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A VERSATILE REGIO- AND STEREOSPECIFIC ANNULATION METHOD - II.

FORMATION OF SUBSTITUTED FIVE- OR SIX- MEMBERED RING SYSTEMS BY ACIDIC FRAGMENTATION OF 1-ETHOXY-2-OXATRICYCLO[4.2.1.$0^{4,8}$]NONAN-7-ONE DERIVATIVES

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Abstract: Smooth fragmentation of the strained title compounds under acidic conditions is achieved. Depending on structure, solvent, Lewis acid and nucleophile stereospecifically substituted cyclopentanones as well as cyclohexanones could be gained in good yields.

Introduction

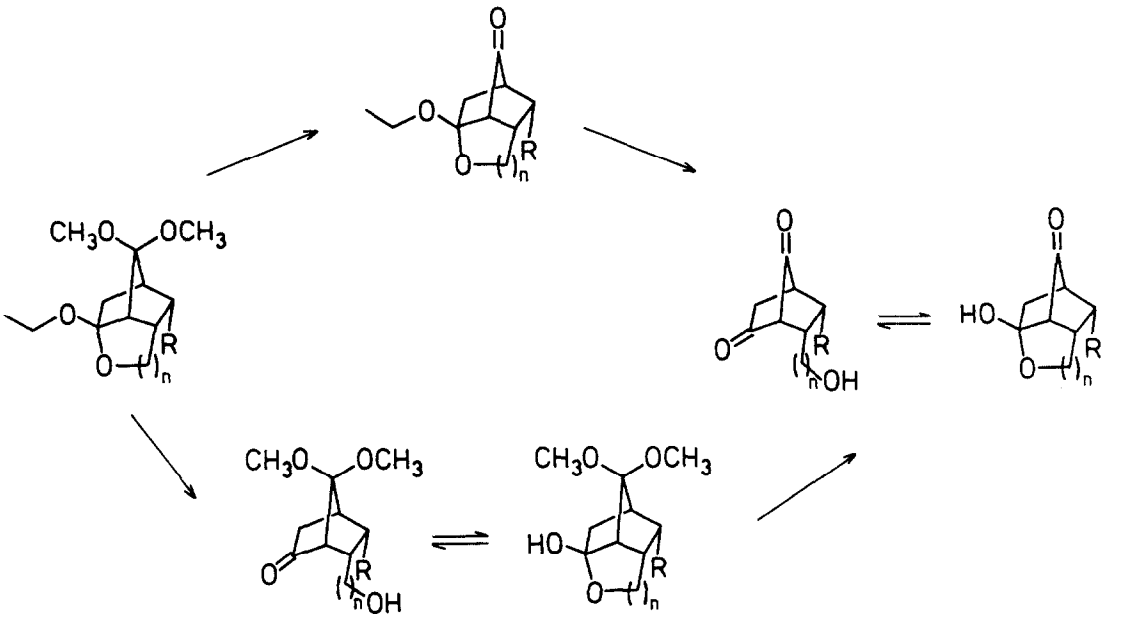
In the preceding publication[1] we have described a simple high yielding preparation of 1-ethoxy-2-oxatricyclo[4.2.1.$0^{4,8}$]nonan-7-one dimethylketal derivatives and their homologues respectively, starting with allylically and homoallylically heterosubstituted olefins and 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene. The structure of these protected 1,3-diketones should permit fragmentation under mild conditions, yielding stereospecifically substituted (mono)cyclic compounds.

The main reasons for this assumption are firstly the substitution pattern of the title compounds, secondly the sterically favourable position of the orbitals involved in the stereoelectronically controlled fragmentation and thirdly the considerable decrease of strain by going from the highly strained tricyclic system to a stereospecifically substituted monocycle.

The substitution pattern should allow hydrolysis to the monoketone and further on to the 1,3-diketone, which should be highly susceptible to retro-Claisen reaction or its acidic equivalent[2], especially so because these bridged 1,3-diketones are unable to enolize to a delocalized π-system (scheme 1).

Generation of the ketones leads to new sp^2-hybridized carbon centers and thus to an increase in strain energy in these molecules. Therefore Grob-type fragmentation under acidic conditions starting directly from the diketals or from the monoketones might be energetically equivalent and has to be considered too.

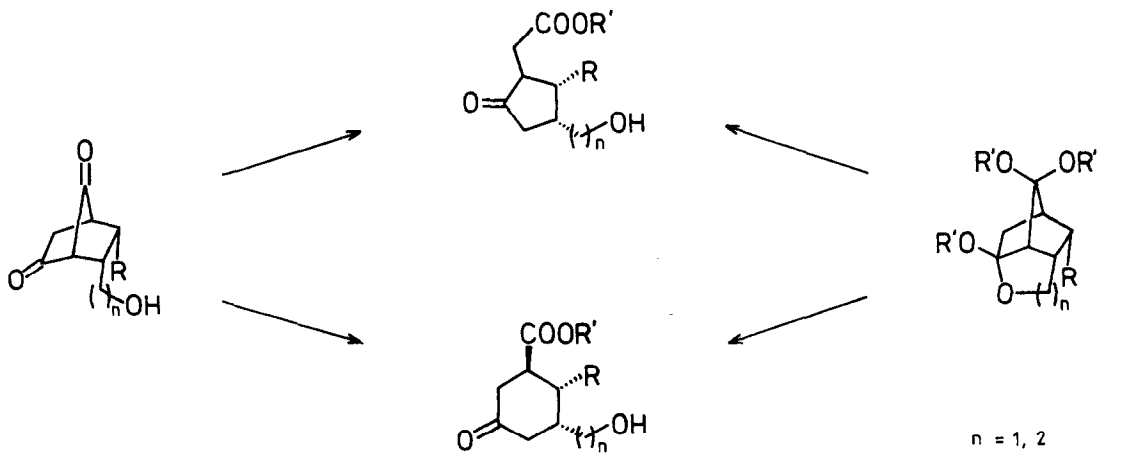
Hydrolyses (deketalizations)[3,4] as well as fragmentations[5,6] are stereoelectronically controlled processes. Molecular models of the title compounds (assuming that the oxygen atoms are sp^3-hybridized[3,4]) show that the orbitals involved in these reactions are in approximately antiperiplanar position to each other



scheme 1

thus indicating smooth transformation to the monocycles.

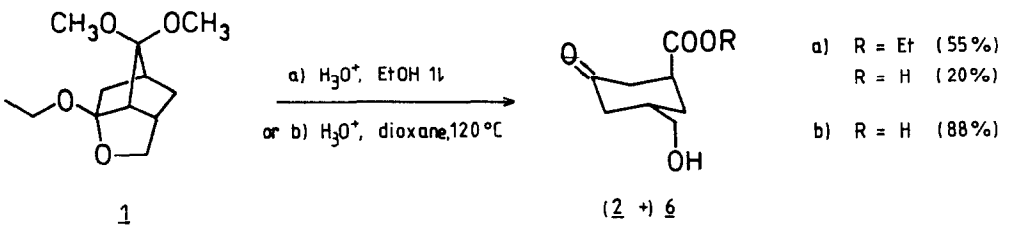
There are two equivalent functional groups in the title compounds, which may function as leaving group or electron donor. Thus two different structural systems, stereospecifically substituted cyclopentanones and cyclohexanones respectively may be generated (scheme 2).In order to attain a useful annulation method, conditions had to be found to steer the fragmentation to but one main product, either the cyclohexanone or the cyclopentanone derivative.



scheme 2

Results and Discussion

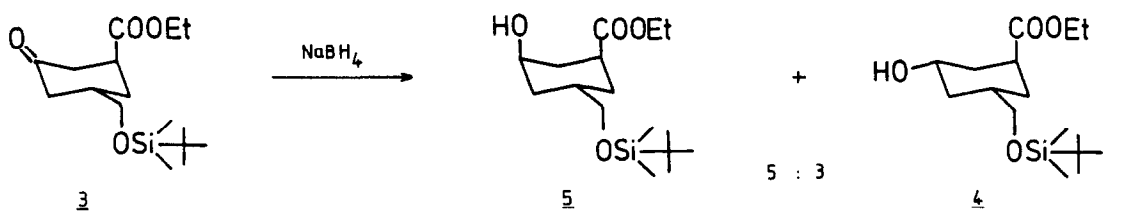
Treatment of 7,7-dimethoxy-1-ethoxy-2-oxatricyclo[4.2.1.$0^{4,8}$]nonane **1** with weakly acidic aqueous ethanol yielded the cyclohexanone derivative **2** as the main product (scheme 3, a).



1 (2 +) 6

scheme 3

The existence of a hydroxy acid ethyl ester was revealed by chemical shift and coupling constants in the ^{1}H-NMR spectrum. The ring size of the monocyclic **2** was determined by the chemical shift of the carbonyl carbon (δ= 208,4ppm) and by chemical conversion. To diminish the water solubility alcohol **2** was etherified to its silyl ether **3**. Reduction of **3** with sodium borohydride afforded the two diastereomeric alcohols **4** and **5**.



3 5 4

scheme 4

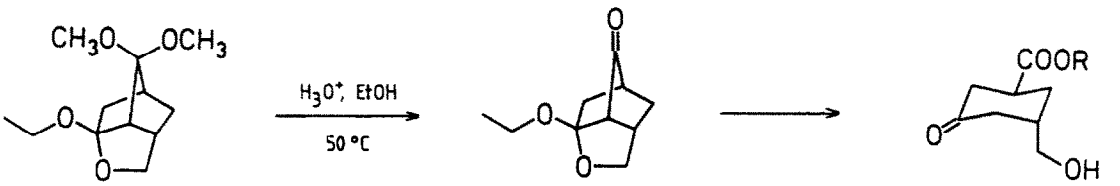
The pattern of the signal of the proton in geminal position to the secondary hydroxyl group in the ^{1}H-NMR spectra of these alcohols permitted unequivocal determination of the ring size by the number of coupling partners and the size of the coupling constants. The coupling constants of the protons attached to the ring showed that the conformational equilibrium of **4** is heavily biased to the conformation shown in scheme 4. Even for the stereoisomeric compound **5** the main conformation is that one indicated in scheme 4.

The main byproduct of this acidic fragmentation in aqueous ethanol was the acid **6**. To optimize the reaction conditions it seemed reasonable to avoid reketalization or more likely esterification by ethanol. For that reason **1** was treated in aqueous dioxane with traces of aqu. HCl at 120°C. The desired acid **6** could be obtained as white crystals by evaporation of the solvent (scheme 3, b). - In this way a simple high yielding

procedure for a stereospecifically substituted cyclohexanone starting with allyl acohol was achieved.

Numerous methods for the stereospecific or stereoselective construction of substituted six-membered rings by annulation have been developed[7]. Contrary to this, the number of generally applicable methods for the stereospecific or stereoselective construction of substituted cyclopentanes by annulation is rather small, despite of several interesting methods published recently[8]. This lack motivated us to try to steer the acidic fragmentation to a reaction pathway leading to the cyclopentanone derivatives.

Pursuing the progress of the reaction in acidic ethanol by TLC as well as by quenching and measuring the ^{1}H-NMR spectra of the reaction mixtures after work up revealed that the monoketone **7** is formed. As is expected in the intermediate of a (pseudo)first order consecutive reaction with similar rate constants the amount of ketone **7** increases in the earlier stage of the reaction but decreases with increasing reaction time.

