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TOWARDS ACYCLIC 1,1-LINKED POLYCYCLOBUTANES AS POTENTIAL PRECURSORS OF POLYSPIRANES WITH A HELICAL PRIMARY STRUCTURE: SYNTHESIS OF TERCYCLOBUTANES AND ATTEMPTED SYNTHESIS OF QUINQUECYCLOBUTANES

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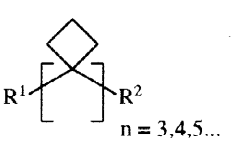
Abstract: Acyclic 1,1-linked polycyclobutanes **1** should be potentially prone to rearrange to polyspiranes with a helical primary structure. In an exploratory study, the synthesis of the tercyclobutanes **8** (**5-6-7-8**) and **15** (**9-10-11-12-16-15** or **14-15**), and several approaches to quinquecyclobutanes with the β- and δ-ketoesters **35** (**15-33-34-35**) and **24b** (**23-24a-24b**), respectively, as most promising precursors are described.

Introduction

Acyclic 1,1-linked polycyclobutanes **1**[1] are an unknown but topologically interesting class of compounds. According to MM3(92)-calculations[2] on the septicyclobutane **2** ($R^1 = R^2 = CH_3$) as a model, they adopt a helical conformation **A** as thermodynamically most stable conformation ($\Delta H_f° = 152.8$ kcal/mol). It is therefore tempting to speculate that a conformationally controlled multiple cyclobutylmethyl to cyclopentyl rearrangement of a suitable functionalized precursor (e.g. **2**, $R^1 = CH_2OH$, $R^2 = H$) could lead to a hexaspirane **3** with a helical primary structure **4**[3] ($\Delta H_f° = 8.8$ kcal/mol) as one of sixteen (eight)[4] possible diastereoisomers. Interestingly, the calculated identity periods of the two helical species **A** (5.5 Å) and **4** (5.7 Å) are nearly identical.



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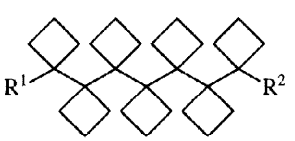

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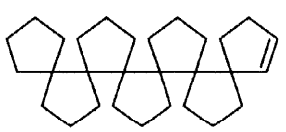

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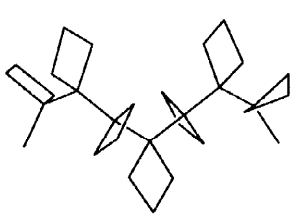
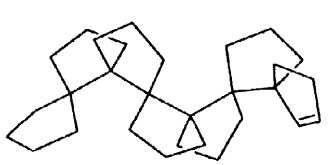


A



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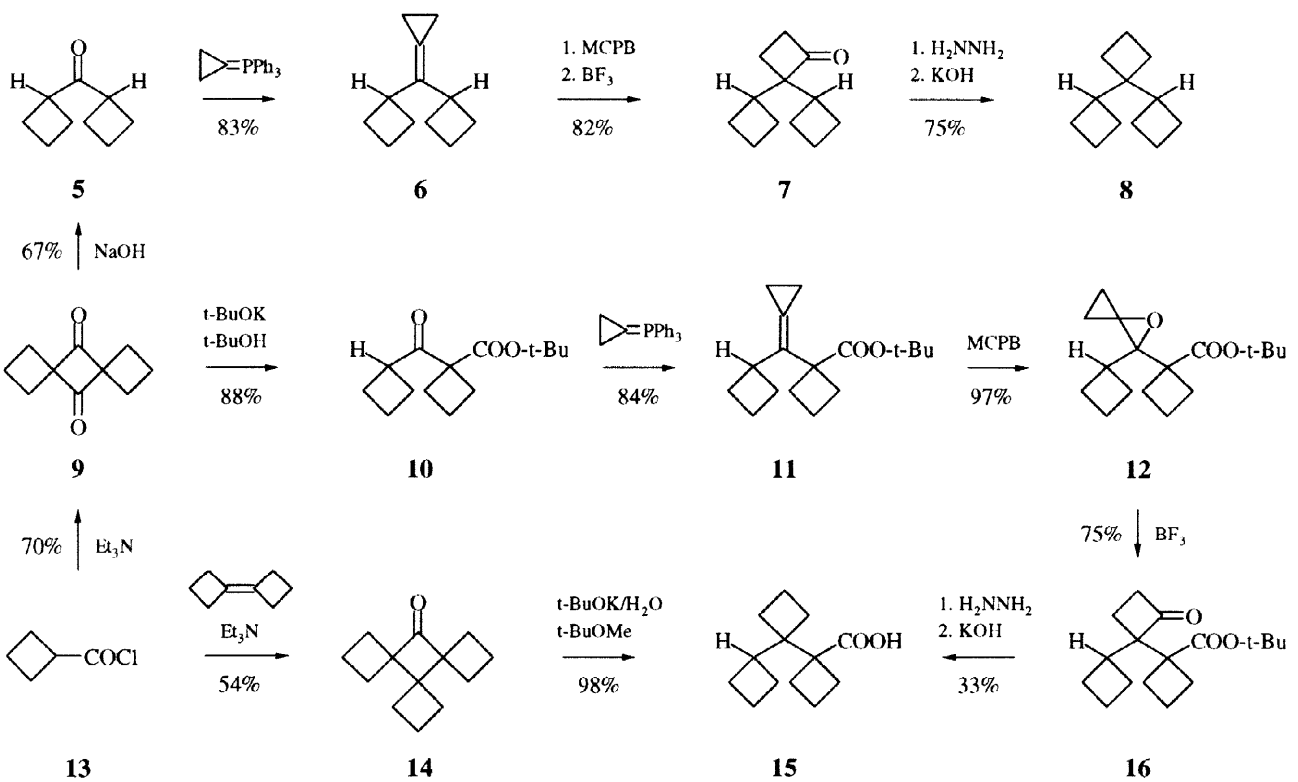
PII: S0040-4020(99)00098-8

From an analytical point of view, a synthesis and rearrangement of a quinquecyclobutane instead of a septicyclobutane was most desirable. In this case, a diastereoselective rearrangement to a helical tetraspirane could still occur, but the number of possible stereoisomers was restricted to four (two).[4] However, also a sexicyclobutane with a possible formation of up to eight (four)[4] stereoisomeric pentaspiranes seemed acceptable. From a synthetic point of view, the synthesis of a sexicyclobutane via a dimerization of a suitable functionalized tercyclobutane appeared most promising. We therefore explored this possibility first.

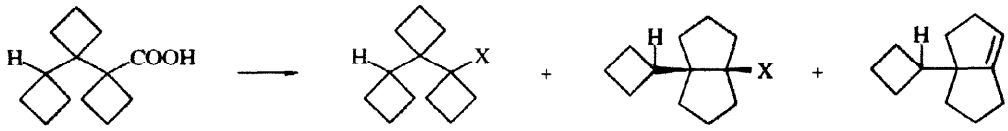
Synthesis of Tercyclobutanes

For the synthesis of tercyclobutanes, we first explored the annelation of a cyclobutane to the readily available dicyclobutyl ketone **5**[5] via a sequence of cyclopropylidenation, epoxidation, rearrangement and reduction (**5-6-7-8**). We then used this sequence to transform the β-ketoester **10**, itself obtained by ring opening of **9**,[5] to the tercyclobutanecarboxylic acid **15** (**10-11-12-16-15**), until we learned that **15** could more conveniently be prepared by ring opening of the trispirane **14**[1] using a modified procedure of Swan.[6a] To our disappointment, this and other methods[6b,c] for the cleavage of nonenolizable ketones failed when applied to higher homologs of **14**[1], and therefore a short and attractive access to higher homologs of **15** was barred.



