New Tandem Ring Enlargements of Bicyclo[3.3.0]octanes to Bicyclo[5.5.0]dodecanes and Subsequent Conversions into Tricyclo[5.5.0.0.^{2,9}]dodecane and Tricyclo[5.5.0.0^{2,10}]dodecane Derivatives

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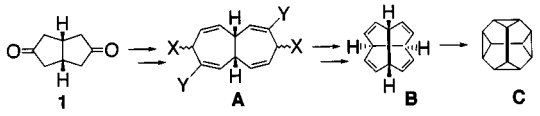
Potential precursors of tetracyclo[5.5.0.0^{4,10}]dodecatetraenes **B** were synthesized by means of ring enlargements of bicyclo[3.3.0]octanes to bicyclo[5.5.0]dodecanes through enol ether/ketene additions and Michael-induced reactions. Base-catalyzed or oxidative ring closures of the highly functionalized compounds that were obtained (most conspicuously **12** and **17**) gave other polycyles (**13**, **14**, **20**). Unexpectedly, the reaction of bicyclooctanedione **15** with dimethyl butynedioate gave a bi(cyclohexadienyl) derivative **18** as well as the expected bicyclododecane derivative **17**.

Introduction

We recently focused our attention on a possible route towards the molecular carbon skeleton representing an Archimedian body, the tetrafold truncated tetrahedrane (“truncahedrane”, **C**[1]), starting from bicyclo[3.3.0]octa-3,7-diones **1**.[2] One-pot twofold double ring-enlargement should transform compound **1** into suitably substituted bicyclo[5.5.0]dodecatetraenes such as **A**. These are potential precursors of (substituted) tetracyclo[5.5.0.0^{4,10}]dodecatetraene (**B**), which in turn is related to the unknown **C** by an unusual photochemical process predicted over 30 years ago by Woodward and Hoffmann which is still under discussion today.[3,4] In the beginning, it seemed to be most efficient for our purposes to apply known methods for cyclopentanone → cycloheptanone transformations using [2+2] additions as one-pot processes, and indeed the reaction of the bis(enamine) of **1** with certain alkynes allowed for the preparation of **A**-type compounds (Scheme 1).[2] Unfortunately, in our earlier work further conversions led to an unwanted intramolecular reaction. We now report initial dichloroketene/**1**-silylenol ether cycloadditions. Such adducts have previously been transformed into various cycloheptane compounds by means of dehalogenation and subsequent direct ring-opening, or by Grignard addition/fragmentation of the four-membered ring.[5−7]



Scheme 1

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The Ketene/Silylenol Ether Addition Pathway

Diketone **1** was converted into a 1:1 mixture of the two isomeric trimethylsilyl enol ethers **2** and **3**. Dichloroketene addition gave the two adducts **4** and **5** in a poor overall yield of approximately 30%, regardless of whether the ketene was generated from trichloroacetyl chloride/activated zinc or from dichloroacetyl chloride/triethylamine (Scheme 2). There was considerable decomposition. In spite of the fact that the starting material was a 50:50 mixture of **2** and **3**, one of the adduct isomers, namely **5** (obtained from **3**), was formed preferentially. This could be crystallized and characterized. Its structure follows from the presence of only one multiplet for the bridgehead hydrogen atoms in the ^{1}H NMR spectrum and the IR carbonyl absorption at 1800 cm^{-1}. The addition must have occurred from the convex, less hindered side of **3**. This stereochemical assignment is corroborated by the stereochemistry of adduct **16a** based on an X-ray structure determination (see below). Minor isomer **4** (formed from **2**) was present in the mother liquor and could only be enriched to the point where the NMR spectrum could be recorded (showing two bridgehead multiplets). The fact that the product mixture did not mirror the starting material composition can be explained similarly to the cycloadditions of the enamines derived from **1**.[2]

Depending on the conditions, **5** could be dehalogenated by tributyltin hydride/AIBN to give either dichloro diketone **6** or the chlorine-free **7**. The stereochemical structure assignment of **6** was based on the relatively large “W-type” coupling of 4.6 Hz between 2-H and the 4-H in the NMR spectrum. The respective *cis*-2,4 coupling in cyclobutanone itself is 4.2 Hz.[18] As can be seen from molecular models, the lower side of **5** is less shielded against radical attack.

Treatment of **5** with methanol and a trace of acid resulted in the formation of diol **8**. A large number of experiments were performed in order to directly convert **5** or any of the three tetracycles **6**−**8** into derivatives of bicyclo[5.5.0]dode-

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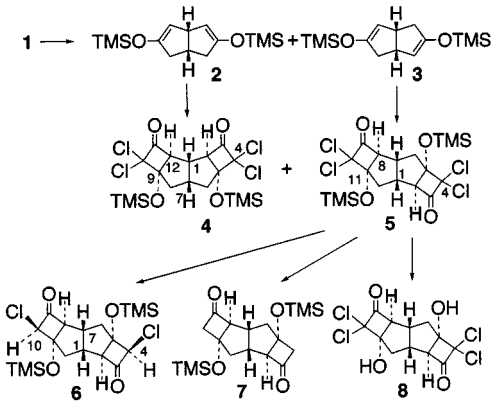
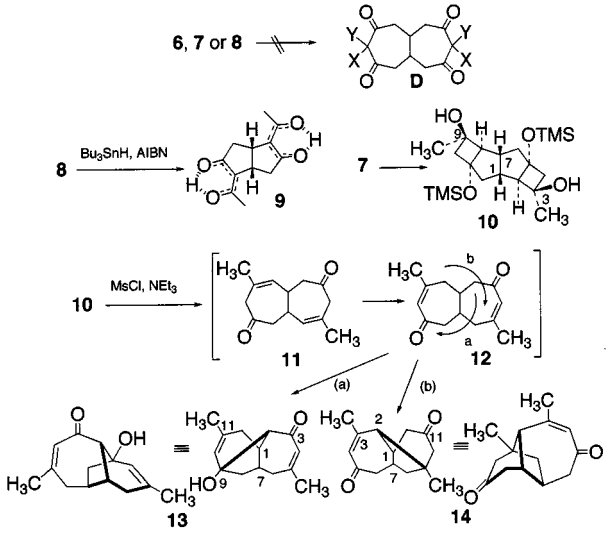


Scheme 2

canes of type **D**. This included the above-mentioned conversions of cyclopentane into cycloheptane derivatives[5−7] initiated by fluoride or by trimethylsilyl iodide. The trapping of **D**-like intermediates by trimethylsilyl chloride as well as intramolecular C-4−C-10 ring-closure with iodine were also attempted as possible ways to arrive at the carbon skeleton of **B**. All these attempts were to no avail. In most cases, intractable mixtures of decomposition or intramolecular follow-up products were obtained. However, when **8** was dehalogenated, a pure product was isolated. Here the four-membered rings had been fragmented in the unwanted direction by a retro-aldol reaction, giving 2,6-diacetylbicyclo-[3.3.0]octa-3,7-dione (**9**, Scheme 3).



