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Helical primary structures of 1,3-spiroannelated five-membered rings: (±)-trispiro[4.1.1.4.2.2]heptadecane and (±)-tetraspiro[4.1.1.1.4.2.2.2]heneicosane☆

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ABSTRACT

A combination of three spiroannelation methods forms the basis for a synthesis of the first two helical hydrocarbons of 1,3-spiroannelated five-membered rings.

1. Introduction

Since the first report in 1996,[1] helical primary structures of 1,2-spiroannelated hydrocarbon rings have been the subject of an intense research.[2–10] Illustrative examples are the rigid helices **1**[3,4] and **2**,[4] and the flexible helices **3**,[5] **4**,[6] **5**,[9] and **6** (Fig. 1). With the exception of **6**,[10] all systems cited have been synthesized both in racemic and in enantiomerically pure form, and striking differences concerning their rotatory power have been observed. As a rule, the rotatory power of the rigid systems (**1**, **2**)[3,4] is high and increases with the length of the helix, while the rotatory power of the flexible systems (**3**–**5**)[5,6,9] is low and decreases with the length of the helix.

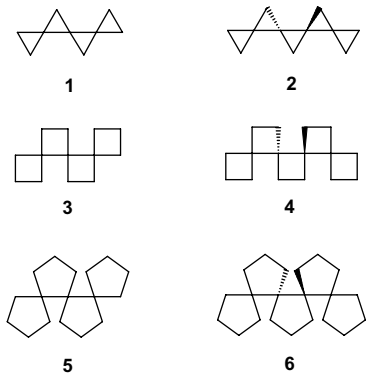

Figure 1.

Interestingly, it was already in 1991 that Trost and Shi[11] recognized that with five-membered rings 1,3-spiroannelation may lead to helical structures as well. Upon palladium catalyzed polycyclization of suitable sized polyenynes they obtained the 1,1-bis-sulfones **7** and **8** with a helical (**7**) and a potentially helical carbon skeleton (**8**), respectively. However, inseparable mixtures of diastereoisomers were formed in both cases and no proof of a helical structure of **8** could be given. We now report on the synthesis of (±)-**9** and (±)-**10**, the first helical hydrocarbons of 1,3-spiroannelated cyclopentane rings that bear no functionalities (Fig. 2).

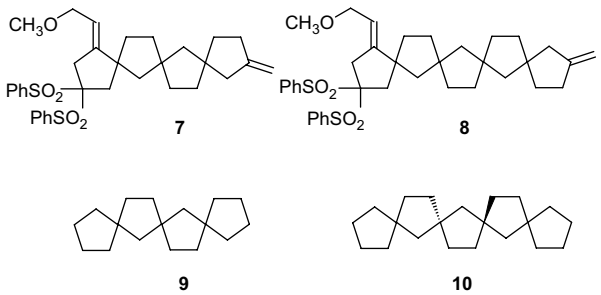

Figure 2.

☆ Polyspiranes, Part 31. For Part 30, see Ref. 10.

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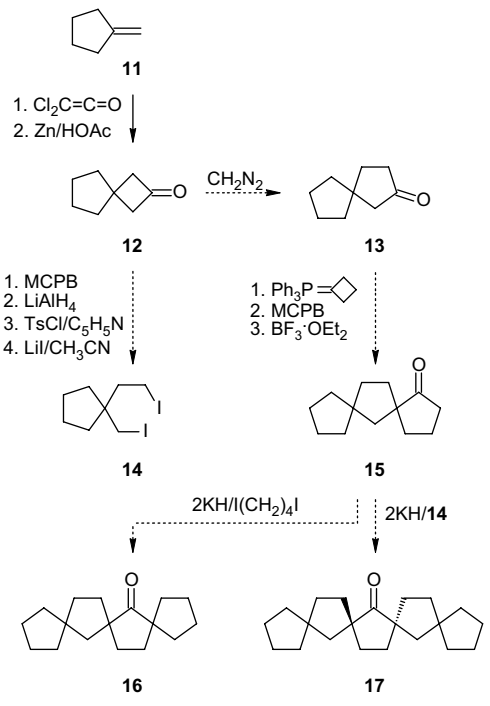
2. Results

Our approach to the desired carbon frameworks relied on three methods for the construction of spiranes[12] (Scheme 1): (i) a cycloaddition of dichloroketene to methylenecyclopentane (**11**) with subsequent dehalogenation and ring enlargement to yield the β-quaternary cyclopentanone **13** (**11**–**12**–**13**), (ii) a cyclobutylidenation of **13** with subsequent epoxidation and oxaspiropentane to cyclopentanone rearrangement to yield the α-quaternary cyclopentanone **15** (**13**–**15**), and (iii) two cycloalkylations of **15** to yield the α,α′-diquaternary cyclopentanones **16** and **17**, respectively [**15**–**16**(**17**)]. The hitherto unknown 1,4-diiodobutane **14**, needed for the synthesis of **17**, was thought to be accessible by standard operations from **12**, and the final deoxygenations of **16** and **17** to **9** and **10**, respectively, seemed difficult, but feasible.