An obvious possibility to transform the carboxylic acid **15** into a sexicyclobutane was a halodecarboxylation with subsequent coupling. However, none of the methods employed[7a-c] delivered a halogenated tercyclobu-

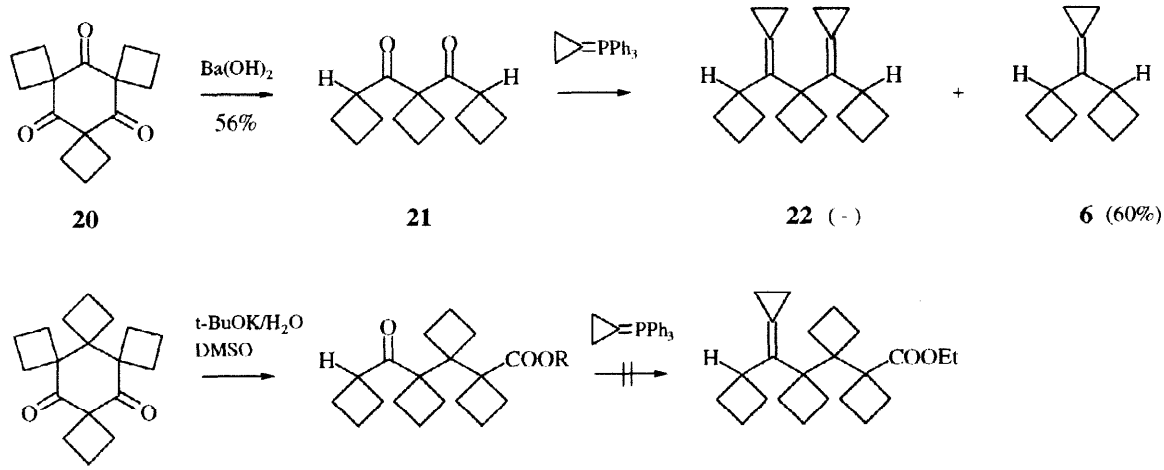
tane (**17a** or **17b**). Mixtures of a halogenated bicyclooctane (**18a** or **18b**) and a bicycloctene (**19**) were formed instead. This demonstrates that the intermediate tercyclobutyl radical rearranges with extreme ease.



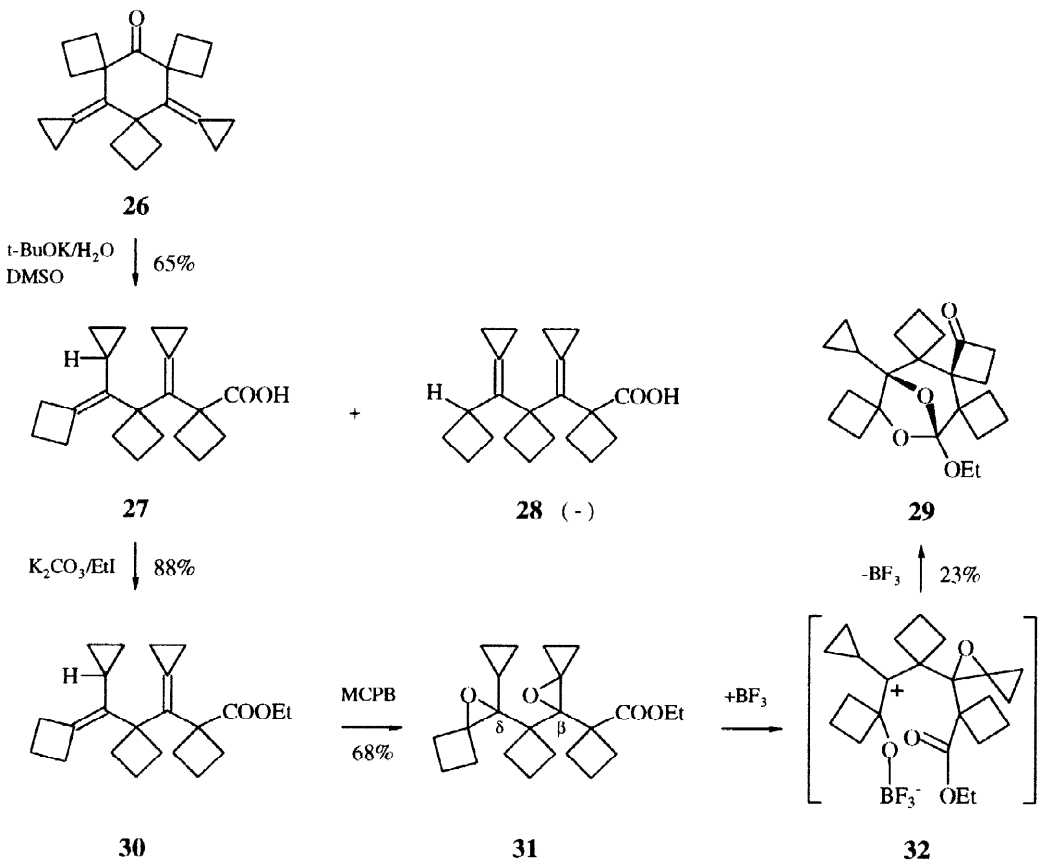
15	17		18		19
$NaOH/AgNO_3/Br_2/CCl_4$	a	X=Br (-)	a	X=Br (32%)	(15%)
Barton bromodecarboxylation	a	X=Br (-)	a	X=Br (17%)	(20%)
$Pb(OAc)_4/LiCl/THF$	b	X=Cl (-)	b	X=Cl (36%)	(12%)

Attempted Synthesis of Quinquecyclobutanes

After a synthesis of halogenated tercyclobutanes as potential precursors of sexicyclobutanes had been failed, we explored the suitability of the 1,3,5-trione **20**[5] and its derivatives **23**[8] and **26**[9] for a synthesis of quinquecyclobutanes. We first learned from an attempted dicyclopropylidenation of 1,3-dione **21**,[5] prepared by cleavage and decarboxylation of **20**, that even weakly basic ylides may provoke a fragmentation. Instead of the desired diolefin **22** we isolated the monoolefin **6** as cyclopropylidenation product of **5**, itself formed by fragmentation of **21**. To avoid this fragmentation, we proceeded to the 1,3-dione **23**. Ring opening using a method of Gassman[6b] delivered the δ-ketocarboxylic acid **24a**, which was esterified to **24b** and subsequently treated with cyclopropylidene triphenylphosphorane. However, this time no reaction occurred.

