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THERMAL GENERATION OF 2-ALKYL-3-CARBETHOXY-CYCLOPENTADIENONES FROM ANGULARLY ALKYLATED TRICYCLO[5.2.1.$0^{2,6}$]DECADIENONES. THEIR USE IN THE SYNTHESIS OF CYCLOPENTENOIDS AND DIHYDROSARKOMYCINS

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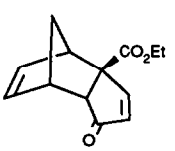
Abstract: Angularly alkylated 2-carboethoxy-tricyclo[5.2.1.$0^{2,6}$]tricyclodecadienones **2** *exhibit a facile and efficient thermal [4+2]-cycloreversion reaction in DMF at 155 °C to produce 2-alkyl-3-carbo-ethoxy-cyclopentadienones* **9**. *Trapping of these relatively stable cyclopentadienones with cyclopentadiene gives the novel tricyclodecadienone esters* **10** *in excellent yields. Regio- and stereospecific enone reduction in* **10** *with zinc in acetic acid, followed by Flash Vacuum Thermolysis (FVT) leads to cyclopentenoids (***20** *and* **25***) which upon catalytic hydrogenation afford dihydrosarkomycins (***22** *and* **30***) in high overall yields.*

In the preceding paper[1] it was demonstrated that 6-alkyl substituted tricyclodecadienones **2** are thermodynamically considerably less stable than the parent ester **1** and rapidly undergo a skeletal Cope rearrangement to bridge ketone **3**. As will be shown in this report, the effect of angular alkyl substitution at C_6 in **1** goes beyond mere promotion of this [3,3]-sigmatropic rearrangement. The alkyl substituteded esters **2**/**3** exhibit an unexpected and facile cycloreversion to give 2-alkyl cyclopentadienone 3-carboxylates upon heating in solution[2]. It should be noted that in all thermal experiments carried out with **2**, the actual starting material consists of an equilibrium mixture of **2** and **3**.



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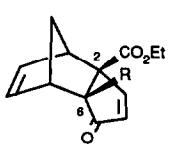

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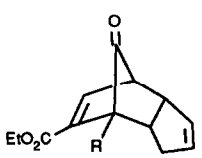
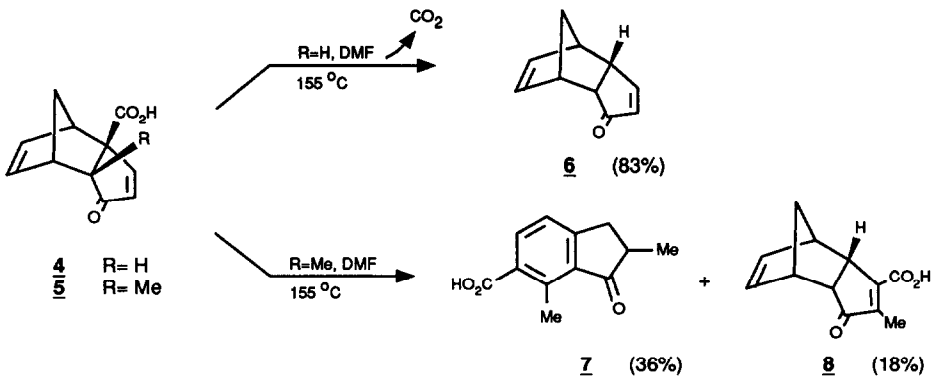


3

An interesting difference in thermal behavior was encountered when the parent acid **4** and the angularly methylated acid **5** were subjected to decarboxylation in DMF at 155 °C. Acid **4**, being a vinylogous β-keto carboxylic acid, readily decarboxylates to furnish the parent tricyclodecadienone **6** in 83 % yield[3,4]. Interestingly, under these conditions, **5** did not show such a decarboxylation, but instead produced a mixture of indanone **7** and the novel tricyclodecadienone **8** as the major products, in yields of 36 % and 18 %, respectively (Scheme 1).

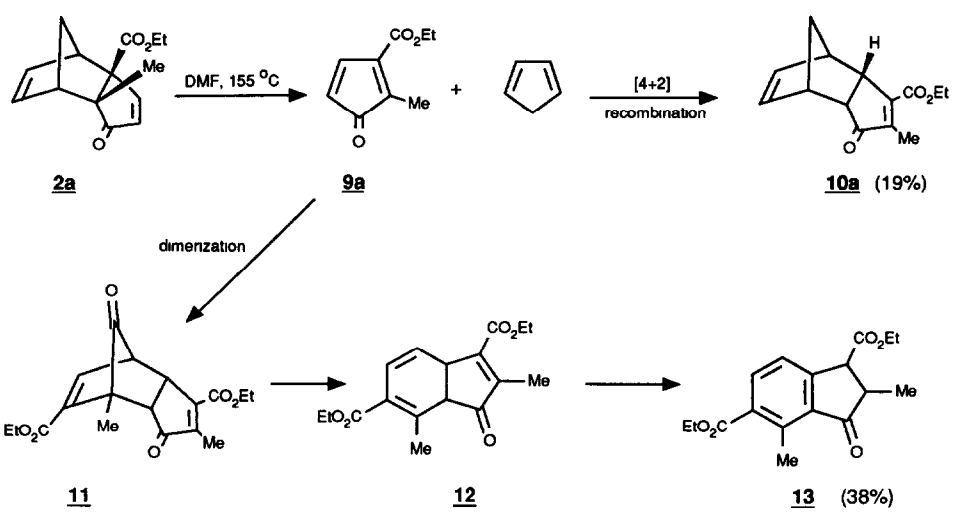
The 6-methyl substituted ester **2a** was rapidly converted into a mixture of tricyclic β-enone ester **10a** and indanone ester **13**, in yields of 19 % and 38 %, respectively, under similar thermal conditions (Scheme 2).

Scheme 1



This concurrent formation of **10a** and **13** during the thermolysis of **2a** in DMF can readily be rationalized by assuming a [4+2] cycloreversion as the initial step to form cyclopentadienone **9a** and cyclopentadiene. Subsequently, **9a** partly recombines with cyclopentadiene to afford tricyclodecadienone **10a**, having a reversed regiochemistry in comparison with the starting material. The stability of **9a** is apparently sufficiently large to find another cyclopentadienone molecule to dimerize with. This dimerization results in the regioselective formation of tricyclic diketone **11**. Under the thermal conditions applied, subsequent decarbonylation occurs to form dihydroindenone **12**, that aromatizes to indanone **13**. In the case of thermolysis of acid **5** a similar pathway is followed, the corresponding bis-carboxylic acid of **13** now decarboxylates to give product **7** (Scheme 1).

Scheme 2

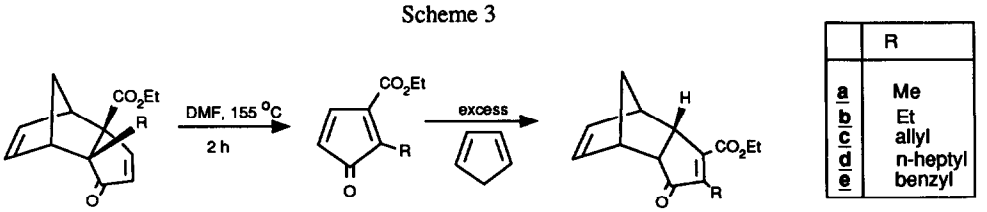


The intermediacy of free cyclopentadienone **9a** was proven by carrying out a crossed Diels-Alder reaction with cyclopentadiene. The addition of a twenty-fold excess of this diene to a solution of **2a** in DMF

and heating this mixture at 155 °C for 2.5 hours, afforded ethyl 4-methyl-tricyclodecadienone 3-carboxylate **10a** in a high yield (79 %). Unambiguous proof for the intermediacy of **11** in the formation of **13** will be given below.

The thermal behavior of **2a** in DMF appeared to be typical for 6-alkyl substituted tricyclodecadienone-2-carboxylates. In all four other cases studied, the thermolysis proceeded smoothly to generate the corresponding 2-alkyl-cyclopentadienone esters **9b-e**, which again were trapped with added excess of cyclopentadiene, to afford tricyclic enones **10b-e** in good yields (Scheme 3). This efficient generation of **9** and its smooth regiospecific cycloaddition reaction with cyclopentadiene makes this thermolysis of practical utility. It will be shown below that these enone esters **10** can serve as efficient precursors for dihydrosarkomycins.

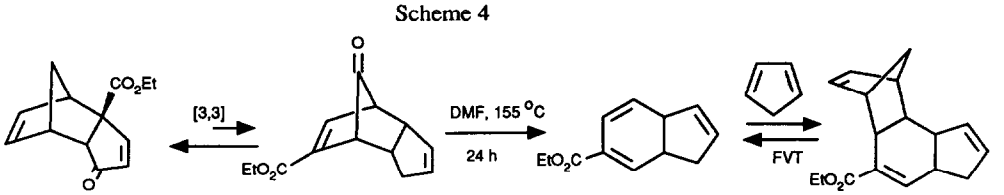
Scheme 3



2 **9** **10** (64-85%)

In contrast to the angularly alkylated tricyclodecadienone carboxylates **2**, parent ester **1** appeared to be thermally relatively stable when heated in DMF. Complete conversion of **1** was only achieved after 24 hours, yielding an intractable mixture. However, when the thermolysis of **1** was carried out in the presence of an excess of cyclopentadiene, with the aim to trap possible cyclopentadienone intermediates, the formation of tetracyclic ester **15** was observed in a yield of 35%, after two successive flash chromatographic purification steps. The rationale for the formation of **15** is outlined in Scheme 4. It involves the cheletropic decarbonylation of the Cope isomer of **1** and Diels-Alder reaction of the intermediate dihydroindene 6-carboxylate **14** with cyclopentadiene. There has been some controversy[5,6] about which olefinic bond of dihydroindenes reacts in a [2+4] cycloaddition with cyclopentadiene. In the cycloaddition of **14** with cyclopentadiene the regiochemistry is similar to that observed by Baxter and Garrath[5] for the Diels-Alder reaction of dihydroindene with cyclopentadiene. The intermediate dihydroindene carboxylate **14** could be generated by subjecting **15** to a thermal cycloreversion reaction at 525 °C by employing the flash vacuum thermolysis technique.