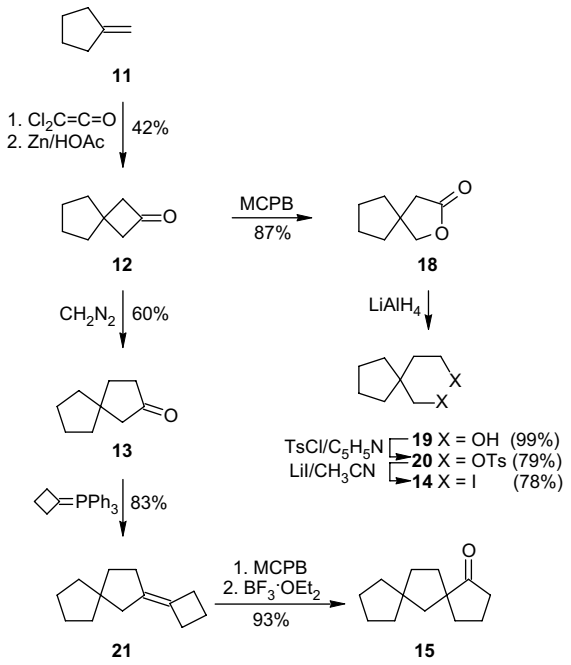
Experimentally, the addition of dichloroketene to methylenecyclopentane (**11**) proceeded regioselectively and yielded, after dehalogenation, the β-quaternary cyclobutanone **12**.[13] Upon treatment with diazomethane, this compound ring enlarged to give the β-quaternary cyclopentanone **13**.[14] The cyclobutylidenation of **13** to **21** proceeded smoothly, and subsequent epoxidation and boron trifluoride etherate catalyzed rearrangement of the resulting oxaspirohexane yielded the desired α-quaternary cyclopentanone **15** (Scheme 2).

For the synthesis of 1,4-diiodobutane **14** we subjected **12** to a Bayer–Villiger oxidation, transformed the resulting spirolactone **18**[15] via diol **19** to ditosylate **20**, and replaced the tosyloxy groups by iodine through reaction with anhydrous lithium iodide in the presence of 12-crown-4[16] (Scheme 2).

The last two steps from **15** to trispirane **9** were straightforward: cycloalkylation with 1,4-diiodobutane in the presence of potassium hydride in ether at room temperature yielded the α,α′-diquaternary cyclopentanone **16**,[17] and subsequent Wolff–Kishner reduction using a high temperature modification developed by Barton et al.[18] yielded the desired trispirane **9** (Scheme 3). This compound (symmetry C_2) was easily recognized by the appearance of only nine resonance lines in the ^{13}C NMR spectrum [δ=24.25 (t), 24.30 (t), 39.14 (t), 40.80 (t), 40.81 (t), 40.88 (t), 50.34 (s), 50.43 (s), 54.24 (t)].

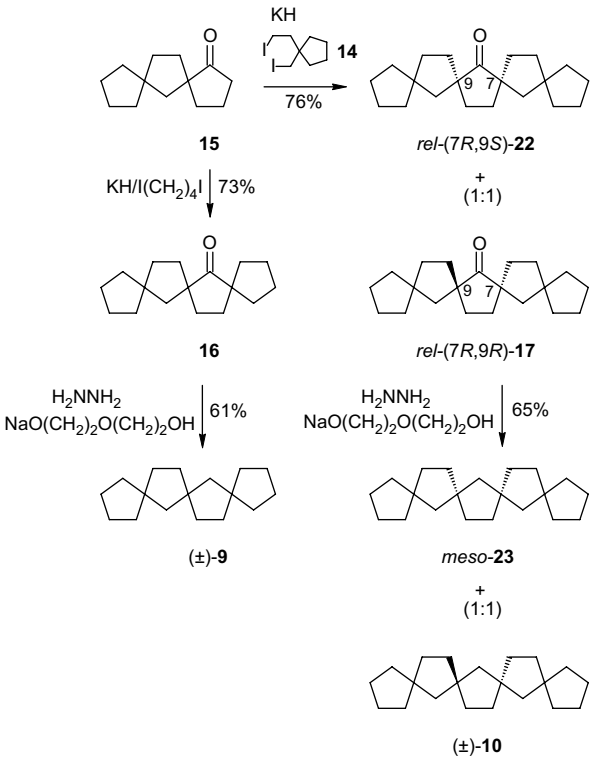


Scheme 1.



Scheme 2.