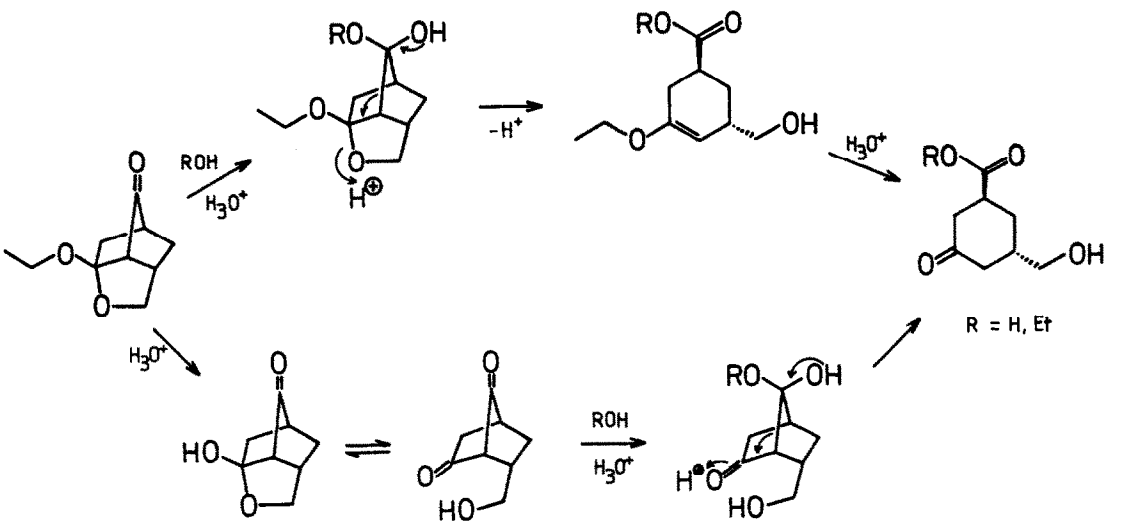


1 **7** **2** (+ **6**)

scheme 5

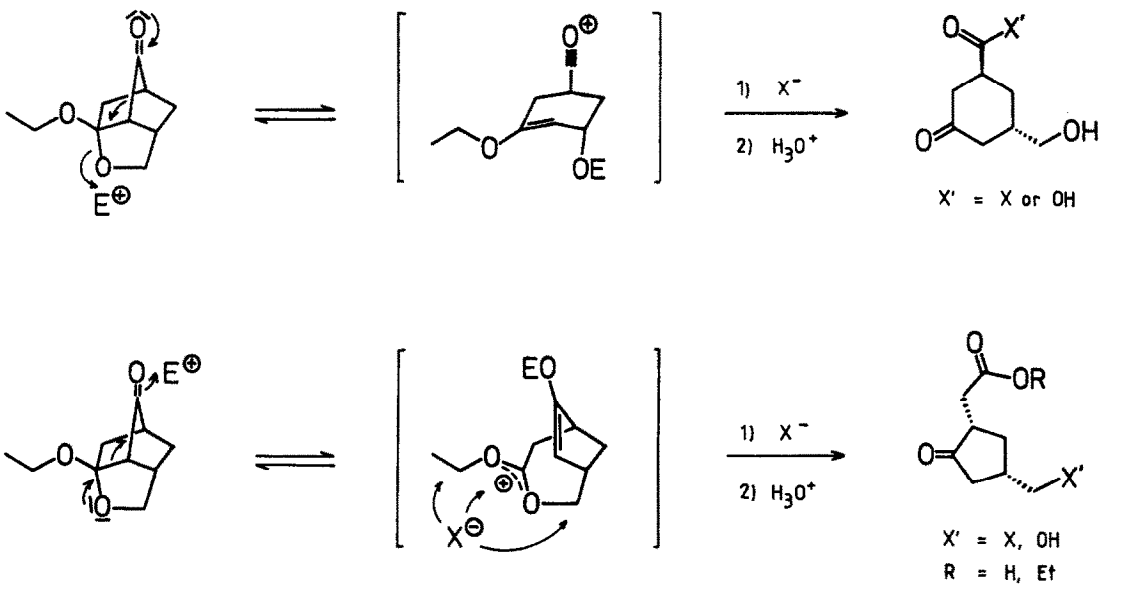
Ketone **7** was isolated in moderate yields when the reaction was quenched after a short reaction period. **7** is labile against acid and even not quite stable against silica gel and fragments to **2** and **6** respectively. These results and the fact that no methylester could be detected even in the earlier stages of the reaction (compare with results published by Anteunis[9]) indicated a reaction mechanism with the monoketone as intermediate. The further steps leading to the cyclohexanone may proceed via hydrolysis to the diketone and very fast retro-Claisen reaction or fragmentation may start directly with monoketone **7** (scheme 6).

At the moment we are unable to decide between these two possible pathways because even in the earlier stages no intermediates could be isolated and no signals corresponding to an ethylenolether or to the diketone and its hemiketal respectively could be detected in the ^{1}H-NMR spectra of the reaction mixtures after quenching and work up. In any case a nucleophile (alcohol, water) has to attack the ketone at C-7. The resulting intermediate (hemiketal, ketohydrate) is converted to the enol(ether) by fragmentation and further transformation leads to the cyclohexanone derivative. Therefore change from the nucleophilic solvent to an inert one and to Lewis acids without moderately hard nucleophiles as counterions should lead to a switch in the reaction pathway.



scheme 6

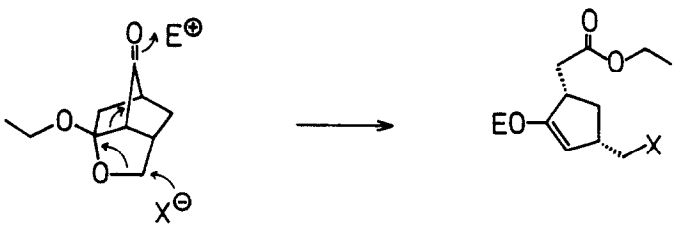
Without simultaneous nucleophilic attack the fragmentation will have to proceed via highly reactive ionic intermediates. Depending on the attack of the Lewis acid either the -C≡O^+ moiety or more likely the resonance stabilized dialkoxycarboniumion will be formed (Scheme 7). Addition of a nucleophile could then produce the corresponding keto acid derivatives.



scheme 7

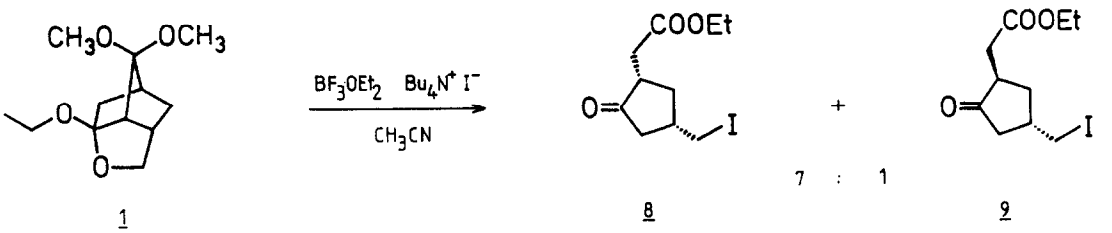
In case of the fragmentation proceeding to the five-membered ring it would depend on the character of the nucleophile if it attacks the sp^2-center of the dialkoxycarbonium ion or the sp^3-centers. With soft nucleophiles substitution at the sp^3-centers should be preferred[10].

If the soft nucleophile is added simultaneously with the Lewis acid displacement initiated fragmentation could occur, which would avoid the strained bicyclic dialkoxycarbonium ion as intermediate.



scheme 8

Since the preparation of the monoketone as described above afforded but moderate yields, diketal **1** itself was treated with boron trifluoride etherate as Lewis acid, iodide as additional soft nucleophile and acetonitrile as solvent[11]. After work up and chromatographic purification compound **8** was obtained in over 70% yield. Contrary to this result treatment of **1** under the same conditions but without the additional iodide led to an unseparable mixture after work up.



scheme 9

The structure of **8** was determined by means of spectroscopic data: The molecular peak in the mass spectrum, the upfield shift of one methylene carbon signal to δ=10.9ppm in the ^{13}C-NMR spectrum, the position of the corresponding proton signals at δ = 3.3ppm (correlated by 2D-NMR) indicate that the iodide indeed attacked position 3. The ^{13}C-NMR- and the IR-spectra confirmed the cyclopentanone. The fragmentation has to render the cis-disubstituted cyclopentanone, but the chiral center in vicinal position to the ketone is easily epimerized. Indeed small amounts of the stereoisomer **9** were formed. The main product is the originally formed cis-disubstituted cyclopentanone **8**. The determination is based on the fact that the 2,4-disubstituted

cyclopentanones assume half chair conformation so that the cis disubstituted stereoisomers are the thermodynamically more stable ones[12,13] and that the NMR spectroscopic data are in accordance with a 2,4-cis-disubstituted cyclopentanone. The rather large and equal coupling constants for one of the C-5′ protons (11Hz) as well as the shift differences of the signals in the ^{13}C-NMR spectra of **8** and **9** which agree with that of cis- and trans-2,4-dimethylcyclopentanone[12] confirm this assumption.

These results show that suitable choice of Lewis acid, solvent and nucleophile allow steering to the desired ring size.

To establish the generality and/or limitations of the new annulation method, the influence of structural variations were examined.

Derivatives of 1-ethoxy-2-oxatricyclo[4.2.1.0^{4,8}]-nonan-7-one dimethylketal and one homologue were treated under identical reaction conditions and are not optimized. The progress of the reactions was pursued by quenching and ^{1}H-NMR spectroscopy of the reaction mixture after work up (scheme 10).

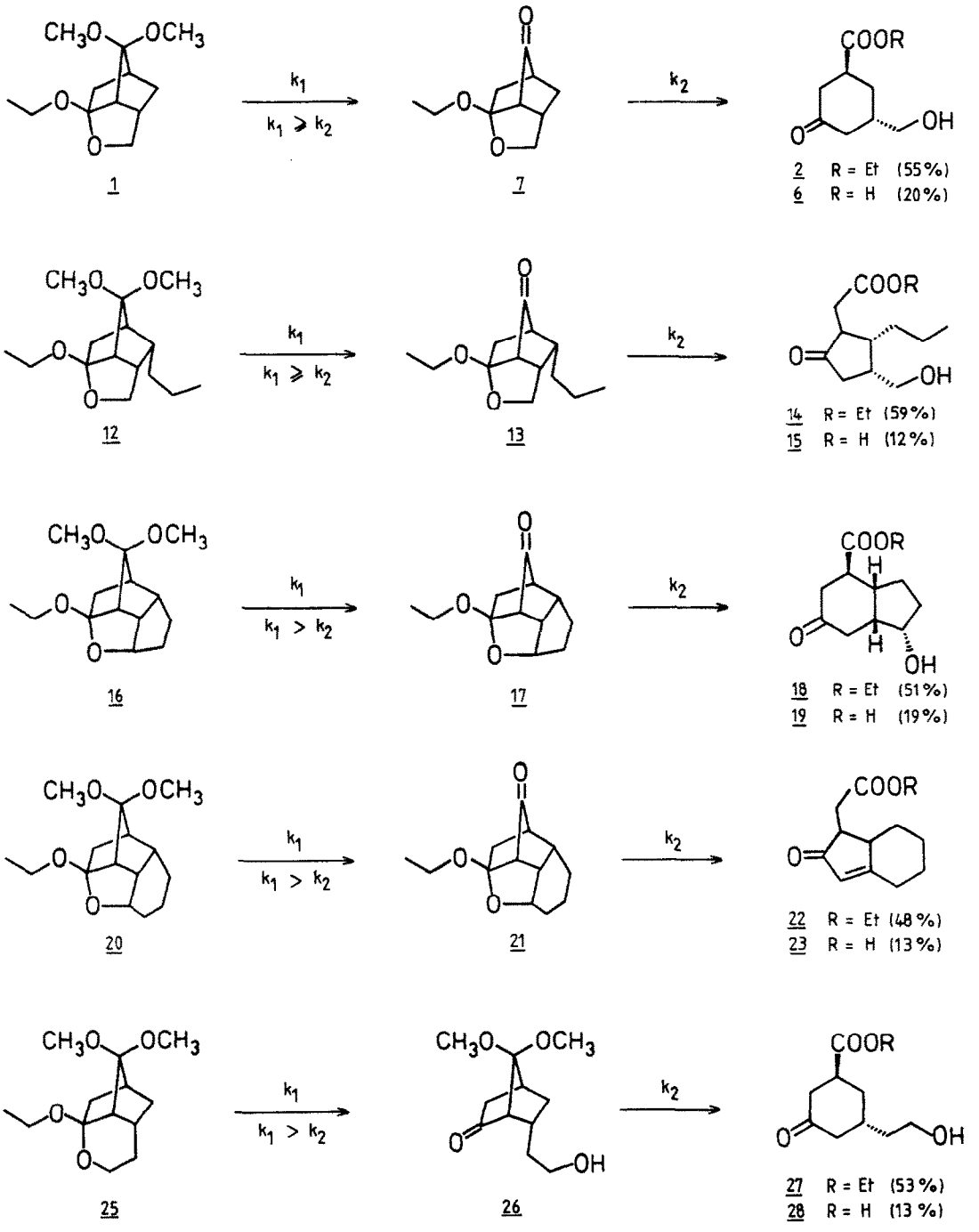
The existence of the additional propyl group in compound **12** was sufficient to drive the system upon an other reaction pathway. The reaction started with hydrolysis to the monoketone **13**, which then was transformed to the trisubstituted cyclopentanones **14** and **15** in good yields. The data of the ^{1}H-NMR spectra did not permit determination of the size of the monocycle. ^{13}C-NMR spectral data pointed to the cyclopentanone system (carbonyl-C: δ= 219ppm). To support this assumption **14** was converted to its tert.-butyldimethylsilyl ether **30** and subsequently reduced to the secondary alcohols. The main stereoisomer **31** was isolated and the signal of its proton in geminal positon to the secondary hydroxyl group showed three coupling partners, thus confirming the cyclopentanone structure of **15**.

