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CYCLIZATION OF 1,3-DISUBSTITUTED 2-(3-BUTENYL)-2-CYCLOHEXEN-1-OLS

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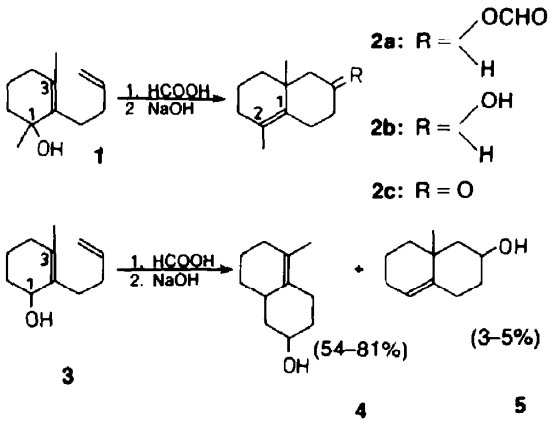
Abstract—The cationic cyclization of cyclohexenols **8a–c** gave mixtures of the octalinols **9a–c** and **10a–c** with **9a–c** as main products. By cyclization of the isomeric educts **13a–c**, the same products were formed in different proportions.

The cationic cyclization of terminally functionalized polyolefins has been developed as a biomimetic method[1] for the stereoselective synthesis of polycyclic systems. In addition to a great number of open-chain educts, cyclic systems such as the 1,3-disubstituted cyclohexenol derivative **1** were tested. Treatment of **1** with formic acid gave the octalin derivative **2a** and after saponification **2b**.[2] The cyclohexenol **3**, unsubstituted at C-1, was preferentially cyclized to **4**,[3,4] the product of bond formation at C-1. Small amounts of the alternative product **5**[4] with an angular Me group were also formed.



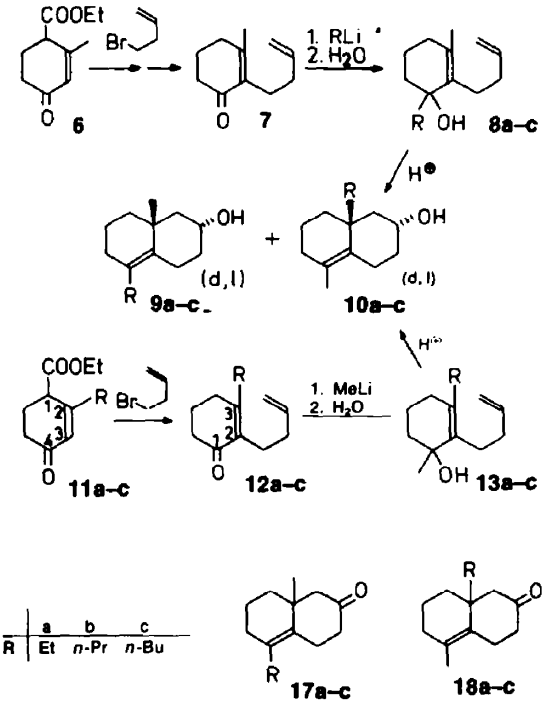
Scheme 1.

Substituted octalin derivatives with angular Me groups are useful intermediates in the syntheses of steroids,[5] terpenoids[6] and fragrance compounds of the ambergris type.[7] We therefore tested the cationic cyclization of the alternatively 1,3-disubstituted 2-(3-butenyl)-2-cyclohexen-1-ols **8a–c** and **13a–c**, as described below.

Cyclization of cyclohexenols **8a–c**

The preparation of cyclization educts **8a–c** started from the cyclohexenone **7**[3], obtained by alkylation[8] of Hagemann's ester (**6**) with 3-butenyl bromide and subsequent saponification and decarboxylation. Treatment of **7** with lithium alkyls and hydrolysis of the addition products resulting thereby, gave the unstable cyclohexenols **8a–c**, which were directly used in the cyclization reactions.

In order to test different cyclization conditions we started with **1** and obtained the known product **2a**[2] in different yield. Substance **2a**, the product of saponification **2b** and the oxidation product **2c** with their demonstrated structures were also used as reference substances in this paper. Compound **2b**, as well as **2c**, easily undergoes partial $\Delta^1 \rightarrow \Delta^2$-double bond isomerization, i.e. during column chromatography (NMR: $\delta = 5.02$, m, 3-H; 0.9 ppm, s, 6-CH_3).



Scheme 2.