Tetraspirane **10** was more difficult to obtain: the cycloalkylation of **15** with 1,4-diiodobutane **14** at reflux in benzene over 48 h went to completion but afforded a 1:1 mixture of the desired trans-configurated α,α′-diquaternary cyclopentanone **17** and its cis-configurated counterpart **22**. Unfortunately, the components of this mixture could not be separated, and the same was found true for



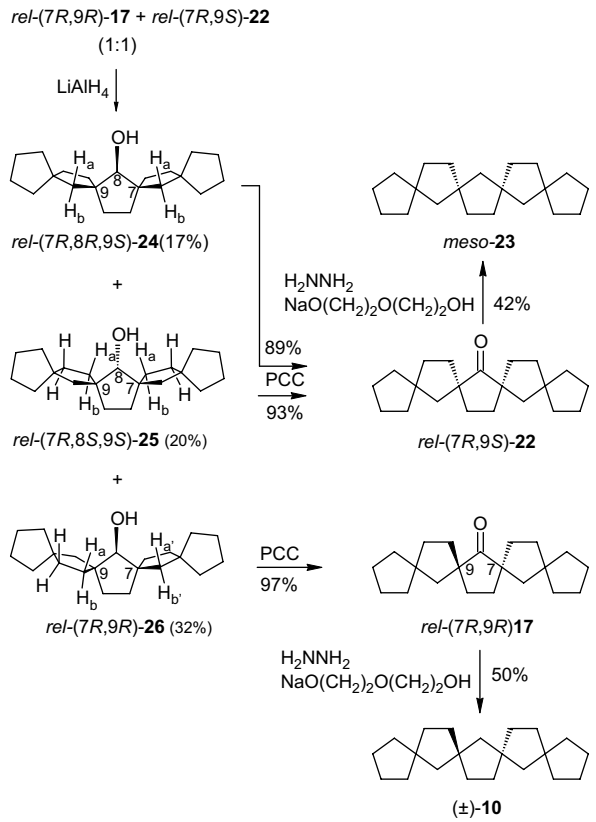
Scheme 3.

the 1:1 mixture of tetraspiranes **10** and **23** obtained therefrom (Scheme 3). Therefore, a possibility for the separation via derivatives was searched for.

Toward this end, the 1:1 mixture of **17** and **22** was reduced with lithium aluminum hydride. Fortunately, the resulting alcohols **24**–**26** could be separated by chromatography on silica gel in pentane/ether (97:3) and identified by NMR and by the outcome of separate oxidations (Scheme 4).

As could have been expected, the ^{13}C NMR data of **24** (symmetry C_s, 11 resonances), **25** (symmetry C_s, 11 resonances), and **26** (symmetry C_1, 21 resonances) allowed only the identification of **26**, but no distinction between **24** and **25**. Fortunately, the ^{1}H NMR data were more instructive. Distinct differences in the chemical shifts and the multiplicity of the four protons of the methylene groups neighboring the hydroxyl group were observed: those nearest to the hydroxyl group (H_a, $H_{a'}$) appeared downfield ($\delta \sim 2.0$ ppm) and those farer away (H_b, $H_{b'}$) appeared upfield ($\delta \sim 1.2$ ppm). Moreover, those being part of a one-carbon bridge appeared as doublet, and those being part of a two-carbon bridge appeared as doublet of doublets of doublets. Thus, the data for the first eluted alcohol [yield 17%, δ=1.23 (d, J=13 Hz, 2H), 2.06 (d, J=13 Hz, 2H)] were conclusive for **24**, those of the second eluted alcohol [yield 32%, δ=1.21 (d, J=13 Hz, 1H), 1.26 (ddd, J=12, 6, 6 Hz, 1H), 1.97 (ddd, J=12, 8, 8 Hz, 1H), 2.04 (d, J=13 Hz, 1H)] were conclusive for **26**, and those of the last eluted alcohol [yield 20%, δ=1.23 (ddd, J=12, 6, 6 Hz, 2H), 1.96 (ddd, J=12, 8, 8 Hz, 2H)] were conclusive for **25**.

A chemical proof resulted from separate oxidations with pyridinium chlorochromate:[19] both **24** and **25** delivered one and the same ketone, and hence **22** (symmetry C_s), while **26** delivered a stereoisomer and hence **17** (symmetry C_2). Of these, **22** was deoxygenated to **23** (symmetry C_s) and **17** to the desired helical **10** (symmetry C_2) (Scheme 4).



Scheme 4.

Having established productive procedures for the synthesis of (±)-**9** and (±)-**10** via cycloalkylations of the α-quaternary cyclopentanone **15**, we shortly investigated whether the methods employed could also be used for the synthesis of higher analogues. Toward this end, we first tried to synthesize the α-quaternary cyclopentanone **33** as higher analogue of **15** (Scheme 5).