As mentioned above chiral centers in the α-position to the ketone of five-membered rings are easily epimerized. We suggest, that **14** is the epimerized product, because this should be the thermodynamically more stable product. Prolonged treatment of pure **14** with diluted acid led to a mixture of **14** and its stereoisomer **14a** in an 22 : 1 ratio which was determined by ^{1}H-NMR data.

In analogy to **1** the tetracyclic compound **16** hydrolyzed to the monoketone **17** and fragmented to the hydrindanone derivative **18**, thus constituting a six-membered ring formation by annulation. Contrary to the fragmentation of **1** the reaction rates of the formation of ketone **17** and fragmentation to **18** differed appreciably, so that ketone **17** could be isolated in high yields. The structure determination of the hydrindanone derivatives **18** and **19** is based on spectral data.

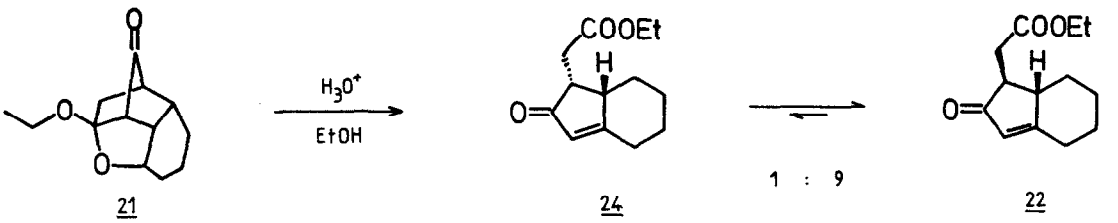
The IR spectrum showed that a hydroxy group, an ester group and a keto group (at a six-membered ring system:1715cm^{-1}) are part of the structure. The molecular peak m/e = 226 and the main fragment M$^+$ - COOEt in the mass spectrum confirmed the structure determination. The C-signal of the keto group at 211,5ppm in the ^{13}C-NMR is consistent with a ketone in a six-membered ring system. The coupling constants in the ^{1}H-NMR spectrum confirmed the relative configuration of the chiral centers.

Although acidic treatment of **20** again led to a monoketone **21**, the course of the fragmentation was quite different. Ketone **21** fragmented to the enone **24**, which was unstable under the reaction conditions and epimerized to the equilibrium mixture **22** : **24** = 9 : 1. This could be demonstrated by treating pure compound **22**


CH3O
OCH3
O
k1
k1 ≥ k2
k2
COOR
OH
1
7
2 R = Et (55%)
6 R = H (20%)
12
13
14 R = Et (59%)
15 R = H (12%)
16
17
18 R = Et (51%)
19 R = H (19%)
20
21
22 R = Et (48%)
23 R = H (13%)
25
26
27 R = Et (53%)
28 R = H (13%)

scheme 10

as well as a 1 : 4 mixture of **22** : **24** under the same acidic conditions. In each case a 9 : 1 mixture of **22** : **24** was obtained.



21 24 22

scheme 11

The structures of these bicyclo[4.3.0]nonenone derivatives were determined by the absorption band at λ_{max}(ethanol)= 231 nm, the wavenumbers of the C=O, C=C and the C-H vibrations, the signal of the olefinic proton in the ^{1}H-NMR spectrum and the shift of the carbonyl-C signal, which all were in agreement with an unsaturated ketone in a five- membered ring system. The position of the side chain on the convex face of the molecule was assumed due to the epimerization equilibrium, which showed **22** to be the thermodynamically more stable diastereomer.

The acidic conversion of the homologue **25** took quite a different course compared to the above mentioned systems. In a comparably fast reaction the cyclic ketal was hydrolyzed to the monoketone **26**. As the ^{1}H-NMR showed this monoketone exists mainly as the hydroxy ketone and not as the cyclic hemiketal. The structure determination of the final products of the fragmentation **27** and **28** is based on spectral data, which very closely resembled that of **2** and **6** respectively.

We shall report steering the course of the fragmentation of the tetracyclic compounds to diquinanones and cis-decalinones, which constitute interesting intermediates in natural product syntheses in a subsequent publication[14].

Conclusion

In the preceding publication we demonstrated the easy accessibility of bridged 1,3 diketals[1]. The present publication dealt with the conversion of these 1,3-diketals to stereospecifically substituted cyclic compounds. This could be achieved by acidic fragmentation. According to the choice of solvent, Lewis acid and nucleophile the fragmentation can be steered to the five as well as to the six-membered ring system. Thus a new versatile annulation method was developed which permits the regio- and stereospecific addition of C-3- or C-4-units respectively to the double bond. - Next to the dependence of the fragmentation on the reaction parameters, the strong influence of structural variations on the reaction pathway was demonstrated.

Experimental

General notes: ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Spectrospin WM 250 (250 MHz). Tetramethylsilane served as internal standard. IR spectra were recorded on a Perkin Elmer 377 spectrometer and mass spectra on a spectrometer CH-7 (Varian). Melting points were obtained using a Reichert "Kofler" hot stage microscope and are uncorrected. Adsorption chromatography was conducted on silica gel (70-230 mesh ASTM, Merck) or aluminium oxide 90 standardized acc. to Brockmann (70-230 mesh ASTM, Merck). Silica gel (230-400 mesh ASTM, Merck) was used for flash chromatography. - Preparation of compounds **1**, **12**, **16**, **20** und **25** is described in the preceding paper[1].

General procedure for the treatment with aqueous acid: 1mmol starting material was dissolved in 20ml ethanol and 4ml 1%aqu. HCl and heated under reflux. After the suitable reaction time the mixture was treated with 15ml 5% aqu. $NaHCO_3$-solution. This solution was extracted four times with dichloromethane. The collected org. layers were dried over $MgSO_4$ and the solvent evaporated yielding the monoketone and/or the ethyl ester(s) (neutral fraction). The aqueous layer was acidified with dil. HCl and extracted with $CHCl_3$ for two days. The chloroform layer was dried over $MgSO_4$ and the solvent evaporated yielding the acid(s) (acidic fraction).

A first charge was used to examine the progress of the reaction by quenching part of the reaction (by extraction of 3 ml with a syringe) work up and analysis of the ^{1}H-NMR spectra of the reaction mixture. Further charges were used to determine the yields of the fragmentation products.

(±)-(1S*,3S*)-Ethyl-3-hydroxymethyl-5-oxocyclohexylcarboxylate (2) and (±)-(1S*,3S*)-3-hydroxymethyl-5-oxocyclohexylcarboxylic acid (6):

A) **1** (460mg) was treated as described under general procedure for 15 h. Flash chromatography of the neutral fraction on silica gel with petroleum ether : diethyl ether = 2 : 3 yielded **2** (220mg; 55%; colourless liquid). The acidic fraction yielded after crystallization (petroleum ether : acetone) **6** (70mg; 20%; white crystals, m.p. 106-107°C).

B) **1** (301.5mg) was dissolved in 5ml dioxane, 1ml H_2O and 3 drops 0,2N HCl and heated in a sealed tube at 120°C for 18 h. The reaction mixture was evaporated at 35°C. The resulting crystalline mass was washed with $CHCl_3$ and crystallized from petroleum ether : acetone yielding **6** (205.0mg; 87.5%).

2: IR(CCl_4)(cm^{-1}): 3640, 3450 br., 1735, 1720sh. **^{1}H-NMR($CDCl_3$)(δ):** 1.27(t)(3H) $J_{2'',1''}$= 7Hz C-H(2"); 1.92(m) $J_{2,2}$= 13.7Hz, $J_{2\alpha,3}$= 8.5Hz, $J_{2\alpha,1}$= 5Hz C-H(2α); 2.1-2.3 (m)(3H) C-H(2β,3,4α); 2.44(m)(1H) $J_{6,6}$= 14.5Hz, $J_{6\alpha,1}$= 5.7Hz C-H(6α); 2.50(m)(1H) $J_{4,4}$= 18Hz, $J_{4\beta,3}$= 8.5Hz C-H(4β); 2.6(1H)(exchangeable with D_2O) O-H; 2.65(m)(1H) $J_{6,6}$= 14.5Hz, $J_{6\beta,1}$= 6Hz, $J_{6\beta,4\beta} \approx J_{6\beta,2\beta} \approx$ 1.5Hz C-H(6β); 3.15(m)(1H) $J_{1,6\alpha}$= $J_{1,6\beta}$= 6Hz, $J_{1,2\alpha}$= $J_{1,2\beta}$= 5Hz C-H(1); 3.59(d)(2H) $J_{1',3}$= 6Hz C-H(1'); 4.16(q)(2H) $J_{1'',2''}$= 7Hz C-H(1"). **^{13}C-NMR($CDCl_3$)(δ):** 14.2 C-2"; 29.6 C-2; 37.0 C-3; 40.3 C-1; 42.2 C-6; 43.3 C-4; 61.0 C-1"; 65.9 C-1'; 174.0 COOEt; 209.2 C-5. **MS:** 200(M^+)(4.3%), 182(M^+-H_2O)(32%), 154(M^+-EtOH)(22%), 127(M^+-COOEt)(44%), 113(M^+-CH_2COOEt)(29%), 109(M^+-COOEt -H_2O)(100%).

6: IR(KBr)(cm^{-1}): 3230, 2990, 2960, 1720, 1702, 1677. **^{1}H-NMR(CD_3OD)(δ) :**1.87(m)(1H) $J_{2,2}$= 13Hz, $J_{2ax,1}$= 4.5Hz, $J_{2ax,3}$= 9.8Hz C-H(2ax); 2.02-2.15(m)(3H) C-H(2e,3ax,4ax); 2.42(m)(1H) C-H(4e); 2.45(m)(1H) $J_{6,6}$= 15.0Hz, $J_{6ax,1}$= 5.7 C-H(6ax); 2.59(m)(1H) $J_{6,6}$= 15.0Hz, $J_{6e,1}$= 4.2Hz C-H(6e); 3.15(m)(1H) $J_{1,6ax}$=5.7Hz, $J_{1,6e}$= 4.2Hz C-H(1); 3.48(d)(2H) $J_{1',3}$= 5.5Hz C-H(1'); 5.00(2H) (exchangeable with D_2O) O-H. **^{13}C-NMR(CD_3OD)(δ):** 30.4 C-2; 38.3 C-3; 41.4 C-1; 42.9 C-6; 44.25 C-4; 66.6 C-1'; 177.7 COOH; 212.1 C-5. **MS:** 172(M^+)(1.8%), 154(M^+-H_2O)(7.5%), 113(M^+-CH_2COOH)(13%), 109(M^+-COOH -H_2O)(12%), 41(allyl$^+$)(100%).