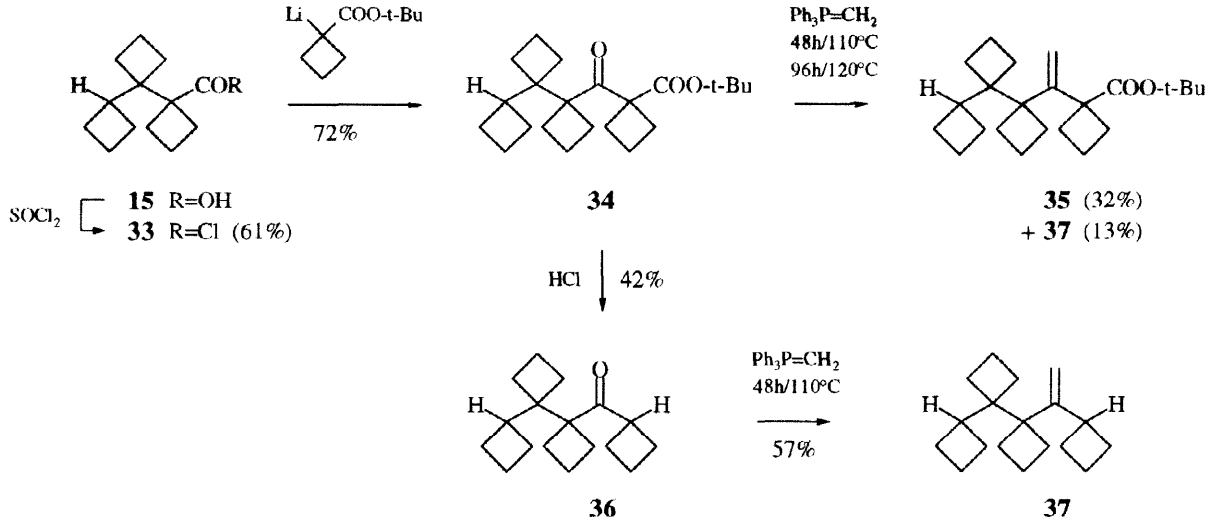


In a last attempt to generate a suitable precursor for the synthesis of a quinquecyclobutane from a spiroalkylated cyclohexane, we opened the monoketone **26** using the same procedure as for **23**. Once again, the result was disappointing. As could have been expected, the ring opening was accompanied by an allylic rearrangement and instead of the desired diolefin **28** we isolated its isomer **27**. Despite of this fact, we used this compound as a model to cheque the feasibility of a twofold ring enlargement. Towards this end, **27** was first esterified to **30**, then epoxidized to a single diepoxide **31** of unknown stereochemistry, and finally treated with boron trifluoride etherate to induce the ring enlargements. To our surprise, the only isolable product was the orthoformate **29**,[10] apparently formed by attack of the ester carbonyl to the ring-opened oxaspirohexane in δ-position (**31**-**32**-**29**). The oxaspiropentane in β-position reacted normally and delivered the expected cyclobutanone. This demonstrates, that the originally chosen olefins **25** and **28** would have been the wrong precursors of a quinquecyclobutane, as they would have been prone to a ring closure via an intermediate oxaspiropentane in δ-position too. We therefore returned to an investigation of the carboxylic acid **15**, but this time as a potential educt for a chain elongation.



For the chain elongation of the carboxylic acid **15**, we reacted the corresponding acid chloride **33** with 1-lithio-cyclobutanecarboxylic acid tert-butyl ester[11] to give the β-ketoester **34**.[14] Treatment with boiling hydrochloric acid yielded the corresponding ketone **36**. As could have been expected from the behaviour of **24b**, an

attempted cyclopropylidenation of **34** and **36** failed. We therefore subjected both compounds to a sterically less demanding methylenation to **35** and **37**, respectively, with the option of an annelation of the missing cyclobutane rings via a [2+1]cycloaddition and a subsequent ring enlargement. In both cases, high temperatures had to be employed,[15] and in the case of the β-ketoester **34**, concomitant fragmentation with formation of **37** was observed. In light of this fact, the δ-ketoester **24b** regains importance. In this case, a fragmentation is impossible and a methylenation could lead to another promising candidate for a synthesis of a functionalized quinquecyclobutane via a [2+1]cycloaddition strategy. Research following these lines is in progress.



EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer 298 spectrophotometer. ^1H and ^{13}C NMR spectra were measured on a Varian FT 80A, XL 200, VXR 200 or a Bruker AMX 300 spectrometer using $CDCl_3$ as solvent, and $CHCl_3$ (δ_H = 7.24 ppm) and $CDCl_3$ (δ_C = 77.00 ppm), respectively, as standards. ^{13}C spectra were studied by APT (attached proton test) to determine the number of protons attached to each carbon. Mass spectra were obtained with a Varian MAT 311A, 711 or Finnigan MAT 95 instrument operated at 70 eV. R_f-values are quoted for Macherey & Nagel Polygram SIL G/UV$_{254}$ plates. Colourless substances were detected by oxidation with 3.5% alcoholic 12-molybdophosphoric acid (Merck) and subsequent warming. Boiling and melting points are not corrected. Of the solvents used, ether ($LiAlH_4$), tetrahydrofuran ($LiAlH_4$) and benzene (Na) were dried as indicated and distilled.

(Cyclobutyl-cyclopropylidene-methyl)-cyclobutane (6): To a stirred suspension of potassium-tert-butoxide (12.4 g, 110 mmol) in dry benzene (340 ml) under nitrogen was added cyclopropyltriphenylphosphonium bromide[16] (42.2 g, 110 mmol) and the mixture heated to 60°C. After 2 h the temperature was lowered to 45°C, a solution of 6.08 g (44 mmol) **5** in dry benzene (20 ml) was added, and after further 2.5 h at 45°C the reaction was complete according to tlc [pentane/ether 9:1; R_f = 0.80 (**6**), 0.40 (**5**)]. The mixture was hydrolyzed with water (200 ml), the aqueous phase was extracted with pentane (50 ml), and the combined organic phases were washed with water (200 ml), dried ($MgSO_4$) and concentrated through a 20 cm Vigreux column (bath temperature 120°C). The residue was fractionated in vacuo yielding 5.95 g (83%) of pure **6** as colourless liquid, b.p. 55°C/0.4 torr. ^1H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): δ = 0.98 (s, 4H), 1.62-1.92 (m, 4H), 1.94-2.14 (m, 8H), 3.00 (quin, J = 9 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$, $CDCl_3$ int): δ = 0.22, 18.76, 28.03 (C_{sek}), 39.98 (C_{tert}),

111.69, 134.00 (C_{quart}); MS m/z 138 (35), 55 (100). Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C 88.87; H, 11.09.

[1,1′;1′,1′′]Tercyclobutan-2′-one (7): To a vigorously stirred mixture of **6** (5.00 g, 32.5 mmol), dichloromethane (420 ml) and saturated sodium bicarbonate (130 ml) was added within 15 min at 0°C a solution of m-chloroperbenzoic acid (8.41 g, 80% w/w, 39.0 mmol) in dichloromethane (40 ml) and the reaction progress monitored by tlc [pentane/ether 9:1; R_f = 0.80 (**6**), 0.55 (epoxide), 0.45 (**7**)]. After 2 h at 0°C, **6** had been completely consumed. The organic layer was separated, washed with 1 N sodium hydroxide (3 x 60 ml), dried ($MgSO_4$) and concentrated on a rotary evaporator (bath temperature 30°C/15 torr). The residue was dissolved in anhydrous ether (100 ml), boron trifluoride etherate (170 mg, 1.20 mmol) was added at 0°C under nitrogen, and after 20 min the rearrangement to **7** was complete. The mixture was washed with saturated sodium bicarbonate (3 x 30 ml), dried ($MgSO_4$) and concentrated on a rotary evaporator (bath temperature 20/15 torr), and the residue was fractionated in vacuo yielding 4.76 (82%) of pure **7** as colourless liquid, b.p. 65°C/0.4 torr. IR (film): 1750 cm^{-1} (C=O); ^1H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): δ = 1.60-2.05 (m, 14H), 2.35-2.53 (m, 2H), 2.70 (t, J = 9 Hz, 2H); ^{13}C NMR (20 MHz, $CDCl_3$, $CDCl_3$ int): δ = 15.73, 18.22, 24.05, 24.63 (C_{sek}), 37.99 (C_{tert}), 43.15 (C_{sek}), 74.19, 215.90 (C_{quart}); MS m/z 178 (4, M^+), 80 (100). Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C 81.07; H, 10.18.

[1,1′;1′,1′′]Tercyclobutane (8): A solution of hydrazine (2.60 g, 80% w/w, 65.0 mmol) and **7** (2.40 g, 13.5 mmol) in diethylene glycol (20 ml) was heated under nitrogen with stirring to 160°C until tlc [pentane/ether 9:1; R_f = 0.73 (**8**), 0.45 (**7**), 0.00 (hydrazone)] indicated that **7** had been consumed (20 h). Powdered potassium hydroxide (4.70 g, 84.0 mmol) was added and a mixture of hydrazine and water was distilled off until the internal temperature reached 190°C. After 3 h at this temperature, the evolution of nitrogen had been ceased. The mixture was diluted with water (30 ml), acidified with concentrated hydrochlorid acid and extracted with pentane (3 x 40 ml). The combined extracts were dried ($MgSO_4$), the solvent was distilled off, and the residue (2.05 g) was chromatographed on silica gel (0.05-0.20 mm) in pentane/ether (9:1; column 60 x 3.5 cm) yielding 1.66 g (75%) of pure **8** as colourless liquid. ^1H NMR (200 MHz, $CDCl_3$, $CHCl_3$ int): δ = 1.60-1.90 (m, 18H), 2.12-2.30 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$, $CDCl_3$ int): δ = 14.94, 17.76, 22.83, 23.62 (C_{sek}), 41.93 (C_{tert}), 44.82 (C_{quart}); MS m/z 136 (25, M^+-C_2H_4), 80 (100). Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C 87.77; H, 12.32.

