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Anomalous Jones Oxidation of Cyclic Hemiacetals. A Method for the Ring Contraction of Polycyclic δ-Lactones into γ-Lactones

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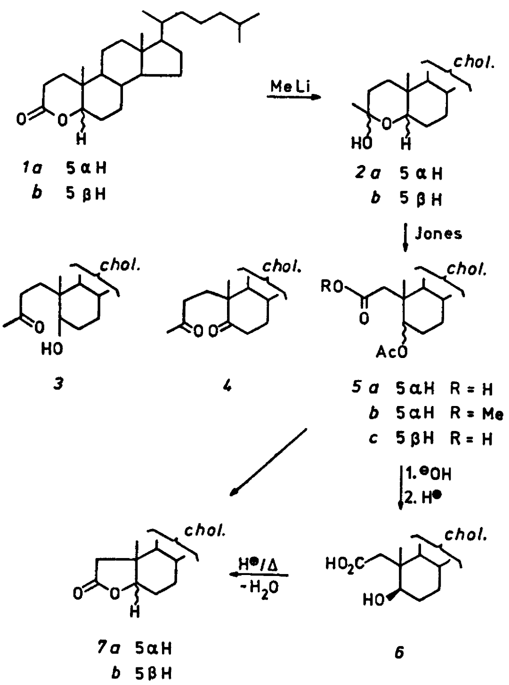
A transformation of δ-lactones into γ-lactones is reported, involving alkylation to give cyclic hemiacetals followed by Jones oxidation, hydrolysis and ring closure of the hydroxy acids.

In connection with studies on improved procedures for the ring A 4,4-bisdemethylation of triterpenes[1] we prepared from 4-oxa-5α-cholestan-3-one (*1a*) the cyclic hemiacetal form

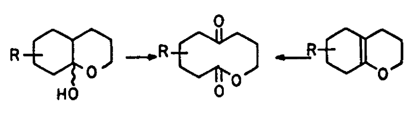


2a of the hydroxy ketone *3* and attempted Jones oxidation of *2a*, a procedure which is reported[2] to readily oxidise an analogous hemiacetal in the lanostane series to the diketone. Instead of the expected diketone *4* we isolated a highly polar compound in 90 % yield which was identified as the acetoxy acid *5a* by hydrolysis to the hydroxy acid *6* and lactonisation to *7a*.

Inspection of the literature reveals that in certain cases unaccountably low yields (48 – 69 %) have been reported[3–5] for Jones and related oxidations of type A cyclic hemiacetals,

Type A Type B

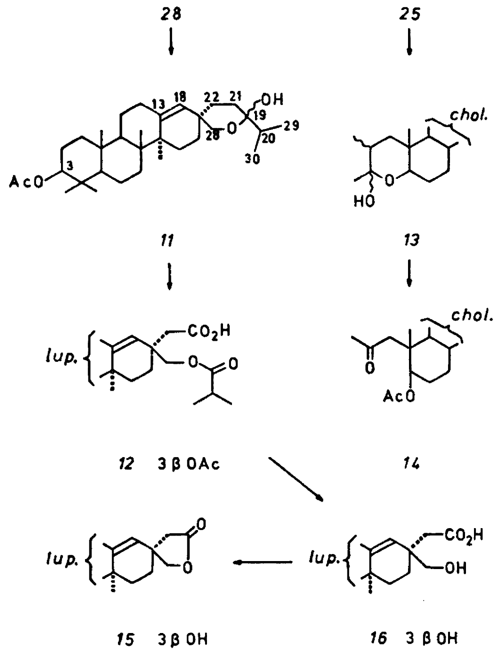
while in other cases[2,5] nearly quantitative yields are reported or implied. With type B cyclic hemiacetals normal Jones oxidation into diketones are known[6] but C – C bond cleavage and macrocyclic keto lactone formation has also been observed[7,8] (*e.g.* *8*→*9*). Similar C – C cleavages result[7–10] when the type B derived enol ethers are oxidised with chromic acid (*e.g.* *10*→*9*). The formation of acyloxy acids