(±)-(1S*,3S*)-Ethyl-3-(tert.-butyldimethylsilyloxy)methyl-5-oxocyclohexylcarboxylate (3): **1** (133mg) in DMF (abs.; 3ml) was treated with tert.-butyldimethylchlorosilane (11mg) and imidazole

(subl.;100.5mg) at room temperature for 20 h. After addition of water the reaction mixture was extracted with petroleum ether. The org. layers were dried over $MgSO_4$ and the solvent evaporated. After purification on silica gel with petroleum ether : diethyl ether = 6 : 1 compound **3** (109mg; 52%) was obtained as colourless oil. **IR(CCl_4)(cm^{-1}):** 1735, 1720 sh. **^{1}H-NMR($CDCl_3$)(δ):** 0.00(s)(6H) Si(C-H_3)$_2$; 0.85(s)(9H) SiC(C-H_3)$_3$; 1.22(t)(3H) $J_{2'',1''}$= 6.8 Hz C-H(2"); 1.89(m)(1H) C-H(2ax); 2.01-2.25(m)(3H) C-H(2e,3,4ax); 2.31-2.46(m)(2H) C-H(4e,6ax); ~2.61(part B of an ABX-system)(1H) $J_{6,6}$= 15Hz, $J_{6e,1}$= 5.8Hz C-H(6e); 3.09(m)(1H) $J_{1,2e} \approx J_{1,2ax} \approx J_{1,6e} \approx J_{1,6ax} \approx$ 5.7Hz C-H(1); 3.51(part A and B of an ABX-system)(2H)$J_{1',1''}$= 11Hz, $J_{1a',3}$= 4Hz, $J_{1'b,3}$= 5.5Hz C-H(1'a,1'b); 4.12(q)(2H) $J_{1'',2''}$= 6.8Hz C-H(1"). **^{13}C-NMR($CDCl_3$)(δ):** -5.6 Si(CH_3)$_2$; 14.0 C-2"; 18.15 Si<u>C</u>(CH_3)$_3$; 25.8 SiC(<u>C</u>H_3)$_3$; 29.6 C-2; 36.7 C-3; 40.0 C-1; 42.0 C-6; 43.2 C-4; 60.7 C-1"; 66.2 C-1'; 174.0 COOEt; 208.4 C-5. **MS:** 299(M^+-CH_3)(12%); 258(93%), 257(M^+-tert.Bu)(100%), 184(99%), 183(M^+-OSiMe$_2$tert.Bu)(100%), 75(100%).

Reduction with sodium borohydride: (±)-(1S*,3S*,5S*)-Ethyl-3-(tert.-butyldimethylsilyloxy)methyl-5-hydroxycyclohexylcarboxylate (4) and (±)-(1S*,3S*,5R*)-ethyl-3-(tert.-butyldimethylsilyloxy)methyl-5-hydroxycyclohexylcarboxylate (5). **3** (77.4mg) in methanol (4ml) at O°C was treated with an excess of sodium borohydride for 2 h. After addition of water the mixture was extracted with dichloromethane several times. The org. layers were washed with brine and dried over $MgSO_4$. Chromatography on silica gel with petroleum ether : acetone = 9 : 1 yielded **4** (38mg; 49%) and **5** (23.2mg; 30%).

4: IR(CCl_4)(cm^{-1}): 3620, 3440br. **^{1}H-NMR($CDCl_3$)(δ):** 0.01(s)(6H) Si(C-H_3)$_2$; 0.87(s)(9H) SiC(C-H_3)$_3$; 1.04(m)(1H) $J_{4,4} \approx J_{4ax,3} \approx J_{4ax,5} \approx$10-12Hz C-H(4ax); 1.17(t)(3H) $J_{2'',1''}$= 7.3Hz C-H(2"); 1.4(m)(1H) $J_{6,6}$= 12.6Hz, $J_{6ax,5}$= 10.5Hz, $J_{6ax,1}$= 5Hz C-H(6ax); 1.7(m)(1H) $J_{3,2ax} \approx J_{3,4ax} \approx$ 10.5Hz, $J_{3,1'b}$= 6Hz, $J_{3,1'a}$= 5Hz, $J_{3,2e} \approx J_{3,4e} \approx$ 3.5Hz C-H(3); ~2.0(m)(3H) C-H(2ax,2e,4e); 2.24(m)(1H) $J_{6,6}$= 12.6Hz, $J_{6e,1} \approx J_{6e,4e} \approx$ 3.5Hz, $J_{6e,2e}$< 1Hz C-H(6e); 2.84(m)(1H) $J_{1,2e} \approx J_{1,2ax} \approx J_{1,6ax} \approx J_{1,6e} \approx$ 4.2Hz C-H(1); 3.47(part A and B of an ABX-system)(2H) $J_{1',1''}$= 10.8Hz, $J_{1'a,3}$= 5Hz, $J_{1'b,3} \approx$ 6.3Hz C-H(1'); 3.85(m)(1H) $J_{5,4ax} \approx J_{5,6ax} \approx$ 9.8Hz, $J_{5,4e} \approx J_{5,6e} \approx$ 4.2Hz C-H(5); 4.1(q)(2H) $J_{1'',2''}$= 7.3Hz C-H(1"). **^{13}C-NMR($CDCl_3$)(δ):** -5.5 Si(CH_3)$_2$; 14.1 C-2"; 18.2 Si<u>C</u>(CH_3)$_3$; 25.8 SiC(<u>C</u>H_3)$_3$; 29.7 C-2; 35.5 C-3; 36.1 C-6; 37.7 C-4; 38.5 C-1; 60.3 C-1"; 66.7 C-1'; 67.7 C-5; 174.9 COOEt. **MS:** 259(M^+-tert.Bu)(17%), 185(M^+-OSiMe$_2$tert.Bu)(6%), 93($C_7H_9^+$)(100%).

5: IR(CCl_4)(cm^{-1}): 3620, 3470 br., 1735,1715. **^{1}H-NMR($CDCl_3$)(δ):** 0.00(s)(6H) Si(C-H_3)$_2$; 0.86(s)(9H) SiC(C-H_3)$_3$; 1.25(t)(3H) $J_{2'',1''}$= 7Hz C-H(2"); 1.42(part A of an ABXY-system)(1H) $J_{4,4}$= 13.5Hz, $J_{4ax,3}$= 9.5Hz, $J_{4ax,5}$= 3Hz C-H(4ax); 1.49(m)(1H) $J_{2,2}$= 14Hz, $J_{2ax,3}$= 10Hz, $J_{2ax,1}$= 5Hz C-H(2ax); 1.65(part B of an ABXY-system)(1H) $J_{4,4}$= 13.5Hz, $J_{4e,3} \approx J_{4e,5} \approx$ 4.7Hz C-H(4e); 1.81(part A of an ABXY-system)(1H) $J_{6,6}$= 13.5Hz, $J_{6ax,1}$= 5Hz, $J_{6ax,5}$= 3.5Hz C-H(6ax); 1.88-2.07(m)(3H) C-H(2e,3,6e); 2.55(br.)(1H) (exchangeable with D_2O) O-H; 2.71(m)(1H) $J_{1,2ax} \approx J_{1,2e} \approx J_{1,6ax} \approx J_{1,6e} \approx$ 5.3Hz C-H(1); 3.39(part A of an ABXY-system)(1H) $J_{1',1''}$= 10Hz, $J_{1'a,3}$= 6.7Hz C-H(1'a); 3.49(part B of an ABX-system)(1H) $J_{1',1''}$=10Hz, $J_{1'b,3}$= 5.5Hz C-H(1'b); 3.98(m)(1H) $J_{5,6ax} \approx J_{5,4ax} \approx$ 5Hz, $J_{5,6e} \approx J_{5,4e} \approx$ 3.7Hz,C-H(5); 4.13(part A and B of an ABX_3-system)(2H) $J_{1'',1''}$= 10.8Hz, $J_{1'',2''}$= 7Hz C-H(1"). **^{13}C-NMR ($CDCl_3$)(δ):** -5.4 Si(CH_3)$_2$; 14.1 C-2"; 18.2 Si<u>C</u>(CH_3)$_3$; 25.9 SiC(<u>C</u>H_3)$_3$; 29.9 C-2; 32.3 C-3; 34.4 C-6; 36.0 C-4; 37.8 C-1; 60.7 C-1"; 65.4 C-5; 66.7 C-1'; 180.0 COOEt. **MS:** 259(M^+-tert.Bu)(14%), 185(M^+-OSiMe$_2$tert.Bu)(5%), 93($C_7H_9^+$)(100%).

(±)-(1R*,4S*,6S*,8S*)-1-Ethoxy-2-oxatricyclo[4.2.1.0^{4,8}]nonan-7-one (7): Treatment of **1** (471 mg) with 0.5% aqu. H_2SO_4 (10ml) in ethanol (20ml) at 50°C for 55 h yielded a mixture with **7** as the main product next to smaller amounts of **1** and **2**. Flash chromatography on silica gel with petroleum ether : diethyl ether with increasing amounts of diethyl ether yielded pure compound **7** (50mg). Since the ratio of **7** : (**1** + **2**) in the isolated compounds is strongly diminished compared to that found by ^{1}H-NMR analysis of the reaction mixture, decomposition of **7** on silica gel is assumed. **IR(CCl_4)(cm^{-1}):**1782. **^{1}H-NMR($CDCl_3$)(δ):** 1.21(t)(3H) $J_{2',1'}$=7Hz C-H(2'); 1.48(dd)(1H) $J_{5,5}$= 12.5Hz, $J_{5endo,4}$= 2.5Hz C-H(5endo); 1.96(d)(1H) $J_{9,9}$= 9.5Hz C-

H(9endo); 2.19(dt)(1H) $J_{9,9}$= 12.5Hz, $J_{9exo,6}$= $J_{9exo,5}$= 3.2Hz C-H(9exo); 2.25(m)(1H) $J_{6,9exo}$= 3.2Hz, $J_{6,5exo}$= 2.5Hz C-H(6); 2.3(m)(1H) $J_{5,5}$= 12.5Hz, $J_{5exo,9exo}$= 3.2Hz, $J_{5exo,6}$= 2.5Hz, $J_{5exo,4}$= 9.5Hz C-H(5exo); 2.5(d)(1H) $J_{8,4}$= 4.5Hz C-H(8); 2.74(m)(1H) $J_{4,8}$= 4.5Hz, $J_{4,3}$= 3.5Hz, $J_{4,5exo}$= 9.5Hz, $J_{4,5endo}$= 2.5Hz C-H(4); 3.53(part A of an ABX_3-system)(1H) $J_{1',1'}$= 9Hz, $J_{1'a,2'}$= 7Hz C-H(1'a); 3.72(part B of an ABX_3-system)(1H) $J_{1',1'}$= 9Hz, $J_{1'b,2'}$= 7Hz C-H(1'b); 3.81(d)(1H) $J_{3endo,3exo}$= 8Hz C-H(3endo); 4.07(dd)(1H) $J_{3endo,3exo}$= 8Hz, $J_{3exo,4}$= 3.5Hz C-H(3exo). **^{13}C-NMR($CDCl_3$)(δ):** 15.4 C-2'; 31.5 C-5; 35.6 C-4; 40.8 C-6; 43.55 C-9; 48.5 C-8; 59.2 C-1''; 73.5 C-3; 111.35 C-1; 211.5 C-7. **MS:** 182(M^+)(11%), 113() (98%), 85()(100%).

(±)-(1'S*,4'S*)-Ethyl-4'-iodomethyl-2'-oxocyclopentylacetate (8) and (±)-(1'R*,4'S*)-ethyl-4'-iodomethyl-2'-oxocyclopentylacetate (9): To 1 (228mg) dissolved in acetonitrile (abs.; 1ml) was added under an argon atmosphere a solution of tetrabutylammonium iodide (780mg; 2.1eq.) in acetonitrile (abs.; 3ml), followed by boron trifluoride etherate (0.31ml; 2.5eq.). This reaction mixture was stirred at room temperature for 3 h. After addition of 1ml sat. aqu. $NaHCO_3$ the aqu. layer was extracted thrice with chloroform. The collected org. layers were washed with 5% aqu. $Na_2S_2O_3$, dried over $MgSO_4$ and the solvent evaporated. By addition of diethyl ether the reaction mixture could be separated from tetrabutylammonium salts. Chromatography on silica gel with petroleum ether : diethyl ether = 4 : 1 yielded 8 (180.8mg; (58%), a 9 : 11 mixture of 8 : 9 (29.3mg; 10%) and pure 9 (9.8mg; 3%).