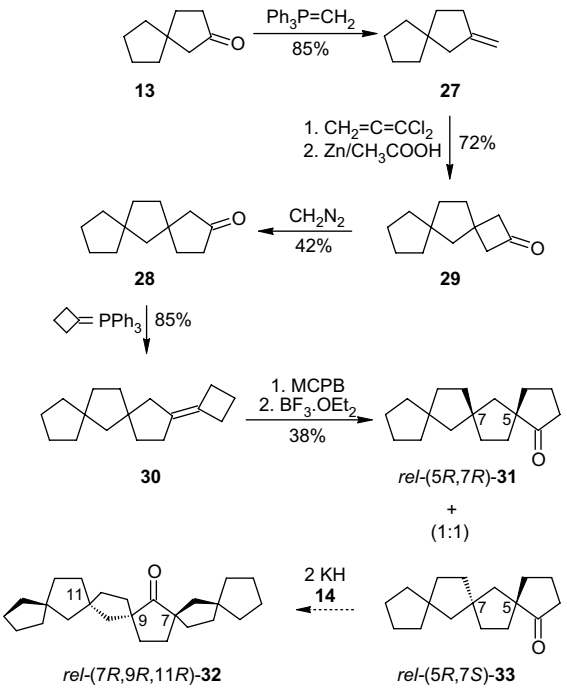
For the experimental realization, we subjected the β-quaternary cyclopentanone **13** first to a methylenation, and then to an addition of dichloroketene, a reductive dehalogenation, and a ring enlargement with diazomethane (**13**–**27**–**29**–**28**). The resulting β-quaternary cyclopentanone **28** was then cyclobutylidenated and subsequently epoxidized and rearranged to yield a 1:1 mixture of the desired α-quaternary cyclopentanone *rel*-(5*R*,7*S*)-**33** and its undesired counterpart *rel*-(5*R*,7*R*)-**31** [**28**–**30**–**33**(**31**)]. Unfortunately, all efforts for the separation of **31** and **33** failed. Therefore, the envisioned spiroalkylation with **14**, which probably would have led to four stereoisomeric α,α′-diquaternary cyclopentanones with (7*R*,9*R*,11*R*)-**32** as the only one with a helical carbon skeleton, was abandoned.

In summary, we have developed productive syntheses of the helical hydrocarbons (±)-**9** and (±)-**10** via spiroalkylations of the hitherto unknown dispiroketone **15**. This means that a resolution of **15** will open the way to enantiopure specimen. Due to lack of stereoselectivity in the synthesis of **33**, experiments directed toward the synthesis of a higher analogue of (±)-**10** were cut off.

3. Experimental

3.1. General

IR spectra were obtained with a Perkin–Elmer 298 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX 300, a Varian VXR 500, or a Varian VXR 600 spectrometer. As standards the following chemical shifts were used: δ_H ($CHCl_3$)=7.24, δ_H (C_6D_5H)=7.15, δ_C ($CDCl_3$)=77.00, δ_C (C_6D_6)=128.00. ^{13}C multiplicities were studied by HMQC measurements. Mass spectra were obtained with a Finnegan MAT 95 spectrometer (EI and HREI)



Scheme 5.

operated at 70 eV. Analytical and preparative GC was carried out on a Carlo Erba 6000 Vega 2 instrument using a thermal conductivity detector and hydrogen as carrier gas. The following columns were used: (A): 3 m×1/4″ all-glass system, 15% OV 210 on Chromosorb W AW/DMCS 60/80 mesh; (B): 3 m×1/4″ all-glass system, 15% FFAP on Chromosorb W AW/DMCS 60/80 mesh. Product ratios were not corrected for relative response. R_f values are quoted for Macherey and Nagel Polygram SIL G/UV_{254} plates. Colorless substances were detected by oxidation with 3.5% alcoholic 12-molybdophosphoric acid and subsequent warming. Melting points were observed on a Reichert microhotstage. Boiling and melting points are not corrected. Microanalytical determinations were done at the Microanalytical Laboratory of the Institute of Organic and Bioorganic Chemistry, Göttingen.