Scheme 4

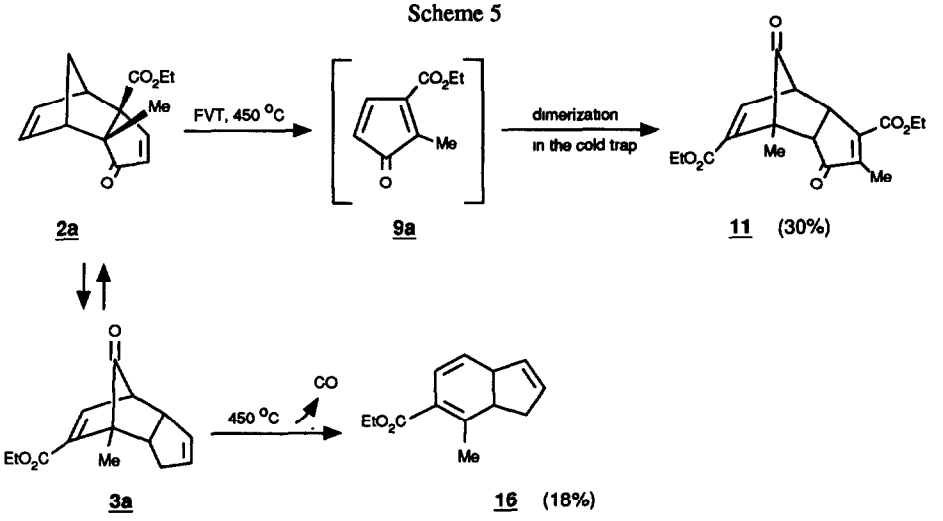


1 **3** (R= H) **14** **15** (35%)

In order to verify the intermediacy of cyclopentadienone dimer **11** during the formation of **13** in the thermolysis of **2a** in DMF (Scheme 2), the isolation of **11** was attempted by performing the thermolysis of **2a** under FVT-conditions. Under these gas phase conditions, it is expected that the cycloreversion of **2a/3a** will

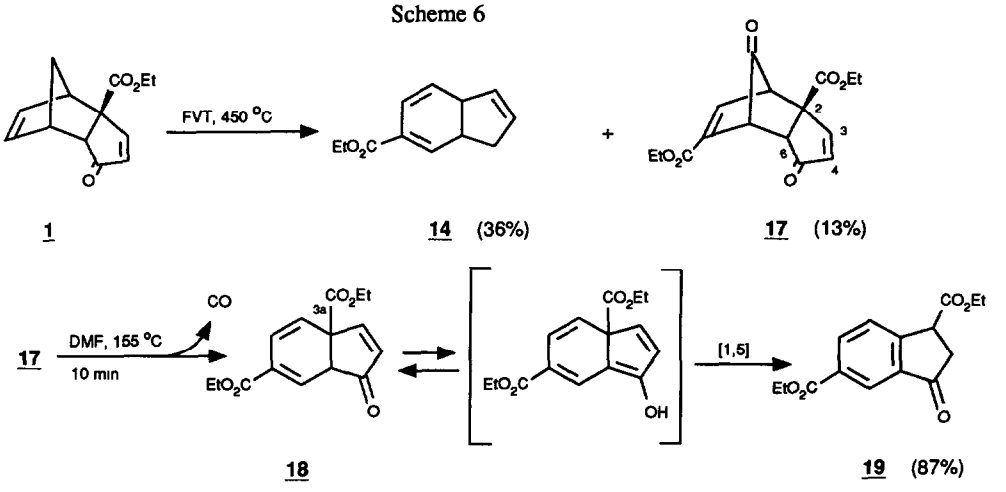
initially produce cyclopentadienone **9a** that subsequently will dimerize in the cold trap. Decarbonylation of the thus-obtained dimer **11** is now unlikely. The gas phase thermolysis yielded a mixture of the expected **11** and dihydroindene **16** in a molar ratio of 2.4:1 (for the isolated yields see Scheme 5). The structure of **11** was unequivocally established by an X-ray diffraction analysis[7]. Subsequent heating of **11** in DMF caused rapid decarbonylation to give indanone **13** as the sole product. The formation of **16** can be rationalized by invoking a thermal cheletropic elimination of CO[8] from **3a** (Scheme 5).

Scheme 5



By employing identical thermal conditions for parent ester **1**, a mixture of cyclopentadienone dimer **17** and dihydroindene **14**[9] was obtained in equimolar amounts (Scheme 6). The substitution pattern in structure

Scheme 6



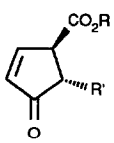
17 could be deduced from its ^{1}H-NMR spectrum: β-enone proton H_3 appeared as a doublet ($^3J_{3,4}$= 5.7 Hz) at δ 7.45 ppm, implying that one of the carbethoxy groups must occupy the angular 2- or 6-position. Determination of all vicinal coupling constants by performing additional homonuclear decoupling experiments

revealed structure **17**. It should be noted that the orientation of the cyclopentadienones in the respective dimerizations, *i.e.* **9a** to **11** and **9** (R=H) to **17**, is different. The formation of **17** shows that for **9** (R=H), the ester conjugated enone moiety is more dienophilic than the unsubstituted enone function in this dimerization. The observed regiochemistry in these two dimerizations with respect to the relative orientation of both ester functions, is explained by invoking minimal dipole interaction between these functions in the transition state, forcing this polar groups as far apart as possible[10,11].

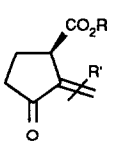
In analogy with the conversion of **11** into **13**, compound **17** was cleanly transformed into **19** by heating in DMF at 155 °C for 10 min. Indanone **19** is most likely formed via decarbonylation of **17** to give **18**, that undergoes successively a [1,5] shift of its 3a-carbethoxy group and an aromatization[12,13] (Scheme 6). The intermediacy of dihydroindenones **12** (*Cf.* Scheme 2) and **18** in the respective formation of **13** and **19** was confirmed by preparing these two compounds by an independent flash vacuum thermolysis (450 °C, 2.10^{-2} torr) of **11** and **17**, respectively.

The results described sofar allow the following conclusions. The introduction of an alkyl group at the 6-position in tricyclic ester **1** drastically alters its thermal behavior in DMF. Whereas in ester **1** thermal fragmentation proceeds by an initial Cope rearrangement, followed by decarbonylation, 6-alkyl esters **2** fragment exclusively by a [4+2] cycloreversion. The ease at which the 2-alkylcyclopentadienone carboxylates **9** are formed in the last-mentioned reaction suggests a considerable stabilization of these cyclic dienones because of the presence of the electron donating 2-alkyl group as well as the electron withdrawing 3-carboxylate function (push-pull effect[13,14]). The ethoxycarbonyl substituent probably stabilizes by extending the conjugation of the enone moiety in **9**. This enhanced stability is apparently sufficient to favor, at least in DMF, the cycloreversion reaction over the alternative decarbonylation process[15]. In the gas phase both processes occur simultaneously for both substrates **1** and **2**. At the relatively low temperature of 150 °C as applied in DMF, there is apparently much more chemoselectivity than under FVT conditions (450 °C) and as a consequence one of the electrocyclic processes predominates. It should be noted that, whereas the decarbonylation of tricyclodecadienones with a bridged ketone function is a well-known process[8,16], the thermal cycloreversion of such simply substituted tricyclodecadienones as **2** in solution, to generate cyclopentadienones, has no precedent[13].

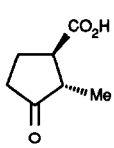
The efficient synthesis of tricyclodecadienones **10** from readily available ester **1** is tempting their use as synthons. In this paper we would like to illustrate the utilization of **10** for the synthesis of the novel cyclopentenoid esters **20** which essentially are structural isomers of sarkomycin esters **21**. These latter



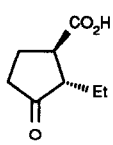
20



21



22a



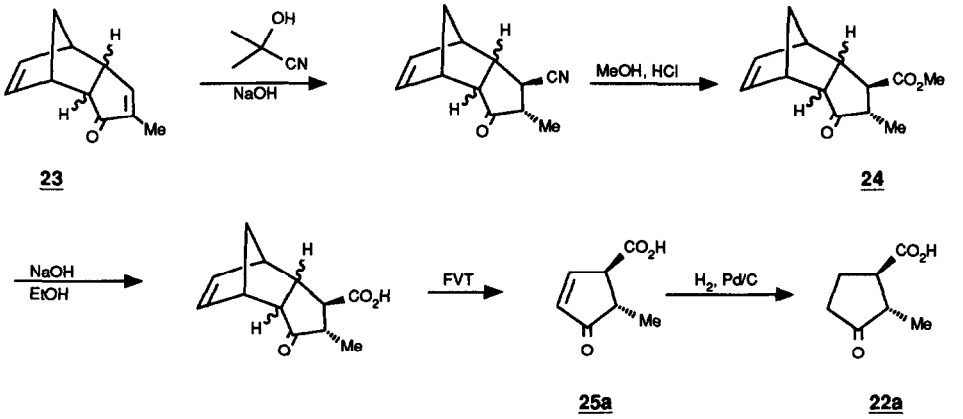
22b

cyclopentenoids have been and still are the subject of numerous synthetic studies because of their anti-tumor and antiviral potential[17]. Obviously, access to their isomers **20** permits screening of the biological activity of these cyclopentenoids. Furthermore, selective reduction of the enone system in esters **20** eventually would

lead to another series of biologically interesting compounds *viz.* the dihydrosarkomycins. These relatively simple cyclopentanones have some promising biological features, *e.g.* dihydrosarkomycin **22a** is completely ineffective against bacteria, however, it exhibits strong oncostatic activity[18], similar to sarkomycin **21** (R=R'= H)[19]. Some derivatives of dihydrosarkomycin, *e.g.* its homologue **22b**, were found[20] to inhibit Ehrlich ascites carcinoma even more strongly than sarkomycin and dihydrosarkomycin **22a**. Some syntheses of dihydrosarkomycin have already been reported in the literature[21].

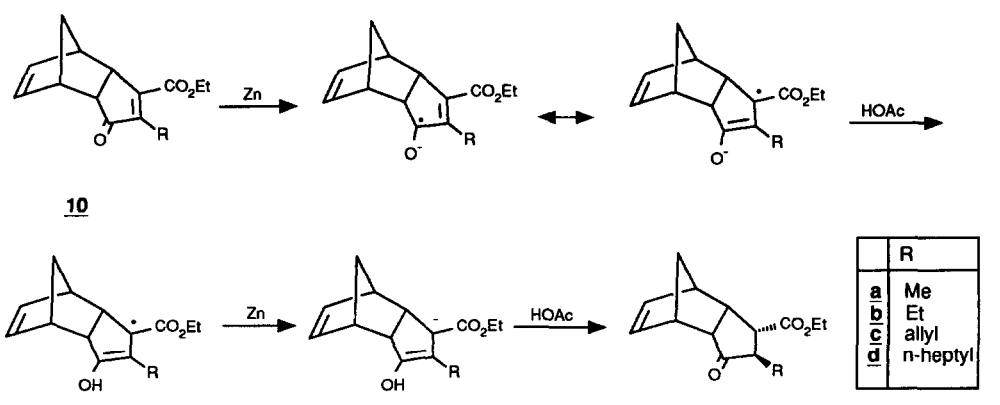
Previously, we[22] accomplished the synthesis of dihydrosarkomycin **22a** in five steps and in an overall yield of 50 % from an *endo/exo*-mixture of 4-methyltricyclodecadienone **23** (Scheme 7). A comparison of