8: IR(CCl_4)(cm^{-1}): 1750, 1735. **^{1}H-NMR($CDCl_3$)(δ):** 1.27(t)(3H) $J_{2'',1''}$= 7.5Hz C-H(2''); 1.41(m)(1H) $J_{5',5'}$= $J_{5',1'}$= $J_{5',4'}$= 11.6Hz C-H(5'); 2.03(dd)(1H) $J_{3',3'}$= 18Hz, $J_{3',4'}$= 11Hz C-H(3'); 2.27-2.67(4H) C-H(1',3',4',5'); 2.50(part A of an ABX-system)(1H) $J_{2,2}$= 16.5Hz, $J_{2a,1'}$= 6.5Hz C-H(2a); 2.74(part B of an ABX-system)(1H) $J_{2,2}$= 16.5Hz, $J_{2b,1'}$= 4Hz C-H(2b); 3.28(part A of an ABX-system)(1H) $J_{1'',1''}$= 10Hz, $J_{1''a,4'}$= 6.5Hz C-H(1"a); 3.33(part B of an ABX-system) $J_{1'',1''}$= 10Hz, $J_{1''b,4'}$= 6.5Hz (1H) C-H(1"b); 4.14(q)(2H) $J_{1'',2''}$= 7.5Hz C-H(1''). **^{13}C-NMR($CDCl_3$)(δ):** 10.9 C-1''; 14.2 C-2''; 33.8 C-5'; 36.5 C-2; 37.15 C-4'; 45.0 C-3'; 47.2 C-1'; 60.7 C-1''; 171.6 C-1; 215.8 C-2'. **MS:** 310(M^+)(20%), 264(M^+-OEt)(23%), 137(M^+-OEt -I)(100%). High resolution mass spectrum: found: $310.007^{04} \pm 0.003$, calc.: 310.006^6.

9: IR(CCl_4)(cm^{-1}): 1748 sh, 1735. **^{1}H-NMR($CDCl_3$)(δ):** 1.26(t)(3H) $J_{2'',1''}$= 7Hz C-H(2''); 1.97(dt)(1H) $J_{5',5'}$= 13.5Hz, $J_{5'\alpha,4'}$= $J_{5'\alpha,1'}$= 7.5Hz C-H(5'α); 2.15(ddd)(1H) $J_{5',5'}$= 13Hz, $J_{5'\beta,4'}$= 9.5Hz, $J_{5'\beta,1'}$= 4.5Hz C-H(5'β); 2.24(dd)(1H) $J_{3',3'}$= 18Hz, $J_{3'\alpha,4'}$= 5Hz C-H(3'α); 2.51(dd)(1H) $J_{2,2}$= 18Hz, $J_{2a,1\alpha'}$= 9Hz C-H(2a); 2.54(dd)(1H) $J_{3',3'}$= 18Hz, $J_{3'\beta,4'}$= 9Hz C-H(3'β); 2.68(dd)(1H) $J_{2,2}$= 18Hz, $J_{2b,1'}$= 5Hz C-H(2b); 2.6-2.8(m)(2H) C-H(1',4'); 3.26(part A of an ABX-system)(1H) $J_{1'',1''}$= 12.5Hz, $J_{1''a,4'}$= 7.5Hz C-H(1"a); 3.30 (part B of an ABX-system)(1H) $J_{1'',1''}$= 12.5Hz, $J_{1''b,4'}$= 5.5Hz C-H(1"b); 4.15(q)(2H) $J_{1'',2''}$= 7Hz C-H(1''). **^{13}C-NMR($CDCl_3$)(δ):** 11.8 C-1''; 14.2 C-2''; 34.8 and 34.9 C-2 and C-5'; 36.4 C-4'; 43.1 C-1'; 45.0 C-3'; 60.8 C-1''; 171.7 C-1; 216.9 C-2'. **MS:** 310(M^+)(27%), 265(M^+-OEt)(27%), 223(M^+-CH_2COOEt)(7%), 183(M^+-I)(7%), 137(M^+-HI -OEt)(100%).

(±)-(1R*,4S*,5R*,6R*,8S*)-1-Ethoxy-5-propyl-2-oxatricyclo[4.2.1.$0^{4,8}$]nonan-7-one (13): 12 (270 mg) was treated as described under general procedure for 1.5 h. Flash chromatography of the neutral fraction on silica gel with petroleum ether : ethyl acetate = 6 : 1 yielded a mixture of starting material 12 and ketone 13 (1 : 5; 120mg). By two further chromatographic separations 13 (60mg; 27%) was obtained as colourless oil. **IR(CCl_4)(cm^{-1}):** 1775. **^{1}H-NMR($CDCl_3$)(δ):** 0.95(t)(3H) $J_{3'',2''}$= 7Hz C-H(3"); 1.20(t)(3H) $J_{2',1'}$= 7Hz C-H(2'); 1.2-1.39(m)(2H) C-H(2"); 1.39-1.55(m)(2H) C-H(1"); 2.04(ddd)(1H) $J_{9,9}$= 12.5Hz, $J_{9exo,6}$= 3.5Hz, $J_{9exo,5}$≈ 2Hz C-H(9exo); 2.11(m)(1H) $J_{6,9exo}$≈ $J_{6,5}$≈ 3.5Hz, $J_{6,8}$≈ 1Hz C-H(6); 2.17(d)(1H) $J_{9,9}$= 12.5Hz C-H(9endo); 2.25-2.39(m)(1H) $J_{5,4}$= 9Hz, $J_{5,6}$≈ 3.5Hz, $J_{5,9exo}$≈ 2Hz C-H(5); 2.56(d)(1H) $J_{8,4}$= 5Hz, $J_{8,6}$≈ 1Hz C-H(8); 2.76(ddd)(1H) $J_{4,8}$= 5Hz, $J_{4,5}$= 9Hz, $J_{4,3exo}$= 3.5Hz C-H(4); 3.51(dq)(1H) $J_{1',1'}$= 9Hz, $J_{1'a,2'}$= 7Hz C-H(1'a); 3.69(dq)(1H) $J_{1',1'}$= 9Hz, $J_{1'b,2'}$= 7Hz C-H(1'b); 3.82(dd)(1H) $J_{3,3}$= 8.5Hz, $J_{3exo,4}$= 3.5Hz C-H(3exo);

3.91(d)(1H) $J_{3,3}$= 8.5Hz C-H(3endo). **^{13}C-NMR($CDCl_3$)(δ):** 14.1 C-3"; 15.5 C-2´; 21.2 C-2"; 28.0 C-1"; 36.1 C-5; 37.9 C-9; 40.0 C-4; 43.9 C-6; 51.0 C-8; 59.1 C-1´; 66.6 C-3; 111.3 C-1; 210.9 C-7. **MS:** 224(M^+)(9%), 196(M^+-CO)(2%), 178(M^+-EtOH)(3.5%), 113()(100%), 85( )(79%).

(±)-(1´R*,2´S*,3´S*)-Ethyl-3´-hydroxymethyl-5´-oxo-2´-propylcyclopentylacetate (14), (±)-(1´S*, 2´S*,3´S*)ethyl-3´-hydroxymethyl-5´-oxo-2´-propylcyclopentylacetate (14a) and (±)-(1´R*,2´S*,3´S*)-3´-hydroxymethyl-5´-oxo-2´-propylcyclopentylacetic acid (15): 12 (540mg; 2mmol) was treated as described under general procedure for 30 h. Flash chromatography of the neutral fraction on silica gel with petroleum ether : ethyl acetate = 3 : 1 yielded the ester **14** (287mg; 59%) and the impure stereoisomeric compound **14a** (20mg). Acid **15** (50mg; 12%; m.p. 98-100°C) was isolated from the acidic fraction after crystallization from petroleum ether/diethyl ether/acetone.

Epimerization of 14: Pure **14** was treated as described under general procedure for 15hrs. The isolated products consisted of a mixture of **14** : **14a** = 22 : 1 separated by flash chromatography on silica gel (pentane : ethyl acetate = 3 : 1).

14: IR(CCl_4)(cm^{-1}): 3660, 3500 br., 1740, 1470, 1415. **^{1}H-NMR($CDCl_3$)(δ):** 0.96(t)(3H) $J_{3",2"}$= 6.5Hz C-H(3"); 1.26(t)(3H) J= 7Hz $COOCH_2C\underline{H}_3$; ~1.2-1.55(m)(4H) C-H(1",2"); 1.7(1H) (exchangeable with D_2O) O-H; 2.18(m)(1H) $J_{2´,1´}$= 11Hz, $J_{2´,3´}$= $J_{2´,1"a}$= $J_{2´,1"b}$= 5Hz C-H(2´); 2.37(m)(1H) $J_{1´,2´}$= 11Hz, $J_{1´,2a}$= $J_{1´,2b}$= 5Hz C-H(1´); 2.47(m)(3H) $w_{1/2}$= 4.5Hz C-H(3´,4´); 2.56 (part A of an ABX-system)(1H) $J_{2,2}$= 16Hz, $J_{2a,1´}$= 4.5Hz C-H(2a); 2.64(part B of an ABX-system)(1H) $J_{2,2}$= 16Hz, $J_{2b,1´}$= 5.5Hz C-H(2b); 3.69(dd)(1H) $J_{1"´,1"}$= 10Hz, $J_{1"´a,3´}$= 5Hz C-H(1"´a); 3.79(dd)(1H) $J_{1"´,1"}$= 10Hz, $J_{1"´b,3´}$= 3Hz C-H(1"´b); 4.13(q)(2H) J= 7Hz $COOC\underline{H}_2CH_3$. **^{13}C-NMR($CDCl_3$)(δ):** 14.2 and 14.3 C-3" and $COOCH_2\underline{C}H_3$; 20.9 C-2"; 31.8 C-1"; 33.7 C-2; 41.8 C-4´; 37.4 C-3´; 43.4 C-2´; 49.5 C-1´; 60.6 $COO\underline{C}H_2CH_3$; 62.0 C-1"´; 172.2 C-1; 219.5 C-5´. **MS:** 242(M^+)(5%), 224(M^+-H_2O)(1.2%), 199(M^+-C_3H_7)(22%), 197(M^+-OEt)(16%), 155(M^+-CH_2COOEt)(43%), 41(100%).

14a: IR(CCl_4)(cm^{-1}): 3630, 3450 br., 1735, 1715 sh. **^{1}H-NMR($CDCl_3$)(δ):** 0.89(t)(3H) $J_{3",2"}$= 7Hz C-H(3"); 1.27(t)(3H) J= 7Hz $COOCH_2C\underline{H}_3$; 1.09-1.32(m)(3 or 4H) C-H(1",2"); 1.68(br. m)(1 or 2H) C-H(1"); 1.96(dd)(1H) $J_{4´,4´}$= 18Hz, $J_{4´a,3´}$= 9Hz C-H(4´a); 2.34(dd)(1H) $J_{2,2}$= 17Hz, $J_{2a,1´}$= 8.5Hz C-H(2a); 2.37-2.64(m)(3H) C-H(2´,3´,4´b); 2.75(dd)(1H) $J_{2,2}$= 17Hz, $J_{2b,1´}$= 5.5Hz C-H(2b); 2.93(ddd)(1H) $J_{1´,2a}$= 8.5Hz, $J_{1´,2b}$= 5.5Hz, $J_{1´,2´}$= 7Hz C-H(1´); 3.75(part A of an ABX-system)(1H) $J_{1"´,1"}$= 10Hz, $J_{1"´a,3´}$= 5.5Hz C-H(1"´a); 3.79(part B of an ABX-system)(1H) $J_{1"´,1"}$= 10Hz, $J_{1"´b,3´}$= 6.5Hz C-H(1"´b); 4.18(q)(2H) J= 7Hz $COOC\underline{H}_2CH_3$. **^{13}C-NMR($CDCl_3$)(δ):** 14.1 and 14.5 $COOCH_2\underline{C}H_3$ and C-3"; 21.9 C-2"; 27.2 C-1"; 30.6 C-2; 39.0 C-4´; 39.4 C-3´; 41.3 C-2´; 51.6 C-1´; 60.7 $COO\underline{C}H_2CH_3$; 63.3 C-1"´; 172.7 C-1; 216.7 C-5´. **MS:** 242(M^+)(14%), 224(M^+-H_2O)(4.6%),199(M^+-C_3H_7)(63%), 197(M^+-OEt)(54%), 155(M^+-CH_2COOEt)(94%), 153(94%), 137(M^+-CH_2COOEt -H_2O)(23%), 41(100%).