3.2. Spiro[3.4]octan-2-one (12)

To a boiling mixture of methylenecyclopentane[20] (12.3 g, 150 mmol) and zinc dust (19.6 g, 300 mmol) in ether (200 mL) was added within 1 h under argon with stirring a solution of trichloroacetyl chloride (41.0 g, 225 mmol) in ether (200 mL); 15–30 min after the addition was complete, a vigorous reaction occurred making occasional cooling necessary. Afterward the mixture was heated for additional 1.5 h to reflux. The mixture was filtered over Celite, the residue was washed with ether (100 mL), and the combined filtrates were washed with water (5×100 mL), saturated sodium bicarbonate (5×100 mL), and brine (5×100 mL), and dried ($MgSO_4$). The solvent was distilled off (bath temperature 50 °C/15 Torr), and the remaining crude dichloroketone resulting from four identical experiments (137 g, purity 65% GC) [column A, 2 min, 60 °C, 10 °C/min to 200 °C; retention time (min): 13.45] was directly used in the next step. To a suspension of zinc dust (231 g, 3.55 mol) in acetic acid (300 mL) was added within 30 min under argon with stirring a solution of the crude dichloroketone (68.5 g, purity 65%) in acetic acid (150 mL) (exothermic effect) until the mixture was heated for 1.5 h to 60 °C. After cooling, the mixture was filtered over Celite and the residue was washed with pentane (2×200 mL). Water (400 mL) was added, the organic phase was separated, the aqueous phase was extracted with pentane (5×100 mL), and the combined organic phases were washed with 1 N sodium hydroxide (2×100 mL) and brine (2×100 mL), and dried ($MgSO_4$). The solvent was distilled off (bath temperature 40 °C/20 Torr) and the remaining crude **12** resulting from two identical experiments (65 g, purity 71% GC) [column A, 80 °C, 10 °C/min to 220 °C; retention time (min): 6.57 (**12**)] was fractionated first over a 20 cm vigreux column and then over a 55 cm vigreux column yielding 31.4 g (42%) of **12** as colorless liquid, bp 78 °C/20 Torr (purity 95% GC). The ^{1}H and ^{13}C NMR data were in accord with the literature data.[13]

3.3. Spiro[4.4]nonan-2-one (13)

The reaction was performed in fire-polished glassware in a well ventilated hood. To a solution of potassium hydroxide (74 g, 1.32 mol) in methanol (170 mL) and water (30 mL) was added dropwise at 0 °C with stirring **12** (13.6 g, 110 mmol), and, within 3 h, a solution of *N*-methyl-*N*-nitroso-*p*-toluenesulfonic acid amide (30.0 g, 140 mmol) in methanol (360 mL). After additional 0.5 h, the mixture was hydrolyzed with acetic acid (60 mL), diluted with water (400 mL), and extracted with pentane (4×150 mL). The combined extracts were washed with water (2×150 mL), dried ($MgSO_4$), and concentrated (bath temperature 40 °C/15 Torr) to yield 13.4 g of crude **13**. The material of two experiments (27.3 g) was fractionated over a 20 cm vigreux column to yield 18.0 g (60%) of **13** as colorless liquid, bp 93–95 °C/16 Torr (purity 94% GC). A pure sample was obtained by preparative GC [column B, 190 °C; retention time (min): 3.80 (**13**)]. The ^{1}H NMR data were in accord with the literature data.[14b] ^{13}C NMR (50 MHz, $CDCl_3$, $CDCl_3$ int): δ=24.01 (t), 34.83 (t), 37.74 (t), 38.00 (t), 47.40 (s), 51.17 (t), 219.50 (s).

3.4. 2-Cyclobutyliden-spiro[4.4]nonane (21)

To a suspension of 4-bromobutyltriphenylphosphonium bromide[21] (96 g, 0.20 mol) in dry benzene (250 mL) was added under argon with stirring potassium-*tert*-butoxide (3×14.9 g, 0.40 mol) and the mixture heated for 3 h to 50 °C. Compound **13** (17.7 g, 0.13 mol) was added and after 1 h at 60 °C the reaction was complete according to GC [column B, 190 °C; retention times (min): 3.23 (**21**), 3.80 (**13**)]. The mixture was hydrolyzed with water (20 mL), the organic layer was decanted, and the residue was extracted with pentane (3×100 mL). The combined organic phases were concentrated (bath temperature up to 120 °C) and the residue diluted with pentane (300 mL). Precipitated triphenylphosphine oxide was filtered off and the filtrate was concentrated and distilled to yield 18.8 g (83%) of **21** as colorless liquid, bp 126–135 °C/20 Torr (purity 94% GC). An analytically pure sample was obtained by preparative GC. ^{1}H NMR (600 MHz, $CDCl_3$, $CHCl_3$ int): δ=1.37–1.45 (m, 4H), 1.50–1.54 (m, 2H), 1.55–1.63 (m, 4H), 1.89–1.96 (m, 4H), 2.06–2.12 (m, 2H), 2.51–2.57 (m, 4H); ^{13}C NMR (150.8 MHz, $CDCl_3$, $CDCl_3$ int): δ=17.13 (t), 24.69 (t, 2C), 28.12 (t), 29.85 (t), 30.04 (t), 38.09 (t, 2C), 38.65 (t), 42.21 (t), 50.67 (s), 129.61 (s), 132.47 (s); MS (EI): *m*/*z*=176 (32, M^+), 147 (100). $C_{13}H_{20}$ requires: C, 88.57; H, 11.43. Found: C, 88.12; H, 11.30.