The carbinols **8a–c** were cyclized under the different typical reaction conditions tested with **1** (Table 1). By treatment with anhydrous formic acid at room temperature, the 1-ethylcyclohexenol **8a** gave a 3:2 mixture of the constitution isomers **9a/10a**, which were separated by preparative glc. The clearest evidence for the postulated structures comes from the ^{1}H-NMR spectra. The angular Me group of **9a** gives a singulet at $\delta = 1.06$ ppm and the C-2 Et group a triplet at $\delta = 0.92$ ppm. In contrast, **10a** shows a triplet at $\delta = 0.77$ ppm (angular Et group) and a broad singulet at $\delta = 1.63$ ppm (C-2 Me group). In addition, the angular substituents were characterized by mass spectrometrical fragmentation (see below). The cyclization of the higher homologues **8b** and **8c** preferentially resulted in **9b** and **9c**, respectively, which likewise are characterized by the ^{1}H-NMR-signals of their angular Me groups ($\delta = 1.05$–1.07 ppm); the by-

Table 1. Product ratio of octalinols **9a–c/10a–c**, the cyclization products of **8a–c** and **13a–c**.

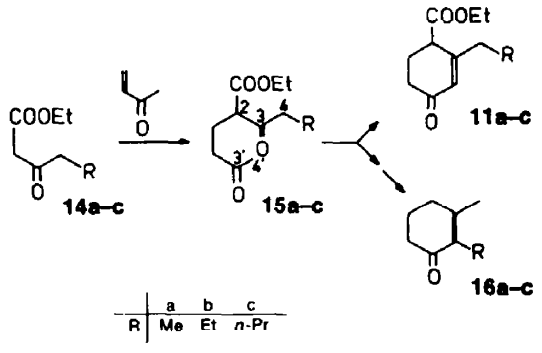
Reaction conditions	Educt	Yield (%)	Product ratio	
			9a	**10a**
HCOOH (room temp.)	**8a**	70	59.5	40.5
	13a		48.0	52.0
HCOOH/Cyclohexane (room temp.)	**8a**	89	59.5	40.5
	13a		47.9	52.1
CF_3COOH/CH_2Cl_2 (-30°C)	**8a**	85	59.6	40.4
	13a		47.9	52.1
CF_3COOH/CH_2Cl_2 (-75°C)	**8a**	83	53.8	46.2
	13a		49.9	50.1
			9b	**10b**
HCOOH/Cyclohexane (room temp.)	**8b**	91	85.6	14.4
	13b		71.8	28.2
CF_3COOH/CH_2Cl_2 (-75°C)	**8b**	84	83.7	16.3
	13b		75.9	24.1
			9c	**10c**
HCOOH/Cyclohexane (room temp.)	**8c**	89	87.6	12.4
	13c		70.0	30.0
CF_3COOH/CH_2Cl_2 (-75°C)	**8c**	82	85.9	14.1
	13c		74.6	25.4

products **10b** and **10c** show broad singulets at $\delta =$ 1.63 ppm. The α-configuration of the C-8 OH group is demonstrated by the ^{1}H-NMR-multiplet ($\delta = 3.4 - 4.2$ ppm, axial proton).[9]

Cyclization of cyclohexenols **13a–c**

The preparation of the alternative cyclization educts **13a–c** was carried out by analogy to the synthesis of **8a–c**. Alkylation of the esters **11a–c** with 3-butenyl bromide and subsequent saponification and decarboxylation led to the C-3 substituted cyclohexenones **12a–c**, which were treated with methyl lithium to give the cyclohexenols **13a–c**.

The cyclic esters **11a–c** were synthesized by Michael addition of methyl vinyl ketone and the oxo-esters **14a–c** and subsequent cyclocondensation of the thereby obtained dioxo-esters **15a–c**. By treatment of **15a–c** with pyrrolidine/acetic acid,[10] the desired esters **11a–c** were formed preferentially by C-3/C-4′ bond formation. The by-products of the alternative cyclo condensation were



Scheme 3.

easily decarboxylated into **16a–c**, which were separated by distillation.

Cyclization reactions with the 1-methyl-3-alkyl-cyclohexenols **13a–c** were carried out under the same reaction conditions as were used for **8a–c**. The resulting produc

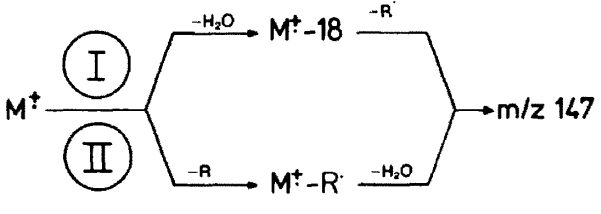
mixtures consisted of the same compounds **9a–c/10a–c**, but in different proportions than obtained from **8a–c** (Table 1). In contrast to the cyclizations of **8a–c**, **13a** and especially the higher homologues **13b,c** lead to a higher proportion of **10b,c**, the products with a voluminous substituent in the angular position. Lowering the cyclization temperature of **13a–c** resulted in an increasing of compounds **9a–c**, while **8a–c** shows an increasing of compounds **10a–c**. The ketones **17a–c** and **18a–c**, useful for the structure elucidation of cyclization products, were synthesized by Jones-oxidation of the product mixtures of cyclization reactions.