1-Cyclobutanecarbonyl-cyclobutanecarboxylic acid tert-butyl ester (10): A solution of potassium-tert-butoxide (1.35 g, 12.0 mmol) and **9**[5] (4.11 g, 25.0 mmol) in tert-butanol (100 ml) was stirred at room temperature under nitrogen until tlc [pentane/ether 9:1; R_f = 0.34 (**10**), 0.18 (**9**)] indicated that **9** had been consumed (30 min). The mixture was diluted with water (50 ml) and extracted with ether (3 x 50 ml). The extracts were dried ($MgSO_4$), concentrated on a rotary evaporator (bath temperature 30°C/15 torr), and the residue was distilled in vacuo yielding 5.23 g (88%) of pure **10** as colourless liquid, b.p. 82-85°C/0.8 torr. ^1H NMR (200 MHz, $CDCl_3$, TMS int): δ = 1.41 (s, 9H), 1.70-2.45 (m, 12H), 3.33 (quin, J = 8 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$, TMS int): δ = 15.57, 18.29, 25.98, 27.41 (C_{sek}), 27.90 (C_{prim}), 42.07 (C_{tert}), 59.17, 81.46, 171.56, 207.23 (C_{quart}); MS m/z 182 (18, M^+-C_4H_8), 82 (100). Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.55; H, 9.30. Found: C 70.67; H, 9.37.

1-(Cyclobutyl-cyclopropyliden-methyl)-cyclobutanecarboxylic acid tert-butyl ester (11): To a stirred suspension of potassium-tert-butoxide (4.94 g, 44.0 mmol) in dry benzene (120 ml) under nitrogen was added cyclopropyltriphenylphosphonium bromide[16] (16.9 g, 44.0 mmol) and the mixture heated to 60°C. After 2 h the temperature was lowered to 45°C, a solution of **10** (3.50 g, 14.7 mmol) in dry benzene (8 ml) was added, and after further 56 h at 45°C the reaction was complete according to tlc [pentane/ether 97:3; R_f = 0.41 (**11**), 0.21 (**10**)]. The mixture was diluted with pentane (50 ml) and hydrolyzed with water (20 ml). The organic phase was decanted, the residue was extracted with ether (2 x 20 ml), the combined organic phases were concentrated through a 20 cm Vigreux column (bath temperature 120°C), and the residue was fractionated in vacuo yielding 3.25 g (84%) of pure **11** as colourless liquid, b.p. 86°C/0.6 torr. IR (film): 1720 cm^{-1} (C=O); ^1H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): δ = 1.03 (AA′-part of a AA′BB′-system, 2H), 1.10 (BB′-part of a AA′BB′-system, 2H), 1.40 (s, 9H), 1.60-2.20 (m, 8H), 2.26-2.44 (m, 4H), 3.00 (quin, J = 9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, $CDCl_3$ int): δ = 0.50, 0.90, 16.70, 18.84 (C_{sek}), 27.99 (C_{prim}), 29.04, 30.84 (C_{sek}), 38.75 (C_{tert}), 55.00, 79.68, 115.77, 132.45, 175.70 (C_{quart}); MS m/z 206 (12, M^+-C_4H_8), 57 (100). Anal. Calcd for $C_{17}H_{26}O_2$: C, 77.82; H, 9.99. Found: C 77.85; H, 9.84.

1-(2-Cyclobutyl-oxiranyl)-cyclobutanecarboxylic acid tert-butyl ester (12): To a vigorously stirred mixture of **11** (2.70 g, 10.3 mmol), dichloromethane (100 ml) and saturated sodium bicarbonate (30 ml) was added within 10 min a solution of m-chloroperbenzoic acid (2.74 g, 80% w/w, 12.7 mmol) in dichloromethane (15 ml) and the reaction progress monitored by tlc [pentane/ether 9:1; R_f = 0.60 (**11**), 0.46 (**12**)]. After 1.5 h, **11** had been consumed. The organic layer was separated, washed with 1 N sodium hydroxide (3 x 30 ml), dried ($MgSO_4$) and concentrated on a rotary evaporator (bath temperature 30°C/15 torr) yielding 2.77 g (97%) of crude **12**. Chromatography of 0.50 g on silica gel (0.05-0.20 mm) in pentane/ether (9:1; column 26 x 1.5 cm) yielded an analytically pure sample as colourless liquid. IR (film): 1720 cm^{-1} (C=O); ^1H NMR (200 MHz, $CDCl_3$, $CHCl_3$ int): δ = 0.65-1.00 (m, 4H), 1.40 (s, 9H), 1.55-2.50 (m, 12H), 2.63 (quin, J = 8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, $CDCl_3$ int): δ = 0.88, 1.45, 16.67, 18.86, 24.28, 25.66 (C_{sek}), 27.50 (C_{prim}), 27.95 (C_{sek}), 36.67 (C_{tert}), 53.10, 59.28, 67.26, 80.20, 174.30 (C_{quart}); MS m/z 166 (14, M^+-$2C_4H_8$), 57 (100). Anal. Calcd for $C_{17}H_{26}O_3$: C, 73.34; H, 9.41. Found: C 73.58; H, 9.29.

2′-Oxo-[1,1′;1′,1′′]tercyclobutane-1-carboxylic acid tert-butyl ester (16): To a solution of crude **12** (2.28 g, 8.2 mmol) in anhydrous ether (80 ml) was added at 0°C under nitrogen with stirring boron trifluoride etherate (1.16 g, 8.2 mmol) and the reaction progress monitored by tlc [pentane/ether 9:1; R_f = 0.46 (**12**), 0.36 (**16**)]. After 1.5 h, more boron trifluoride etherate (0.58 g, 4.1 mmol) was added, and after a further hour the reaction was complete. The mixture was diluted with ether (30 ml), washed with 10% potassium bicarbonate (4 x 30 ml), dried ($MgSO_4$) and concentrated on a rotary evaporator (bath temperature 40°C/15 torr). The residue (2.15 g) was chromatographed on silica gel (0.05-0.20 mm) in pentane/ether (9:1; column 70 x 3.5 cm) yielding 1.70 g (75%) of pure **16** as colourless liquid. IR (film): 1760, 1720 cm^{-1} (C=O); ^1H NMR (200 MHz, $CDCl_3$, $CHCl_3$ int): δ = 1.45 (s, 9H), 1.60-2.65 (m, 15H), 2.72-2.85 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$, $CDCl_3$ int): δ = 15.97, 17.52, 18.80, 25.31, 25.75, 26.03 (C_{sek}), 28.04 (C_{prim}), 29.99 (C_{sek}), 37.25 (C_{tert}), 44.69 (C_{sek}), 51.82, 74.21, 80.51, 174.67, 214.25 (C_{quart}); MS m/z 166 (38, M^+-$2C_4H_8$), 57 (100). Anal. Calcd for $C_{17}H_{26}O_3$: C, 73.34; H, 9.41. Found: C 73.28; H, 9.27.