3.5. Dispiro[4.1.4.2]tridecan-1-one (15)

To a stirred solution of **21** (17.6 g, 100 mmol) in dichloromethane (100 mL) was added within 2 h a solution of 3-chloroperoxybenzoic acid (49.4 g, 70% w/w, 200 mmol) in dichloromethane (400 mL). After 1 h, the reaction was complete according to GC [column B, 190 °C; retention times (min): 3.21 (**21**), 6.12 (epoxide), 10.79 (**15**)]. NaOH (1 N, 200 mL) was added with stirring, the phases were separated, and the organic phase was washed with water (2×200 mL), dried ($MgSO_4$), and concentrated to approximately 300 mL by distillation over a 40 cm vigreux column. Solid potassium carbonate (1.0 g) was added to the remaining solution until it was cooled to 5 °C and boron trifluoride etherate (260 mg, 1.8 mmol) was added drop by drop, causing an exothermic reaction, which with the last drops subsided. After the addition was complete, the mixture was stirred for 30 min at room temperature, until it was washed with 1 N NaOH (50 mL), water (2×150 mL), and dried ($MgSO_4$). The solvent was distilled off over a 40 cm vigreux column and the residue fractionated to yield 17.7 g (93%) of **15** as colorless liquid, bp 108–110 °C/1 Torr (purity 97% GC). An analytically pure sample was obtained by preparative GC. IR (neat): 1740 cm^{-1} (C=O); ^{1}H NMR (600 MHz, $CDCl_3$, $CHCl_3$ int): δ=1.34 (d, *J*=13 Hz, 1H), 1.39–1.63 (m, 11H), 1.76–1.90 (m, 6H), 2.11–2.25 (m, 2H); ^{13}C NMR (150.8 MHz, $CDCl_3$, $CDCl_3$ int): δ=19.47 (t), 24.31 (t), 24.59 (t), 36.33 (t), 36.92 (t), 38.94 (t), 39.02 (t), 39.35 (t), 39.44 (t), 48.60 (t), 51.47 (s), 56.11 (s), 223.74 (s); MS (EI): *m*/*z*=192 (26, M^+), 97 (100). $C_{13}H_{20}O$ requires: C, 81.20; H, 10.48. Found: C, 81.21; H, 10.42.

3.6. Trispiro[4.1.1.4.2.2]heptadecan-6-one (16)

To a suspension of potassium hydride (240 mg, 6.0 mmol) in ether (15 mL) were added under argon with stirring **15** (384 mg, 2.0 mmol) and 1,4-diiodobutane (775 mg, 2.5 mmol). According to GC [column B, 230 °C; retention times (min): 4.29 (**15**), 9.61 (**16**)], after 20 h at room temperature the reaction was complete. The mixture was diluted with pentane (15 mL) and hydrolyzed with saturated ammonium chloride (1 mL). The organic phase was

decanted, the residue was extracted with pentane (5 mL), and the combined organic phases were washed with water (2×15 mL) and dried ($MgSO_4$). The solvents were distilled off (bath temperature 50 °C/15 Torr), and the residue (458 mg) was chromatographed on silica gel (0.05–0.20 mm) in pentane/ether (95:5, column 50×2.5 cm, control by GC) to yield 350 mg (73%) of **16** as colorless oil (purity 98% GC). An analytically pure sample was obtained by preparative GC. IR (neat): 1735 cm^{-1} (C=O); ^1H NMR (600 MHz, C_6D_6, C_6D_5H int): δ=1.23–1.31 (m, 2H), 1.25 (d, J=13 Hz, 1H), 1.32–1.41 (m, 3H), 1.42–1.73 (m, 16H), 1.71–1.84 (m, 1H), 1.88–1.96 (m, 2H), 1.99 (d, J=13 Hz, 1H); ^{13}C NMR (150.8 MHz, C_6D_6, C_6D_6 int): δ=24.68 (t), 24.96 (t), 26.08 (t), 26.18 (t), 35.65 (t), 37.12 (t), 37.59 (t), 37.64 (t), 37.81 (t), 39.31 (t), 39.48 (t), 39.86 (t), 50.08 (t), 51.79 (s), 55.65 (s), 56.02 (s), 225.50 (s); MS (EI): m/z=246 (14, M^+), 151 (100). $C_{17}H_{26}O$ requires: C, 82.87; H, 10.64. Found: C, 83.07; H, 10.43.