The acid catalyzed cyclization of cyclohexenols **8a–c** may occur by formation of an intermediate allylic cation. By attack of the side-chain double bond, bond formation is possible at C-1 and C-3, respectively. The ratio of products formed thereby would be determined by steric (conformative) or inductive effects of the substituents. Starting with the alternative educts **8a–c** and **13a–c**, respectively, the same allylic cation would be formed as an intermediate in an asynchronous course of the cyclization reaction. The product ratio **9a–c/10a–c** of both types of educts (**8a–c** or **13a–c**) would be identical.

A synchronous course of cyclization, also named "non stop reaction,"[1] would be achieved by dehydration and simultaneous attack of the side chain double bond at C-1 and, alternatively, at C-3 by $\Delta^2 \rightarrow \Delta^1$-double bond shift. The results given above (Table 1), especially the different ratio of products obtained from **8b,c** or **13b,c**, point to a partial occurrence of a synchronous mechanism at room temperature. At lower temperatures the asynchronous cyclization mechanism is favored.

Differentiation between the octalinols **9a–c/10a–c** *and the ketones* **17a–c/18a–c** *by mass spectrometry*

The octalinols **9a–c/10a–c** may decompose by the fragmentation paths I and II, respectively.



Scheme 4.

The compounds **10a–c** intensively eliminate an alkyl radical from the quarternary centre by breaking of an allylic bond. By subsequent elimination of water an additional stabilization of the ring system is possible. The peaks at *m/z* 147 correspond to this process. The fragmentation of **9a–c** is more complex. A double bond in the allylic position favours the loss of a Me radical; also the M^+-H_2O fragment intensively occurs. As expected, the loss of an alkyl radical from the molecular ion is considerably decreased compared to the octalinols **10a–c**.

The ketones **18a–c** also show the intensive loss of alkyl radicals in analogy to the corresponding alcohols **10a–c**. By high resolution mass measurements of **17a–c** the occurrence of an O atom in the M^+-43 and M^+-57-ions was confirmed. The octalins **10a–c/18a–c** preferentially fragmentate along way II and—in contrast—the constitution isomers **9a–c/17a–c** according to way I. The two types of substituted octaline-derivatives are easily distinguished by mass spectrometry.

EXPERIMENTAL

Glc: HP 5711 (Hewlett-Packard), 25 m glass capillary, WG 11 as stationary phase, N_2 as carrier gas, retention time (t_r) relative to methane, temp-programme 100–220°, 4°C/min. Preparative Glc: 700—Autoprep (Wilkens Instruments) 3/8" steel column, 3 m Carbowax C 20 M. Preparative tlc: 1 part Kieselgel 60 $Pf_{254+366}$ (Merck) was dispersed with 2.5 parts water and deposited (1 mm thickness) on glass plates (20 × 20 cm); after air drying they were activated (4 h at 160°). NMR: (CCl_4, TMS as internal standard): Varian A 60 spectrometer. IR spectra as capillary films: PE-125 (Perkin–Elmer). Mass spectra (MS) as glc/MS-combination: HP 5992 (Hewlett-Packard), 50 m glass capillary WG 11; CH-5 + GC-1740 (Varian MAT), 50 m glass capillary OV 101. Elementary analyzes: Mikroanalytisches Laboratorium Ilse Beetz, Kronach (Germany).

2-Alkyl-1-carbethoxy-4-oxo-2-cyclohexenes **11a–c**

At a reaction temp of 5–10°, 70 g (1 mol) methyl vinyl ketone were added dropwise (30 min) to a stirred soln of 4.5 g NaOMe in 8 ml MeOH and 130 g (1 mol) ethyl acetoacetate, resp. 144 g (1 mol) ethyl-3-oxo-hexanoate, resp. 158 g (1 mol) ethyl-3-oxo-heptanoate. Each of the resulting mixtures was stirred for 1 hr at room temp and then treated with 5 ml AcOH, 150 ml MeOH/water (9:1) and a soln of 6 g pyrrolidine in 6.5 g AcOH. The resulting soln was heated under reflux for 2 hr. Evaporation of solvents, addition of 100 ml water, extraction with ether, working up and distillation gave the esters **11a–c**.