Scheme 7



structure **24** in this scheme with that of **10a** immediately suggests a reduction of the C_3-C_4 olefinic bond of **10a** as a possible route to *endo*-**24**. For this selective reduction of **10a**, Ohkata's method[23] using zinc in acetic acid was chosen. This method was shown to produce *trans*-products, exclusively. Application of Ohkata's method for the reduction of **10** indeed gave a single product with a *trans*-configuration (Scheme 8). Spectral

Scheme 8

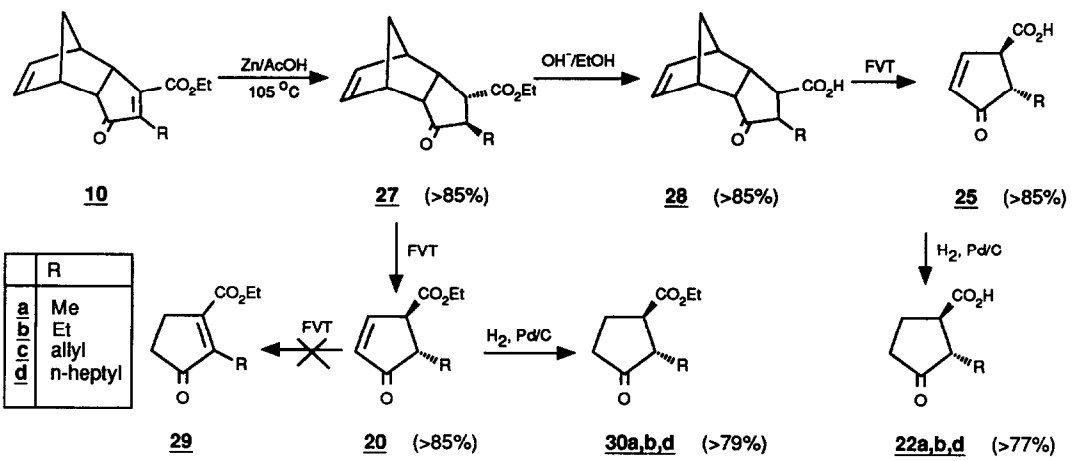


analysis revealed however, that the reduction product has structure **27**, thus with opposite configurations at C_4

and C_5 as compared with compound 24. The ^{1}H-NMR coupling constant $^3J_{H\,3,4}$ in 27a amounted to 11.7 Hz. This value agrees well with that of *endo*-24[22] ($^3J_{H\,3,4}$ = 12 Hz) pointing to a *trans*-relationship of the 3-carboalkoxy- and the 4-alkyl substituent in both compounds. The rationale[24] for this diastereospecific formation of 27 is depicted in Scheme 8. The observed stereospecificity in this reduction with Zn/AcOH appeared to be characteristic for all tricyclic esters 10, because in the five cases studied, the reaction afforded *trans*-diastereomer 27 as the sole product. Apparently, the final protonation of the intermediate anion 26 leading to 27 takes place exclusively from its less hindered *convex* face. By conducting this reduction in the presence of excess reducing agent (zinc) and a proton donor (AcOH), the reduction and protonation steps that follow radical anion formation are favored and accordingly diminishing competing side reactions, such as dimer formation[24].

Hydrolysis of 27 in alkaline ethanol produced the corresponding carboxylic acids 28 in high yields after acid-base extraction (Scheme 9). However, these carboxylic acids 28 were obtained as equimolar *trans*-mixtures, suggesting that the alkaline reaction conditions cause an isomerization of 27 (double epimerization).

Scheme 9



Subsequent flash vacuum thermolysis (FVT) of 28 afforded the labile carboxylic acids 25 in high yields. Formally, these compounds are isomers of sarkomycins. As acids 25 were difficult to purify, they were immediately hydrogenated catalytically[22] to the desired dihydrosarkomycins 22, which were obtained as NMR-pure compounds after acid-base extraction. The overall yields of dihydrosarkomycins 22, calculated on 1, amounted to 40 %. The spectral data of dihydrosarkomycin 22a and its homologue 22b were in good agreement with those reported[20-22]. Tricyclic esters 27 were also utilized for the synthesis of dihydrosarkomycin ethyl esters. FVT of esters 27 produced the surprisingly stable cyclopentenone carboxylates 20a-d in excellent yields and as single compounds. Unexpectedly, under the FVT-conditions applied, no formation of the thermodynamically more stable cyclopentenones 29 was observed. Due to both the presence of the ester function and the alkyl group, which considerably lower the potential energy of 29 relative to 20, a facile migration of the double bond in 20 to form 29 seemed apparent[25]. However, under the gas phase conditions applied (510 °C, 2.10^{-2} torr), the barrier for double bond migration, which is either a sigmatropic or a radical

rearrangement, is apparently large enough to prevent such an isomerization. On the other hand access to esters **29** is quite feasible either by base or catalyzed isomerisation of **20**[25] or by selective reduction of the enone double bond in **2** followed by cycloreversion using FVT[26].

The cyclopentenones **20a,b,d** were subsequently converted into the desired dihydrosarkomycin carboxylates **30a,b,d** in high overall yields by catalytic hydrogenation on Pd/C, using Verlaak's conditions[22].

In conclusion, we have shown that angular alkylated tricyclic esters **2** readily undergo thermal cycloreversion in DMF at 155 °C to produce 2-alkyl-3-carboethoxycyclopentadienones **9**. Trapping of these relatively stable cyclopentadienones with cyclopentadiene lead to the novel tricyclodecadienone esters **10** in a surprisingly effective process. The tricyclic structures **10** are suitable precursors for the syntheses of cyclopentenoids **20** and **25**, and of dihydrosarkomycins **22**.

Experimental

General remarks

^{1}H-NMR spectra were recorded on a Bruker WH-90 spectrometer in $CDCl_3$ solution with $SiMe_4$ as internal reference. ^{13}C-NMR spectra were recorded on a Bruker WP-60 spectrometer or Bruker WM200 (in $CDCl_3$). Mass spectra were obtained using a double-focusing VG 7070E mass spectrometer. Melting points were determined using a Reichert melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 298 infrared spectrophotometer. UV spectra were measured on a Perkin-Elmer 555 spectrophotometer. Elemental analyses were carried out in the Microanalytical Department of the University of Nijmegen. Capillary GC (CapGC) analyses were performed using a HP 5790 A, containing a cross-linked methyl silicone column; L=25 m, ID= 0.31 mm, film 0.17 µm applying a temperature program: 100 °C to 250 °C; 15 °C/min unless indicated otherwise. Flash chromatographic purifications (pressure (p): 1.5-2 atm) were carried out using either silica gel (Kieselgel 60 H (Merck)) or Al_2O_3 (150 neutral typ T (Merck)). THF was dried by subsequent treatment with $CaCl_2$, CaH_2 and distillation from $LiAlH_4$, before use. All reactions with LDA or alkyllithium compounds were performed in a nitrogen atmosphere. Alkyl halides were distilled before use. Glass equipment and syringes were oven-dried.

Syntheses

*6-Methyl-5-oxo-*endo*-tricyclo*[5.2.1.0^{2,6}]*deca-3,8-diene 2-carboxylic acid* **5**

Ester **2a** (0.528 g, 2.276 mmol) was added to a stirred soln of 10 % methanolic NaOH and the resulting mixture was stirred for 1.5 h at r.t. After removal of MeOH *in vacuo*, water (20 ml) was added and the mixture was extracted twice with Et_2O. The aqueous residue was acidified by addition of HCl (20 % aq) and extracted with Et_2O (3 x 50 ml), washed with water (2 x 20 ml), dried and concentrated *in vacuo* to yield pure **5** (0.446 g, 96 %) as a white-yellow solid. ^{1}H-NMR (CD_3COCD_3): δ 1.29 (s, 3H, C_6-Me), 1.69 (dt, ^{2}J=9.0 Hz, J=1.6 Hz, 1H, H_{10}), 2.43 (d, ^{2}J=9.0 Hz, 1H, H_{10}), 2.62-2.73 (m, 1H, H_7), 3.11-3.22 (m, 1H, H_1), 5.93 (d, J=5.9 Hz, 1H, H_4), 5.96 (s, 2H, H_8, H_9), 5.32-6.22 (br s, 1H, C_2-COOH), 7.48 (d, J=5.9 Hz, 1H, H_3); IR (KBr): ν 1732 (C=O, acid), 1668 (C=C), 1580 (C=C, unsat.), 1220 cm^{-1}; EI/MS: m/e 204 (M^+), 176 (M-CO), 161 (M-CO-Me), 66 (C_5H_6); Found 204.0781. $C_{12}H_{12}O_3$ requires 204.0786.

Thermal fragmentation of **5** *in DMF*

A stirred soln of **5** (100 mg, 0.49 mmol) in DMF (5 ml) was heated at 155 °C for 2.5 h in a N_2 atmosphere. The reaction mixture was then allowed to cool and most of the DMF was removed *in vacuo*, Et_2O (50 ml) was added and the organic layer was thoroughly washed with water (8 x 5 ml) to remove the remaining DMF. After drying ($MgSO_4$) and concentration *in vacuo* a mixture of *2,7-dimethyl-1-oxo-indane 6-carboxylic acid* **7** and *4-methyl-5-oxo-*endo*-tricyclo*[5.2.1.0^{2,6}]*deca-3,8-diene 3-carboxylic acid* **8** (86 mg crude yield) was obtained in a molar ratio of 2:1 (^{1}H-NMR). Flash chromatography (silica gel, acetone) gave pure **7** as a viscous oil (17 mg, 17 %). ^{1}H-NMR: δ 1.31 (d, J=7.0 Hz, 3H, C_2-Me), 2.60-2.85 (m, 2H, H_2, H_3), 2.98 (s, 3H, C_7-Me), 3.38 (dd, ^{2}J=18.7 Hz, ^{3}J=9.4 Hz, 1H, H_3), 7.34 (d, J=7.9 Hz, 1H, H_4), 8.18 (d, J=7.9 Hz, 1H, H_5), 8.50-9.14 (br s, 1H, C_6-COOH); IR (CCl_4): ν 3500-2500 (COOH), 2950, 2930, 1710 (C=O, acid), 1600, 1580 (C=C, unsat.) cm^{-1}; EI/MS: m/e 204 (M^+), 189 (M-CH_3), 158, 115, 91 (benzyl), 77; CI/MS: m/e 205 (M^++1); Found 204.0791. $C_{12}H_{12}O_3$ requires 204.0786. These carboxylic acids **7** and **8** were further characterized as their methyl esters. Esterification of a mixture of **7** and **8** with CH_2N_2 (0.3 M soln in Et_2O) in CH_2Cl_2 for 15 min at r.t. quantitatively converted them into a 2:1 mixture of the corresponding methyl esters: *methyl 2,7-dimethyl-1-oxo-indane 6-carboxylate* (^{1}H-NMR: δ 1.27 (d, J=7 Hz, 3H, C_2-Me), 2.49-2.87 (m, 2H, H_2, H_3), 2.89 (s, 3H, C_7-Me), 3.35 (dd, ^{2}J=19 Hz, ^{3}J=9 Hz, 1H, H_3), 3.93 (s, 3H,

OMe), 7.30 (d, J=7.9 Hz, 1H, H_4), 8.01 (d, J=7.9 Hz, 1H, H_5); CapGC/EI/MS: m/e 218 (M^+), 203 (M-CH_3), 187 (M-OMe), 159 (M-COOMe), 115, 91 (benzyl), 77; Found 218.0941. $C_{13}H_{14}O_3$ requires 218.0943) and *methyl* 4-*methyl*-5-*oxo*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*deca*-3,8-*diene* 3-*carboxylate* (^{1}H-NMR: δ 1.55-1.82 (m, 2H, H_{10}), 1.91 (d, ^{4}J=1.8 Hz, 3H, C_4-Me), 2.82-2.98 (m, 1H, H_6), 3.11-3.27 (m, 2H, H_1, H_7), 3.40-3.57 (m, 1H, H_2), 3.84 (s, 3H, OMe), 5.64-5.98 (m, 2H, H_8, H_9); CapGC/EI/MS: m/e 218 (M^+), 159 (M-COOEt), 66 (C_5H_6)).