[1,1′;1′,1′′]Tercyclobutane-1-carboxylic acid (15): A. From 16: A mixture of hydrazine (130 mg, 80% w/w, 3.24 mmol), powdered potassium hydroxide (303 mg, 5.40 mmol) and **16** (300 mg, 1.08 mmol) in diethylene glycol (1.5 ml) was heated under nitrogen with stirring to 160°C until tlc [pentane/ether 7:3; R_f = 0.56 (**16**), 0.33 (**15**), 0.21, 0.11], indicated that **16** had been consumed (3 h). After additional 2 h at 190°C the mixture was diluted with water (15 ml), acidified with concentrated hydrochlorid acid to pH 2 and extracted with ether (3 x 20 ml). The extracts were dried ($MgSO_4$), evaporated to dryness (bath temperature 30/15 torr), and the residue was chromatographed on silica gel (0.05-0.20 mm) in pentane/ether (7:3; column 26 x 1.5 cm) yielding 75 mg (33%) of pure **15** as colourless solid, m.p. 65°C. IR (KBr): 3600-2500 (OH_{ass}), 1700 cm^{-1} (C=O); ^1H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): δ = 1.60-2.00 (m, 12H), 2.10-2.40 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$, $CDCl_3$ int): δ = 15.11, 15.72, 18.17, 23.72, 24.63, 26.92 (C_{sek}), 41.02 (C_{tert}), 46.85, 53.42, 184.26 (C_{quart}); MS m/z 208 (8, M^+), 79 (100). Calculated for $C_{13}H_{20}O_2$: 208.1463. Found: 208.1463 (MS).

B. From 14: To a suspension of potassium-tert-butoxide (44.9 g, 0.400 mol) in tert-butyl-methylether (320 ml) was added at room temperature under nitrogen with stirring water (2.40 g, 0.133 mol) and **14**[1] (7.61 g, 0.040 mol), causing a slightly exothermic effect. After 1 h, the mixture was hydrolyzed with 2 N hydrochloric acid (280 ml), and the organic phase washed with water (3 x 100 ml) and dried ($CaCl_2$). Evaporation of the solvent (bath temperature 45°C/15 torr) yielded 8.16 g (98%) of **15** as nearly colourless solid, m.p. 65°C. The ^1H and ^{13}C NMR data were identical with those of an authentic sample.

3a-Bromo-6a-cyclobutyl-octahydro-pentalene (18a) and 3a-cyclobutyl-1,2,3,3a,4,5-hexahydro-pentalene (19): A. From 15 by Hunsdiecker degradation: At 60°C, a solution of **15** (625 mg, 3.00 mmol) in water (10 ml) was titrated with 2 N sodium hydroxide against phenolphthalein. A solution of silver nitrate (510 mg, 3.00 mmol) in water (2 ml) was added, causing a white precipitate. After 8 h at room temperature the precipitate was filtered off, washed with water (3 x 5 ml), methanol (3 x 5 ml) and ether (3 x 5 ml) and dried (50°C/12 torr, 12 h) yielding 800 mg (85%) silver salt of **15**. 630 mg (2.00 mmol) of this salt were added portionwise at -35°C under nitrogen with stirring to a solution of bromine (320 mg, 2.00 mmol) in tetrachloromethane (2 ml). After the addition was complete, the temperature was raised to -25°C until the gas evolution had been ceased (30 min). The mixture was filtered, the residue washed with ether (20 ml), and the combined filtrates were washed with saturated sodium bicarbonate (2 x 5 ml) and dried ($MgSO_4$). The solvents were distilled off (bath temperature 50°C/15 torr), and the residual slightly yellow oil (470 mg) was chromatographed on silica gel (0.05-0.20 mm) in pentane [column 30 x 3 cm; R_f = 0.80 (**19**), 0.62 (**18a**)] yielding 50 mg (15%) of **19**

and 152 mg (32%) of **18a** as colourless liquids. **18a**: ^{1}H NMR (200 MHz, $CDCl_3$, $CHCl_3$ int): δ = 1.25-2.35 (m, 18H), 2.62-2.82 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, $CDCl_3$ int): δ = 17.60, 23.05, 25.57, 35.47 (C_{sek}), 45.66 (C_{tert}), 45.73 (C_{sek}), 58.48, 83.00 (C_{quart}); MS m/z 242 (2, M^+), 163 (100). **Calculated for $C_{12}H_{19}Br$**: 242.0670. Found: 242.0670 (MS). **19:** ^{1}H NMR (200 MHz, $CDCl_3$, TMS int): δ = 1.10-1.30 (m, 2H), 1.45-2.20 (m, 13H), 2.25-2.70 (m, 3H), 5.21 (m_c, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, $CDCl_3$ int): δ = 17.93, 23.93, 24.96, 25.03, 26.25, 34.80, 35.77, 36.72 (C_{sek}), 42.42 (C_{tert}), 61.28 (C_{quart}), 117.98 (C_{tert}), 155.47 (C_{quart}); MS m/z 162 (8, M^+), 91 (100). Calculated for $C_{12}H_{18}$: 162.1408. Found: 162.1408 (MS).

B. From 15 by Barton bromodecarboxylation: To a solution of **15** (417 mg, 2.00 mmol) in dry benzene (10 ml) were added under nitrogen with stirring oxalyl chloride (1 ml) and a drop of N,N-dimethylformamide. After 3 h at room temperature, the solvent and excess oxalyl chlorid were distilled off (bath temperature 60°C/15 torr), and the residual crude acid chloride was dissolved in 2-bromo-2-chloro-1,1,1-trifluoroethane (7 ml). 2-Mercaptopyridine N-oxide sodium salt (298 mg, 2.00 mmol) and a catalytic amount of 4-dimethylaminopyridine were added, and the mixture was irradiated with a 500 W tungsten lamp while heated to reflux. After 1 h, tlc [pentane/ether 2:1; R_f = 0.95 (**18a**, **19**)] indicated that the reaction was complete. The mixture was diluted with pentane, washed with saturated sodium bicarbonate (2 x 5 ml) and saturated sodium chloride (1 x 5 ml) and dried ($MgSO_4$). The solution was concentrated (bath temperature 50°C/15 torr) and the residual brown oil (400 mg) chromatographed as described above to yield 82 mg (17%) of **18a** and 65 mg (20%) of **19**. The ^{1}H and ^{13}C NMR data were identical with those of authentic samples.

3a-Chloro-6a-cyclobutyl-octahydro-pentalene (18b) and 3a-cyclobutyl-1,2,3,3a,4,5-hexahydro-pentalene (19): A stirred solution of **15** (417 mg, 2.00 mmol) and lead tetraacetate (913 mg, 95% w/w, 2.00 mmol) in anhydrous tetrahydrofuran (8 ml) was saturated with nitrogen (30 min) until lithium chloride (10 mg + 75 mg, 2.00 mmol) was added in two portions. After the first portion the mixture was cooled to 0°C, and after the second portion this temperature was maintained. Tlc [pentane/ether 9:1; R_f = 0.78 (**18b**, **19**), 0.15 (**15**)] indicated that after 40 min the reaction was nearly complete. The mixture was warmed up and after 1 h diluted with pentane (15 ml), washed with saturated sodium bicarbonate (1 x 10 ml), water (2 x 10 ml) and dried ($MgSO_4$). The solvent was distilled off (bath temperature 50°C/15 torr) and the residual yellow oil (305 mg) chromatographed on silica gel (0.05-0.20 mm) in pentane [column 30 x 3 cm; R_f = 0.80 (**19**), 0.64 (**18b**)] yielding 141 mg (36%) of **18b** and 40 mg (12%) of **19** as colourless liquids. The ^{1}H and ^{13}C NMR data of **19** were identical with those of an authentic sample. **18b**: ^{1}H NMR (200 MHz, $CDCl_3$, $CHCl_3$ int): δ = 1.25-2.15 (m, 18H), 2.58-2.78 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, $CDCl_3$ int): δ = 17.87, 22.84, 25.43, 36.04 (C_{sek}), 43.47 (C_{tert}), 44.54 (C_{sek}), 58.01, 86.20 (C_{quart}); MS m/z 79 (100). Anal. Calcd for $C_{12}H_{19}Cl$: C, 72.52; H, 9.64. Found: C 72.73; H, 9.60.