8 9 10

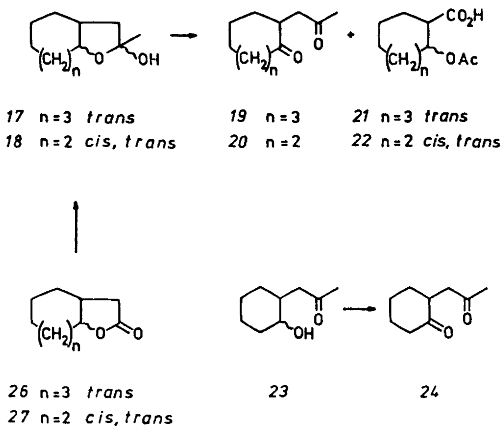
from type A hemiacetals, having an unsubstituted ring α-carbon, would easily escape notice owing to their polarity and poor visualisation characteristics (H_2SO_4, I_2, phosphomolybdic acid *etc.*) on TLC, or their disappearance under standard bicarbonate work-up procedure.

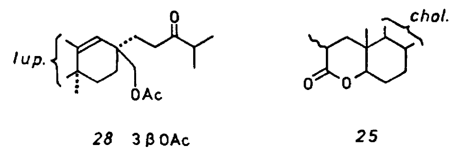
We have now prepared some further type A hemiacetals and found that this anomalous Jones oxidation is a useful reaction for C–C cleavage of such hydroxy ketones which exist in the hemiacetal form. This reaction permits also a convenient ring contraction of δ-lactones to γ-lactones. Thus hemiacetals *2a,b* and *11* give almost quantitatively the acyloxy acids *5a,c* and *12*, and the C–2 methylated hemiacetal *13* the acetoxy ketone *14*. The acids *5a,c* and *12* were hydrolysed and cyclised to the γ-lactones *7a,b* and *15*. The intermediate



hydroxy acids *6* and *16* were also isolated. The lower aliphatic bicyclic hemiacetals *17* and *18* give mixtures of the diketones *19* and *20* and acetoxy acids *21* and *22*. The acid-diketone ratio is roughly 2:1 for the eight membered ring compounds *21:19* and 1:2.5 for the seven membered ring compounds *22:20*. The hemiacetal *18* has been reported [5] to give 48 % of *20* on Jones oxidation and it was suggested that hemiacetal formation was at least partly responsible for the low yield of diketone. No comment was made, however, on the products of oxidation from the hemiacetal form and no carboxylic acids were isolated.

These hydroxy ketones, which undergo the anomalous Jones oxidation, exist in solution essentially in the hemiacetal form *2, 8, 11, 13, 17*, as do *2, 11*, and *13* in the solid state. Both isomers of the hydroxy ketone *23* exist in the open chain form and are known [5,11] to produce





high yields of the diketone *24* on Jones oxidation. Apparently the anomalous Jones oxidation will result if the hydroxy ketone exists as a cyclic hemiacetal tautomer. Very possibly an enol ether intermediate is involved [7–10] in the oxidation *via* the preferred endocyclic double bond formation.

The hydroxy ketones *2, 13, 17*, and *18* in hemiacetal form are readily available from the corresponding lactones (*1, 25, 26*, and *27*) *via* Grignard type reactions (MeLi or *in situ* Grignard procedure [12] was used). The hemiacetal *11* was prepared from the baccharane derivative *28* [13] by hydrolysis.

Some hemiacetals may eliminate water on standing, but this has no effect on the final product.

Thus in cases where the hemiacetal tautomer prevails, the overall sequence constitutes a convenient 3-step route for the ring contraction of polycyclic δ-lactones with unsubstituted α-carbon into corresponding γ-lactones.

EXPERIMENTAL

Melting points are uncorrected. ^{1}H NMR spectra were recorded on a Jeol JNM-PMX 60 spectrometer ($CDCl_3$ as solvent unless otherwise stated), IR spectra on a Perkin-Elmer 125 or 700 spectrophotometer using KBr pellets for solid compounds and liquid film between NaCl discs for liquid compounds, mass spectra on a Perkin-Elmer 270 B mass spectrometer, specific rotations in $CHCl_3$ solutions (unless otherwise stated) on a Perkin-Elmer 141 polarimeter. Silica Gel Woelm was used for dry column chromatography and Merck precoated silica gel 60F-254 plates for TLC.