Thermal fragmentation of **2a** *in DMF*

Ester **2a** (286 mg, 1.23 mmol) was dissolved in DMF (5 ml) and heated, while stirring, at 155 °C in a N_2 atmosphere. After work-up (see 'Thermal fragmentation of **5** in DMF'), a mixture containing **10a** and **13** was obtained (molar ratio 1:2, ^{1}H-NMR) that could not be separated by chromatographic means. Therefore, **10a** and **13** were synthesized independently by the two following procedures:

Preparation of **13**: A stirred soln of **11** (24 mg, 0.072 mmol; see for the preparation of **11** below) was heated in DMF at 155 °C for 10 min. Flash chromatography (Al_2O_3, EtOAc /*n*-hexane = 1/10) gave pure **13** (20 mg, 91 %) as an oil. *Diethyl* 2,4-*dimethyl*-3-*oxo*-*indane* 1,5-*dicarboxylate* **13**: ^{1}H-NMR: δ 1.22-1.50 (m, 9H, C_2-Me, 2xOCH_2CH_3), 2.90 (s, 3H, C_4-Me), 2.93-3.28 (m, 1H, H_2), 3.78 (d, J=4.7 Hz, 1H, H_1), 4.28 (q, J=7 Hz, 2H, C_1-$COOCH_2$), 4.39 (q, J=7 Hz, 2H, C_5-$COOCH_2$), 7.51 (d, J=8.2 Hz, 1H, H_7), 8.04 (d, J=8.2 Hz, 1H, H_6); IR (CCl_4): ν 1730 (C=O), 1600, 1182 cm^{-1}; EI/MS: m/e 304 (M^+), 276 (M-CO), 231 (M-COOEt), 203 (M-CO-COOEt), 175 (M-2CO-COOEt); Found 304.1317. $C_{17}H_{20}O_5$ requires 304.1311.

Preparation of **10a**: A soln of **2a** (900 mg, 3.879 mmol) and cyclopentadiene (7 ml) in DMF was heated at 155 °C for 2.5 h. After cooling to 140 °C most of the cyclopentadiene was removed by blowing through N_2. Subsequently, the mixture was cooled to 50 °C and the DMF was removed *in vacuo*. The resulting crude **10a** was separated by flash chromatography (Al_2O_3, gradient: *n*-hexane to EtOAc /*n*-hexane = 1/20; Rf = 0.3, EtOAc /*n*-hexane = 1/20) from the remaining cyclopentadiene dimers (Rf = 0.8, purple spots with 25 % aqueous H_2SO_4 spray) to produce pure **10a** (708 mg, 79 %) as an oil. *Ethyl* 4-*methyl*-5-*oxo*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*deca*-3,8-*diene* 3-*carboxylate* **10a**: ^{1}H-NMR: δ 1.37 (t, J=7.1 Hz, 3H, OCH_2CH_3), 1.62 A of AB (d, J=9.0 Hz, 1H, H_{10}), 1.77 (dt, ^{2}J =9.0 Hz, J=1.6 Hz, 1H, H_{10}), 1.91 (d, ^{4}J=1.8 Hz, 3H, C_4-Me), 2.90 (t, J=5.1 Hz, 1H, H_6), 3.09-3.31 (m, 2H, H_1, H_7), 3.40-3.60 (m, 1H, H_2), 4.31 (q, J=7.1 Hz, 2H, OCH_2CH_3), 5.76 (dd, ^{3}J=5.5 Hz, ^{4}J=3.0 Hz, 1H, H_8 or H_9), 5.91 (dd, ^{3}J=5.5 Hz, ^{4}J=3.0 Hz, 1H, H_8 or H_9); ^{13}C-NMR: δ 8.9 (q, C_3-$COOCH_2CH_3$), 13.9 (q, C_4-Me), 44.4 (d), 44.6 (d), 45.4 (d), 50.2 (d, C_1, C_2, C_6, C_7), 52.0 (t, C_{10}), 60.9 (t, C_3-$COOCH_2$), 132.9 (d, C_8, C_9), 150.2 (s), 155.1 (s, C_3, C_4), 165.9 (s, C_3-CO), 210.8 (s, C_5); IR (CCl_4): ν 2990, 2940, 1709 (C=O, ester), 1210 cm^{-1}; EI/MS: m/e 232 (M^+), 158 (M-CO-HOEt), 131 (M-CO-COOEt), 66 (C_5H_6); Found 232.1097. $C_{14}H_{16}O_3$ requires 232.1099.

Ethyl 4-*ethyl*-5-*oxo*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*deca*-3,8-*diene* 3-*carboxylate* **10b**

The procedure for the synthesis of **10a** was followed, using **2b** (236 mg, 0.959 mmol) and an excess of cyclopentadiene (3.0 ml) in DMF (15 ml). After heating for 1 h, the usual work-up and flash chromatography (Al_2O_3, gradient: *n*-hexane to EtOAc /*n*-hexane = 1/20; Rf = 0.25, EtOAc /*n*-hexane = 1/20) pure **10b** (190 mg, 81 %) was obtained as an oil. ^{1}H-NMR: δ 0.94 (t, J=7.4 Hz, 3H, C_4-CH_2CH_3), 1.37 (t, J=7.0 Hz, 3H, OCH_2CH_3), 1.62 A of AB (d, ^{2}J=8.7 Hz, 1H, H_{10}), 1.78 (dt, ^{2}J =8.7 Hz, J=1.5 Hz, 1H, H_{10}), 2.40 (q, J=7.4 Hz, 2H, C_4-CH_2), 2.87 (dd, J=5.7 Hz, J=4.8 Hz, 1H, H_6), 3.09-3.33 (m, 2H, H_1, H_7), 3.52 (t, J=4.8 Hz, 1H, H_2), 4.31 (q, J=7.0 Hz, 2H, OCH_2CH_3), 5.75 (dd, ^{3}J=5.4 Hz, ^{4}J=2.8 Hz, 1H, H_8 or H_9), 5.93 (dd, ^{3}J=5.4 Hz, ^{4}J=2.8 Hz, 1H, H_8 or H_9); ^{13}C-NMR: δ 12.7 (q, C_4-CH_2CH_3), 13.9 (q, C_3-$COOCH_2CH_3$), 17.2 (t, C_4-CH_2), 44.7 (d), 45.0 (d), 45.4 (d), 50.2 (d, C_1, C_2, C_6, C_7), 52.2 (t, C_{10}), 60.8 (t, C_3-$COOCH_2$), 132.8 (d, C_8, C_9), 154.8 (s), 155.6 (s, C_3, C_4), 165.7 (s, C_3-CO), 210.8 (s, C_5); IR (CCl_4): ν 2960, 1708 (C=O, ester), 1205 cm^{-1}; EI/MS: m/e 246 (M^+), 66 (C_5H_6); Found 246.1250. $C_{15}H_{18}O_3$ requires 246.1256.

Ethyl 4-*allyl*-5-*oxo*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*deca*-3,8-*diene* 3-*carboxylate* **10c**

A mixture of **2c** (206 mg, 0.798 mmol) and cyclopentadiene (3.0 ml) in DMF (15 ml) was reacted as described for **10b** to yield **10c** (176 mg, 85 %) as a pure oil after flash chromatography (Al_2O_3, gradient: *n*-hexane to EtOAc /*n*-hexane = 1/20; Rf = 0.30, EtOAc /*n*-hexane = 1/20). ^{1}H-NMR: δ 1.37 (t, J=7.0 Hz, 3H, OCH_2CH_3), 1.62 A of AB (d, ^{2}J=9.2 Hz, 1H, H_{10}), 1.78 (dt, ^{2}J=9.2 Hz, J=1.6 Hz, 1H, H_{10}), 2.91 (t, J=4.8 Hz, 1H, H_6), 3.08-3.38 (m, 4H, H_1, H_7, C_4-CH_2), 3.53 (dd, J=4.8 Hz, J=4.4 Hz, 1H, H_2), 4.31 (q, J=7.0 Hz, 2H, OCH_2CH_3), 4.87-5.16 (m, 2H, C_4-CH_2CHCH_2), 5.49-6.00 (m, 3H, H_8, H_9, C_4-CH_2CH); ^{13}C-NMR: δ 13.7 (q, C_3-$COOCH_2CH_3$), 27.7 (t, C_4-CH_2), 44.6 (d), 44.8 (d), 45.6 (d), 50.1 (d, C_1, C_2, C_6, C_7), 51.8 (t, C_{10}), 60.8 (t, C_3-$COOCH_2$), 116.0 (C_4-CH_2CHCH_2), 132.8 (d), 133.0 (d), 133.9 (d, C_8, C_9, C_4-CH_2CH), 151.0 (s), 155.8 (s, C_3, C_4), 165.4 (s, C_3-CO), 209.8 (s, C_5); IR (CCl_4): ν 2980, 1710 (C=O, ester), 1635 (C=C), 1195 cm^{-1}; EI/MS: m/e 258 (M^+), 66 (C_5H_6); Found 258.1266. $C_{16}H_{18}O_3$ requires 258.1256.

Ethyl 4-n-*heptyl*-5-*oxo*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*deca*-3,8-*diene* 3-*carboxylate* **10d**

A mixture of **2d** (650 mg, 2.06 mmol) and cyclopentadiene (4 ml) in DMF (15 ml) was reacted as described for **10b** to afford **10d** (530 mg, 82 %) as a pure oil after flash chromatography (2xAl_2O_3, gradient:

n-hexane to EtOAc /*n*-hexane = 1/20; Rf = 0.50, EtOAc /*n*-hexane = 1/20), ^{1}H-NMR: δ 0.73-1.37 (m, 13H, C_4-$CH_2(CH_2)_5CH_3$), 1.38 (t, J=7.0 Hz, 3H, OCH_2CH_3), 1.60 A of AB (d, ^{2}J=8.5 Hz, 1H, H_{10}), 1.78 B of AB (d, ^{2}J =8.5 Hz, 1H, H_{10}), 2.27-2.49 (m, 2H, C_4-CH_2), 2.87 (t, J=4.8 Hz, 1H, H_6), 3.20 (br s, 2H, H_1, H_7), 3.51 (t, J=4.8 Hz, 1H, H_2), 4.31 (q, J=7.0 Hz, 2H, OCH_2CH_3), 5.69-5.84 (m, 1H, H_8 or H_9), 5.85-5.96 (m, 1H, H_8 or H_9); IR (CCl_4): ν 2920, 1708 (C=O, ester), 1220, 1107 cm^{-1}; EI/MS: m/e 316 (M^+), 66 (C_5H_6); Found 316.2034. $C_{20}H_{28}O_3$ requires 316.2038.

