46%); 94 (M^+-C_2H_4-H_2O, 69%); 79 (76%); 67 ($C_6H_7^+$, 100%); $C_8H_{12}O_2$: calc.: 140.0837; found: 140.0839.

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