Preparation of hemiacetals from lactones with methyllithium (MeLi). General procedure. MeLi in Et_2O was added to a solution of lactone (0.1 – 0.9 M) in dry Et_2O or THF under argon with stirring. In different runs, the temperature ranged between – 90 °C and room temperature. Stirring was continued for 15 – 30 min followed by the usual work-up.

The Jones oxidation of the hemiacetals. General procedure. The Jones reagent [14] was added dropwise to a stirred solution of a hemiacetal (0.02 – 0.08 M) in acetone at room temperature until the orange colour of the reagent persisted for about 20 min. The reaction mixture was poured into water and extracted with ether. Ether extracts were washed with brine, dried over Na_2SO_4 and the solvent was evaporated.

4-Oxa-5β-cholestan-3-one (1b). 5-Oxo-A-nor-3,5-secocholestan-3-oic acid [15b,16] (2.5 g, 6.18 mmol) in dry THF (20 ml) was reduced with L-Selectride [17] (22 ml, 22 mmol) at – 27 °C under argon. Stirring was continued at this temperature for 24 h. Oxidative work-up [17,18] and column chromatography (3:1 $CHCl_3$ – EtOAc as eluent) yielded a 3:1 mixture of lactones *1b* and *1a* (2.33 g, 97 %) according to TLC ($Pr^i{}_2O$ as eluent) and ^{1}H NMR: δ 4.12 (5β H of *1b*) [19] and partially superimposed δ 3.93 (5α H of *1a*).[19,20] Recrystallisation from MeOH (5 ml) gave 4-oxa-5β-cholestan-3-one (*1b*) (1.27 g. 53 %), m.p. 103 °C; $[\alpha]_D$ + 24.2° (*c* 0.97) (Ref. 15b, m.p. 109.5 – 110 °C, $[\alpha]_D$ + 18.3°). The mother liquor contained about 1:1 mixture of *1b* and *1a*.

3ξ-Methyl-4-oxa-5α-cholestan-3-ol (2a). 4-Oxa-5α-cholestan-3-one (*1a*) [15] (0.5 g, 1.29 mmol) and MeLi (1.98 mmol) at room temperature gave after recrystallisation (acetone-water) 3ξ-methyl-4-oxa-5α-cholestan-3-ol (*2a*) (0.33 g, 63 %), m.p. 133 °C; $[\alpha]_D$ + 71.4° (*c* 1.05, CCl_4); $\bar{\nu}$ 3410; δ 0.65 (3 H, s, 18-Me), 1.40 (3 H, s, C-3 Me), 1.90 (1 H, br s, OH), 3.59 (1 H, dd, *J* 9 and 6 Hz, 5-H); *m/e* 386 (M – 18).

3ξ-Methyl-4-oxa-5β-cholestan-3-ol (2b). 4-Oxa-5β-cholestan-3-one (*1b*) (1.0 g, 2.57 mmol) and MeLi (3.6 mmol) at – 75 °C yielded 3ξ-methyl-4-oxa-5β-cholestan-3-ol (*2b*) (0.95 g), which after recrystallisation from acetone-water (0.55 g, 53 %) had m.p. 90 °C; $[\alpha]_D$ – 6.6° (*c* 1.03); $\bar{\nu}$ 3400; δ 0.65 (3 H, s, 18-Me), 1.40 and 1.54 (3 H, two s, C-3 methyls of different isomers), 1.97 (1 H, br s, OH), 3.70 (1 H, tr, *J* 2 Hz, 5-H). Concentration of mother liquor gave more *2b* (0.23 g, 22 %), m.p. 80 – 85 °C; *m/e* 386 (M – 18).