2-Ethyl-1-carbethoxy-4-oxo-2-cyclohexene (**11a**): from ethyl-acetoacetate. 153 g (78%). Bp. (2 mm) = 130–135°. Purity: 94% (glc). NMR: δ = 1.10, t, J = 7 Hz ($-CH_2-CH_3$), 1.27, t, J = 7 Hz ($-O-CH_2-CH_3$), 3.30, "t", J = 5 Hz (4-H), 4.20, q, J = 7 Hz ($-O-CH_2-CH_3$), 5.85 ppm (2-H). IR: ν = 1730 (ester); 1675, 1630 cm^{-1} (α,β-unsat. ketone). MS: *m/z* (%) = 196 (48, M^+), 160 (25), 151 (10), 140 (40), 123 (96), 112 (100). Found: C, 67.73; H, 8.15. Calc. for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22%.

2-Propyl-1-carbethoxy-4-oxo-2-cyclohexene (**11b**). from ethyl 3-oxo-hexanoate. 145 g (79%). Bp. (1 mm) = 132–138°. Purity: 90% (glc). NMR: δ = 0.95, "t", J = 7 Hz ($-CH_2-CH_3$), 1.28, t, J = 7 Hz ($-O-CH_2-CH_3$), 3.27, "t", J = 5 Hz (4-H), 4.16, q, J = 7 Hz ($-O-CH_2-CH_3$), 5.80 ppm, (2-H). IR: ν = 1730 (ester); 1670, 1625 cm^{-1} (α,β-unsat. ketone). MS: *m/z* (%) = 210 (69, M^+), 181 (58). Found: C, 68.49; H, 8.58. Calc. for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63%.

2-Butyl-1-carbethoxy-4-oxo-2-cyclohexene (**11c**). from ethyl-3-oxo-heptanoate. 166 g (74%). Bp. (1 mm) = 140–145°. Purity: 78% (glc); an analytical amount was purified by prep. tlc (cyclohexane-EtOAc, 4:1). NMR: δ = 0.93, "t", J = 7 Hz ($-CH_2-CH_3$), 1.27, t, J = 7 Hz ($-O-CH_2-CH_3$), 3.32, "t", J = 5 Hz (4-H), 4.15, q, J = 7 Hz ($-O-CH_2-CH_3$), 5.83 ppm (2-H). IR: ν = 1730 (C=O, ester); 1675, 1625 cm^{-1} (α,β-unsat. ketone). MS: *m/z* (%) = 224 (76, M^+), 195 (67), 182 (18), 179 (15), 167 (16), 154 (100), 151 (88). Found: C, 69.60; H, 8.94. Calc. for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99%.

3-Alkyl-2-cyclohexen-1-ones **6**, **12a–c**

Under N_2 81 g (0.5 mol) **6**, resp. 98 g (0.5 mol) **11a**, resp. 105 g

Table 2. Fragmentations and relative intensities* of the compounds **9a–c** and **10a–c**

	9 (angular CH_3-group)					10 (angular substituent)				
R	$M^{+\cdot}-CH_3$	$M^{+\cdot}-H_2O$	$M^{+\cdot}-33$	$M^{+\cdot}-R^{\cdot}$	m/z 147	$M^{+\cdot}-CH_3$	$M^{+\cdot}-H_2O$	$M^{+\cdot}-33$	$M^{+\cdot}-R^{\cdot}$	m/z 147
a) C_2H_5	30 %	41 %	100 %	20 %	77 %	-	1 %	3 %	69 %	100 %
b) C_3H_7	27 %	38 %	100 %	23 %	91 %	2 %	2 %	5 %	76 %	100 %
c) C_4H_9	30 %	26 %	65 %	31 %	100 %	-	1 %	1 %	75 %	100 %

+)

Intensities correlated to the base peak

(0.5 mol) **11b**, resp. 112 g (0.5 mol) **11c** were added to a suspension of 15 g (0.5 mol) sodium hydride (80% in paraffin). After boiling the mixtures under reflux (H_2-formation) and cooling to room temp, 0.1 g KI and 66 g (0.5 mol) 1-bromo-butene-3 were added. The mixtures were heated to reflux under N_2 (40 h) and then cooled to room temp. The product mixture, obtained by addition of 200 ml water, separation of the organic layer, drying and evaporation, was solved in a soln of 40 g KOH in 400 ml EtOH and heated to reflux for 24 hr (under N_2). Evaporation of the EtOH, addition of water, neutralization with dil H_2SO_4 extraction with ether, washing of the combined organic layers with brine, drying with Na_2SO_4 and evaporation resulted in 65–80 g of the crude products, which were purified by distillation.