1´´-Cyclobutanecarbonyl-[1,1´;1´,1´´]tercyclobutane-1-carboxylic acid (24a): To a solution of potassium-tert-butoxide (22.2 g, 198 mmol) in dimethyl sulphoxide (40 ml) and water (1.08 g, 60 mmol) was added under nitrogen with stirring within 10 min at 40°C a solution of **23**[8] (9.00 g, 60% w/w, 19.8 mmol) in dimethyl sulphoxide (40 ml). After 20 min, tlc [pentane/ether 7:3; R_f = 0.50 (**23**), 0.30, 0.26 (**24a**)] indicated that the reaction was complete. The mixture was diluted with water (120 ml), acidified with 20% hydrochloric acid to pH 2 and extracted with ether (1 x 100 ml, 3 x 40 ml). The combined extracts were dried ($MgSO_4$) and concentrated on a rotary evaporator (bath temperature 30°C/15 torr), and the residual oil was chromatographed on silica gel (0.05-0.20 mm) in pentane/ether (7:3; column 60 x 7 cm) yielding 5.63 g (98%) of crude **24a** (purity 75%). A second chromatography yielded analytically pure **24a** as colourless solid, m.p. 125°C. IR (CCl_4): 3500-2800 (OH_{ass}), 1740, 1685 cm^{-1} (C=O); ^{1}H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): δ = 1.53-1.73 (m, 3H), 1.73-2.15 (m, 9H), 2.15-2.45 (m, 12H), 3.69 (quin, J = 8 Hz, 1H), 11.0 (br s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$, $CDCl_3$ int): δ = 15.49, 15.62, 15.74, 17.72, 25.05, 25.99, 28.01, 28.85 (C_{sek}), 44.25 (C_{tert}), 51.95, 52.68, 58.68, 182.37, 219.45 (C_{quart}); MS m/z 290 (1, M^+), 55 (100). Anal. Calcd for $C_{18}H_{26}O_3$: C, 74.45; H, 9.02. Found: C 74.62; H, 9.08.

1´´-Cyclobutanecarbonyl-[1,1´;1´,1´´]tercyclobutane-1-carboxylic acid ethyl ester (24b): To a stirred solution of crude **24a** (5.13 g, 75% w/w, 13.3 mmol) in acetone (100 ml) was added potassium carbonate (3.46 g, 25.0 mmol) and ethyl iodide (31.2 g, 200 mmol) and the mixture heated to reflux. After 2 h, tlc [pentane/ether 7:3; R_f = 0.53 (**24b**), 0.27, 0.23 (**24a**)] indicated that the reaction was complete. Most of the solvent and the excess ethyl iodide were distilled off (bath temperature 85°) until 10% potassium carbonate (50 ml) was added. The mixture was extracted with ether (2 x 50 ml), and the extracts were washed with water (2 x 40 ml) and dried ($MgSO_4$). The solvent was distilled off (bath temperature 50°C/15 torr) and the residue (5.7 g)

was chromatographed on silica gel (0.05-0.20 mm) in pentane/ether [9:1; column 40 x 6 cm; R_f = 0.41, 0.33 (**24b**)] yielding 3.52 g (91%) of pure **24b** as colourless oil. IR (film): 1710, 1670 cm^{-1} (C=O); ^1H NMR (200 MHz, $CDCl_3$, $CHCl_3$ int): δ = 1.27 (t, J = 7 Hz, 3H), 1.45-2.45 (m, 24H), 3.84 (quin, J = 8 Hz, 1H), 4.07 (q, J = 7 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$, $CDCl_3$ int): δ = 13.98 (C_{prim}), 15.47, 15.50, 15.93, 17.67, 24.98, 25.90, 27.90, 28.31 (C_{sek}), 43.92 (C_{tert}), 51.71, 52.56, 58.40 (C_{quart}), 60.32 (C_{sek}), 177.37, 217.82 (C_{quart}); MS m/z 318 (5, M^+), 55 (100). Anal. Calcd for $C_{20}H_{30}O_3$: C, 75.43; H, 9.50. Found: C 75.30; H, 9.43.

1-{[1-(Cyclobutylidene-cyclopropyl-methyl)-cyclobutyl]-cyclopropylidene-methyl}-cyclobutane-carboxylic acid (27): To a solution of potassium-tert-butoxide (4.49 g, 40.0 mmol) in dimethyl sulphoxide (15 ml) and water (216 mg, 12.0 mmol) was added **26**[9] (1.00 g, 3.40 mmol) and the mixture heated under nitrogen with stirring to 70°C. After 18 h, tlc [pentane/ether 7:3; R_f = 0.67 (**26**), 0.44 (**27**)] indicated that the reaction was complete. The mixture was diluted with water (50 ml), acidified with 10% hydrochloric acid to pH 2 and extracted with ether (3 x 50 ml). The combined extracts were dried ($MgSO_4$), concentrated on a rotary evaporator (bath temperature 30°C/15 torr), and the residual oil was chromatographed on silica gel (0.05-0.20 mm) in pentane/ether (7:3; column 62 x 3.5 cm) yielding 690 mg (65%) pure **27** als colourless solid, m.p. 110°C. IR (CCl_4): 3200-2700 (OH_{ass}), 1685 cm^{-1} (C=O); ^1H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): δ = 0.42-0.47 (m, 4H), 1.02-1.12 (m, 3H), 1.18-1.28 (m, 2H), 1.60-1.85 (m, 5H), 1.98 (m_c, 1H), 2.20-2.32 (m, 2H), 2.38-2.75 (m, 10H), 11.0 (br s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$, $CDCl_3$ int): δ = 1.43, 3.82, 4.85 (C_{sek}), 12.86 (C_{tert}), 17.22, 17.57, 18.14, 32.35, 32.43, 32.68, 33.82 (C_{sek}), 55.05, 55.14, 119.64, 132.11, 133.83, 137.53, 183.74 (C_{quart}); MS m/z 312 (2, M^+), 185 (100). Anal. Calcd for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03. Found: C 80.75; H, 8.96.

1-{[1-(Cyclobutylidene-cyclopropyl-methyl)-cyclobutyl]-cyclopropylidene-methyl}-cyclobutane-carboxylic acid ethyl ester (30): To a solution of **27** (606 mg, 1.94 mmol) in acetone (20 ml) was added potassium carbonate (450 mg, 3.26 mmol) and ethyl iodide (3.90 g, 25 mmol) and the mixture heated to reflux. After 2 h, tlc [pentane/ether 9:1; R_f = 0.55 (**30**), 0.32, 0.18 (**27**)] indicated that the reaction was complete. Most of the solvent and the excess ethyl iodide were distilled off (bath temperature 85°C) until 10% potassium carbonate (6 ml) was added. The mixture was extracted with ether (2 x 10 ml), and the extracts were washed with water (2 x 6 ml) and dried ($MgSO_4$). The solvent was evaporated (bath temperature 30°C/15 torr) and the residue (685 mg) chromatographed on silica gel (0.05-0.20 mm) in pentane/ether (9:1; column 30 x 2.5 cm) yielding 580 mg (88%) of pure **30** as colourless oil. IR (film): 1710 cm^{-1} (C=O); ^1H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): δ = 0.37-0.43 (m, 4H), 0.98-1.08 (m, 3H), 1.15-1.25 (m, 2H), 1.20 (t, J = 7 Hz, 3H), 1.58-2.75 (m, 18H), 4.09 (q, J = 7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, $CDCl_3$ int): δ = 1.56, 3.89, 4.82 (C_{sek}), 12.76 (C_{tert}), 14.14 (C_{prim}), 17.36, 17.66, 18.21, 32.54, 32.90, 33.90 (C_{sek}), 55.20, 55.60 (C_{quart}), 60.34 (C_{sek}), 119.45, 132.31, 134.09, 136.52, 176.89 (C_{quart}); MS m/z 340 (9, M^+), 185 (100). Calculated for $C_{23}H_{32}O_2$: 340.2402. Found: 340.2402 (MS).