Scheme 3

Addition of a methyl Grignard reagent to **7** furnished a single isomer. In analogy to halo ketone **6** (attack from the lower side of the molecule), its stereochemical structure is **10**. In the monocyclic series, such compounds were transformed into cycloheptenones.[6,7] Therefore, **10** was mesylated and fragmented by using base. It was expected that the unconjugated bis(enone) **11** or possibly the conjugated analogue **12** would be formed. In this case, polymerization was the main course of the reaction. However, two crystalline products were isolated in low yields, neither of which were **11** or **12**, as shown by the relatively complex spectral data. X-ray structure determinations were used to clarify the situation.[8] As can be seen from Figure 1 and 2, the compounds were identified as **13** and **14**, which contain tricyclo[5.5.0.0^{2,9}]dodecane systems.

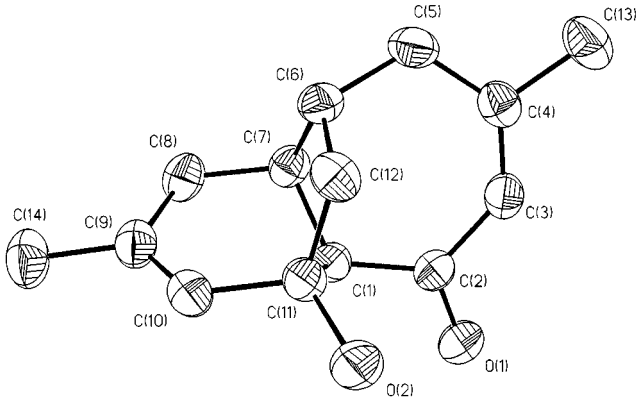


Figure 1. Single-crystal X-ray structure of 9-hydroxy-5,11-dimethyltricyclo[5.5.0.0^{2,9}]dodeca-4,10-dien-3-one (**13**)[19]

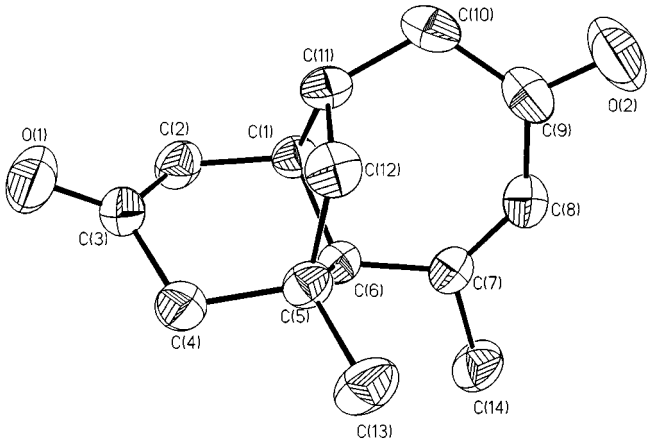


Figure 2. Single-crystal X-ray structure of 3,9-dimethyltricyclo-[5.5.0.0^{2,9}]dodec-3-ene-5,11-dione (**14**)

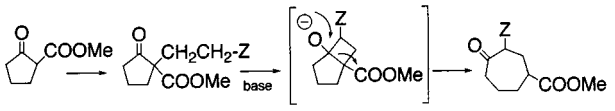
The formation of the novel cage compounds can be rationalized by starting with the transformation of **10** into **11**, and subsequently into **12**. An intramolecular aldol reaction (path a) leads to **13**, whereas the Michael addition of path (b) gives **14**. On repetition of the reaction, either **13** or **14** was formed preferentially under seemingly identical conditions. Thus, the relative amounts of the two pathways seem to depend on subtle differences in the reaction protocol.

From these results it became clear that the ketene addition route was not amenable to the generation of **B**-like structures.

The MIRC Route

A different enlargement of five- to seven-membered rings is known in the literature as the "MIRC" reaction (Michael-initiated ring closure).[9,10] For example, when 2-(methoxycarbonyl)cyclopentanone is treated with Michael acceptors, under certain conditions the primary adduct *may*

undergo the sequence shown in Scheme 4. Applications to acetylenic esters are also known.[11,12]



Scheme 4

Double Michael addition of methyl acrylate and acrylonitrile to compound **15** gave **16a** or **b**, respectively, after extensive optimization work. Best yields and fastest conversions were achieved in a new variation on the reaction, carried out in acetonitrile with catalytic *cis*-tetrakis(triphenylphosphane)ruthenium(II) dihydride.[13] Exclusive attack from the convex side was expected. This was ascertained by an X-ray structure determination of **16a**[8] (Figure 3). In spite of the fact that the MIRC ring-enlargements to the monocyles can be reproduced easily, all base-catalyzed experiments with compounds **16a**,**b** led only to complex, partially polymerized mixtures from which no bicyclo[5.5.0]dodecanes could be isolated. Numerous evasive intramolecular cross-ring condensations can be formulated, and evidently some do proceed. Therefore, the MIRC reactions with methyl propynoate and dimethyl butynedioate were used as alternatives. It was hoped that the unsaturated side-chains of the primary adducts would be less likely to give unwanted evasive results. The MIRC conversion of the monocyclic compound with acetylenic esters was described using NaH as base.[11] Under these conditions and with LDA, only decomposition occurred with **15** and the two alkynes. Using sodium bis(trimethylsilyl)amide as base, a relatively clean reaction with dimethyl butynedioate was observed, whereas the reaction of the propynoate again led to polymerization. The substance isolated from the butynedioate reaction had analytical and spectroscopic data corresponding to the desired product of double ring enlargement, **17**. However, it was surprising that a minor compound was isolated from some reaction runs (under seemingly identical conditions) and had very similar ^{13}C NMR spectral data: Both isomers had 12 resonances, 9 of which were almost identical. X-ray structure determinations (Figure 4 and 5) established that the major isomer was, indeed, bicyclo[5.5.0]-dodecane derivative **17**. The other isomer was the bi(cyclohexadienyl) derivative **18** (Scheme 5).

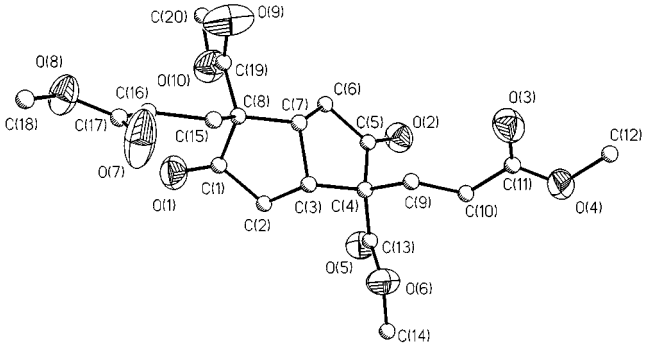


Figure 3. Single-crystal X-ray structure of dimethyl (1α,2β,5α,6β)-2,6-bis(methoxycarbonyl)-3,7-dioxobicyclo[3.3.0]octane-2,6-dipropionate (**16a**)[19]