3-*Methyl*-2-(3-*butenyl*)-*cyclohex*-2-*en*-1-*on* (**6**)[3]. 45 g (55%). Bp. (1 mm) = 80–84°. NMR: δ = 1.93, s (3-CH_3), 4.7–4.8 and 4.85–5.1, 2 m (4'-H), 5.4–6.1 ppm, m (3'-H). IR: ν = 3080, 1640 (–CH=CH_2); 1665, 1630 cm^{-1} (α,β-unsat. ketone). MS: *m/z* (%) = 164 (54, M^+), 149 (83), 146 (12), 135 (51), 131 (25), 123 (55), 95 (65), 67 (100). $C_{11}H_{16}O$(164.24).

3-*Ethyl*-2-(3-*butenyl*)-*cyclohex*-2-*en*-1-*on* (**12a**). Fraction 1: 37 g (42%) **12a**. Bp. (0.8 mm) = 77–80°. Fraction 2: 8 g (60% **12a** + 40% γ-alkylation product). NMR: δ = 1.10, t, J = 7.5 H (–CH_2–CH_3), 4.70–4.85 + 4.85–5.15, 2 m (4'-H), 5.45–6.15 ppm (3'-H). IR: ν = 3080, 1640 (–CH=CH_2); 1665, 1620 cm^{-1} (α,β-unsat. ketone). UV (EtOH): λ_{max} = 247 nm, ϵ = 12 300. MS: *m/z* (%) = 178 (15, M^+), 163 (12), 160 (2), 149 (100), 137 (34), 136 (43), 131 (16), 123 (12), 109 (25). Found: C, 80.89, H, 10.08. Calc. for $C_{12}H_{18}O$: C, 80.85; H, 10.18%.

3-*Propyl*-2-(3-*butenyl*)-*cyclohex*-2-*en*-1-*on* (**12b**). 33 g (34%). B.p. (1 mm) = 90–92°C. NMR: δ = 0.93, "t" (–CH_2–CH_3), 4.70–4.85 + 4.90–5.15, 2 m (4'-H), 5.35–6.10 ppm (3'-H). IR: ν = 1665, 1620 (α,β-unsat. ketone), 1640 cm^{-1} (–CH=CH_2). MS: *m/z* (%) = 192 (14, M^+), 177 (15), 174 (4), 163 (23), 159 (5), 149 (100), 136 (54). Found: 81.23; H, 10.41. Calc. for $C_{13}H_{20}O$: C, 81.20; H, 10.48%.

3-*Butyl*-2-(3-*butenyl*)-*cyclohex*-2-*en*-1-*on* (**12c**). 30 g (29%) raw product, 80% (glc); purification by column-chromatography on 400 g alumina (activity II), elution with cyclohexane gave 12 g tlc-pure **12c**. NMR: δ = 0.94, "t" (–CH_2–CH_3), 4.70–4.85 + 4.90–5.10, 2 m (4'-H), 5.4–6.1 ppm (3'-H). IR: ν = 1670, 1620 (α,β-unsat. ketone), 1640 cm^{-1} (–CH=CH_2). MS: *m/z* (%) = 206 (9, M^+), 191 (5), 177 (28), 165 (11), 164 (15), 163 (11), 159 (5), 149 (100), 136 (61). Found: C, 81.45; H, 10.75. Calc. for $C_{14}H_{22}O$ C, 81.50; H, 10.75%.

1-*Alkyl*-3-*methyl*-2-(3-*butenyl*)-*cyclohex*-2-*en*-1-*ols* (**1, 8a–c**). Under stirring 35.5 g (0.25 mol) MeI, resp. 27.3 g (0.25 mol) EtBr, resp. 30.8 g (0.25 mol) n-PrBr, resp. 34.3 g (0.25 mol) n-BuBr, each solved in 200 ml dry ether, were dropped into a mixture of 3.5 g (0.5 mol) Li in 300 ml dry ether. To the solns of organo lithium compounds, formed thereby, 18.2 g (0.1 mol) **6** and 100 ml dry ether were added dropwise. After refluxing for 30 min, the mixtures were hydrolysed. The organic layers were dried and evaporated by the usual way.