Ethyl 4-*benzyl*-5-*oxo*-endo-*tricyclo*[5.2.1.0^{2,6}]*deca*-3,8-*diene* 3-*carboxylate* **10e**

A mixture of **2e/3e** (25 mg, 0.081 mmol) and cyclopentadiene (1 ml) in DMF (5 ml) was reacted as described for **10b** to furnish **10e** (16 mg, 64 %, 98 % purity by CapGC) after flash chromatography (Al_2O_3, EtOAc /*n*-hexane = 1/20, Rf = 0.25). ^{1}H-NMR: δ 1.34 (t, J=7.0 Hz, 3H, OCH_2CH_3), 1.61 A of AB (d, J=8.4 Hz, 1H, H_{10}), 1.76 (dt, ^{2}J =8.4 Hz, J=1.8 Hz, 1H, H_{10}), 2.88 (t, J=5.0 Hz, 1H, H_6), 3.11-3.33 (m, 2H, H_1, H_7), 3.53 (t, J=5.0 Hz, 1H, H_2), 3.76 (s, 2H, C_4-CH_2), 4.30 (q, J=7.0 Hz, 2H, OCH_2CH_3), 5.60-5.87 (m, 2H, H_8, H_9), 7.18 (s, 5H, Ph); IR (CCl_4): ν 1710 (C=O, ester), 1230 cm^{-1}; EI/MS: m/e 308 (M^+), 242, 196, 91 ($PhCH_2^+$), 66 (C_5H_6); Found 308.1414. $C_{20}H_{20}O_3$ requires 308.1412.

Ethyl tetracyclo[9.2.1.0^{2,10}.0^{5,9}]*tetradeca*-3,7,12-*triene* 3-*carboxylate* **15**

A soln of **1** (450 mg, 2.064 mmol) and cyclopentadiene (2 ml) in DMF (10 ml) was heated at 155 °C for 24 h. After removal of DMF and cyclopentadiene at 50 °C *in vacuo*, flash chromatography (Al_2O_3, EtOAc /*n*-hexane = 1/10, Rf = 0.35) gave crude **15** (360 mg). Repeating this purification twice (Al_2O_3, EtOAc /*n*-hexane = 1/20) afforded **15** (209 mg, 35 %, 88 % purity by CapGC). ^{1}H-NMR: δ 1.26 (t, J=7.0 Hz, 3H, OCH_2CH_3), 1.55-2.00 (m, 2H, H_{14}), 2.24-3.06 (m, 7H, H_1, H_5, H_6, H_9, H_{10}, H_{11}), 3.26 (br s, 1H, H_2), 4.16 (q, J=7.0 Hz, 2H, OCH_2CH_3), 5.33-5.60 (m, 4H, H_7, H_8, H_{12}, H_{13}), 7.07 (dd, J=6.8 Hz, J=1.6 Hz, 1H, H_4); IR (CCl_4): ν 3050, 2920, 1706 (C=O, ester), 1625 (C=C), 1230 cm^{-1}; EI/MS: m/e 256 (M^+), 190 (M-C_5H_6), 117 (M-C_5H_6-COOEt), 66 (C_5H_6); Found 256.1467. $C_{17}H_{20}O_2$ requires 256.1463.

Flash-vacuum thermolysis: general remarks.

The polycyclic substrates were distilled or sublimed in vacuo through a hot quartz tube (25 x 1.3 cm). The pyrolysates were collected immediately after the pyrolysis tube in a cold trap at -78 °C. By carefully varying the pressure, the preheating temperature (T_1) and the oven temperature (T_2) optimum conditions were established for the majority of the reactions. Usually several runs were needed before the best conditions were found.

Flash Vacuum Thermolysis (FVT) of **2a**

Flash vacuum thermolysis [T_1 60-70 °C/ T_2 450 °C/ 0.04 mbar] of **2a** (572 mg, 2.466 mmol) afforded a mixture of **11** and **16** (378 mg) in a molar ratio of 2.4:1 (^{1}H-NMR) together with a small amount of a regioisomer of **11** (8 %, according to CapGC/MS). Crystallization from *n*-hexane gave *diethyl* 4,7-*dimethyl*-5,10-*dioxo*-endo-*tricyclo*[5.2.1.0^{2,6}]*deca*-3,8-*diene* 3,8-*dicarboxylate* **11** (103 mg) as an analytically pure solid. M.p. 77-79 °C; ^{1}H-NMR: δ 1.27 (t, J=7.0 Hz, 3H, C_8-$COOCH_2CH_3$), 1.39 (t, J= 7.0 Hz, 3H, C_3-$COOCH_2CH_3$), 1.70 (s, 3H, C_7-CH_3), 2.00 (s, 3H, C_4-CH_3), 2.63 (d, J=5.7 Hz, 1H, H_6), 3.55-3.81 (m, 2H, H_1, H_2), 4.17 (q, J= 7.0 Hz, 2H, C_8-$COOCH_2CH_3$), 4.34 (q, J=7 Hz, 2H, C_3-$COOCH_2CH_3$), 7.00 (d, J=3.6 Hz, 1H, H_9); IR (CCl_4): ν 1790 (C=O, bridged), 1720 (C=O), 1365, 1270, 1210, 1070 cm^{-1}; CI/MS: m/e 333 (M^++1), 259 (M-COOEt), 167 (M+1-$C_9H_{10}O_3$); Found 333.1343. $C_{18}H_{21}O_6$ requires 333.1338; Found C, 64.95; H, 6.00. $C_{18}H_{20}O_6$ requires C, 65.05; H, 6.07. Subsequent flash chromatography (silica gel, EtOAc /*n*-hexane = 1/3) of the remaining mother liquor gave another crop of **11** (142 mg, total yield 30 %) and **16** (90 mg, 18 %). **16** was also prepared by the following procedure: A soln of ethyl 7-methyl-11-oxo-*endo*-10-oxatricyclo[5.2.2.0^{2,6}]undeca-3,8-diene 8-carboxylate[1] (80 mg, 0.322 mmol) in DMF (10 ml) was heated for 10 min at 155 °C. After cooling and removal of DMF *in vacuo*, the residue was taken up in Et_2O , thoroughly washed with water (8 x 5 ml), dried and concentrated to afford pure *ethyl* 7-*methyl*-cis-3*a*,7*a*-*dihydroindene* 6-*carboxylate* **16** (57 mg, 87 %). ^{1}H-NMR: δ 1.31 (t, J=7.1 Hz, 3H, OCH_2CH_3), 2.19 (s, 3H, C_7-Me), 2.24-2.51 (m, 1H, H_1), 2.64-3.11 (m, 2H, H_1, H_{7a}), 3.40-3.69 (m, 1H, H_{3a}), 4.21 (q, J=7.1 Hz, 2H, OCH_2), 5.40 (dd, J=10.0 Hz, J=2.8 Hz, 1H, H_4), 5.67-5.98 (m, 2H, H_2, H_3), 6.15 (dd, J=10.0 Hz, J=2.8 Hz, 1H, H_5); IR (CCl_4): ν 1715 (C=O), 1650, 1595, 1250, 1240, 1070 cm^{-1}; EI/MS: m/e 204 (M^+), 189 (M-CH_3), 131 (M-COOEt), 91 (benzyl); Found 204.1152. $C_{13}H_{16}O_2$ requires 204.1150.

Flash vacuum thermolysis of **1**

Flash vacuum thermolysis [T_1 60-70 °C/ T_2 550 °C/ 0.02 mbar] of **1** (305 mg, 1.40 mmol) produced a mixture of **14** and **17** (196 mg, molar ratio 1:1, ^{1}H-NMR, Cap.GC). Variation of the oven temp.(400-600 °C) did not affect the product ratio. Flash chromatography (silica gel, EtOAc /*n*-hexane = 1/3) gave **14** (97 mg, 36 %, Rf = 0.50) and **17** (55 mg, 13 %, Rf = 0.15). *Ethyl* cis-3*a*,7*a*-*dihydroindene* 6-*carboxylate* **14**: ^{1}H-NMR: δ 1.30 (t, J=7.1 Hz, 3H, OCH_2CH_3), 2.16-2.51 (m, 1H, H_1), 2.62-3.00 (m, 1H, H_1), 3.02-3.43 (m, 1H, H_{7a}), 3.43-3.61 (m, 1H, H_{3a}), 4.21 (q, J=7.1 Hz, 2H, OCH_2), 5.53-5.97 (m, 3H, H_2, H_3, H_4), 6.25 (dt,

J=9.9 Hz, J=1.7 Hz, 1H, H_5), 6.83 (d, J=4.7 Hz, 1H, H_7); IR (CCl_4): ν 3050, 1715 (C=O), 1640, 1590, 1250, 1075 cm^{-1}; EI/MS: m/e 190 (M^+), 161, 145, 117 (M-COOEt), 91 (benzyl); Found 190.0998. $C_{12}H_{14}O_2$ requires 190.0994. *Diethyl* 5,10-*dioxo*-endo-*tricyclo[5.2.1.0^{2,6}]deca*-3,8-*diene* 2,8-*dicarboxylate* **17**: ^{1}H-NMR: δ 1.38 (t, J=7.0 Hz, 6H, 2xOCH$_2$CH$_3$), 3.38 (d, J=5.0 Hz, 1H, H_6), 3.69 (dd, J =3.9 Hz, ^{4}J=1.3 Hz, 1H, H_1), 3.99 (br d, J=5.0 Hz, 1H, H_7), 4.08-4.40 (m, 4H, 2xOCH$_2$CH$_3$), 6.37 (d, ^{3}J=5.7 Hz, 1H, H_4), 7.12 (dd, J=3.9 Hz, ^{4}J=1.3 Hz, 1H, H_9), 7.45 (d, J=5.7 Hz, 1H, H_3); IR (CCl_4): ν 1800 (C=O, bridged), 1720 (C=O), 1590 (C=C, unsat.), 1265, 1225, 1100, 910 cm^{-1}; CapGC/CI/MS: m/e 305 (M^++1), 277 (M+1-CO), 231 (M-COOEt), 203 (M-CO-COOEt); Found 305.1037. $C_{16}H_{17}O_6$ requires 305.1025. Analogously, by using 6-*D*-**1** instead of **1**, 7-*deuterio*-**14** and 6,7-*dideuterio*-**17** were prepared.