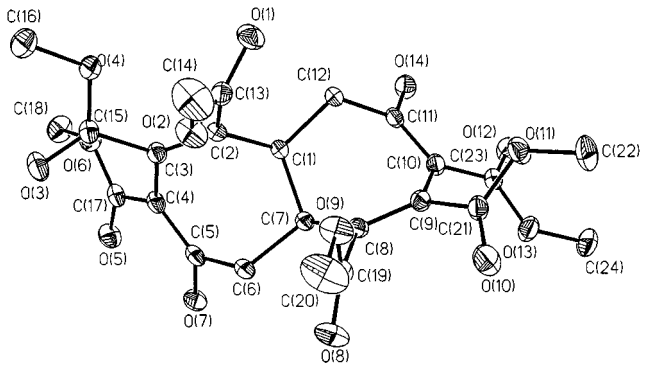


Figure 4. Single-crystal X-ray structure of hexamethyl α,α-5,11-dihydroxybicyclo[5.5.0]dodeca-2,4,8,10-tetraene-2,3,4,8,9,10-hexacarboxylate (**17**)

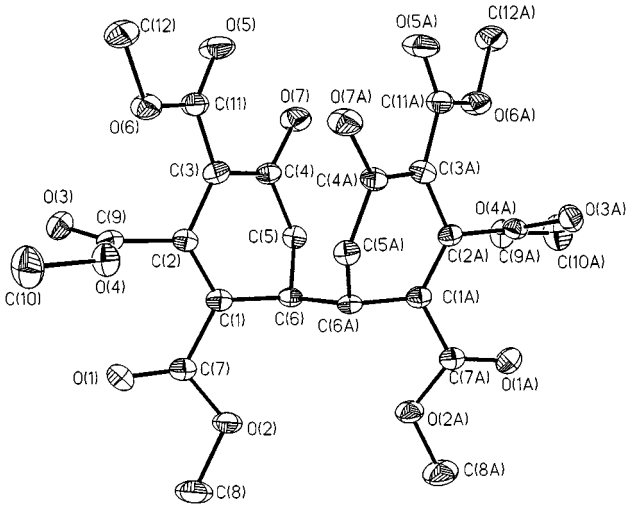
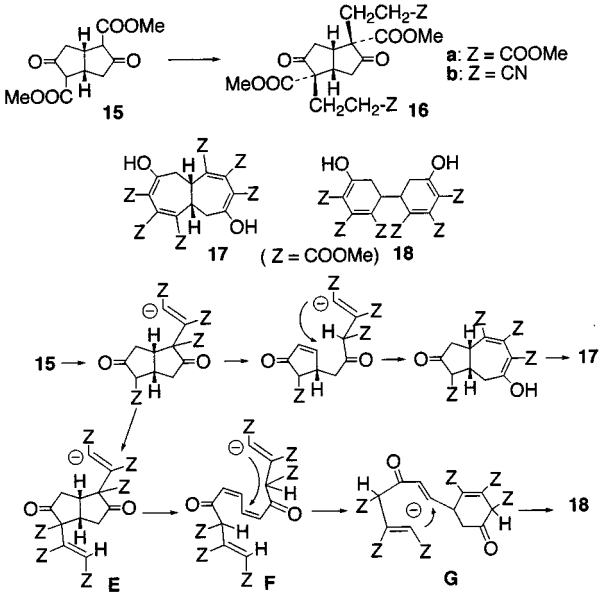


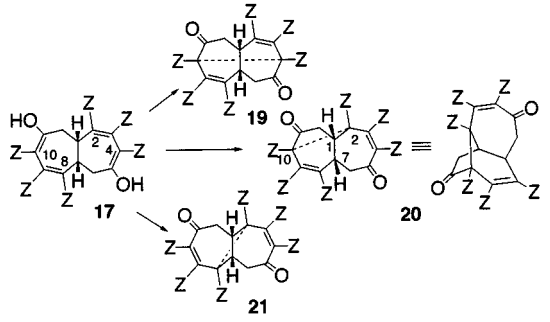
Figure 5. Single-crystal X-ray structure of bis[5-hydroxy-2,3,4-tris-(methoxycarbonyl)cyclohexa-2,4-dienyl] (**18**)



Scheme 5

The formation of **17** can be understood, by following a mechanism analogous to Scheme 4 or alternatively, a retro-Michael/new Michael addition as indicated in Scheme 5. Compound **18**, on the other hand, must be the product of a base-catalyzed rearrangement. However, treatment of **17** with base did not result in the formation of **18**. We assume therefore that reaction branching occurs at an earlier stage of the sequence. Following the idea of Michael fragmentation/new addition, we tentatively suggest that some intermediate, for instance **E**, might lead to **18** via **F** and **G** as shown in Scheme 5.

With **17** in hand, one is very close to the target skeleton of **B**: A simple oxidation of the oxo ester itself or of its dianion might finish the task. There is, however, more than one mode of bridging available to the molecule (Scheme 6): (a) The wanted symmetrical C-4−C-10 coupling, giving a tricyclododecane **19** with two new seven-membered rings; (b) an unsymmetrical C-2−C-10 bridging, giving **20** with new five-, six-, and nine-membered rings; and (c) a path connecting C-2 with C-8, resulting in **21** with a new four-membered and two new seven-membered rings.



Scheme 6

Oxidations of **17** with bromine or iodine in the presence or absence of base or with active manganese dioxide gave tar-like mixtures. But the use of CAN in dichloromethane/methanol or of DDQ in dioxane allowed for the preparation of a single, crystalline product in 40 or 56%, respectively (as well as tar-like residues). The presence of 24 signals in the ^{13}C NMR spectrum immediately showed that the new compound could not be **19** or **21**, and a detailed inspection of all the data showed that **20** had been obtained. The direction of the ring closure is reflected by AM1 calculations.[14] The calculated heats of formation **19** and **20** (without the ester substituents) indicate that the basic skeleton of **20** is more stable than that of **19** by 10 kcal/mol. The undesired direction of ring-closure would evidently have been avoided if the ring enlargements with acrylic esters or acrylonitrile had been successful.

Thus, as in our previous study,[2] the synthesis ended one step short of the target molecule **19**, because the last precursor possesses too many functional groups. This, however, was a necessary prerequisite of the chosen reaction pathway. As a result, interesting insights into the reactivity of such bicyclic systems were obtained, and polycycles **13**, **14** and **20** became available.

Experimental Section

General: X-ray structure determinations:[8,15] Instrument: Siemens P2(1); programs used: Siemens SHELXTL plus/SHELXL-97. Table 1 gives crystal data and structure-refinement parameters. − NMR spectra in $CDCl_3$ with TMS as internal standard; AC 250-P (Bruker; ^1H: 250 MHz, ^{13}C: 62.89 MHz) or DRX 500 (Bruker; ^1H: 500 MHz, ^{13}C:125.78 MHz). − IR: Genesis FT Instrument (Mattson). − MS: VG AutoSpec of Fisons Instruments. − Melting points: Büchi apparatus (type "Dr. Tottoli"). − Boiling points of kugelrohr distillations refer to air bath temperatures.