3.7. (±)-Trispiro[4.1.1.4.2.2]hexadecane [(±)-9]

Sodium metal (140 mg, 6.0 mmol) was dissolved in diethyleneglycol (8.0 mL). Anhydrous hydrazine (1.30 g, 40 mmol) and **16** (119 mg, 0.50 mmol) were added under argon with stirring, and the resulting mixture was heated to 140 °C. According to GC [column A, 200 °C; retention times (min): 1.75 (**9**), 4.52 (**16**), 6.28 (hydrazone)], after 24 h the mixture contained >90% hydrazone. The temperature was raised to 200 °C and after additional 48 h the mixture contained >90% **9**. The mixture was diluted with water (50 mL), extracted with pentane (2×50 mL), and the extracts were washed with water (2×50 mL) and dried ($MgSO_4$). The solvent was distilled off (bath temperature 30 °C/15 Torr) and the residue (100 mg) was chromatographed on silica gel (0.05–0.20 mm) in pentane (column 10×1 cm) to yield 69 mg (61%) of **9** as colorless liquid (purity 96% GC). An analytically pure sample was obtained by preparative GC. ^1H NMR (600 MHz, $CDCl_3$, $CHCl_3$ int): δ=1.40–1.49 (m, 12H), 1.51–1.58 (m, 16H); ^{13}C NMR (150.8 MHz, $CDCl_3$, $CDCl_3$ int): δ=24.25 (t, 2C), 24.30 (t, 2C), 39.14 (t, 2C), 40.80 (t, 2C), 40.81 (t, 2C), 40.88 (t, 2C), 50.34 (s, 2C), 50.43 (s), 54.24 (t, 2C); MS (EI): m/z=232 (58, M^+), 175 (100). $C_{17}H_{28}$ requires: C, 87.86; H, 12.14. Found: C, 88.00; H, 11.89.

3.8. 2-Oxa-spiro[4.4]nonan-3-one (18)

To a vigorously stirred solution of **12** (9.3 g, 75 mmol) in dichloromethane (100 mL) was added a 0.7 M aqueous solution of sodium bicarbonate (150 mL), and, within 2 h at 20–25 °C, a solution of 3-chloroperoxybenzoic acid (24.7 g, 70% w/w, 100 mmol) in dichloromethane (300 mL). According to GC [column B, 190 °C; retention times (min): 2.16 (**12**), 12.05 (**18**)], after additional 0.5 h the reaction was complete. The organic phase was washed with 1 N NaOH (150 mL), water (150 mL), and dried ($MgSO_4$). The solvent was distilled off and the residue fractionated to yield 9.1 g (87%) of **18** as colorless liquid, bp 86 °C/0.4 Torr (purity 99% GC) (lit.[15a] 120–121 °C/11 Torr). The ^1H and ^{13}C NMR data were in accord with the literature data.[15b]

3.9. 1-Hydroxymethyl-1-(2-hydroxyethyl)-cyclopentane (19)

To a suspension of lithium aluminum hydride (3.8 g, 100 mmol) in anhydrous ether (110 mL) was added at room temperature under argon with stirring **18** (9.1 g, 65 mmol) causing an exothermic effect. Afterward the mixture was heated to reflux. According to GC [column A, 180 °C; retention times (min): 4.51 (**18**), 11.21 (**19**)], after 2 h the reduction was complete. Water (3.8 mL), 15% aqueous potassium hydroxide (3.8 mL), and water (11.4 mL) were added, the liquid phase was decanted, and the residue was extracted with ether (3×100 mL). The combined organic phases were dried ($MgSO_4$) and concentrated on a rotary evaporator (bath temperature 60 °C/15 Torr) to yield 9.3 g (99%) of **19** as colorless oil (purity 96% GC). This material was used for the synthesis of **20**. Analytically pure **19** was obtained by preparative GC. ^1H NMR (600 MHz, $CDCl_3$, $CHCl_3$ int): δ=1.26–1.33 (m, 2H), 1.45–1.52 (m, 2H), 1.54–1.61 (m, 4H), 1.64 (m_c, 2H), 3.37 (s, 2H), 3.68 (m_c, 2H), 4.08 (br s, 2H); ^{13}C NMR (150.8 MHz, $CDCl_3$, $CDCl_3$ int): δ=24.51 (t, 2C), 35.02 (t, 2C), 41.92 (t), 47.06 (s), 59.89 (t), 69.03 (t); MS (CI): m/z=289 (5, $[2M+H]^+$), 162 (100, $[M+NH_4]^+$), 145 (14, $[M+H]^+$). $C_8H_{16}O_2$ requires: C, 66.63; H, 11.18. Found: C, 66.90; H, 10.93.