15: IR(CCl_4)(cm^{-1}): 3620, 3500 br., 1735, 1710. **^{1}H-NMR($CDCl_3$)(δ):** 0.96(t)(1H) $J_{3",2"}$= 6.5Hz C-H(3"); 1.22-1.57(m)(4H) C-H(1",2"); 2.15(m)(1H) $w_{1/2}$= 24Hz C-H(2´); 2.41(m)(1H) $J_{1´,2a}$= 5.4Hz, $J_{1´,2b}$= 4.7Hz, $J_{1´,2´}$= 5Hz C-H(1´); 2.46(m)(3H) $w_{1/2}$= 5Hz C-H(3´,4´); 2.57(part A of an ABX-system)(1H) $J_{2,2}$= 17.4Hz, $J_{2a,1´}$= 5.4Hz C-H(2a); 2.69(part B of an ABX-system)(1H) $J_{2,2}$= 17.4Hz, $J_{2b,1´}$= 4.7Hz C-H(2b); 3.72(part A of an ABX-system)(1H) $J_{1"´,1"}$= 10.5Hz, $J_{1"´a,3´}$= 4.7Hz C-H(1"´a); 3.78(part B of an ABX-system)(1H) $J_{1"´,1"}$= 10.5Hz, $J_{1"´b,3´}$= 3.3Hz C-H(1"´b); 4.5(br.m)(2H)(exchangeable with D_2O) O-H. **^{13}C-NMR($CDCl_3$)(δ):** 14.3 C-3"; 20.8 C-2"; 31.7 C-1"; 33.4 C-2; 37.4 C-2´; 41.7 C-4´; 43.4 C-3´; 49.3 C-1´; 62.2 C-1"´; 176.6 C-1; 220.1 C-5´. **MS:** 214(M^+)(6.7%), 196(M^+-H_2O)(1.5%), 171(M^+-C_3H_7)(13%), 85(HO-CH=CH_2-C=O^+)(100%).

(±)-(1´R*,2´S*,3´S*)-Ethyl-3´-(tert.-butyldimethylsilyloxy)methyl-5´-oxo-2´-propylcyclopentylacetate (30): 14 (140mg) was stirred with tert.-butyldimethylchlorosilane (100mg), imidazole (subl., 87mg)

and DMF (abs., 0.17mg) at room temperature for 15 h. After addition of water the reaction mixture was extracted with petroleum ether. The org. layers were dried over $MgSO_4$ and the solvent evaporated. After purification by chromatography on silica gel with petroleum ether : diethyl ether = 6 : 1 as eluent **30** (130mg; 63%) was obtained. **IR(CH_2Cl_2)(cm^{-1}):** 1740. **^{1}H-NMR($CDCl_3$)(δ):** -0.016(s)(3H) Si(C-H_3)$_2$; 0.03(s)(3H) Si(C-H_3)$_2$; 0.82(s)(9H) SiC(C-H_3)$_3$; 0.91(t)(3H) $J_{3'',2''}$= 7Hz C-H(3"); 1.21(t)(3H) J= 7Hz $COOCH_2$C-H_3; ~1.3(br. m)(2H) C-H(2"); 1.45(m)(2H) C-H(1"); 2.09(m)(1H) $J_{2',3'}\approx$ 13Hz, $J_{2',1''a}\approx J_{2',1''b}\approx J_{2',1'}\approx$ 6.5Hz C-H(2'); 2.29(part A of an ABX-system)(1H) $J_{4',4'}$= 19Hz, $J_{4'\alpha,3'}\leq$ 1Hz C-H(4'α); 2.43(part B of an ABX-system)(1H) $J_{4',4'}$= 19Hz, $J_{4'\beta,3'}$= 10Hz C-H(4'β); 2.26-2.45(m)(2H) C-H(1',3'); 2.50(part A of an ABX-system)(1H) $J_{2,2}$= 17Hz, $J_{2a,1'}$= 5Hz C-H(2a); 2.56(part B of an ABX-system)(1H) $J_{2,2}$= 17Hz, $J_{2b,1'}$= 6Hz C-H(2b); 3.58(dd)(1H) $J_{1'',1''}$= 10Hz, $J_{1''a,3'}$= 3Hz C-H(1''a); 3.74(dd)(1H) $J_{1'',1''}$= 10Hz, $J_{1''b,3'}$= 3.5Hz C-H(1''b); 4.08(q)(2H) J= 7Hz COOC-H_2CH_3. **^{13}C-NMR($CDCl_3$)(δ):** -5.8 Si(CH_3)$_2$; 14.2 und 14.3 C-3" und $COOCH_2\underline{C}H_3$; 18.0 Si$\underline{C}$(CH_3)$_3$; 20.9 C-2"; 25.7 SiC($\underline{C}H_3$)$_3$; 31.8 C-1"; 33.7 C-2; 41.8 C-4'; 37.4 C-3'; 43.4 C-2'; 49.5 C-1'; 60.6 $COO\underline{C}H_2CH_3$; 62.0 C-1''; 172.2 C-1; 219.5 C-5'. **MS:** 341(M^+-CH_3)(2%), 311(M^+-OEt)(3%), 299(M^+-tert.Bu)(100%), 225(M^+-OSiMe_2tert.Bu)(17%), 179(76%).

(±)-(1'R*,2'S*,3'S*)-Ethyl-3'-(tert.-butyldimethylsilyloxy)methyl-5'-hydroxy-2'-propylcyclopentylacetate (31): **30** (320mg) was dissolved in a mixture of methanol (2ml) and diethyl ether (3ml) and cooled to 0°C. After addition of an excess of sodium borohydride the reaction mixture was stirred with slow warming to room temperature for 2 h. Addition of water was followed by extraction with dichloromethane, drying of the org. layers over $MgSO_4$ and evaporation of the solvent. The product was purified by chromatography on silica gel with petroleum ether : diethyl ether yielding **31** (150mg; 46% starting from **14**). **IR(CCl_4)(cm^{-1}):** 3500 br., 1725. **^{1}H-NMR($CDCl_3$)(δ):** 0.05(s)(6H) Si(C-H_3)$_2$; 0.87(s)(t)(12H) J= 7Hz $COOCH_2$C-H_3; SiC(C-H_3)$_3$; 1.24(t)(3H) $J_{3'',2''}$= 7Hz C-H(3"); 1.17-1.45(m)(4H) C-H(1",2"); ~1.5(m)(1H) C-H(2'); 1.58(m)(1H) $J_{4',4'}$= 16.5Hz, $J_{4'\beta,3'}$= 8Hz, $J_{4'\beta,5'}$= 4.5Hz C-H(4'β); 1.86(m)(1H) $J_{1',2b}$= $J_{1',2'}$= 10Hz, $J_{1',5'}$= 4.5Hz, $J_{1',2a}$= 4Hz C-H(1'); 2-2.16(m)(1H) C-H(3'); 2.08(m)(1H) $J_{4',4'}$= 16.5Hz, $J_{4'\alpha,3'}$= 8Hz, $J_{4'\alpha,5'}$= 6.5Hz C-H(4'α); 2.24(dd)(1H) $J_{2,2}$= 16Hz, $J_{2b,1'}$= 10Hz C-H(2b); 2.54(dd)(1H) $J_{2,2}$= 16Hz, $J_{2a,1'}$= 4Hz C-H(2a); 3.62(d)(2H) $J_{1'',3'}$= 5.5Hz C-H(1''); 3.89(m)(1H) $J_{5',1'}$= $J_{5',4'\beta}$= 4.5Hz, $J_{5',4'\alpha}$= 6.5Hz C-H(5'); 4.12(q)(2H) J= 7Hz COOC-H_2CH_3. **^{13}C-NMR($CDCl_3$)(δ):** -5.6 and -5.5 Si(CH_3)$_2$; 14.2 and 14.3 C-3" und $COOCH_2\underline{C}H_3$; 18.2 Si$\underline{C}$(CH_3)$_3$; 21.3 C-2"; 25.9 SiC($\underline{C}H_3$)$_3$; 31.5 C-1"; 37.2 C-2; 41.1 C-4'; 38.4 C-3'; 45.8 C-2'; 49.8 C-1'; 60.4 $COO\underline{C}H_2CH_3$; 63.6 C-1''; 78.4 C-5'; 174.1 C-1. **MS:** 313(M^+-OEt)(0.4%), 301(M^+-tert.Bu)(5%), 271(M^+-COOEt)(1.2%), 75(100%).

(±)-(1S*,3R*,5R*,7S*,8S*,9R*)-3-Ethoxy-2-oxatetracyclo[6.3.0.0^{3,7}.0^{5,9}]undecan-6-one (17): **16** (254mg) was treated as described under general procedure for 1 hr. Flash chromatography of the neutral fraction on silica gel with petroleum ether : ethyl acetate = 9 : 1 yielded the monoketone **17** (154mg; 74%) as colourless oil. **IR(CCl_4)(cm^{-1}):** 1775. **^{1}H-NMR($CDCl_3$)(δ):** 1.19(t)(3H) $J_{2',1'}$= 7.5Hz C-H(2'); 1.56-1.87(m)(2H) C-H(10endo,11); 1.87-2.15(m)(3H) C-H(4exo,10exo,11); 2.18(d)(1H) $J_{4,4}$= 14Hz C-H(4endo); 2.21(m)(1H) $w_{1/2}$= 5Hz C-H(5); 2.68(m)(2H) $J_{7,8}$= 4.8Hz, $J_{9,10exo}$= 11Hz, $J_{9,8}$= 9.6Hz, $J_{9,10endo}$= 4Hz C-H(7,9); 2.83(m)(1H) $J_{8,9}$= 9.6Hz, $J_{8,7}$= 4.8Hz, $J_{8,1}$= 4Hz C-H(8); 3.52(dq)(1H) $J_{1',1'}$= 9Hz, $J_{1'a,2'}$= 7.5Hz C-H(1'a); 3.72(dq)(1H) $J_{1',1'}$= 9Hz, $J_{1'b,2'}$= 7.5Hz C-H(1'b); 4.65(m)(1H) $J_{1,8}$= 4Hz, $J_{1,11}$= 3Hz, $J_{1,11}\leq$ 1Hz C-H(1). **^{13}C-NMR($CDCl_3$)(δ):** 15.4 C-2'; 23.4 C-10; 34.0 C-11; 36.5 C-9; 37.8 C-4; 44.7 C-8; 47.4 C-5; 51.7 C-7; 59.2 C-1'; 83.4 C-1; 111.2 C-3; 210.4 C-6. **MS:** 208(M^+)(72%), 180(M^+-CO)(51%), 162(M^+-EtOH)(43%), 134(M^+-CO -EtOH)(100%).

(±)-(1R*,2R*,6R*,7S*)-Ethyl-7-hydroxy-4-oxobicyclo[4.3.0]non-2-ylcarboxylate (18) and (±)-(1R*,2R*,6R*,7S*)-7-hydroxy-4-oxobicyclo[4.3.0]non-2-ylcarboxylic acid (19): **16** (254mg) was treated as described under general procedure for 55 h. The neutral fraction yielded ester **18**. Pure ester **18** (115mg;

51%; m.p. 73-75°C) was obtained by flash chromatography on silica gel with petroleum ether : diethyl ether = 1 : 3 or by crystallization from petroleum ether/diethyl ether. The acidic fraction could be purified by flash chromatography on silica gel with dichloromethane : methanol = 19 : 1 and crystallization from chloroform/petroleum ether yielding acid **19** (18mg; 9%; m.p. 138-143°C).