***cis*-3,7-Bis(trimethylsilyloxy)bicyclo[3.3.1]octa-2,7-diene (2) and *cis*-3,7-Bis(trimethylsilyloxy)bicyclo[3.3.1]octa-2,6-diene (3) (Isomer Mixture):** A solution of LDA was prepared from dry diisopropylamine (52.3 g, 517 mmol) in dry THF (360 mL), and a solution of butyllithium in hexane (1.6 M, 317 mL, 507 mmol) at −78 °C. This cold solution was added dropwise into a solution of **1**[16] (30.0 g, 217 mmol) and chlorotrimethylsilane (61.8 g, 72.2 mL, 569 mmol) in dry THF (480 mL), also cooled to −78 °C. The mixture was stirred for 1 h in the cold, then warmed to room temp. overnight. The solvent was removed under vacuum, and the residue was taken up in petroleum ether (250 mL, b.p. 50−70 °C) and washed twice with saturated $NaHCO_3$ in water. After drying (Na_2SO_4), the solvent was removed, and the remaining oily liquid was distilled in a kugelrohr oven, b.p. 82−90 °C/0.2 Torr); yield 59.9 g (98%) as a 1:1 **2/3** mixture [see NMR]. − IR (Film): $\tilde{\nu}$ = 3062, 2958, 2912, 2850, 1646, 1442, 1407, 1334, 1311, 1253, 1211, 921, 844, 755 cm^{-1}. − ^1H NMR (500 MHz): δ = 0.19 (s, 18 H), 1.95−2.10 (m, CH_2) and 2.50−2.62 (m, CH_2) [1:1; together 4 H], 2.80−2.90 (m, CH of **2**) and 3.55−3.57 (m, CH of **2**) and 3.23−3.25 (m, CH of **3**) [1:1:2; together 2 H), 4.51 (d, ^3J = 1.2 Hz, =CH) and 4.63 (d, ^3J = 2.0 Hz, =CH) [1:1; together 2 H].

(1α,2β,5β,7α,9β,12β)-4,4,10,10-Tetrachloro-5,9-bis(trimethylsilyloxy)tetracyclo[5.5.0.0^{2,5}.0^{9,12}]dodecane-3,11-dione (4) and (1α,2β,5β,7α,8β,11β)-4,4,10,10-Tetrachloro-5,11-bis(trimethylsilyloxy)tetracyclo[5.5.0.0^{2,5}.0^{8,11}]dodecane-3,9-dione (5): A suspension of activated zinc dust (50.2 g, 768 mmol) in a solution of the **2/3** isomer mixture (25.0 g, 88.5 mmol) in dry diethyl ether (1100 mL) was treated dropwise with a solution of freshly distilled trichloroacetyl chloride (41.9 g, 230 mmol) in dry diethyl ether (350 mL) at 0 °C within about 8 h. The grey suspension was stirred overnight at room temp., then filtered, and the solid was washed with further diethyl ether. The combined diethyl ether solution was concentrated in vacuo to approximately 250 mL, then kept in a refrigerator at −18 °C. The crystallized solid, **5**, was filtered off, recrystallized from *tert*-butyl methyl ether and dried under vacuum, m.p. 208 °C; yield 11.3 g (25%). − IR (KBr): $\tilde{\nu}$ = 2954, 2923, 2869, 1801, 1457, 1411, 1346, 1311, 1253, 1214, 1122, 1068, 971, 948, 833, 844, 767, 752, 671, 620, 520, 447 cm^{-1}. − ^1H NMR (500 MHz): δ = 0.27 (s, 18 H), 2.16 (dd, ^2J = 13.9, ^3J = 11.3 Hz, 2 H), 2.67−2.70 (m, 2 H), 2.86 (dd, ^2J = 13.9, ^3J = 7.6 Hz, 2 H), 3.69 (s, 2 H). − ^{13}C NMR (126 MHz): δ = 1.7 (CH_3), 40.3 (CH_2), 46.6 (CH), 71.8 (CH), 88.8 (CCl_2), 92.0 (COTMS), 195.9 (CO). − MS (EI, 70 eV); *m/z* (%): 502 [M^{+}] (1), 468 (1), 441 (2), 405 (1), 379 (1), 349 (4), 329 (1), 315 (1), 287 (1), 266 (1), 241 (1), 213 (1), 195 (1), 175 (1), 157 (2), 131 (1), 115 (2), 103 (1), 73 (100), 45 (10). − $C_{18}H_{26}Cl_4O_4Si_2$ (504.4): calcd. C 42.86, H 5.20; found C 42.75, H 5.17. − Compound **4** could be enriched (by concentrating the mother liquor of **5** and by repeated fractionating recrystallization from diethyl ether and acetonitrile) to the point that its ^1H NMR could be recorded in the mixture with **5**. The raw yield of **4** was approximately 4%. − ^1H NMR (500 MHz): δ = 0.30 (s, 18 H), 2.44 (dd, ^2J = 14.5 Hz, ^3J = 6.4 Hz, 2 H), 2.57 (dd, ^2J = 14.5,

Table 1. Crystal data and structure refinements for compounds **13**, **14**, **16a**, **17**, and **18** (wavelength: 0.71073 nm; absorption corrections: none; full-matrix least-squares refinements on F^2)

	13	**14**	**16a**	**17**	**18**
Empirical formula	$C_{14}H_{18}O_2$	$C_{14}H_{18}O_2$	$C_{20}H_{26}$	$C_{24}H_{26}O_{14}$	$C_{24}H_{26}O_{14}$
Molecular mass	218.28	218.28	426.41	538.45	538.45
Temperature [K]	293	293	173	173	173
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$C2/c$
Unit cell [Å; °]	a = 8.029(3) b = 8.469(2) c = 17.688(6) β = 92.64(3)	a = 12.318(3) b = 11.397(3) c = 8.338(3) β = 92.92(2)	a = 10.758(3) b = 24.309(4) c = 16.009(3) β = 91.98(2)	a = 8.486(6) b = 11.023(10) c = 13.669(10) α = 86.06(7) β = 82.07(6) γ = 84.75(6)	a = 14.836(15) b = 11.884(10) c = 15.056(11) β = 111.62(6)
Volume [Å^3]	1201.5(7)	1169.0(6)	4184.1(16)	1259.0(17)	2468(4)
Z; calcd. density	4; 1.207	4; 1.240	8; 1.354	2; 1.420	4; 1.449
Abs. coeff. [mm^{-1}]	0.079	0.081	0.109	0.119	0.121
F(000)	472	472	1808	564	1128
Crystal size [mm]	0.7 × 0.4 × 0.3	1.1 × 0.7 × 0.3	0.3 × 0.2 × 0.2	1.2 × 0.8 × 0.7	1.1 × 0.2 × 0.1
Colour and shape	colourless, rhombic	colourless plates	colourless, irregular	colourless, irregular	colourless needles
θ range [°]	2.31−30	2.44−30	2.07−25	1.86−30	2.26−27
Index ranges	$0 \le h \le 11$ $0 \le k \le 11$ $-24 \le l \le 24$	$-17 \le h \le 16$ $-15 \le k \le 0$ $0 \le l \le 11$	$0 \le h \le 12$ $0 \le k \le 28$ $-19 \le l \le 19$	$0 \le h \le 11$ $-15 \le k \le 15$ $-19 \le l \le 19$	$0 \le h \le 18$ $0 \le k \le 15$ $-19 \le l \le 17$
Reflect. total/unique	7443/3498	3416/3217	7829/7413	7774/7318	2798/2697
R(int)	0.0391	0.0215	0.0381	0.0748	0.1033
Data/restr./param.	3498/0/217	3217/0/217	7392/0/350	7318/0/357	2697/0/176
Goodness-of-fit on F^2	1.012	1.029	1.039	1.016	1.018
Final R indices	R_1 = 0.0495	R_1 = 0.0556	R_1 = 0.0800	R_1 = 0.0462	R_1 = 0.0641
[$I \le 2\sigma(I)$][a]	wR_2 = 0.1192 [2419]	wR_2 = 0.1293 [2185]	wR_2 = 0.1995 [3009]	wR_2 = 0.1172 [5928]	wR_2 = 0.1440 [1687]
R indices (all data)	R_1 = 0.0772 wR_2=0.1330	R_1 = 0.0877 wR_2=0.1476	R_1 = 0.1644 wR_2=0.3059	R_1 = 0.0607 wR_2 = 0.1268	R_1 = 0.1160 wR_2 = 0.1706
Largest diff. peak/hole [e Å^{-3}]	0.215/−0.192	0.235/−0.221	0.496/−0.471	0.393/−0.264	0.370/−0.332
Treatment of H atoms	Isotropically refined	Isotropically refined	Riding model	Riding model	Riding model