Diethyl 2,7-*dimethyl*-1-*oxo*-cis-3*a*,7*a*-*dihydroindene* 3,6-*carboxylate* **12**

Flash vacuum thermolysis [T_1 120 °C/ T_2 450 °C/ 0.04 mbar] of **11** (43 mg, 0.13 mmol) gave **12** and **13** (33 mg, 1:1 molar mixture, 35 % yield each (^{1}H-NMR)). These compounds were not separated. **12**: ^{1}H-NMR: δ 1.31 (t, J=7.0 Hz, 3H, C_6-CO$_2$CH$_2$CH$_3$), 1.40 (t, J=7.0 Hz, 3H, C_3-CO$_2$CH$_2$CH$_3$), 2.09 (d, J=1.8 Hz, 3H, C_2-CH$_3$), 2.40 (s, 3H, C_7-CH$_3$), 3.24 (d, J=9.4 Hz, 1H, H_{7a}), 4.00-4.53 (m, 5H, H_{3a}, 2xOCH$_2$CH$_3$), 5.78 (dd, J=10 Hz, J=2.8 Hz, 1H, H_4), 6.19 (dd, J=10 Hz, J=2.4 Hz, 1H, H_5).

Diethyl 1-*oxo*-cis-3*a*,7*a*-*dihydroindene* 3*a*,6-*dicarboxylate* **18**

Flash vacuum thermolysis [T_1 120 °C/ T_2 450 °C/ 0.04 mbar] of **17** (88 mg, 0.289 mmol) gave **18** and **19** (62 mg, 1:1 molar mixture, 32 % yield each (^{1}H-NMR)). ^{1}H-NMR of **18**: δ 1.19-1.53 (m, 6H, 2xOCH$_2$CH$_3$), 4.09-4.58 (m, 5H, H_{7a}, 2xOCH$_2$CH$_3$), 5.97 (d, J=10 Hz, 1H, H_4), 6.38 (d, J=5.7 Hz, 1H, H_2), 6.50 (d, J=10 Hz, 1H, H_5), 6.95 (d, J=5.1 Hz, 1H, H_7), 7.67 (d, J=5.7 Hz, 1H, H_3).

Diethyl 3-*oxo*-*indane* 1,5-*dicarboxylate* **19**

Ester **17** (134 mg, 0.441 mmol) was heated in DMF as described for the preparation of **13**, to yield **19** (106 mg, 87 %) as a pure oil after flash chromatography (Al_2O_3, EtOAc /*n*-hexane = 1/10). ^{1}H-NMR: δ 1.19-1.53 (m, 6H, 2xOCH$_2$CH$_3$), 2.91 A of ABX (dd, J=19.5 Hz, J=8.1 Hz, 1H, H_2), 3.27 B of ABX (dd, J=19.5 Hz, J=3.9 Hz, 1H, H_2), 4.09-4.58 (m, 5H, 2xOCH$_2$, H_1), 7.78 (d, J=8.1 Hz, 1H, H_7), 8.33 (dd, J=8.1 Hz, J=1.5 Hz, 1H, H_6), 8.43 (d, J=1.5 Hz, 1H, H_4); ^{13}C-NMR: δ 14.0 (q, 2xOCH$_2$CH$_3$), 39.5 (t, C_2), 43.8 (d, C_1), 61.3 (t, OCH$_2$), 61.7 (t, OCH$_2$), 125.1 (d), 126.5 (d), 131.6 (s), 135.5 (d), 136.6 (s, C_{3a}, C_4, C_6, C_7, C_{7a}), 155.2 (s, C_5), 165.7 (s), 171.5 (s, C_1-CO, C_5-CO), 204.2 (s, C_3); IR (CCl_4): ν 2980, 1725 (C=O), 1610, 910 cm^{-1}; EI/MS: m/e 276 (M^+), 231 (M-OEt), 203 (M-COOEt), 175 (M-CO-COOEt); Found 276.0997. $C_{15}H_{16}O_5$ requires 276.0998.

Ethyl exo-4-*methyl*-5-*oxo*-endo-*tricyclo*[5.2.1.0^{2,6}]*dec*-8-*ene* endo-3-*carboxylate* **27a**

Excess Zn powder (995 mg, 15.2 mmol) was added to a soln of **10a** (405 mg, 1.746 mmol) in AcOH (10 ml) in a N_2 atmosphere and stirred for 1.5 h at 110 °C. After cooling to r.t. the remaining Zn was removed by filtration. AcOH was concentrated *in vacuo* to afford **27a** (342 mg, 84 %), that solidified after flash chromatography (EtOAc /*n*-hexane = 1/3, Rf = 0.30, I_2, purity by Cap GC > 99 %). M.p. 73-75 °C (after recrystallization from *n*-hexane). ^{1}H-NMR: δ 0.97 (d, J=6.4 Hz, 3H, C_4-Me), 1.36 (t, J=7 Hz, 3H, OCH$_2$CH$_3$), 1.49 (br s, 1H, H_{10}), 1.62 (br s, 1H, H_{10}), 2.47 (dq, $J_{3,4}$=11.7 Hz, J=6.4 Hz, 1H, H_4), 2.60-3.36 (m, 5H, H_1, H_2, H_3, H_6, H_7), 4.26 and 4.28 (q,q, J=7 Hz, 2H, diastereotopic OCH$_2$CH$_3$), 5.96-6.20 (m, 2H, H_8, H_9); ^{13}C-NMR: δ 13.7 (q), 13.9 (q, C_3-COOCH$_2$CH$_3$, C_4-CH$_3$), 41.2 (d), 45.9 (d), 46.9 (d), 47.4 (d), 48.9 (d, C_1, C_2, C_4, C_6, C_7), 52.2 (t, C_{10}), 53.8 (d, C_3), 60.3 (t, C_3-COOCH$_2$), 134.7 (d), 135.9 (d, C_8, C_9), 173.0 (s, C_3-CO), 219.6 (s, C_5); IR (KBr): ν 2975, 1725 (C=O), 1365, 1230, 1220, 1185 cm^{-1}; EI/MS: m/e 234 (M^+), 169 (M-$C_5H_5^+$), 161 (M-COOEt), 66 (C_5H_6); MS: Found 234.1246. $C_{14}H_{18}O_3$ requires 234.1256. Found C, 70.93; H, 7.71. $C_{14}H_{18}O_3$ requires C, 71.77; H, 7.74.

Ethyl exo-4-*ethyl*-5-*oxo*-endo-*tricyclo*[5.2.1.0^{2,6}]*dec*-8-*ene* endo-3-*carboxylate* **27b**

The zinc reduction of **10b** was carried out as described for the synthesis of **10a** starting from Zn powder (550 mg, 8.41 mmol), **10b** (165 mg, 0.671 mmol) and AcOH (8 ml) to afford **27b** (143 mg, 85 %) as a pure oil after flash chromatography (silica gel, EtOAc /*n*-hexane = 1/3, Rf = 0.3, I_2). ^{1}H-NMR: δ 0.82 (t, J=7 Hz, 3H, C_4-CH$_2$CH$_3$), 1.13-1.82 (m, 7H, OCH$_2$CH$_3$, H_{10}, C_4-CH$_2$), 2.26-2.54 (m, 1H, H_4), 2.78-3.34 (m, 5H, H_1, H_2, H_3, H_6, H_7), 4.05-4.42 (m, 2H, diastereotopic OCH$_2$CH$_3$), 5.96-6.20 (m, 2H, H_8, H_9); IR (CCl_4): ν 2960, 1732 (C=O, ester), 1220, 1170, 1157 cm^{-1}; EI/MS: m/e 248 (M^+), 220 (M-CO), 203 (M-OEt$^+$), 183 (M-$C_5H_5^+$), 66 (C_5H_6); Found 248.1418. $C_{15}H_{20}O_3$ requires 248.1412.

Ethyl exo-4-*allyl*-5-*oxo*-endo-*tricyclo*[5.2.1.0^{2,6}]*dec*-8-*ene* endo-3-*carboxylate* **27c**

Application of the same procedure as described for the preparation of **27a** using Zn (300 mg, 4.59 mmol), AcOH (5 ml) and **10c** (70 mg, 0.271 mmol) gave **27c** (70 mg, 90 %, purity by CapGC = 90 %) after flash chromatographic purification (silica gel, EtOAc /*n*-hexane = 1/3, Rf = 0.37, I_2). ^{1}H-NMR: δ 1.34 (t, J=7.2 Hz, 3H, OCH$_2$CH$_3$), 1.58 (s, 2H, H_{10}), 1.87-2.73 (m, 3H, H_4, C_4-CH$_2$), 2.80-3.31 (m, 5H, H_1, H_2, H_3, H_6, H_7), 4.11-4.38 (m, 2H, diastereotopic OCH$_2$CH$_3$), 4.85-5.11 (m, 2H, C_4-CH$_2$CHCH$_2$), 5.40-5.89 (m, 1H,

C_4-CH_2CH), 5.98-6.23 (m, 2H, H_8, H_9); IR (CCl_4): ν 1735 (C=O, ester), 1635 (C=C), 1160 cm^{-1}; EI/MS: m/e 260 (M^+), 195 (M-$C_5H_6^+$), 187 (M-COOEt), 66 (C_5H_6); Found 260.1414. $C_{16}H_{20}O_3$ requires 260.1412.

Ethyl exo-4-n-*heptyl*-5-*oxo*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*ene* endo-3-*carboxylate* **27d**

The same procedure as employed for the preparation of **27a** using Zn (700 mg, 10.7 mmol), AcOH (10 ml) and **10d** (207 mg, 0.655 mmol) produced **27d** (174 mg, 83 %) as a pure oil after flash chromatography (silica gel, gradient: EtOAc /*n*-hexane = 1/10 to 1/3, Rf = 0.40, EtOAc /*n*-hexane = 1/3, I_2). ^{1}H-NMR: δ 0.71-1.67 (m, 20H, C_4-$(CH_2)_6CH_3$, OCH_2CH_3, H_{10}), 2.22-2.56 (m, 1H, H_4), 2.67-3.31 (m, 5H, H_1, H_2, H_3, H_6, H_7), 4.23 and 4.24 (q,q, J=7.0 Hz, 2H, diastereotopic OCH_2CH_3), 5.96-6.20 (m, 2H, H_8, H_9); IR (CCl_4): ν 2920, 1732 (C=O), 1157 cm^{-1}; EI/MS: m/e 318 (M^+), 253 (M-$C_5H_5^+$), 66 (C_5H_6); Found 318.2200. $C_{20}H_{30}O_3$ requires 318.2195.