5β-Acetoxy-3,4-dinor-2,5-secocholestan-2-oic acid (5a) and its methyl ester (5b). The Jones oxidation of 3ξ-methyl-4-oxa-5α-cholestan-3-ol (*2a*) (1.2 g) gave 5β-acetoxy-3,4-dinor-2,5-secocholestan-2-oic acid (*5a*) (1.2 g), m.p. 116 °C (light petroleum, b.p. 40 – 60 °C); $[\alpha]_D$ + 10.3° (*c* 1.03); $\bar{\nu}$ 3600 – 2500, 3450, 3100, 1735, 1705; δ 0.65 (3 H, s, 18-Me), 1.03 (3 H, s, 19-Me), 2.02 (3 H, s, $OCOCH_3$), 2.24 and 2.40 (2 H, AB quart., *J* 14 Hz, 1-H), 4.78 (1 H, dd, *J* 10 and 5 Hz, 5-H), 9.30 (1 H, br s, CO_2H); *m/e* 374 (M-60). Treatment of *5a* with ethereal CH_2N_2 gave methyl ester (*5b*), m.p. 41 – 43 °C (crude); $[\alpha]_D$ + 9.8° (*c* 0.95); $\bar{\nu}$ 1740; δ 0.65 (3 H, s, 18-Me), 0.99 (3 H, s, 19-Me), 2.00 (3 H, s, $OCOCH_3$), 2.25 and 2.35 (2 H, AB quart., *J* 14 Hz, 1-H), 3.58 (3 H, s, CO_2CH_3), 4.67 (1 H, dd, *J* 10 and 5 Hz, 5-H); *m/e* 388 (M-60).

5β-Hydroxy-3,4-dinor-2,5-secocholestan-2-oic acid (6) and its γ-lactone (7a). Hydrolysis of *5a* with NaOH in EtOH gave after acidification (2 N HCl) 5β-hydroxy-3,4-dinor-2,5-secocholestan-2-oic acid (*6*), m.p. 189 – 190 °C (acetone), $[\alpha]_D$ + 44.9° (c 1.19); $\bar{\nu}$ 3480, 3300 – 2400, 1710; δ 0.65 (3 H, s, 18-Me), 0.92 (3 H, s, 19-Me), 2.31 and 2.61 (2 H, AB quart., *J* 14 Hz, 1-H), 3.68 (1 H, dd, *J* 11 and 5 Hz, 5-H), 4.90 (2 H, br, CO_2H and *OH*); *m/e* (%) 392 (2, M), 374 (86, M – 18), 359 (13, M – 18 – 15), 332 (100, M – 60). Lactonisation was carried out by slowly distilling a benzene solution of *6* in the presence of *p*-toluenesulfonic acid monohydrate giving A-nor-3-oxa-5α-cholestan-2-one (*7a*), m.p. 103 °C (light petroleum, b.p. 40 – 60 °C); $[\alpha]_D$ + 76.9° (*c* 1.08); $\bar{\nu}$ 1785; δ 0.67 (3 H, s, 18-Me), 0.98 (3 H, s, 19-Me), 2.23 (2 H, br s, 1-H), 3.83 (1 H, dd, *J* 11 and 5 Hz, 5-H); *m/e* 374 (M).

5α-Acetoxy-3,4-dinor-2,5-secocholestan-2-oic acid (5c). The Jones oxidation of 3ξ-methyl-4-oxa-5β-cholestan-3-ol (*2b*) (0.67 g) gave 5α-acetoxy-3,4-dinor-2,5-secocholestan-2-oic acid (*5c*) (0.66 g), m.p. 154 – 155 °C (light petroleum, b.p. 40 – 60 °C); $[\alpha]_D$ + 80.5 (*c* 1.06); $\bar{\nu}$ 3600 – 2500, 3450, 3050, 1740, 1705; δ 0.66 (3 H, s, 18-Me), 1.09 (3 H, s, 19-Me), 2.01 (3 H, s, $OCOCH_3$), 2.10 (2 H, br s, 1-H), 4.79 (1 H, tr, *J* 2 Hz, 5-H), 10.9 (1 H, br s, CO_2H); *m/e* 374 (M – 60).