[a] Number of reflections used in the refinement in square brackets.

^3J = 6.7 Hz, 2 H), 2.76−2.80 (m, 1 H), 2.83 −2.88 (m, 1 H), 3.73 (d, ^3J = 2.7 Hz, 2 H).

(1α,2β,4α,5β,7α,8β,10α,11β)-4,10-Dichloro-5,11-bis(trimethyl)-silyloxytetracyclo[5.5.0.^{2,5}.0^{8,11}]dodecane-3,9-dione (6): Freshly distilled tributyltin hydride (3.49 g, 12.0 mmol) was added dropwise to a solution of **5** (3.03 g, 6.0 mmol) and AIBN (50 mg) in dry toluene (60 mL) over 1−2 h. The resulting mixture was stirred at room temp. for 3 d. The solvent was removed completely, and the oily residue was taken up in hot hexane. The hot solution was filtered, and the filtrate was concentrated and kept at −18 °C, resulting in crystallization, m.p. 145−148 °C; yield 1.8 g (69%). − IR (KBr): ṽ = 2962, 1793, 1454, 1419, 1342, 1315, 1253, 1222, 1180, 1126, 1079, 1041, 948, 871, 848, 755, 694 cm^{-1}. − ^{1}H NMR (250 MHz): δ = 0.22 (s, 18 H), 1.98 (dd, ^2J = 13.0, ^3J = 10.7 Hz, 2 H, H_A of CH_2), 2.48−2.56 (m, 2 H, 1- and 7-H), 2.69 (dd, ^2J = 13.0 and ^3J = 7.7 Hz, 2 H, H_B of CH_2), 3.48 (d, ^4J = 4.6 Hz, 2 H, 2- and 8-H), 4.95 (d, ^4J = 4.6 Hz, 2 H, CHCl). − ^{13}C NMR (62 MHz): δ = 1.5 (CH_3), 38.5 (CH_2), 46.5 (C-1 and -7), 70.1 (C-2 and -8), 72.3 (CHCl), 84.0 (COTMS), 201.9 (CO). −$C_{18}H_{28}Cl_2O_4Si_2$ (435.5): calcd. C 49.64, H 6.48; found C 49.37, H 6.43.

(1α,2β,5β,7α,8β,11β)-5,11-Bis(trimethylsilyloxy)tetracyclo-[5.5.0.0^{2,5}0^{8,11}]dodecane-3,9-dione (7): Freshly distilled tributyltin hydride (20.5 g, 70.4 mmol) was added dropwise to a solution of **5** (8.07 g, 16.0 mmol) and AIBN (160 mg) in dry toluene (250 mL) over 1−2 h. The resulting mixture was stirred for 4 h at 80 °C. After cooling, the solvent was completely removed, and the oily residue was taken up in hot petroleum ether (b.p. 60−80 °C) and the hot solution was filtered. The light-green filtrate was concentrated and kept at −18 °C, resulting in crystallization. To remove residual Bu_3SnCl, the product was dissolved in diethyl ether, and this solution was equilibrated with aqueous KF (10%). The Bu_3SnF that formed was filtered off, the solution was dried (Na_2SO_4) and concentrated. Fine "cotton-like" crystals (4.0 g, 68%) were obtained from petroleum ether; m.p. 113−116 °C. − IR (KBr): ṽ = 2958, 1781, 1338, 1268, 1253, 1218, 1122, 1076, 933, 871, 836, 752, 686 cm^{-1}. − ^{1}H NMR (250 MHz): δ = 0.18 (s, 18 H), 2.04 ("t", J = 11.6 Hz, 2 H), 2.32 (dd, J = 12.9 and J = 7.2 Hz, 2 H), 2.47−2.55 (m, 2 H), 3.03 (dd, J = 17.5 Hz, J' = 3.1 Hz, 2 H), 3.26 (dd, J = 17.5 Hz, J' = 3.8 Hz, 2 H), 3.36 (dd, J = 5.0 and J = 3.1 Hz, 2 H). − ^{13}C NMR (62 MHz): δ = 1.6 (CH_3), 43.7 (C-6 and -12), 45.3 (C-1 and -7), 59.6 (C-4 and -10), 74.7 (C-2 and -8), 94.8 (COTMS), 209.3 (CO). − $C_{18}H_{30}O_4Si_2$ (366.6): calcd. C 58.97, H 8.25; found C 58.54, H 8.16.

(1α,2β,5β,7α,8β,11β)-4,4,10,10-Tetrachloro-5,11-dihydroxy-tetracyclo[5.5.0.0^{2,5}.0^{8,11}]dodecane-3,9-dione (8): A stirred suspension of **5** (5.04 g, 10.0 mmol) in methanol (100 mL) was treated with a few drops of HCl (1 M). Dissolution of the solid occurred within 2−3 h, but stirring was continued for 19 h. The solvent was removed, the residue was taken up in diethyl ether, and the solution was washed with water and brine. Concentration of the dried (Na_2SO_4) solution resulted in the separation of a slightly discoloured solid, which was recrystallized from chloroform. Yield 3.31 g (92%), m.p. 163−164 °C (dec.). − IR (KBr): ṽ = 3507, 3372, 2969, 2939, 1797, 1338, 1303, 1265, 1214, 1130, 1091, 1045, 971, 833, 732, 682, 617, 528, 489 cm^{-1}. − ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 2.12 (dd, ^2J = 14.2 and ^3J = 11.3 Hz, 2 H, H_A of CH_2), 2.42−2.51 (m, 2 H, 1- and 7-H), 2.73 (dd, ^2J = 14.2 and ^3J = 7.6 Hz, 2 H, H_B of CH_2), 3.91 (s, 2 H, 2- and 8-H), 7.24 (s, 2 H, OH). − ^{13}C NMR (62 MHz, [D$_6$]DMSO): δ = 40.3 (CH_2), 46.6

(CH), 69.4 (CH), 85.9 (CCl_2), 92.5 (COH),197.6 (CO). − MS (EI, 70 eV); *m/z* (%): 358 (8) [$M^{\cdot+}$], 342 (1), 324 (7), 297 (5), 287 (15), 275 (99), 261 (8), 251 (25), 239 (45), 223 (24), 211 (100), 175 (17), 161 (28), 141 (29), 131 (20), 115 (25), 103 (33), 91 (41), 77 (74), 63 (53), 51 (78), 36 (86), 28 (53). − $C_{12}H_{10}Cl_4O_4$ (360.0): calcd. C 40.03, H 2.80; found C 39.95, H 2.87.