1,3-*Dimethyl*-2-(3-*butenyl*)-*cyclohex*-2-*en*-1-*ol* (**1**). 17.5 g (97%) colourless oil. NMR: δ = 1.23, s (1-CH_3), 1.63 "s" (3-CH_3), 4.75–4.90 + 4.90–5.15, 2 m (4'-H), 5.40–6.15 ppm (3'-H). IR: ν = 3420 (–O–H); 3000, 1640 cm^{-1} (–CH=CH_2). $C_{12}H_{20}O$ (180.28).

1-*Ethyl*-3-*methyl*-2-(3-*butenyl*)-*cyclohex*-2-*en*-1-*ol* (**8a**). 1.84 g (95%), colourless oil. NMR: δ = 0.82, t, J = 7 Hz (–CH_2–CH_3), 1.66, "s" (3-CH_3), 4.75–4.90 + 4.90–5.15, 2 m (4'-H), 5.40–6.15 ppm, m (3'-H). IR: ν = 3460 (O–H), 3080, 1640 cm^{-1} (–CH=CH_2). $C_{13}H_{22}O$ (194.31).

3-*Methyl*-1-*propyl*-2-(3-*butenyl*)-*cyclohex*-2-*en*-1-*ol* (**8b**): 20.4 g (98%), colourless oil. NMR: δ = 1.63, s (3-CH_3), 4.73–4.90 + 4.90–5.15 (4'-H), 5.40–6.15 ppm, m (3'-H). IR: ν = 3460 (O–H); 3080, 1640 cm^{-1} (–CH=CH_2). $C_{14}H_{24}O$ (208.33).

1-*Butyl*-3-*methyl*-2-(3-*butenyl*)-*cyclohex*-2-*en*-1-*ol* (**8c**). 20.9 g (94%), colourless oil. NMR: δ = 0.90, "t" (–CH_2–CH_3), 1.65, "s" (3-CH_3), 4.75–4.90 + 4.90–5.15, 2 m (4'-H), 5.50–6.20 ppm, m (3'-H). IR: ν = 3440 (OH); 3070, 1640 cm^{-1} (–CH=CH_2). $C_{15}H_{26}O$ (222.36).

3-*Alkyl*-1-*methyl*-2-(3-*butenyl*)-*cyclohex*-2-*en*-1-*ols* (**13a–c**). A soln of 1.78 g (0.01 ml) **12a**, resp. 1.92 g (0.01 mol) **12b**, resp. 2.06 g (0.01 mol) **12c** and 20 ml dry ether was added to a soln of MeLi, prepared with 0.35 g (0.05 mol) Li and 3.55 g (0.25 mol) MeI in 50 ml dry ether. After 30 min reflux the reaction solns were hydrolysed. The organic layers were dried and evaporated.

3-*Ethyl*-1-*methyl*-2-(3-*butenyl*)-*cyclohex*-2-*en*-1-*ol* (**13a**). 1.80 g (92%), colourless oil. NMR: δ = 0.98, t, J = 7 Hz (–CH_2–CH_3), 1.25, s (1-CH_3), 4.75–4.90 + 4.90–5.15, 2 m (4'-H), 5.40–6.20 ppm, m (3'-H). IR: ν = 3380 (–OH), 1640 cm^{-1} (–CH=CH_2). $C_{13}H_{22}O$ (194.31).

3-*Propyl*-1-*methyl*-2-(3-*butenyl*)-*cyclohex*-2-*en*-1-*ol* (**13b**). 1.85 g (89%), colourless oil. NMR: δ = 0.92, t, J = 7 Hz (–CH_2–CH_3), 1.22, s (1-CH_3), 4.75–4.90 + 4.90–5.15, 2 m (4'-H), 5.40–6.20 ppm, m (3'-H). IR: ν = 3400 (–OH), 1638 cm^{-1} (–CH=CH_2). $C_{14}H_{24}O$ (208.33).

3-*Butyl*-1-*methyl*-2-(3-*butenyl*)-*cyclohex*-2-*en*-1-*ol* (**13c**). 1.93 g (87%), colourless oil. NMR: δ = 1.24, s (1-CH_3), 4.75–4.90 + 4.90–5.20, 2 m (4'-H), 5.40–6.15 ppm, m (3'-H). IR: ν = 3400 (O–H), 1640 cm^{-1} (–CH=CH_2). $C_{15}H_{26}O$ (222.36).