A-Nor-3-oxa-5β-cholestan-2-one (7b). Hydrolysis and lactonisation of *5c* was conducted as above affording A-nor-3-oxa-5β-cholestan-2-one (*7b*), m.p. 128 – 129 °C (EtOH); $[\alpha]_D$ + 6.0 (*c* 1.0); $\bar{\nu}$ 1765; δ 0.67 (3 H, s, 18-Me), 1.07 (3 H, s, 19-Me), 2.23 and 2.48 (2 H, AB quart., *J* 16 Hz, 1-H), 4.17 (1 H, tr, *J* 2 Hz, 5-H); *m/e* 374 (M).

3β-Acetoxy-19,28-epoxy-19ξ-hydroxy-18,19-secolup-13(18)-ene (11). 3β,28-Diacetoxy-18,19-secolup-13(18)-en-19-one (*28*) [13] (0.5 g) and KOH (0.06 g) in EtOH (30 ml) were stirred at

50 °C for 1 h. Work-up and chromatography on silica plates gave 3β-acetoxy-19,28-epoxy-19ξ-hydroxy-18,19-secolup-13(18)-ene (*11*) (0.35 g), m.p. 116 – 117 °C (water-acetone); $[\alpha]_D$ – 15.6° (*c* 1.0); ν̄ 3470, 1735; δ (CCl_4) 1.97 (3 H, s, $OCOCH_3$), 3.3 (2 H, AB quart., *J* 11 Hz, 28-H), 4.4 (1 H, m, 3-H), 4.82 (1 H, br s, 18-H); *m/e* 482 (M – 18).

3β-Acetoxy-28-isobutyryloxy-19,20,29,30-tetranor-18,19-secolup-13(18)-en-21-oic acid (*12*). The Jones oxidation of 3β-acetoxy-19,28-epoxy-19ξ-hydroxy-18,19-secolup-13(18)-ene (*11*) yielded over 90 % 3β-acetoxy-28-isobutyryloxy-19,20,29,30-tetranor-18,19-secolup-13(18)-en-21-oic acid (*12*), m.p. 178 °C; $[\alpha]_D$ – 43.2° (*c* 1.0); ν̄ 1740, 1705; δ 2.3 (1 H, sept., *J* 7 Hz, $OCOCH(CH_3)_2$), 2.35 (2 H, s, 22-H), 4.02 (2 H, AB quart., *J* 12 Hz, 28-H), 4.5 (1 H, m, 3-H); *m/e* (%) 470 (11, M – 60), 382 (18), 249 (9), 203 (50), 190 (53), 189 (47), 43 (100).

3β,28-Dihydroxy-19,20,29,30-tetranor-18,19-secolup-13(18)-en-21-oic acid (*16*) *and its γ-lactone* (*15*). Hydrolysis of *12* with KOH in EtOH, acidification (2 N H_2SO_4) and addition of benzene gave a precipitate of the dihydroxy acid *16* and the evaporation of benzene gave the lactone *15*. 3β,28-Dihydroxy-19,20,29,30-tetranor-18,19-secolup-13(18)-en-21-oic acid (*16*), m.p. 205 °C; $[\alpha]_D$ – 30,5° (*c* 0.39, dioxan); ν̄ 3370, 1700. 3β-Hydroxy-19,20,29,30-tetranor-18,19-secolup-13(18)-en-21→28-olide (*15*), m.p. 212 °C; $[\alpha]_D$ – 14.7° (*c* 0.5); ν̄ 3380, 1763; δ 2.35 (2 H, AB quart., *J* 14 Hz, 22-H), 3.2 (1 H, m, 3-H), 3.98 (2 H, AB quart., *J* 9 Hz, 28-H), 5.15 (1 H, br s, 18-H).