2,6-Diacetyl-α,α-bicyclo[3.3.0]octane-3,7-dione (9): Dione **8** (3.00 g, 8.33 mmol) was suspended in dry toluene (90 mL) and AIBN (80 mg) was added. Bu_3SnH (10.7 g, 36.0 mmol) was added dropwise over 10 min, and the mixture was stirred at 80 °C for 20 h. Solvent removal was followed by dissolution in diethyl ether and treatment with aqueous KF as described for **7** (above). Crystallization from *tert*-butyl methyl ether at −18 °C gave rise to the product (0.87 g, 47%), m.p. 138−140 °C. − IR (KBr): $\tilde{\nu}$ = 2954, 2923, 2854, 1658, 1616, 1511, 1411, 1376, 1230, 1164, 1072, 1022, 929, 998, 856, 744, 667, 605, 474 cm^{-1}. − ^1H NMR (500 MHz): δ = 2.06 (s, 6 H), 2.41 (dd, ^2J = 18.8 and ^3J = 6.1 Hz, 2 H, H_A of CH_2), 2.90 (dd, ^2J = 18.8 and ^3J = 9.3 Hz, 2 H, H_B of CH_2), 3.57−3.59 (m, 2 H, CH), 13.84 (m, 2 H, OH). − ^{13}C NMR (62 MHz): δ = 21.7 (CH_3), 37.8 (CH), 42.9 (CH_2), 114.0 (C=COH), 180.7 (C=COH), 200.7 (CO). − MS (EI, 70 eV); *m/z* (%): 222 [$M^{\cdot+}$] (32), 195 (9), 179 (17), 165 (11), 153 (13), 137 (34), 123 (9), 111 (24), 95 (17), 83 (8), 69 (14), 43 (100). − $C_{12}H_{14}O_4$ (222.3): calcd. C 64.85, H 6.35; found C 64.56, H 6.49.

(1α,2β,3α,5β,7α,8β,9α,11β)-3,9-Dimethyl-5,11-bis(trimethylsilyloxy)tetracyclo[5.5.0.0^{2,5}.0^{8,11}]dodecane-3,9-diol (10): A solution of **7** (1.00 g, 2.73 mmol) in absolute THF (30 mL) was treated over 10−15 min with of a solution of CH_3MgBr in diethyl ether (3 M, 6.0 mL) at −78 °C. The mixture was stirred for 30 min while cold, then brought to room temp. and decomposed by careful addition of water (3 mL). Saturated aqueous NH_4Cl (30 mL) was added, and the mixture was extracted with diethyl ether (2 × 100 mL). The combined organic phases were washed with water (10 mL) and dried with Na_2SO_4. Removal of the solvent was followed by crystallization from petroleum ether, yield 760 mg (70%); m.p. 167−170 °C. −IR(KBr): $\tilde{\nu}$ = 3286, 2962, 2865, 1454, 1454, 1415, 1322, 1187, 1068, 960, 906, 840, 806, 752, 686 cm^{-1}. − ^1H NMR (250 MHz): δ = 0.11 (s, 18 H), 1.45 (s, 6 H), 1.60−1.71 (m, 2 H), 1.90 (dd, ^2J = 12.1 and ^3J = 6.9 Hz, 2 H), 2.15 (d, *J* = 3.0 Hz, 4 H), 2.26 (d, *J* = 2.4 Hz, 2 H), 2.51−2.62 (m, 2 H), 3.20 (s, 2 H). − ^{13}C NMR (62 MHz): δ = 1.9 (CH_3), 30.7 (CH_3), 42.3 (CH), 44.9 (CH_2), 49.3 (CH_2), 61.7 (CH), 67.6 (C_{quart}), 79.6 (C_{quart}). − $C_{20}H_{38}O_4Si_2$ (398.7): calcd. C 60.25, H 9.61; found C 59.97, H 9.47.

9-Hydroxy-5,11-dimethyltricyclo[5.5.0.0^{2,9}]dodeca-4,10-dien-3-one (13) and 3,9-dimethyltricyclo[5.5.0.0^{2,9}]dodec-3-ene-5,11-dione (14): A stirred solution of **10** (400 mg) and triethylamine (400 mg, 1.0 mmol) in dichloromethane (15 mL) was treated dropwise with methanesulfonyl chloride (650 mg, 5.67 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The mixture was stirred at room temp. for 20 h, then concentrated, while cold, in vacuo and left for a while under vacuum. At this point, a brown discoloration and partial polymerization sometimes occurred. The solid was dissolved in a mixture of diethyl ether (80 mL) and water (30 mL), the phases were separated, and the organic layer was washed with water, aqueous $NaHCO_3$ (10%), saturated brine, and again with aqueous $NaHCO_3$. After drying (Na_2SO_4), the solvent was removed in vacuo, and the residue was purified by chromatography with petroleum ether (b.p. 40−60 °C)/ethyl acetate (2:1) on silica gel. In several, seemingly identical runs of the reaction, either **13** or **14** (7−8 mg, 3−4%) was obtained by chromatography as the main product. − **13**: M.p. 127−129 °C. − IR (KBr): $\tilde{\nu}$ = 3413, 3008, 2962, 2915, 2877, 1693, 1627, 1438, 1369, 1288, 1172, 1099, 1052, 1022, 806 cm^{-1}. − ^1H NMR (500 MHz): δ = 1.62 (s, 3 H), 1.71−1.75 (m, 2 H), 1.90 (s, 3 H), 1.97 (d, *J* = 17.7 Hz, 1 H), 2.26−2.38 (m, 4 H), 2.55−2.64 (m, 3 H), 5.65 (s, 1 H), 6.00 (s, 1 H). − ^{13}C NMR (62 MHz): δ = 21.7 (CH_3), 27.5 (CH_3), 39.3 (CH), 39.6 (CH), 40.2 (CH_2), 43.2 (CH_2), 44.9 (CH_2), 63.6 (CH), 81.1 (C_{quart}), 129.1 (=CH), 130.6 (=C_{quart}), 133.1 (=CH), 153.5 (=C_{quart}), 203.8 (CO). − $C_{14}H_{18}O_2$ (218.3): calcd. C 77.04, H 8.31; found C 76.97, H 8.56. − **14**: M.p. 135−137 °C. − IR (KBr): $\tilde{\nu}$ = 3397, 2962, 2931, 2869, 1708, 1635, 1457, 1415, 1369, 1334, 1295, 1265, 1222, 1180, 1095, 1029, 956, 894, 806, 713, 493 cm^{-1}. − ^1H NMR (500 MHz): δ = 1.10 (s, 3 H), 1.24−1.63 (m, 1 H), 2.10 (s, 3 H), 1.89−2.02 (m, 1 H), 2.16−2.26 (m, 1 H), 2.38−2.42 (m, 2 H), 2.47−2.61 (m, 6 H), 6.09 (s, 1 H). − ^{13}C NMR (62 MHz): δ = 23.8 (CH_3), 29.9 (CH_3), 37.4 (CH), 47.5 (CH), 60.6 (CH), 41.5 (CH_2), 48.5 (CH_2), 50.2 (CH_2), 57.3 (CH_2), 48.9 (C_{quart}),131.4 (=CH),157.5 (=C_{quart}), 200.7 (CO), 209.5 (CO). − $C_{14}H_{18}O_2$ (218.3): calcd. C 77.04, H 8.31; found C 76.90, H 8.48.