Trans-4-*methyl*-5-*oxo*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*ene* 3-*carboxylic acid* **28a**

Ester **27a** (205 mg, 0.876 mmol) was dissolved in EtOH (4.5 ml)/2 N NaOH (1.5 ml) and refluxed for 10 min[22]. After cooling to r.t., the mixture was poured into water (25 ml) and extracted with Et_2O (3 x 30 ml). The water layer was acidified to pH 1 using HCl (20 % aq) and again extracted three times with Et_2O (acid-base extraction). The combined ether extracts were washed (H_2O), dried ($MgSO_4$) and concentrated to afford **28a** (155 mg, 86 %) as a 1:1 diastereomeric mixture of *trans*-acids. M.p. 140-190 °C (after recrystallization from *n*-hexane). ^{1}H-NMR: δ 1.00 (d, J=6.8 Hz, 3H, C_4-CH_3), 1.16-1.78 (m, 2H, H_{10}), 1.91-3.38 (m, 6H, H_1, H_2, H_3, H_4, H_6, H_7), 5.98-6.27 (m, 2H, H_8, H_9), 7.00 (br s, 1H, COOH); Homonuclear decoupling at δ 1.00 gave δ 2.42 (d, J=11.2 Hz) and δ 2.78 (d, J=12 Hz); IR (CCl_4): ν 3500-2450 (COOH), 1736 (C=O), 1705 (C=O), 1260 cm^{-1}; CapGC/EI/MS of diastereomer 1 and 2: m/e 206 (M^+), 191 (M-CH_3), 141 (M-$C_5H_5^+$), 66 (C_5H_6); Found 206.0939. $C_{12}H_{14}O_3$ requires 206.0943.

Trans-4-*ethyl*-5-*oxo*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*ene* 3-*carboxylic acid* **28b**

The same procedure as employed for the synthesis of **28a** was applied to **27b** (140 mg, 0.565 mmol) using EtOH (2 ml)/2 N NaOH (2ml). **28b** (128 mg, 100 %) was obtained as a 1:1 mixture of *trans*-diastereomers (Cap GC, ^{1}H-NMR). ^{1}H-NMR: δ 0.82 (t, J=7 Hz, 3H, C_4-CH_2CH_3), 1.11-1.78 (m, 4H, H_{10}, C_4-CH_2), 2.22-3.33 (m, 6H, H_1, H_2, H_3, H_4, H_6, H_7), 5.98-6.31 (m, 2H, H_8, H_9), 7.80 (br s, 1H, COOH); IR (CCl_4): ν 3500-2500 (COOH), 1735 (C=O), 1705 (C=O), 1235 cm^{-1}; CapGC/EI/MS of diastereomer 1 and 2: m/e 220 (M^+), 175 (M-COOH), 155 (M-$C_5H_5^+$), 66 (C_5H_6); Found 220.1099. $C_{13}H_{16}O_3$ requires 220.1099.

Trans-4-*allyl*-5-*oxo*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*ene* 3-*carboxylic acid* **28c**

The same procedure as employed for the synthesis of **28a** using **27c** (75 mg, 0.288 mmol) and EtOH (1.5 ml)/NaOH (1.5 ml) gave **28c** (68 mg, 100 %) as a 1:1 mixture of *trans*-diastereomers. ^{1}H-NMR: δ 1.49 A of AB (d, J=9 Hz, 1H, H_{10}), 1.70 B of AB (d, J= 9 Hz, 1H, H_{10}), 2.11-2.69 (m, 3H, H_4, C_4-CH_2), 2.73-3.36 (m, 5H, H_1, H_2, H_3, H_6, H_7), 4.87-5.16 (m, 2H, C_4-CH_2CHCH_2), 5.44-5.89 (m, 1H, C_4-CH_2CH), 6.00-6.27 (m, 2H, H_8, H_9), 7.35 (br s, 1H, COOH); IR (CCl_4): ν 3500-2500 (COOH), 1735 (C=O), 1705 (C=O, acid), 920 cm^{-1}; CapGC/EI/MS of diastereomer 1 and 2: m/e 232 (M^+), 167 (M-$C_5H_5^+$), 66 (C_5H_6); Found 232.1095. $C_{14}H_{16}O_3$ requires 232.1099.

Trans-4-n-*heptyl*-5-*oxo*-endo-*tricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*ene* 3-*carboxylic acid* **28d**

The same procedure as employed for the preparation of **28a**, using **27d** (240 mg, 0.755 mmol) and EtOH (6.3 ml)/NaOH (6.3 ml), gave **28d** (202 mg, 92 %) as a 1:1 mixture of *trans*-diastereomers. ^{1}H-NMR: δ 0.73-1.78 (m, 17H, C_4-$(CH_2)_6CH_3$, H_{10}), 2.16-2.58 (m, 1H, H_4), 2.62-3.36 (m, 5H, H_1, H_2, H_3, H_6, H_7), 6.00-6.31 (m, 2H, H_8, H_9), 7.40 (br s, 1H, COOH); IR (CCl_4): ν 3500-2450 (COOH), 1735 (C=O), 1705 (C=O, acid) cm^{-1}; EI/MS: m/e 290 (M^+), 272 (M-H_2O), 225 (M-$C_5H_5^+$), 66 (C_5H_6); Found 290.1874. $C_{18}H_{26}O_3$ requires 290.1882.

Ethyl trans-5-*methyl*-4-*oxocyclopent*-2-*ene carboxylate* **20a**

Flash vacuum thermolysis [T_1 70 °C/ T_2 510 °C/ 0.02 mbar] of **27a** (50 mg, 0.214 mmol) yielded **20a** (33 mg, 92 %, 99 % purity by CapGC) as a pure oil after flash chromatography (silica gel, EtOAc /*n*-hexane = 1/3, Rf = 0.2). ^{1}H-NMR: δ 1.29 (d, J=7.2 Hz, 3H, C_5-CH_3), 1.30 (t, J=7.2 Hz, 3H, OCH_2CH_3), 2.68 (qd, J=7.2 Hz, J=3.2 Hz, 1H, H_5), 3.42 (q, J≅3 Hz, 1H, H_1), 4.22 (q, J=7.2 Hz, 2H, OCH_2), 6.23 (dd, $^3J_{cis}$=5.8 Hz, ^{4}J=2.2 Hz, 1H, H_3), 7.63 (dd, $^3J_{cis}$=5.8 Hz, ^{4}J=2.6 Hz, 1H, H_2); IR (CCl_4): ν 2970, 1735 (C=O, ester), 1720 (C=O, ketone), 1590 (C=C, unsat.), 1320, 1180 cm^{-1}; EI/MS: m/e 168 (M^+), 122 (M-HOEt), 95 (M-COOEt), 67; Found 168.0792. $C_9H_{12}O_3$ requires 168.0786.

Ethyl trans-5-*ethyl*-4-*oxocyclopent*-2-*ene carboxylate* **20b**

Flash vacuum thermolysis [T_1 70 °C/ T_2 510 °C/ 0.02 mbar] of **27b** (30 mg, 0.121 mmol) gave **20b** (20 mg, 90 %) as a pure oil after flash chromatography (silica gel, EtOAc /*n*-hexane = 1/3, Rf = 0.3, I_2). ^{1}H-NMR: δ 0.98 (t, J=7.4 Hz, 3H, C_5-CH_2CH_3), 1.30 (t, J=7.1 Hz, 3H, OCH_2CH_3), 1.44-2.13 (m, 2H,

C_5-CH_2), 2.56-2.78 (m, 1H, H_5), 3.52 (q, J≅2.4 Hz, 1H, H_1), 4.22 (q, J=7.1 Hz, 2H, OCH_2), 6.23 (dd, $^3J_{cis}$=5.8 Hz, ^4J= 2.2 Hz, 1H, H_3), 7.63 (dd, $^3J_{cis}$=5.8 Hz, ^4J=2.6 Hz, 1H, H_2); IR (CCl_4): ν 2960, 1740 (C=O, ester), 1710 (C=O, ketone), 1590 (C=C, unsat.) cm^{-1}; EI/MS: m/e 182 (M^+), 154 (M-CO), 109 (M-COOEt), 81 ($C_5H_5O^+$); Found 182.0934. $C_{10}H_{14}O_3$ requires 182.0943.

Ethyl trans-5-*allyl*-4-*oxocyclopent*-2-*ene carboxylate* **20c**
Flash vacuum thermolysis [T_1 95 °C/ T_2 510 °C/ 0.02 mbar] of **27c** (30 mg, 0.115 mmol) (sample temp.: 95 °C, oven temp.: 510 °C, cold trap temp.: -78 °C, p: 2.10^{-2} mm Hg) gave **20c** (19 mg, 85 %, 98 % purity by CapGC) as a pure oil after flash chromatography (silica gel, EtOAc /*n*-hexane = 1/3, Rf = 0.20). ^{1}H-NMR: δ 1.30 (t, J=7.2 Hz, 3H, OCH_2CH_3), 2.16-2.71 (m, 2H, C_5-CH_2), 2.71-2.93 (m, 1H, H_5), 3.56 (q, J≅2.6 Hz, 1H, H_1), 4.21 (q, J=7.2 Hz, 2H, OCH_2), 4.96-5.25 (m, 2H, C_5-CH_2CHCH_2), 5.49-5.96 (m, 1H, C_5-CH_2CH), 6.22 (dd, ^{3}J=5.8 Hz, ^{4}J=2.4 Hz, 1H, H_3), 7.62 (dd, ^{3}J=5.8 Hz, ^{4}J=2.6 Hz, 1H, H_2); IR (CCl_4): ν 2975, 2920, 1740 (C=O, ester), 1715 (C=O, ketone), 1637 (C=C), 1587 (C=C, unsat.), 1325, 1030 cm^{-1}; EI/MS: m/e 194 (M^+), 166 (M-CO), 148 (M-HOEt), 121 (M-COOEt); Found 194.0947. $C_{11}H_{14}O_3$ requires 194.0943.

Ethyl trans-5-n-*heptyl*-4-*oxocyclopent*-2-*ene carboxylate* **20d**
Ester **27d** (67 mg, 0.211 mmol) was subjected to flash vacuum thermolysis [T_1 130 °C/ T_2 510 °C/ 0.02 mbar] to give **20d** (50 mg, 94 %) as a pure oil. ^{1}H-NMR: δ 0.73-2.03 (m, 18H, C_5-C_7H_{15}, OCH_2CH_3), 2.56-2.78 (m, 1H, H_5), 3.49 (q, J≅2.5 Hz, 1H, H_1), 4.20 (q, J=7.1 Hz, 2H, OCH_2), 6.23 (dd, $^3J_{cis}$=5.6 Hz, ^{4}J= 2.4 Hz, 1H, H_3), 7.61 (dd, $^3J_{cis}$=5.6 Hz, ^{4}J=2.6 Hz, 1H, H_2); IR (CCl_4): ν 2920, 1740 (C=O, ester), 1720 (C=O, ketone), 1590 (C=C, unsat.) cm^{-1}; EI/MS: m/e 253 (M^++1), 179 (M-COOEt), 154 (M+1-C_7H_{15}), 108 (M+1-C_7H_{15}-HOEt); Found 252.1727. $C_{15}H_{24}O_3$ requires 252.1725.