2ξ,3ξ-Dimethyl-4-oxa-5α-cholestan-3-ol (*13*). 2ξ-Methyl-4-oxa-5α-cholestan-3-one (*25*) (0.78 g, 1.94 mmol) and MeLi (2.24 mmol) at – 80 °C gave 2ξ,3ξ-dimethyl-4-oxa-5α-cholestan-3-ol (*13*) (0.72 g, 89 %), m.p. 156 °C (crude); $[\alpha]_D$ + 73.6° (*c* 1.0); ν̄ 3480; δ 0.65 (3 H, s, 18-Me), 1.39 (3 H, s, C-3 Me), 1.80 (1 H, br s, OH), 3.48 (1 H, dd, *J* 12 and 6 Hz); *m/e* 400 (M – 18).

5β-Acetoxy-A-nor-3,5-secocholestan-2-one (*14*). The Jones oxidation of 2ξ,3ξ-dimethyl-4-oxa-5α-cholestan-3-ol (*13*) (0.52 g) gave a viscous oil (0.52 g), which was crystallised from aqueous EtOH to give 5β-acetoxy-A-nor-3,5-secocholestan-2-one (*14*) (0.22 g), m.p. 76 °C; $[\alpha]_D$ + 12.5° (*c* 1.07); ν̄ 1735, 1695; δ 0.65 (3 H, s, 18-Me), 0.99 (3 H, s, 19-Me), 2.00 (3 H, s, $OCOCH_3$), 2.06 (3 H, s, 3-Me), 2.30 and 2.44 (2 H, AB quart., *J* 15 Hz, 1-H), 4.88 (1 H, dd, *J* 10 and 5 Hz, 5-H); *m/e* (%) 372 (3, M – 60), 357 (2), 354 (4), 332 (20), 314 (100).

trans-*10ξ-Methyl-9-oxabicyclo*[*6.3.0*]*undecan-10-ol* (*17*). *trans*-9-Oxabicyclo[6.3.0]undecan-10-one (*26*) (2.4 g, 14.3 mmol) and MeLi (16.2 mmol) at – 80 °C gave *trans*-10ξ-methyl-9-oxabicyclo[6.3.0]undecan-10-ol (*17*) (2.3 g) as a viscous oil which was used without purification for the Jones oxidation, ν̄ 3410; δ 1.47 (3 H, s, C-10 Me), 3.17 (1 H, br s, OH), 3.95 (1 H, br m, 8-H).

cis- *and* trans-*9ξ-Methyl-8-oxabicyclo*[*5.3.0*]-*decan-9-ol* (*18*). A mixture of *cis*- and *trans*-8-oxabicyclo[5.3.0]decan-9-one (*27*) (1.05 g, 6.8 mmol) was treated with methyl iodide (7.5 mmol) in the presence of lithium pieces [12] to afford a mixture (0.72 g) of *cis*-9ξ-methyl-8-oxabicyclo[5.3.0]decan-9-ol (55 – 60 %) and *trans*-9ξ-methyl-8-oxabicyclo[5.3.0]decan-9-ol (40 – 45 %) (*18*),[5] as a viscous oil which was used without purification for the Jones oxidation, ν̄ 3400; δ 1.50 (3 H, s, C-9 Me), 3.03 (1 H, br s, OH), 3.70 and 4.30 (1 H, two br m, 7-H of *trans* and *cis*-isomer).

trans-8-Oxabicyclo[5.3.0]decan-9-one [21] (0.58 g, 3.76 mmol) and MeLi (4.2 mmol) at – 90 °C gave *trans*-9ξ-methyl-8-oxabicyclo[5.3.0]decan-9-ol (*trans-18*) (0.47 g) as a viscous oil which was used without purification for the Jones oxidation. *Trans-18* had in the ^1H NMR spectrum the 7-H signal at δ 3.70 only.

2-(2-Oxopropyl)cyclooctanone (*19*) *and* trans-*2-acetoxy-cyclooctanecarboxylic acid* (*21*). The Jones oxidation of *trans*-10ξ-methyl-9-oxabicyclo[6.3.0]undecan-10-ol (*17*) (1.7 g) gave an oil (1.5 g), which showed on TLC two main compounds and had in ^1H NMR two methyl signals at δ 1.99 and 2.11 in the intensity ratio of 2:1. Column chromatography gave liquid 2-(2-oxopropyl)-cyclooctanone (*19*) ν̄ 1705; δ 1.0 – 2.1 (10 H, m), 2.11 (3 H, s), 2.1 – 3.5 (5 H, m); and oily *trans*-2-acetoxy-cyclooctanecarboxylic acid (*21*), ν̄ 3700 – 2400, 1735, 1705 sh; δ 1.1 – 2.1 (12 H, m), 1.99 (3 H, s), 2.77 (1 H, m, 1-H), 5.20 (1 H, m, $J_{2,1}$ 10 Hz, 2-H), 10.0 (1 H, br s, CO_2H).