1-{2-[1-(2-Cyclopropyl-1-oxa-spiro[2.3]hex-2-yl)-cyclobutyl]-1-oxa-spiro[2.2]pent-2-yl}-cyclobutanecarboxylic acid ethyl ester (31): To a vigorously stirred mixture of **30** (650 mg, 1.91 mmol), dichloromethane (30 ml) and saturated sodium bicarbonate (8 ml) was added within 10 min a solution of m-chloroperbenzoic acid (1.03 g, 80% w/w, 4.78 mmol) in dichloromethane (8 ml). After 2 h, tlc [pentane/ether 9:1; R_f = 0.52 (**30**), 0.35, 0.30 (**31**)] indicated that the reaction was complete. The organic layer was separated, washed with 1 N sodium hydroxide (3 x 20 ml), dried ($MgSO_4$) and concentrated on a rotary evaporator (bath temperature 30°C/15 torr). The residual crude diepoxide (955 mg) was chromatographed on silica gel (0.05-0.20 mm) in pentane/ether (7:3; column 34 x 4 cm) yielding 485 mg (68%) of pure **31** as colourless solid, m.p. 84-86°C. IR (CCl_4): 1720 cm^{-1} (C=O); ^1H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): δ = -0.12-0.04 (m, 1H), 0.09-0.19 (m, 1H), 0.24-0.34 (m, 2H), 0.95-1.15 (m, 3H), 1.21 (t, J = 7 Hz, 3H), 1.26-1.38 (m, 2H), 1.50-1.90 (m, 8H), 2.00-2.15 (m, 2H), 2.20-2.90 (m, 8H), 3.97-4.10 (m, 1H), 4.15-4.28 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, $CDCl_3$ int): δ = -0.57, 1.68, 2.41, 4.05 (C_{sek}), 9.92 (C_{prim}), 13.91 (C_{tert}), 13.98, 16.20, 16.42, 26.25, 26.90, 27.25, 30.95, 31.72, 32.03 (C_{sek}), 49.84, 53.99 (C_{quart}), 60.74 (C_{sek}), 61.27, 66.80, 68.40, 71.21, 175.36 (C_{quart}); MS m/z 175 (100). Anal. Calcd for $C_{23}H_{32}O_4$: C, 74.16; H, 8.66. Found: C 74.28; H, 8.60.

Rearrangement of 31 to orthoester 29: The crude diepoxide **31** obtained from epoxidation of **30** (580 mg, 1.70 mmol) was dissolved in ether (20 ml), cooled to 0°C and treated with boron trifluoride etherate (284 mg, 2.00 mmol). After 20 min, tlc [pentane/ether 9:1; R_f = 0.49, 0.38, 0.31 (**31**), 0.24 (**29**), 0.16, 0.10] indicated that the reaction was complete. The solution was washed with saturated sodium bicarbonate (3 x 10 ml), dried ($MgSO_4$) and concentrated on a rotary evaporator (bath temperature 30°C/15 torr), and the residue (690 mg) was chromatographed on silica gel in pentane/ether (9:1; column 50 x 3.5 cm) yielding 140 mg (23%) of pure **29**

as colourless solid, m.p. 143°C. IR (CCl_4): 1760 cm^{-1} (C=O); ^1H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): δ = 0.57-0.67 (m, 1H), 0.70-0.83 (m, 2H), 0.86-0.96 (m, 1H), 1.19 (t, J = 7 Hz, 3H), 1.29-1.39 (m, 1H), 1.45-2.60 (m, 18H), 2.78-2.90 (m, 3H), 3.04 (m_c, 1H), 3.58 (m_c, 2H); ^{13}C NMR (50 MHz, $CDCl_3$, $CDCl_3$ int): δ = 1.57, 4.12, 10.76 (C_{sek}), 13.02 (C_{prim}), 15.09 (C_{sek}), 15.38 (C_{tert}), 15.62, 20.49, 25.15, 25.56 (coincidence of two lines), 27.67, 32.48, 35.74, 45.28 (C_{sek}), 48.77, 50.51 (C_{quart}), 56.49 (C_{sek}), 76.15, 83.65, 88.61, 121.54, 215.79 (C_{quart}); MS m/z 372 (3, M^+), 123 (100). Anal. Calcd for $C_{23}H_{32}O_4$: C, 74.16; H, 8.66. Found: C 74.06; H, 8.51.

[1,1′;1′,1′′]Tercyclobutyryl chloride (33): To a solution of **15** (39.5 g, 0.190 mol) in thionyl chloride (29.7 g, 0.250 mol) was added under nitrogen with stirring a drop of N,N-dimethylformamide and the mixture heated to reflux until the gas evolution had been ceased (2.5 h). Fractional distillation yielded 26.1 g (61%) of pure **33** as colourless liquid, b.p. 110°C/0.5 torr. IR (film): 1785 cm^{-1} (C=O); ^1H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): δ = 1.55-2.05 (m, 12H), 2.15-2.45 (m, 7H); ^{13}C NMR (50 MHz, $CDCl_3$, $CDCl_3$ int): δ = 15.08, 15.24, 18.23, 24.19, 24.64, 27.70 (C_{sek}), 41.36 (C_{tert}), 46.25, 63.47, 178.13 (C_{quart}); MS m/z 91 (100). Anal. Calcd for $C_{13}H_{19}ClO$: C, 68.86; H, 8.45. Found: C 68.77; H, 8.57.

1-([1,1′;1′,1′′]Tercyclobut-1-carbonyl)-cyclobutanecarboxylic acid tert-butyl ester (34): To a 1.6 M solution of n-butyllithium in hexane (45 ml, 72 mmol) was added at 0°C under nitrogen with stirring a solution of diisopropylamine (7.29 g, 72 mmol) in anhydrous tetrahydrofuran (6 ml). After 1 h at 0°C the solution was cooled to -78°C until cyclobutanecarboxylic acid tert-butylester[11] (11.2 g, 72 mmol) was added. After 30 min at -78°C the mixture was warmed up to room temperature, a solution of **33** (18.1 g, 80 mmol) in pentane (30 ml) was added, and after 1 h at room temperature the mixture was hydrolyzed with saturated ammonium chloride (50 ml). The organic phase was dried ($MgSO_4$) and concentrated on a rotary evaporator (bath temperature 30°C/15 torr), and the residue (26.5 g yellow oil) was chromatographed on silica gel (0.05-0.20 mm) in pentane/ether [8:2; column 25 x 10 cm; R_f = 0.75 (**34**), 0.31 (**15**)] yielding 17.9 g (72%) of **34** (purity 95%) and 4.0 g (27%) of **15** as colourless solids. The ^1H NMR data of **15** were in accord with those of an authentic sample. An analytically pure sample of **34** was obtained by a second chromatography in pentane/ether (95:5; R_f = 0.35). Colourless solid, m.p. 70-77°C. IR (KBr): 1715, 1680 cm^{-1} (C=O); ^1H NMR (300 MHz, $CDCl_3$, TMS int): δ = 1.50 (s, 9H), 1.65-1.90 (m, 8H), 1.90-2.10 (m, 6H), 2.10-2.58 (m, 11H); ^{13}C NMR (50 MHz, $CDCl_3$, $CDCl_3$ int): δ = 15.30, 15.48, 16.02, 18.13, 24.26, 25.22, 27.01, 27.83 (C_{prim}), 28.21 (C_{sek}), 41.23 (C_{tert}), 49.02, 57.10, 60.64, 81.65, 171.67, 211.18 (C_{quart}).; MS m/z 346 (M^+, 1), 57 (100). Anal. Calcd for $C_{22}H_{34}O_3$: C, 76.26; H, 9.89. Found: C 76.25; H, 9.97.