Dimethyl (1α,2β,5α,6β)-2,6-Bis(methoxycarbonyl)-3,7-dioxobicyclo-[3.3.0]octane-2,6-dipropionate (16a). − a) With NaOMe in DME: Compound **15** (10.0 g, 39.4 mmol) was dissolved in absolute DME (75 mL) and combined with a fresh solution of sodium methoxide (1.00 mL, 2.20 mmol) [prepared from Na (500 mg) in dry methanol (10.0 mL)]. After stirring for 1 h, freshly distilled methyl acrylate (10.2 g, 118 mmol) in absolute DME (25 mL) was added over 30 min. The orange-coloured mixture was stirred overnight at room temp., then kept for 11 d at room temp., and heated at reflux for 20 h in an attempt to effect ring enlargements. Concentration in vacuo gave a brownish oil which was dissolved in diethyl ether and washed with saturated brine. The latter was again extracted three times with a little diethyl ether, and the combined organic phases were dried (Na_2SO_4) and concentrated to give an orange-coloured semi-crystalline residue (17.0 g). This was recrystallized from methanol to yield colourless fine needles (13.3 g, 79%), m.p. 105−110 °C. − **b) With $RuH_2(PPh_3)_4$ Catalysis:** A mixture of **15** (1.0 g, 3.93 mmol) and $RuH_2(PPh_3)_4$ [13,17] (136 mg, 0.12 mmol) in dry acetonitrile (12 mL) was treated with freshly distilled methyl acrylate (713 mg, 8.3 mmol) and stirred for 23 h at room temp. The solvent was removed, and the residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to yield, after crystallization from methanol, the product (1.33 g, 80%). − IR (KBr): $\tilde{\nu}$ = 2958, 2923, 2850, 1747, 1442, 1380, 1245, 1199, 1176, 1049, 975, 809 cm^{-1}. −^1H NMR (250 MHz): δ = 2.07−2.19 (m, 2 H), 2.24−2.38 (m, 2 H), 2.41−2.65 (m, 8 H), 2.98- 3.04 (m, 2 H), 3.67 (s, 6 H), 3.73 (s, 6 H). − ^{13}C NMR (62 MHz): δ = 29.0 (CH_2), 29.1 (CH_2), 39.9 (CH_2), 44.6 (CH), 51.8 (CH_3), 52.8 (CH_3), 62.2 (C_{quart}), 170.1 (COOR), 173.1 (COOR), 210.0 (CO). − MS (EI, 70 eV): *m/z* (%) = 426 (27)[$M^{\cdot+}$], 398 (7), 363 (54), 338 (49), 321 (8), 307 (21), 292 (9), 275 (20), 261 (12), 243 (5), 233 (10), 213 (29), 201 (6), 181 (90), 173 (7), 153 (18), 139 (70), 126 (19), 111 (17), 91 (17), 77 (13), 67 (17), 55 (100), 41 (19). − $C_{20}H_{26}O_{10}$(426.4): calcd. C 56.33, H 6.15; found C 56.24, H 6.13.

Dimethyl (1α,2β,5α,6β)-2,6-Bis(2-cyanoethyl)-3,7-dioxobicyclo[3.3.0]-octane-2,6-dicarboxylate (16b). − a) The reaction was carried out with NaOMe in DME analogously to the preparation (a) of **16a**. Mostly polymerization occurred; traces of crystalline **16b** were found after prolonged chromatography. − **b)** A similar protocol as for **16a** was applied with $RuH_2(PPh_3)_4$ catalysis, except that the reaction mixture was stirred for 4 d at room temp., then heated at reflux for 2 d. Yield after chromatography as with **16a** was 736 mg, 52%; m.p. 146 °C. − IR (KBr): $\tilde{\nu}$ = 2954, 2923, 2854, 2248, 1758, 1724, 1442, 1353, 1241, 1203, 1157, 1052 cm^{-1}. − ^1H NMR (500 MHz): δ = 2.05−2.11 (m, 2 H), 2.37−2.43 (m, 2 H), 2.48−2.65 (m, 8 H), 2.99−3.03 (m, 2 H), 3.78 (s, 6 H). − ^{13}C NMR

(126 MHz): δ = 12.9 (CH_2), 29.9 (CH_2), 40.0 (CH_2), 44.4 (CH), 53.0 (CH_3), 61.3 (C_{quart}), 118.6 (CN), 169.2 (COOR), 208.8 (CO). − MS (EI, 70 eV): *m/z* (%) = 360 [$M^{\cdot+}$] (3), 329 (9), 301 (7), 292 (14), 269 (6), 260 (12), 228 (9), 213 (5), 200 (7), 180 (100), 152 (42), 139 (8), 121 (9), 111 (13), 91 (12), 65 (17), 53 (30), 39 (14), 28 (11). − $C_{18}H_{20}N_2O_6$ (360.4): calcd. C 59.99, H 5.59, N 7.77; found C 60.24, H 5.59, N 7.47.