Ethyl trans-2-*methyl*-3-*oxocyclopentane carboxylate* **30a**
Ester **20a** (20 mg, 0.119 mmol) was hydrogenated in EtOH for 30 min at r.t. at normal pressure using Pd/C as catalyst, to furnish **30a** (18 mg, 89 %) as a pure oil. ^{1}H-NMR: δ 1.15 (d, J≅7.0 Hz, 3H, C_2-CH_3), 1.26 (t, J=7.2 Hz, 3H, OCH_2CH_3), 1.90-2.75 (m, 6H, H_1, H_2, H_4, H_5), 4.20 (q, J=7.2 Hz, 2H, OCH_2); IR (CCl_4): ν 2920, 1745 (C=O, ketone), 1730 (C=O, ester), 1145 cm^{-1}; EI/MS: m/e 170 (M^+), 142 (M-CO), 97 (M-COOEt); Found 170.0937. $C_9H_{14}O_3$ requires 170.0943.

Ethyl trans-2-*ethyl*-3-*oxocyclopentane carboxylate* **30b**
Ester **20b** (15 mg, 0.0824 mmol) was hydrogenated as described for the preparation of **30a** to yield pure **30b** (12 mg, 79 %) as an oil after flash chromatography (silica gel, EtOAc /*n*-hexane = 1/3, Rf = 0.3, I_2). ^{1}H-NMR: δ 0.91 (t, J=7.2 Hz, 3H, C_2-CH_2CH_3), 1.29 (t, J=7.1 Hz, 3H, OCH_2CH_3), 1.36-2.60 (m, 7H, H_2, H_4, H_5, C_2-CH_2), 2.62-3.00 (m, 1H, H_1), 4.20 (q, J=7.1 Hz, 2H, OCH_2); IR (CCl_4): ν 2960, 1745 (C=O, ketone), 1735 (C=O, ester), 1375, 1195, 1177, 1155 cm^{-1}; EI/MS: m/e 184 (M^+), 156 (M-CO), 111 (M-COOEt), 83 ($C_5H_7O^+$); Found 184.1093. $C_{10}H_{16}O_3$ requires 184.1099.

Ethyl trans-2-n-*heptyl*-3-*oxocyclopentane carboxylate* **30d**
Ester **20d** (18 mg, 0.0714 mmol) was hydrogenated as described for **30a** to afford **30d** (18 mg, 99 %) as an oil. ^{1}H-NMR: δ 0.73-2.97 (m, 24H, C_2-C_7H_{15}, H_1, H_2, H_4, H_5, OCH_2CH_3), 4.20 (q, J=7.0 Hz, 2H, OCH_2); IR (CCl_4): ν 2920, 1745 (C=O, ketone), 1730 (C=O, ester), 1375 cm^{-1}; EI/MS: m/e 254 (M^+), 226 (M-CO), 209 (M+1-HOEt), 181 (M-COOEt), 156 (M+1-C_7H_{15}), 83 ($C_5H_7O^+$); Found 254.1873. $C_{15}H_{26}O_3$ requires 254.1882.

Trans-5-*methyl*-4-*oxocyclopent*-2-*ene carboxylic acid* **25a**
Carboxylic acid **28a** (72 mg, 0.35 mmol) was subjected to flash vacuum thermolysis [T_1 110 °C/ T_2 510 °C/ 0.02 mbar] to produce **25a**[22] (48 mg, 98 %) as a pale-yellow pure oil. ^{1}H-NMR: δ 1.28 (d, J=7 Hz, 3H, C_5-CH_3), 2.68 (qd, J=7.2 Hz, J=3.2 Hz, 1H, H_5), 3.44 (m, 1H, H_1), 6.25 (dd, $^3J_{cis}$=5.8 Hz, ^{4}J= 2.1 Hz, 1H, H_3), 7.63 (dd, $^3J_{cis}$=5.8 Hz, ^{4}J=2.5 Hz, 1H, H_2), 7.78 (br s, 1H, COOH); IR (CCl_4): ν 3500-2500 (COOH), 1710 (C=O), 1590 (C=C, unsat.) cm^{-1}; EI/MS: m/e 140 (M^+); Found 140.0471. $C_7H_8O_3$ requires 140.0473.

Trans-5-*ethyl*-4-*oxocyclopent*-2-*ene carboxylic acid* **25b**
Acid **28b** (97 mg, 0.441 mmol) was subjected to flash vacuum thermolysis [T_1 110-115 °C/ T_2 510 °C/ 0.02 mbar] to furnish **25b** (58 mg, 85 %) as a pale-yellow pure oil. ^{1}H-NMR: δ 0.99 (t, J=7.3 Hz, 3H, C_5-CH_2CH_3), 1.29-2.13 (m, 2H, C_5-CH_2), 2.69 (qd, J=4.8 Hz, J=3.2 Hz, 1H, H_5), 3.59 (q, J≅2.6 Hz, 1H, H_1), 6.29 (dd, J=5.8 Hz, J=2.2 Hz, 1H, H_3), 7.66 (dd, J=5.8 Hz, J=2.6 Hz, 1H, H_2), 7.71(br s, 1H, COOH); IR (CCl_4): ν 3500-2500 (COOH), 1710 (C=O) cm^{-1}; EI/MS: m/e 154 (M^+), 126 (M-CO), 108 (M-COOH), 81 ($C_5H_5O^+$); Found 154.0635. $C_8H_{10}O_3$ requires 154.0630.

Trans-5-*allyl*-4-*oxocyclopent*-2-*ene carboxylic acid* **25c**
Acid **28c** (53 mg, 0.228 mmol) was subjected to flash vacuum thermolysis [T_1 110 °C/ T_2 510 °C/ 0.02 mbar] to yield **25c** (35 mg, 92 %) as a pure oil. ^{1}H-NMR: δ 2.18-2.69 (m, 2H, C_5-CH_2), 2.73-2.98 (m, 1H,

H_5), 3.63 (q, J≅2.5 Hz, 1H, H_1), 4.98-5.20 (m, 2H, C_5-CH_2CHCH_2), 5.47-5.96 (m, 1H, C_5-CH_2CH), 6.27 (dd, J=5.8 Hz, J=2.2 Hz, 1H, H_3), 7.30 (br s, 1H, COOH), 7.65 (dd, J=5.8 Hz, J=2.6 Hz, 1H, H_2); IR (CCl_4): ν 3500-2500 (COOH), 1715 (C=O), 1590 (C=C, unsat.) cm^{-1}; EI/MS: m/e 166 (M^+), 149 (M-OH); Found 166.0628. $C_9H_{10}O_3$ requires 166.0630.

Trans-5-n-*heptyl*-4-*oxocyclopent*-2-*ene carboxylic acid* **25d**

Acid **28d** (197 mg, 0.679 mmol) was subjected to flash vacuum thermolysis [T_1 110 °C/ T_2 510 °C/ 0.02 mbar] to yield **25d** (138 mg, 91 %) as a pure oil. ^{1}H-NMR: δ 0.73-2.89 (m, 16H, C_5-C_7H_{15}, H_2), 3.56 (q, J≅2.5 Hz, 1H, H_1), 6.27 (dd, J=5.6 Hz, J=2.6 Hz, 1H, H_3), 7.64 (dd, J=5.6 Hz, J=2.4 Hz, 1H, H_2), 7.30 (br s, 1H, COOH); IR (CCl_4): ν 3500-2500 (COOH), 1710 (C=O) cm^{-1}; CI/MS: m/e 225 (M^++1), 181 (M+1-CO_2); Found 225.1483. $C_{13}H_{21}O_3$ requires 225.1491.

Trans-2-*methyl*-3-*oxocyclopentane carboxylic acid* **22a**

Acid **25a** (41 mg, 0.293 mmol) was hydrogenated in EtOH for 30 min at r.t. at normal pressure using Pd/C as catalyst, to furnish **22a** (35 mg, 84 %) as a viscous oil after acid-base extraction. **22a** slowly solidified by stirring in *n*-hexane. M.p. 83-88 °C (lit.[21]: 94-95 °C, lit.[27]: 91-92.5 °C). ^{1}H-NMR: δ 1.16 (d, J≅7 Hz, 3H, C_2-CH_3), 1.90-2.90 (m, 6H, H_1, H_2, H_4, H_5), 8.10 (br s, 1H, COOH); IR (KBr): ν 3400-2600 (COOH), 1740 (C=O) cm^{-1}; EI/MS: m/e 142 (M^+), 97 (M-COOH); Found 142.0635. $C_7H_{10}O_3$ requires 142.0630.

Trans-2-*ethyl*-3-*oxocyclopentane* 1-*carboxylic acid* **22b**

Acid **25b** (56 mg, 0.364 mmol) was hydrogenated as described for **25a** to afford **22b** (51 mg, 90 %) which slowly solidified after acid-base extraction (Et_2O). M.p. 37-42 °C (after recrystallization from *n*-hexane)(lit.[20]: 42-45 °C). ^{1}H-NMR: δ 0.96 (t, J=7.2 Hz, 3H, C_2-CH_2CH_3), 1.33-2.62 (m, 7H, H_2, H_4, H_5, C_2-CH_2), 2.69-3.07 (m, 1H, H_1), 9.05 (br s, 1H, COOH); IR (CCl_4): ν 3500-2500 (COOH), 1745 (C=O, ketone), 1705 (C=O, acid) cm^{-1}; EI/MS: m/e 156 (M^+), 128 (M-CO), 111 (M-COOH), 83 ($C_5H_7O^+$); Found 156.0795. $C_8H_{12}O_3$ requires 156.0786.

Trans-2-n-*heptyl*-3-*oxocyclopentane carboxylic acid* **22d**

Acid **25d** (138 mg, 0.616 mmol) was hydrogenated as described for **25a** to produce **22d** (107 mg, 77 %) which solidified after acid-base extraction (Et_2O). M.p. 57-59.5 °C (after recrystallization from *n*-hexane). ^{1}H-NMR: δ 0.73-2.66 (m, 20H, C_2-C_7H_{15}, H_2, H_4, H_5), 2.66-3.02 (m, 1H, H_1), 9.96 (br s, 1H, COOH); ^{13}C-NMR: δ 13.8 (CH_3), 22.4 (CH_2CH_3), 24.6 ($CH_2CH_2CH_3$), 26.5 ($CH_2C_3H_7$), 28.8 (($CH_2)_2C_4H_9$), 29.4 (C_2-CH_2), 31.6 (C_5), 37.1 (C_4), 46.4 (C_2), 51.9 (C_1), 180.4 (COOH), 217.5 (C_3); IR (KBr): ν 3300-2500 (COOH), 2915, 1732 (C=O, ketone), 1707 (C=O, acid), 1190 cm^{-1}; CI/MS: m/e 227 (M^++1), 181 (M-COOH), 128 (M+1-$C_7H_{15}^+$); Found 227.1645. $C_{13}H_{23}O_3$ requires 227.1647. Found C, 69.01; H, 9.81. $C_{13}H_{22}O_3$ requires C, 68.99; H, 9.80.

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