1-(1-[1,1′;1′,1′′]Tercyclobut-1-yl-vinyl)-cyclobutanecarboxylic acid tert-butyl ester (35): To a stirred suspension of potassium-tert-butoxide (1.07 g, 9.5 mmol) in dry benzene (10 ml) under nitrogen was added methyltriphenylphosphonium bromide (3.57 g, 10.0 mmol). After 2 h at reflux most of the benzene was distilled off under nitrogen until the temperature of the remaining slurry reached 110°C. **34** (1.73 g, 5.00 mmol) was added and after 48 h at 110°C and 96 h at 120°C tlc [pentane/ether 95:5; R_f = 0.80 (**37**), 0.51 (**35**), 0.29 (**34**)] indicated that most of the starting material had been consumed. The mixture was diluted with benzene (15 ml) and hydrolyzed with water (1 ml), the organic phase was decanted, the residue was extracted with benzene (5 ml), and the combined organic phases were washed with water (5 ml) and dried ($MgSO_4$). The solution was concentrated (bath temperature 40°C/15 torr), and the residue (3.1 g) was chromatographed on silica gel (0.05-0.20 mm) in pentane/ether [9:1; column 16 x 3 cm; R_f = 0.89 (**37**), 0.76 (**35**), 0.59 (**34**)] yielding 1.14 g of a mixture of **37**, **35** and **34** as yellow oil. A second chromatography on silica gel (0.05-0.20 mm) in pentane ether (95:5; colum 95 x 3 cm) yielded 160 mg (13%) of **37** and 550 mg (32%) of **35** as colourless liquids, and 160 mg (9%) of **34** as colourless solid. The ^1H NMR data of **37** and **34** were identical with those of authentic samples. **35**: IR (film): 1715 (C=O), 1620 cm^{-1} (C=C); ^1H NMR (200 MHz, $CDCl_3$, $CHCl_3$ int): δ = 1.50 (s, 9H), 1.60-2.60 (m, 25H), 4.90 (s, 1H), 4.98 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, $CDCl_3$ int): δ = 15.36, 15.64, 16.28, 18.42, 24.93, 25.88 (C_{sek}), 27.77 (C_{prim}), 30.24, 32.55 (C_{sek}), 41.49 (C_{tert}), 49.16, 52.02, 55.98, 79.95 (C_{quart}), 112.89 (C_{sek}), 157.66, 175.83 (C_{quart}); MS m/z 344 (M^+, 1), 180 (100). Anal. Calcd for $C_{23}H_{36}O_2$: C, 80.18; H, 10.53. Found: C 80.42; H, 10.28.

Cyclobutyl-[1,1′;1′,1′′]tercyclobut-1-yl-methanone (36): A mixture of **34** (10.4 g, 30 mmol) and 18% hydrochloric acid (60 ml) was heated to reflux. After 8 h, tlc [pentane/ether 95:5, R_f = 0.83, 0.56 (**36**), 0.43 (**34**)] indicated the formation of an undesired unpolar component. The mixture was cooled and extracted with ether (1 x 40 ml, 1 x 20 ml), the extracts were neutralized over solid sodium carbonate, the solvent was evaporated (bath temperature 30°C/15 torr), and the residue (8.1 g yellow oil) was chromatographed on silica gel (0.05-0.20 mm) in pentane/ether (95:5; column 95 x 5 cm) yielding 3.10 g (42%) of **36** as colourless oil and

2.90 g (28%) of unchanged **34** as colourless solid. The ^{1}H NMR data of **34** were identical with those of an authentic sample. **36**: IR (film): 1720, 1690 cm^{-1} (C=O); ^{1}H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): δ = 1.50-2.35 (m, 25H), 3.28 (quin, J = 9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, $CDCl_3$ int): δ = 15.38, 15.53, 18.23 (coincidence of two lines), 24.41, 24.78, 25.55, 26.24 (C_{sek}), 41.74 42.43 (C_{tert}), 47.02, 59.70, 215.50 (C_{quart}); MS m/z 246 (M^+, 8), 55 (100). Anal. Calcd for $C_{17}H_{26}O$: C, 82.87; H, 10.64. Found: C 83.08; H, 10.46.

1-(1-Cyclobutyl-vinyl)-[1,1′;1′,1′′]tercyclobutane (37): To a stirred suspension of potassium-tert-butoxide (3.25 g, 29.0 mmol) in dry benzene (100 ml) under nitrogen was added methyltriphenylphosphonium bromide (10.4 g, 29.0 mmol) and the mixture heated to reflux. After 2 h most of the benzene was distilled off under nitrogen until the temperature of the remaining slurry reached 110°C. **36** (986 mg, 4.00 mmol) was added and the temperature maintained until tlc [pentane/ether 95:5; R_f = 0.80 (**37**), 0.55 (**36**)] indicated that the reaction was complete (48 h). The mixture was diluted with pentane (50 ml) and hydrolyzed with water (2 ml). The organic phase was decanted, the residue was extracted with pentane (3 x 50 ml), and the combined organic phases were washed with water (3 x 50 ml) and dried ($MgSO_4$). The solvent was evaporated (bath temperature 30°C/15 torr) and the residue chromatographed on silica gel (0.05-0.20 mm) in pentane/ether (95:5; column 48 x 3.5 cm) yielding 555 mg (57%) of pure **37** als colourless oil. IR (film): 1625 cm^{-1} (C=C); ^{1}H NMR (200 MHz, $CDCl_3$, $CHCl_3$ int): δ = 1.50-2.30 (m, 25H), 2.69 (quin, J = 9 Hz, 1H), 4.97 (s, 1H), 5.08 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, $CDCl_3$ int): δ = 15.38, 15.53, 18.11, 18.62, 24.72, 25.06, 27.86, 31.38 (C_{sek}), 38.86, 41.86 (C_{tert}), 47.90, 53.58 (C_{quart}), 108.11 (C_{sek}), 157.92 (C_{quart}); MS m/z 244 (M^+, 2), 108 (100). Anal. Calcd for $C_{18}H_{28}$: C, 88.45; H, 11.55. Found: C 88.75; H, 11.44.

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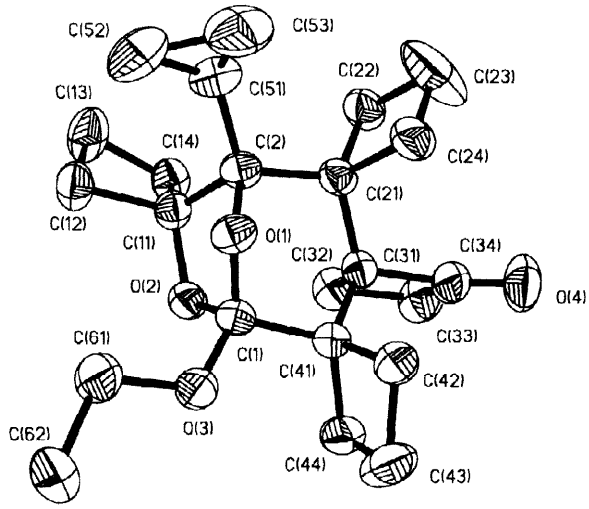
10. **29** ($C_{23}H_{32}O_4$, M = 372.5, mp 143°C) formed colourless monoclinic crystals from pentane, space group $P2_1/c$, a = 1347.7(2), b = 1104.2(2), c = 1463.4(2) pm, $\alpha = \gamma = 90$, β = 114.96(1)°, V = 1.9743(5) nm^3. 8566 reflections with $4.05 < \Theta < 25.08°$ were measured on a Stoe four-circle diffractometer using monochromated radiation Mo K_α. Of these, 3491 were unsed for the structure determination and refinement. The structure was solved by direct methods. The anisotropic refinement with geometrically positioned H atoms (riding model: C-H = 96 pm, ∠HCH = 109.5°) converged at R_1 = 0.0468 (wR_2 = 0.1213). All calculations were performed with the program SHELX TL. All relevant crystallographic data have been deposited with the Cambridge Crystallographic Data Centre.



Molecular structure of **29** (hydrogen atoms omitted)

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