2-(2-Oxopropyl)-cycloheptanone (*20*) *and 2-acetoxy-cycloheptanecarboxylic acids* (*22*). The Jones oxidation of the mixture of *cis*- and *trans*-9ξ-methyl-8-oxabicyclo[5.3.0]decan-9-ol (*18*) (0.72 g) gave an oil (0.65 g), which showed on TLC two main compounds and had in ^1H NMR two methyl signals at δ 2.00 and 2.13 in the intensity ratio of 1:2.5. Column chromatography gave liquid 2-(2-oxopropyl)-cycloheptanone [5,22] (*20*), ν̄ 1705; δ 1.0 – 2.1 (8 H, m), 2.13 (3 H, s), 2.1 – 3.4 (5 H, m); and oily mixture of *cis*- and *trans*-2-acetoxycycloheptanecarboxylic acid [23] (*22*) in the ratio of 5:1, ν̄ 3700 – 2400, 1740, 1710; δ 1.0 – 2.2 (10 H, m), 2.00 (3, H, s), 2.4 – 2.9 (1 H, m, 1-H of *trans* and *cis*),[23] 5.16 and 5.38 (1 H, two partly superimposed m, 2-H of *trans* and *cis* respectively in the ratio of 1:5),[23] 9.3 (1 H, br s, CO_2H). *Trans-18* when subjected to the Jones oxidation gave only minor amounts (5 – 10 %) of *trans*-acetoxy acid (*22*), the main product being the diketone *20*.

2ξ-Methyl-4-oxa-5α-cholestan-3-one (*25*). 4-Oxa-5α-cholestan-3-one [15] (0.5 g, 1.29 mmol) (*1a*) was 2-methylated [24] to furnish after work-up and recrystallisation from EtOH (3 ml) 2ξ-methyl-4-oxa-5α-cholestan-3-one (*25*) (0.39 g, 75 %), m.p. 145 °C; $[\alpha]_D$ + 72.7° (*c* 0.99); ν̄ 1735; δ 0.66 (3 H, s, 18-Me), 0.95 (3 H, s, 19-Me), 1.28 (3 H, d, *J* 7 Hz, C-2 Me), 2.2 – 3.0

(1 H, m, 2-H), 3.92 (1 H, dd, *J* 11 and 5 Hz, 5-H); *m/e* 402 (M).

trans-*9-Oxabicyclo[6.3.0]undecan-10-one* (*26*). This compound was prepared according to Heiba *et al.*,[25] who stated that cyclooctene produced only one lactone isomer of unknown configuration. Our product had the IR and ^{1}H NMR spectral values identical with those described for *trans*-9-oxabicyclo[6.3.0]-undecan-10-one (*26*), recently prepared by a different unambiguous way.[26]

cis- *and* trans-*8-Oxabicyclo[5.3.0]decan-9-one* (*27*). These compounds were prepared according to the general procedure of Heiba *et al.*[25] from cycloheptene (4.0 g). Distillation afforded a mixture (1.1 g, 17 %) of *cis*-8-oxabicyclo[5.3.0]decan-9-one (*cis-27*) (55 – 60 %) and *trans*-8-oxabicyclo[5.3.0]decan-9-one (*trans-27*) (40 – 45 %), b.p. 115 – 120 °C/1 mmHg (Ref. 21., b.p. 94 – 96 °C/0.4 mmHg for *cis* and 91 – 92 °C/0.3 mmHg for *trans*). The IR and ^{1}H NMR spectra of the mixture were consistent with those given in the literature [21] separately for *cis*- and *trans*-isomer.

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