Hexamethyl α,α-5,11-Dihydroxybicyclo[5.5.0]dodeca-2,4,8,10-tetraene-2,3,4,8,9,10-hexacarboxylate (17) and Bis[5-hydroxy-2,3,4-tris(methoxycarbonyl)cyclohexa-2,4-dienyl] (18): A solution of **15** (2.03 g, 8.00 mmol) in dry THF (140 mL) at 0 °C was treated dropwise over 1 h under vigorous stirring with an LDA solution in dry THF (1 M, 20 mL, 20 mmol). Stirring was continued for 1 h at room temp. The mixture was then brought to 0 °C again, and a solution of freshly distilled dimethyl butynedioate (3.30 g, 23.2 mmol) in THF (90 mL) was added over 90 min. The mixture gradually turned dark brown. It was heated at reflux overnight, then quenched by the addition of HOAc (3.0 mL) in diethyl ether (10 mL). The solvents were removed, the residue was taken up in CH_2Cl_2 (300 mL), washed with water (2 × 100 mL) and then with saturated brine, and finally dried (Na_2SO_4). Concentration gave a brownish, viscous paste. This was stirred with methanol until dissolved, then kept at −18 °C. A beige-coloured precipitate formed which was recrystallized from a little methanol to give colourless fine crystals of **17** (1.64 g, 38%), m.p.184−186 °C. − IR (KBr): $\tilde{\nu}$ = 3436, 3031, 3000, 2954, 1727, 1654, 1600, 1442, 1361, 1307, 1280, 1245, 1207, 1122, 1037, 1010, 960, 840 cm^{-1}. − ^1H NMR (250 MHz): δ = 2.47 ("t", *J* = 12.7 Hz, 2 H), 2.73 (dd, ^2J = 12.7 and ^3J = 4.3 Hz, 2 H), 3.57−3.62 (m, 2 H), 3.71 (s, 6 H), 3.73 (s, 6 H), 3.76 (s, 6 H), 12.74 (s, 2 H). − ^{13}C NMR (62 MHz): δ = 34.5 (CH_2), 51.5 (CH), 52.0 (CH_3), 52.3 (CH_3), 52.4 (CH_3), 98.7 (=C_{quart}), 131.8 (=C_{quart}),140.6 (=C_{quart}),166.0 (COOR),167.3 (COOR), 170.3 (COOR), 178.8 (=COH). − MS (EI, 70 eV); *m/z* (%): 506 [(M − MeOH)$^{\cdot+}$] (4), 478 (6), 450 (8), 446 (28), 431 (3), 418 (23), 415 (9), 388 (5), 386 (25), 364 (7), 358 (22), 355 (13), 345 (10), 327 (23), 313 (9), 296 (6), 299 (15), 271 (12), 268 (8), 243 (5), 237 (72), 221 (10), 209 (15), 206 (35), 181 (12), 179 (15), 163 (10), 153 (17), 148 (12), 139 (7), 120 (22), 115 (10), 105 (8), 92 (16), 77 (20), 65 (11), 53 (13). − $C_{24}H_{26}O_{14}$ (538.5): calcd. C 53.53, H 4.87; found C 53.44, H 5.10. − The combined mother liquor of **17** was concentrated, redissolved in dichloromethane, and purified by chromatography on silica gel with petroleum ether/ethyl acetate (1:1). After some **17**, compound **18** (15%, average of 5 experiments) was eluted, m.p. 178−184 °C. − IR (KBr): $\tilde{\nu}$ = 3031, 3000, 2950, 2842, 1735, 1643, 1612, 1562, 1450, 1400, 1349, 1292, 1261, 1118, 1087, 1025, 1002, 964, 898, 871, 786, 748, 713, 613, 559, 485, 451 cm^{-1}. − ^1H NMR (250 MHz): δ = 2.45 (d, 2 H, *J* = 18.2 Hz), 2.63 (dd, 2 H, ^2J = 18.2 Hz, ^3J = 8.6 Hz), 3.38 (d, 2 H, *J* = 8.6 Hz), 3.77 (s, 6 H), 3.80 (s, 6 H), 3.83 (s, 6 H), 13.41 (s, 2 H). − ^{13}C NMR (62 MHz): δ = 29.8 (CH_2), 33.9 (CH), 52.2 (CH_3), 52.4 (CH_3), 52.5 (CH_3), 98.7 (=C_{quart}), 117.5 (=C_{quart}), 140.0 (=C_{quart}), 166.1 (COOR), 168.3 (COOR), 169.6 (COOR), 180.0 (=C(OH)]. − MS (CI); *m/z* (%): 507 [(M − MeO)$^+$] (4), 475 (7), 444 (2), 443 (10), 415 (2), 268 (4), 239 (10), 238 (27), 237 (100), 236 (7), 223 (4), 207 (8), 206 (18), 191 (4), 179 (15), 153 (2), 148 (5), 135 (2), 120 (7), 119 (3), 92 (3). − $C_{24}H_{26}O_{14}$ (538.5): calcd. C 53.53, H 4.87; found C 53.83, H 5.14.

Hexamethyl 5,11-Dioxotricyclo[5.5.0.0^{2,10}]dodeca-3,8-diene-2,3,4,8,9,10-hexacarboxylate (20). − a) By Oxidation of 17 with DDQ: Compound **17** (500 mg, 0.093 mmol) and DDQ (232 mg, 1.02 mmol) were heated at reflux for 43 h in absolute dioxane (30 mL). On cooling, 2,3-dichloro-4,5-dicyanohydroquinone crystallized and was filtered off. The solvent was removed, and the residue was taken up in chloroform and filtered again. When the solvent was distilled off, a beige-coloured residue was obtained which was recrystallized from methanol, then purified by chromatography on silica gel with petroleum ether (b.p. 50−70 °C)/ethyl acetate (1:1).Yield: 280 mg (56%); m.p.208−210 °C (dec.). − **b) By Oxidation of 17 with CAN:** A solution of CAN (2.74 g, 5.00 mmol) in methanol (30 mL) was added dropwise over 1 h to a solution of **17** (500 mg, 0.093 mmol) in dichloromethane (30 mL). The deep orange coloration faded rapidly in the beginning, and a precipitate formed, which dissolved again in the course of the reaction. Stirring was continued for 3 h. Thereafter the mixture was concentrated, taken up in chloroform and washed twice each with water and saturated brine. The solution was dried (Na_2SO_4), the solvent was distilled off, and the residue was purified by flash chromatography with ethyl acetate as eluent to yield **20** (200 mg, 40%), m.p. 208−210 °C (dec.). − IR (KBr): $\tilde{\nu}$ = 2996, 2958, 1735, 1627, 1438, 1261, 1099, 1029, 802 cm^{-1}. − ^1H NMR (250 MHz): δ = 2.22−3.33 (m, 6 H), 3.70, 3.75, 3.76, 3.77, 3.79, 3.81 (6 s, 3 H each). − ^{13}C NMR (62 MHz): δ = 38.9, 39.1 (both CH), 43.5, 46.7 (both CH_2), 52.7, 52.8, 53.0, 53.1, 53.2, 53.8 (6 × CH_3), 59.9, 65.4 (both C_{quart}), 132.2, 136.4, 136.9, 140.9 (4 × =C_{quart}), 164.2, 164.7, 165.6, 165.8, 165.9, 169.4 (6 × COOR), 193.6, 197.2 (2 × CO). − $C_{24}H_{24}O_{14}$ (536.4): calcd. C 53.74, H 4.51; found C 53.70, H 4.51.

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[15] Other details of the crystal-structure investigation have been deposited at the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-149319 (**13**), -149320 (**14**), -149321 (**16a**), -149322 (**17**) and -149323 (**18**). Copies of the data are available free of charge on application to The Director, CCDC, 12 Union Road, Cambridge

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[19] Figure 1 and 3 show the enantiomers of the drawn structures **13** and **16a**.

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