Cyclization reactions of the cyclohexenols **1**, **8a–c** *and* **13a–c**

Cyclizations A. 2 g of the carbinol (**1**, **8a–c** and **13a–c**, respectively) were treated with 100 ml anhyd formic acid for 10 min. At 0° the mixture was dropped into a soln of 180 g NaOH in 250 ml water. Stirring 1 hr at room temp, extraction with ether, drying and evaporation of the organic layers gave 2.2 g product mixture, which was treated with a soln of 2 g NaOH in 50 ml EtOH (15 min at 45°C). Evaporation, addition of 100 ml H_2O, extraction with ether and evaporation of the dried organic layers gave 1.6–1.8 g product.

Cyclizations B. A soln of 2 ml trifluoroacetic acid in 100 ml CH_2Cl_2 was added dropwise to a stirred and cooled (–75°) soln of 2 g carbinol (**1**, **8a–c** and **13a–c**, respectively) in 100 ml CH_2Cl_2. The mixture was stirred at –75° for 1 hr, then washed with sat $NaHCO_3$ aq and evaporated. The residue was saponified as described with cyclization A.

Cyclizations C. A mixture of 100 ml anhyd formic acid and a soln of 2 g carbinol (**1**, **8a–c** and **13a–c**, respectively) in 100 ml cyclohexane were stirred intensively for 30 min. The organic layer was separated, washed with brine, and evaporated. The residue was saponified as described with cyclization A.

rac. 2,6β-*Dimethyl*-Δ^1-*bicyclo*[4.4.0]*decen*-8α-*ol* (**2b**). Cyclization A of **1**. t_r = 24.3 min. NMR: δ = 1.05, s (6-CH_3), 1.60, "s" (2-CH_3), 3.4–4.2 ppm, m (8β-H). IR: ν = 3340 cm^{-1} (–O–H). MS: *m/z* (%) = 180 (23, M^+), 165 (31), 162 (36), 147 (100). $C_{12}H_{20}O$ (180.28).

rac. 2-*Ethyl*-6β-*methyl*-Δ^1-*bicyclo*[4.4.0]*decen*-8α-*ol* (**9a**). Cyclization C of **8a**, separation of **8a**/**9a** by prep. glc t_r = 25.2 min. NMR: δ = 0.92, t, J = 7 Hz (–CH_2–CH_3), 1.06, s (6-CH_3), 3.4–4.2 ppm, m (8β-H). IR: ν = 3340 cm^{-1} (–OH). MS: *m/z* (%) = 194 (29, M^+), 179 (30), 176 (41), 165 (20), 161 (100), 147 (77), 135 (18), 133 (19), 119 (38). Found: C, 80.31; H, 11.35. Calc. for $C_{13}H_{22}O$: C, 80.35; H, 11.41%.

rac. 6β-*Ethyl*-2-*methyl*-Δ^1-*bicyclo*[4.4.0]*decen*-8α-*ol* (**10a**). Cyclization C of **8a**, separation by prep glc. t_r = 26.5 min. NMR: δ = 0.77, t, J = 7 Hz (–CH_2–CH_3), 1.63, "s" (2-CH_3), 3.4–4.2 ppm, m (8β-H). MS: *m/z* (%) = 194 (14, M^+), 176 (1), 165 (69), 161 (3), 147 (100). Found: C, 80.29; H, 11.33. Calc. for $C_{13}H_{22}O$: C, 80.35; H, 11.41%.

rac. 6β-*Methyl*-2-*propyl*-Δ^1-*bicyclo*[4.4.0]*decen*-8α-*ol* (**9b**) *and rac.* 2-*methyl*-6β-*propyl*-Δ^1-*bicyclo*[4.4.0]*decen*-8α-*ol* (**10b**). Cyclization B of **8b**. t_r = 27.1 (**9b**) and 27.8 min (**10b**). NMR: δ = 0.89, "t" (–CH_2–CH_3), 1.07; s (6-CH_3 in **8b**), 1.62, "s" (2-CH_3 in **9b**), 3.4–4.2 ppm, m (8β-H). IR: ν = 3320 cm^{-1} (O-H). MS [**9b**]: *m/e* (%) = 208 (17, M^+), 193 (27), 190 (38), 175 (100), 165 (23), 147 (91). MS [**10b**]: *m/z* (%) = 208 (14M^+), 193 (2), 190 (2), 175 (5), 166 (10), 165 (76), 147 (100). $C_{14}H_{24}O$ (208.33).