18: **IR(CCl_4)(cm^{-1}):** 3620, 3440 br.,1730, 1715sh. **^{1}H-NMR($CDCl_3$)(δ):** 1.27(t)(3H) $J_{2',1'}$= 7Hz C-H(2'); 1.73-2.0(m)(4H) C-H(8,9); 2.05(1H)(exchangeable with D_2O) O-H; 2.33-2.66(m)(4H) C-H(1,5,6); 2.44(part A of an ABX-system)(1H) $J_{3,3}$= 17Hz, $J_{3\beta,2}$= 11Hz C-H(3β); 2.57(part B of an ABX-system)(1H) $J_{3,3}$= 17Hz, $J_{3\alpha,2}$= 4.5Hz C-H(3α); 2.97(ddd)(1H) $J_{2,3\beta}$= 11Hz, $J_{2,1}$= 10Hz, $J_{2,3\alpha}$= 4.5Hz C-H(2); 4.17(q)(2H) $J_{1',2'}$=7Hz C-H(1'); 4.26(m)(1H) $w_{1/2}$= 8Hz C-H(7). **^{1}H-NMR(C_6D_6)(δ):** 0.91(t)(3H) $J_{2',1'}$=7Hz C-H(2'); 1.40(m)(1H) $J_{8,8}$= 13Hz, $J_{8\alpha,9\alpha}$=$J_{8\alpha,9\beta}$=9Hz, $J_{8\alpha,7}$= 4.5Hz C-H(8α); 1.56(m)(1H) $J_{8,8}$=13Hz, $J_{8\beta,9\alpha}$=$J_{8\beta,9\beta}$=4Hz, $J_{8\beta,7}$=2Hz C-H(8β); 1.59-1.72(m)(2H) C-H(9); 1.66(m)(1H) $J_{6,1}$= 8.5Hz, $J_{6,5\beta}$= 7.5Hz, $J_{6,5\alpha}$= 6.5Hz, $J_{6,7}$= 4Hz C-H(6); 2.15(dd)(1H) $J_{5,5}$= 16Hz, $J_{5\beta,6}$=7.5Hz C-H(5β); 2.17(1H)(exchangeable with D_2O) O-H; 2.28(m)(1H) C-H(1); 2.36(dd)(1H) $J_{3,3}$= 16Hz, $J_{3\beta,2}$= 11Hz C-H(3β); 2.40(dd)(1H) $J_{5,5}$= 16Hz, $J_{5\alpha,6}$= 6.5Hz C-H(5α); 2.53(dd)(1H) $J_{3,3}$= 16Hz, $J_{3\alpha,2}$= 5Hz C-H(3α); 2.89(ddd)(1H) $J_{2,3\beta}$= 11Hz, $J_{2,1}$= 9Hz, $J_{2,3\alpha}$= 5Hz C-H(2); 3.72(m)(1H) $J_{7,8\alpha}$= 4.5Hz, $J_{7,6}$= 4Hz, $J_{7,8\beta}$= 2Hz C-H(7); 3.90(q)(2H) $J_{1',2'}$= 7Hz C-H(1'). **^{13}C-NMR($CDCl_3$)(δ):**14.2 C-2'; 28.5 C-8; 34.1 C-9; 38.2 C-5; 38.8 and 43.2 C-6 and C-1; 40.9 C-3; 45.1 C-2; 60.8 C-1'; 74.9 C-7; 174.5 COOEt; 211.5 C-4. **MS:** 226(M^+)(47%), 208(M^+-H_2O)(9%), 180(M^+-EtOH)(84%), 153(M^+-COOEt)(100%), 135(M^+-COOEt -H_2O)(96%), 125(94%).

19: **IR(Fluorolube)(cm^{-1}):** 3405, 3390, 1700. **^{1}H-NMR(CD_3OD)(δ):** 1.70-2.00(m)(4H) C-H(8,9); 2.30-2.66(m)(4H) C-H(1,5,6); 2.39(part A of an ABX-system)(1H) $J_{3,3}$= 17.3Hz, $J_{3ax,2}$= 10.5Hz C-H(3ax); 2.55(part B of an ABX-system)(1H) $J_{3,3}$= 17.3Hz, $J_{3e,2}$= 5Hz C-H(3e); 2.89(ddd)(1H) $J_{2,3ax}$= 10.5Hz, $J_{2,1}$= 9.5Hz, $J_{2,3e}$= 5Hz C-H(2ax); 4.16(m)(1H) $w_{1/2}$= 10Hz C-H(7); 4.95(s)(2H)(exchangeable with D_2O) O-H. **^{13}C-NMR(CD_3OD)(δ):** 29.5 C-8; 34.5 C-9; 38.7 C-5; 40.0 C-2; 41.6 C-3; 43.8 and 45.9 C-1 and C-6; 75.5 C-7; 177.9 C-1'; 214.4 C-4. **MS:** 198(M^+)(25%), 180(M^+-H_2O)(33%), 152(M^+-HCOOH)(40%), 125(M^+-CH_2=CHCOOH) (82%), 41(100%).

(±)-(1S*,3R*,5R*,7S*,8S*,9R*)-3-Ethoxy-2-oxatetracyclo[6.4.0.0^{3,7}.0^{5,9}]dodecan-6-one (21): **20** (300mg) was dissolved in 30ml THF and after addition of 15ml 3% aqu. HCl heated under reflux for 2 h. The reaction mixture was extracted several times with ethyl acetate. The org. layers were washed with aqu. sat. $NaHCO_3$ and brine, dried over $MgSO_4$ and the solvent evaporated. After purification on silica gel with petroleum ether : diethyl ether = 7 : 1 by flash chromatography **21** (210mg; 85%) was obtained. **IR(KCl)(cm^{-1}):** 1780, 1770,1595. **^{1}H-NMR($CDCl_3$)(δ):** 1.21(t)(3H) $J_{2',1'}$= 6.8Hz C-H(2'); 1.44(m)(2H) C-H(11endo,12endo); 1.78(m)(3H) C-H(10endo,10exo,11exo); 2.06(m)(3H) C-H(4endo,5,12exo); 2.37(m)(1H) C-H(9); 2.53(m)(1H) $J_{4,4}$= 14Hz C-H(4exo); 2.63(m)(1H) C-H(8); 2.67(m)(1H) $J_{7,8}$= 4.9Hz C-H(7); 3.53(part A of an ABX_3-system)(1H) $J_{1',1'}$= 9Hz, $J_{1'a,2'}$= 6.8Hz C-H(1'a); 3.74(part B of an ABX_3-system)(1H) $J_{1',1'}$= 9Hz, $J_{1'b,2'}$= 6.8Hz C-H(1'b); 4.37(m)(1H) $w_{1/2}$= 9.7Hz $J_{1,12exo}$= 3Hz, $J_{1,12endo}$= 1.5Hz C-H(1). **^{13}C-NMR($CDCl_3$)(δ):** 15.4 C-2'; 16.8 C-11; 23.5 C-10; 27.2 C-12; 30.0 C-9; 38.7 C-8; 39.1 C-4; 46.9 C-5; 53.0 C-7; 59.0 C-1'; 74.6 C-1; 110.6 C-3; 210.3 C-6. **MS:** 222(M^+)(34%),. 176(M^+-EtOH)(53%), 148(M^+-EtOH - CO)(100%).

(±)-(6'S*,7'S*)-Ethyl-8'-oxobicyclo[4.3.0]non-9'-en-7'-ylacetate (22), (±)-(6'S*,7'S*)-8'-oxobicyclo[4.3.0]non-9'-en-7'-ylacetic acid (23) and (±)-(6'S*,7'R*)-ethyl-8'-oxobicyclo[4.3.0]non-9'-en-7'-ylacetate (24): **20** (1.07g; 4mmol) was treated as described under general procedure for 30 h. The acidic fraction was extracted with ethyl acetate. The neutral fraction was purified by flash chromatography on silica gel with petroleum ether : ethyl acetate = 7 : 1 yielding pure **22** (111.7mg), a mixture of **22** : **24** = 9 : 1 (256.6mg) and a mixture of **22** : **24** = 3 : 4 (47.0mg). The overall yield of **22** and **24** is 415.3mg (48%). By preparative TLC

(2mm, silica gel 60 F_{254}, Merck) with petroleum ether : diethyl ether = 3 : 1 pure **24** (3mg; m.p. 44-46°C) was obtained. The acidic fraction was purified by flash chromatography on silica gel with dichloromethane (1.5% methanol) followed by preparative TLC (2mm, silica gel 60 F_{254}, Merck) with toluene : chloroform : methanol as eluent yielding **23** (111.1mg; 13.3%).

Epimerization: pure **22** as well as a 4 : 1 mixture of **22** : **24** were treated as described under general procedure for 15 h. In both cases a mixture of **22** : **24** = 9 : 1 resulted. The ratio of the components **22** : **24** was determined by glas capillary - gas chromatography with a 15m x 0.32mm DB-WAX column at 180°C (isotherm).

22: IR(CCl_4)(cm^{-1}): 3070, 1735, 1710, 1625. **^{1}H-NMR($CDCl_3$)(δ):** 1.18(td)(1H) $J_{5',5'}$= $J_{5'ax,4'ax}$= 12Hz, $J_{5'ax,6'}$= 12Hz, $J_{5'ax,4'e}$= 3Hz C-H(5'ax); 1.29(t)(3H) $J_{2'',1''}$= 7.3Hz C-H(2"); 1.40(m)(1H) $J_{3',3'}$= $J_{3'ax,2'ax}$= $J_{3'ax,4'ax}$= 13Hz, $J_{3'ax,2'e}$= $J_{3'ax,4'e}$= 3Hz C-H(3'ax); 1.50(m)(1H) $J_{4',4'}$= $J_{4'ax,3'ax}$= $J_{4'ax,5'ax}$= 13Hz, $J_{4'ax,3'e}$= $J_{4'ax,5'e}$= 3Hz C-H(4'ax); 1.87(m)(1H) C-H(4'e); 2.02(m)(1H) C-H(3'e); 2.19-2.40(m)(4H) C-H(2'ax,5'e,6',7'); 2.41(dd)(1H) $J_{2,2}$= 15.6Hz, $J_{2a,7'}$= 9Hz C-H(2a); 2.83(m)(2H) $J_{2,2}$= 15.6Hz, $J_{2b,7'}$= 3.5Hz C-H(2b,2'e); 4.14(q)(2H) $J_{1'',2''}$= 7.3Hz C-H(1"); 5.87(s)(1H) C-H(9). **^{13}C-NMR($CDCl_3$)(δ):** 14.1 C-2"; 25.2 and 26.7 C-3' and C-4'; 30.9 C-5'; 34.2 and 34.6 C-2 and C-2'; 48.5 C-6'; 49.5 C-7'; 60.5 C-1"; 125.7 C-9'; 172.1 C-1; 182.7 C-1'; 208.15 C-8'. **MS:** 222(M^+)(30%), 176(M^+-EtOH)(49%), 148(M^+-HCOOEt)(100%), 120(M^+-HCOOEt-CO)(50%). High resolution mass spectrum: found: 222.125[6], calc.: 222.125[7] ±0.001. **UV:** λ_{max}(ethanol)= 231nm, λ_{max}(hexane)= 226nm.

23: IR(CCl_4)(cm^{-1}): 3530, 3500-2400, 3040, 2660, 1735, 1710, 1705, 1675, 1625. **^{1}H-NMR($CDCl_3$)(δ):** 1.18(m)(1H) $J_{5',5'}$= $J_{5'ax,4'ax}$= $J_{5'ax,6'ax}$= 12Hz, $J_{5'ax,4'e}$= 2.5Hz C-H(5'ax); 1.40(m)(1H) $J_{3',3'}$= $J_{3'ax,2'ax}$= $J_{3'ax,4'ax}$= 13Hz, $J_{3'ax,2'e}$= $J_{3'ax,4'e}$= 3Hz C-H(3'ax); 1.50(m)(1H) $J_{4',4'}$= $J_{4'ax,3'ax}$= $J_{4'ax,5'ax}$= 12Hz, $J_{4'ax,3'e}$= $J_{4'ax,5'e}$= 2.7Hz C-H(4'ax); 1.88(m)(1H) $J_{4',4'}$= 12Hz C-H(4'e); 2.02(m)(1H) $J_{3',3'}$= 13Hz C-H(3'e); 2.2-2.45(m)(4H) $J_{2',2'}$= 13Hz, $J_{2'ax,3'e}$= 6.5Hz, $J_{2'ax,3'ax}$= 13Hz C-H(2'ax (~2.26ppm), 5'e, 6', 7'(~2.35ppm)); 2.48(dd)(1H) $J_{2,2}$= 16Hz, $J_{2a,7'}$= 8.5Hz C-H(2a); 2.84(m)(1H) $J_{2',2'}$= 13Hz, $J_{2'e,3'ax}$= 3Hz C-H(2'e); 2.85(dd)(1H) $J_{2,2}$= 16Hz, $J_{2b,7'}$= 4Hz C-H(2b); 5.90(m)(1H) C-H(9'); 7.25-8.5(1H)(exchangeable with D_2O) COO-H. **^{13}C-NMR($CDCl_3$)(δ):** 25.3 and 26.8 C-3'and C-4'; 31.1 C-5'; 34.2 and 34.6 C-2 and C-2'; 48.7 C-6'; 49.4 C-7'; 125.7 C-9'; 176.9 C-1; 183.7 C-1'; 209.0 C-8'. **MS:** 194(M^+)(33%), 176(M^+-H_2O)(27%), 148(M^+-HCOOH)(100%), 134(M^+-CH_2COOH)(27%), 120(M^+-HCOOH,-CO)(70%). **UV:** λ_{max}(ethanol)= 231nm.

24: IR(CCl_4)(cm^{-1}): 3070 w, 1735, 1705, 1625. **^{1}H-NMR($CDCl_3$)(δ):** 1.05(qd)(1H) $J_{5',5'}$= $J_{5'ax,6'}$= $J_{5'ax,4'ax}$= 12.5Hz, $J_{5'ax,4'e}$= 3Hz C-H(5'ax); ~1.25(m)(1H) $w_{1/2}$= 5Hz C-H(4'e); 1.27(t)(3H) $J_{2'',1''}$= 7Hz C-H(2"); ~1.36(m)(1H) $J_{3',3'}$= $J_{3'ax,2'ax}$= $J_{3'ax,4'ax}$= 12.5Hz, $J_{3'ax,2'e}$= $J_{3'ax,4'e}$= 3Hz C-H(3'ax); 1.52(m)(1H) $J_{4',4'}$= $J_{4'ax,3'ax}$= $J_{4'ax,5'ax}$= 12.5Hz, $J_{4'ax,3'e}$= $J_{4'ax,5'e}$= 3Hz C-H(4'ax); 1.82-2.12(m)(3H) C-H(2'ax, 3'e, 5'e); 2.28(m)(1H) $J_{2',2'}$= 19Hz, $J_{2'e,3'e}$= 8Hz, $J_{2'e,3'ax}$= 3Hz, $J_{2'e,9'}$= 1Hz C-H(2'e); 2.30(dd)(1H) $J_{2,2}$= 18Hz, $J_{2a,7'}$= 12Hz C-H(2a); 2.77-2.92(m)(1H) C-H(6'); 2.82(dd)(1H) $J_{2,2}$= 18Hz, $J_{2b,7'}$= 4Hz C-H(2b); 2.97(m)(1H) $J_{7',2a}$= 12Hz, $J_{7',6'}$= 7Hz, $J_{7',2b}$= 4Hz C-H(7'); 4.18(q)(2H) $J_{1'',2''}$= 7Hz C-H(1"); 5.85(m)(1H) $w_{1/2}$= 4Hz C-H(9'). **^{13}C-NMR($CDCl_3$)(δ):** 14.2 C-2"; 25.3 and 27.8 C-3' and C-4'; 30.7, 30.9 and 31.5 C-2, C-2' and C-5'; 45.1 and 45.8 C-6' and C-7'; 60.7 C-1"; 125.1 C-9'; 173.0 C-1; 184.3 C-1'; 208.9 C-8'. **MS:** 222(M^+)(51%), 176(M^+-EtOH)(67%), 148(M^+-HCOOEt)(100%), 134(M^+-CH_3COOEt)(59%).

(±)-(1R*,4S*,6R*)-6-(2'-Hydroxyethyl)-7,7-dimethoxybicyclo[2.2.1]heptan-2-one (26): **25** (242mg) was treated as described under general procedure for 1/2 h. The neutral fraction was purified by flash chromatography on silica gel with petroleum ether : ethyl acetate = 2 : 1 for two times yielding the monoketone **26** (68mg; 29%) and equal amounts of the product of fragmentation **27**. **IR(CCl_4)(cm^{-1}):** 3640, 3480 br., 1750. **^{1}H-NMR($CDCl_3$)(δ):** 1.06(dd)(1H) $J_{5,5}$= 12.5Hz, $J_{5endo,6}$= 4Hz C-H(5endo); 1.40(part A of an $ABMX_2$-sys-

tem)(1H) $J_{1',1}$= 14Hz, $J_{1'a,6}$≈ 7.5Hz, $J_{1'a,2}$≈ 6.5Hz C-H(1'a); 1.45(part B of an $ABMX_2$-system) (1H) $J_{1',1}$= 14Hz, $J_{1'b,6}$= $J_{1'b,2}$= 6.5Hz C-H(1'b); 1.86(part A of an ABXY-system)(1H) $J_{3,3}$= 17.5Hz C-H(3endo); 2.31(m)(1H) $J_{5,5}$= 12.5Hz, $J_{5exo,6}$= 11Hz, $J_{5exo,4}$= 4.5Hz, $J_{5exo,3exo}$= 3Hz C-H(5exo); 2.49(part B of an ABXY-system)(1H) $J_{3,3}$= 17.5Hz, $J_{3exo,4}$= 4.5Hz, $J_{3exo,5exo}$= 2.5Hz C-H(3exo); 2.50(m)(1H) $J_{6,5exo}$= 11Hz, $J_{6,1'b}$≈ 6.5Hz, $J_{6,1'a}$≈ 7.5Hz, $J_{6,1}$= 4.5Hz, $J_{6,5endo}$= 4Hz C-H(6); 2.58(t)(1H) $J_{4,3exo}$≈ $J_{4,5exo}$≈ 4.5Hz C-H(4); 2.68(d)(1H) $J_{1,6}$= 4.5Hz C-H(1); 3.25(s)(3H) OC-H_3; 3.28(s)(3H) OC-H_3; 3.62(t)(2H) $J_{2',1'a}$= $J_{2',1'b}$= 6.5Hz C-H(2'). **^{13}C-NMR($CDCl_3$)(δ):** 31.3 C-6; 33.6 C-1"; 36.6 C-5; 38.6 C-4; 44.9 C-3; 50.2 and 50.8 OCH_3 and OCH_3; 57.4 C-1; 60.9 C-2'; 112.0 C-7; 212.6 C-2. **MS:** 214(M^+)(17%), 183(M^+-OCH_3)(7%), 169(M^+-CH_2CH_2OH)(31%), 145(M^+-O≡C-CH_2-CH=CH_2)(100%).

(±)-(1S*,3R*)-Ethyl-3-(2'-hydroxyethyl)-5-oxocyclohexylcarboxylate (27) and (±)-(1S*,3R*)-3-(2'-hydroxyethyl)-5-oxocyclohexylcarboxylic acid (28)

A) 25 (484mg; 2mmol) was treated as described under general procedure for 11 h. The neutral fraction was purified by flash chromatography on silica gel with petroleum ether : ethyl acetatee = 2 : 1 yielding the ester 27 (227mg; 53%) next to the monoketone 26 (55mg; 13%). After flash chromatography on silica gel with dichloromethane : methanol = 19 : 1 the acidic fraction yielded compound 28 (50mg; 13%).

B) 26 (100mg; 0.47mmol) was treated as described under general procedure for 7 h and purified as described above yielding a mixture of 27 : 26 = 4 : 3.

27: **IR(CCl_4)(cm^{-1}):** 3630, 3450br., 1735, 1720 sh. **^{1}H-NMR($CDCl_3$)(δ):** 1.26(t)(3H) $J_{2'',1''}$= 7.4Hz C-H(2"); 1.53(part A of an $ABMX_2$-system)(1H) $J_{1',1}$= 15Hz, $J_{1'a,2'a}$≈ $J_{1'a,2'b}$≈ $J_{1'a,3}$≈ 7Hz C-H(1'a); 1.59(part B of an $ABMX_2$-system)(1H) $J_{1',1}$= 15Hz, $J_{1'b,2'a}$≈ $J_{1'b,2'b}$≈ $J_{1'b,3}$≈ 7Hz C-H(1'b); 1.79(part A of an ABXY-system)(1H) $J_{2,2}$= 13.7Hz, $J_{2\alpha,3}$= 9.5Hz, $J_{2\alpha,1}$= 4.8Hz C-H(2α); 2.0(1H)(exchangeable with D_2O) O-H; 2.09(part A of an ABX-system)(1H) $J_{4,4}$= 14Hz, $J_{4\alpha,3}$= 9Hz C-H(4α); 2.14-2.3(2H) C-H(3,2β); 2.42(part A of an ABX-system)(1H) $J_{6,6}$= 15Hz, $J_{6\alpha,1}$= 6Hz C-H(6α); 2.53(part B of an ABX-system)(1H) $J_{4,4}$= 14.4Hz, $J_{4\beta,3}$= 4Hz C-H(4β); 2.65(part B of an ABX-system)(1H) $J_{6,6}$= 15Hz, $J_{6\beta,1}$= 6Hz C-H(6β); 3.06(m)(1H) $J_{1,2\alpha}$≈ $J_{1,2\beta}$≈ $J_{1,6\alpha}$≈ $J_{1,6\beta}$≈ 5.5Hz C-H(1); 3.67(t)(2H) $J_{2',1'a}$= $J_{2',1'b}$= 7Hz C-H(2'); 4.16(t)(2H) $J_{1'',2''}$= 7.4Hz C-H(1"). **^{13}C-NMR($CDCl_3$)(δ):** 14.2 C-2"; 31.4 C-3; 32.6 C-1'; 37.8 C-2; 40.3 C-1; 42.2 C-6; 46.6 C-4; 59.7 C-2'; 61.0 C-1"; 174.2 COOEt; 209.2 C-5. **MS:** 214(M^+)(16%), 196(M^+-H_2O)(5%), 169(M^+-OEt)(26%), 141(M^+-COOEt)(28%), 123(M^+-COOEt -H_2O)(40%), 41(allyl$^+$)(100%).

28: **IR($CHCl_3$)(cm^{-1}):** 3450 br., 1720. **^{1}H-NMR(CD_3OD)(δ):** 1.50(part A of an $ABMX_2$-system)(1H) $J_{1',1}$= 13Hz, $J_{1'a,2'a}$= $J_{1'a,2'b}$= 6.5Hz, $J_{1'a,3}$= 6.3Hz C-H(1'a); 1.59(part B of an $ABMX_2$-system)(1H) $J_{1',1}$= 13Hz, $J_{1'b,2'a}$= $J_{1'b,2'b}$= 6.5Hz, $J_{1'b,3}$= 5.6Hz C-H(1'b); 1.80(part A of an ABXY-system)(1H) $J_{2,2}$= 15Hz, $J_{2ax,3}$= 10.7Hz, $J_{2ax,1}$= 4.4Hz C-H(2ax); 2.02-2.24(m)(3H) C-H(1,4ax,2e); 2.44(part A of an ABX-system)(1H) $J_{6,6}$= 15Hz, $J_{6ax,1}$= 6.3Hz C-H(6ax); 2.45(dd)(1H) $J_{4,4}$= 13Hz, $J_{4e,3}$= 8.8Hz C-H(4e); 2.67(part B of an ABX-system)(1H) $J_{6,6}$= 15Hz, $J_{6e,1}$= 5Hz C-H(6e); 3.09(m)(1H) $J_{1,6ax}$= 6.3Hz, $J_{1,6e}$= 5Hz, $J_{1,2ax}$= 4.4Hz, $J_{1,2e}$= 5Hz C-H(1e); 3.59(t)(2H) $J_{2',1'}$= 6.5Hz C-H(2'); 4.94(2H)(exchangeable with D_2O) O-H. **^{13}C-NMR(CD_3OD)(δ):** 32.6 C-3; 33.8 and 39.2 C-2 and C-1'; 41.6 C-1; 43.0 C-6; 47.5 C-4; 60.2 C-2'; 177.8 COOH; 212.2 C-5. **MS:** 186(M^+)(2.5%), 168(M^+-H_2O)(17%), 141(M^+-COOH)(24%), 123(M^+-COOH -H_2O)(28%), 41(allyl$^+$)(100%).

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