rac. 2-*Butyl*-6β-*methyl*-Δ^1-*bicyclo* [4.4.0] *decen*-8α-*ol* (**9c**) *and rac.* 6β-*butyl*-2-*methyl*-Δ^1-*bicyclo* [4.4.0] *decen*-8α-*ol* (**10c**). Cyclization C of **8c**. t_r = 29.0 (**9c**) and 30.1 min (**10c**). NMR: δ = 0.90, "t" (–CH_2–CH_3), 1.05, s (6-CH_3 in **9c**), 1.62, "s" (2-CH_3 in **10c**), 3.4–4.2 ppm, m (8β-H). IR: ν = 3330 cm^{-1} (O–H). MS [**9c**]: *m/z* (%) = 222 (29, M^+) 207 (30), 204 (26), 189 (65), 175 (6), 165 (31), 161 (16), 147 (100), 133 (31), 119 (33), 105 (42). MS [**10c**]: *m/z* (%) = 222 (7, M^+), 204 (1), 189 (1), 165 (75), 147 (100), 133 (11), 121 (23), 119 (17), 105 (55). $C_{15}H_{26}O$ (222.36).

Oxidation of cyclization products. 4 ml oxidation reagent (22 g

CrO_3 in 66 ml H_2O and 14 ml conc H_2SO_4) were added dropwise to a stirred and cooled (0°) soln of 1.7 g cyclization product (**2b**, **9a–c** and **10a–c**, respectively). After 10 min stirring at room temp 5 ml of a sat $NaHCO_3$-aq were added. Evaporation, addition of saturated brine, extraction with ether and working up resulted in 1.5–1.7 g product (**2d**, **17a–c** and **18a–c**, respectively).

2,6-*Dimethyl*-Δ^1-*bicyclo*[4.4.0]*decen*-8-*on* (**2c**). NMR: $\delta = 1.02$, s (6-CH_3), 1.69 ppm, s (2-CH_3). IR: $\nu = 1710\,cm^{-1}$ (C=O). MS: *m/z* (%) = 178 (49, M^+), 163 (100), 160 (3), 150 (42), 145 (12), 135 (21), 121 (43), 107 (36), 105 (32). $C_{12}H_{18}O$ (178.26).

2-*Ethyl*-6-*methyl*-Δ^1-*bicyclo*[4.4.0]*decen*-8-*on* (**17a**). NMR: $\delta =$ 0.97, t, $J = 7$ Hz (–CH_2–CH_3), 1.04, s (6-CH_3). IR: $\nu = 1710\,cm^{-1}$ (C=O). MS: *m/z* (%) = 192 (65, M^+), 177 (92), 174 (4), 163 (100), 159 (4), 150 (69), 145 (12), 135 (44). MS (high resolution): Found: 192.1511. Calc. for $C_{13}H_{22}O$: 192.1514.

6-*Ethyl*-2-*methyl*-Δ^1-*bicyclo*[4.4.0]*decen*-8-*on* (**18a**): MS: *m/z* (%) = 192 (17, M^+), 177 (3), 163 (100), 145 (10), 135 (15), 121 (34).

2-*Propyl*-6-*methyl*-Δ^1-*bicyclo*[4.4.0]*decen*-8-*on* (**17b**). Cyclization A; purification by prep tlc (cyclohexane, ethylacetate, 6:1). NMR: $\delta = 0.88$, "t" (–CH_2–CH_3), 1.05 ppm, s (6-CH_3). IR: $\nu =$ $1710\,cm^{-1}$ (C=O). MS: *m/z* (%) = 206 (38, M^+), 191 (54), 188 (2), 178 (7), 163 (100), 150 (37). MS (high resolution): Found: 206.1671. Calc. for $C_{14}H_{22}O$: 206.1670.

2-*Methyl*-6-*propyl*-Δ^1-*bicyclo*[4.4.0]*decen*-8-*on* (**18b**). MS: *m/z* (%) = 206 (10, M^+), 163 (100), 150 (3), 144 (6).

2-*Butyl*-6-*methyl*-Δ^1-*bicyclo*[4.4.0]*decen*-8-*on* (**17c**). Cyclization A; purification by prep tlc (cyclohexane, ethylacetate, 6:1). NMR: $\delta = 0.87$, "t" (–CH_2–CH_3), 1.05 ppm, s (6-CH_3). IR: $\nu =$ $1710\,cm^{-1}$ (C=O). MS: *m/z* (%) = 220 (24, M^+), 205 (40), 202 (2), 192 (4), 163 (100), 150 (35), 135 (17), 121 (21), 107 (33), 105 (25). MS (high resolution): Found: 220.1826. Calc. for $C_{15}H_{24}O$: 220.1827.

2-*Methyl*-6-*butyl*-Δ^1-*bicyclo*[4.4.0]*decen*-8-*on* (**18c**). MS: *m/z* (%) = 220 (18, M^+), 187 (6), 163 (100).

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