3.10. 1-Tosyloxymethyl-1-(2-tosyloxyethyl)-cyclopentane (20)

To a solution of *p*-toluenesulfonic acid chloride (48.8 g, 256 mmol) in pyridine (100 mL) was added under argon with stirring a solution of **19** (9.2 g, 64 mmol) in pyridine (60 mL) such that the internal temperature did not exceed 3 °C (2 h). After having been stirred at 0 °C overnight, the mixture was poured into ice-cold water (1 L) and the separating oil extracted with dichloromethane (400 mL). The extract was washed with water (200 mL), 5% H_2SO_4 (200 mL), and water (200 mL), and dried ($MgSO_4$). The solvent was distilled off on a rotary evaporator (bath temperature up to 60 °C/15 Torr) to yield 22.8 g (79%) of **20** as slightly yellow sticky gum (purity 94% ^1H NMR). An analytically pure sample was obtained by thick layer chromatography on silica gel in pentane/ether [1:1, R_f=0.32 (**20**)], colorless sticky gum. ^1H NMR (600 MHz, $CDCl_3$, $CHCl_3$ int): δ=1.27–1.33 (m, 2H), 1.34–1.40 (m, 2H), 1.40–1.54 (m, 4H), 1.71 (pseudo t, J=7 Hz, 2H), 2.42 (s, 6H), 3.65 (s, 2H), 3.95 (pseudo t, J=7 Hz, 2H), 7.30–7.33 (m, 4H), 7.69–7.73 (m, 4H); ^{13}C NMR (150.8 MHz, $CDCl_3$, $CDCl_3$ int): δ=21.55 (q), 21.56 (q), 24.32 (t, 2C), 34.52 (t, 2C), 35.66 (t), 44.39 (s), 67.48 (t), 74.10 (t), 127.72 (d, 2C), 127.73 (d, 2C), 129.81 (d, 2C), 129.87 (d, 2C), 132.49 (s), 132.79 (s), 144.79 (s), 144.88 (s); MS (EI): m/z=452 (<1, M^+), 109 (100); (CI): m/z=922 (7, $[2M+NH_4]^+$), 470 (100, $[M+NH_4]^+$). $C_{22}H_{28}O_6S_2$ requires: C, 58.38; H, 6.24. Found: C, 58.55; H, 6.31.

3.11. 1-Iodomethyl-1-(2-iodoethyl)-cyclopentane (14)

A mixture of **20** (22.6 g, 50 mmol), anhydrous lithium iodide (26.8 g, 200 mmol), and 12-crown-4 (1.76 g, 10 mmol) in anhydrous acetonitrile (300 mL) was heated to reflux. According to TLC in pentane/ether [1:1; R_f=0.32 (**20**), 0.58, 0.75 (**14**)] after 20 h the reaction was complete. Most of the solvent was distilled off on a rotary evaporator (bath temperature 40 °C/30 Torr) and the residue was extracted with ether (3×200 mL). The combined extracts were washed with water (300 mL), $Na_2S_2O_3$ solution (10%, 350 mL), and water (300 mL), and dried ($MgSO_4$). The solvent was distilled off and the residue fractionated to yield 14.2 g (78%) of pure **14** as slightly yellow liquid, bp 108–109 °C/0.1 Torr. ^1H NMR (600 MHz, $CDCl_3$, $CHCl_3$ int): δ=1.52–1.58 (m, 4H), 1.61–1.67 (m, 4H), 2.12 (AA′ part of an AA′BB′ system, 2H), 3.07 (BB′ part of an AA′BB′ system, 2H), 3.16 (s, 2H); ^{13}C NMR (150.8 MHz, $CDCl_3$, $CDCl_3$ int): δ=−0.53 (t), 19.52 (t), 24.84 (t, 2C), 37.01 (t, 2C), 45.19 (t), 48.26 (s); MS (EI): m/z=364 (<1, M^+), 237 (66, M^+-I), 109 (100, M^+-I-HI). $C_8H_{14}I_2$ requires: C, 26.40; H, 3.88. Found: C, 26.69; H, 3.68.

3.12. *rel*-(7*R*,9*R*)-Tetraspiro[4.1.1.1.4.2.2.2]heneicosan-8-one [*rel*-(7*R*,9*R*)-17] and *rel*-(7*R*,9*S*)-tetraspiro[4.1.1.1.4.2.2.2]-heneicosan-8-one [*rel*-(7*R*,9*S*)-22]

To a suspension of potassium hydride (1.20 g, 30 mmol) in benzene (75 mL) were added under argon with stirring **15** (0.96 g, 5.0 mmol) and **14** (2.73 g, 7.5 mmol). Afterward, the mixture was heated to reflux. The reaction progress was monitored by GC [column A, 200 °C; retention times (min): 3.08 (**15**), 3.53 (**14**), 18.85 (**17**/**22**)], and, after 24 and 30 h, more **14** (2×0.91 g, 2×2.5 mmol) was added. After 48 h, the reaction was complete. The mixture was

diluted with pentane (75 mL), hydrolyzed with saturated ammonium chloride (50 mL), and the organic phase was washed with water (2×50 mL) and dried ($MgSO_4$). The solvents were distilled off (bath temperature 50 °C/15 Torr), and the residue (3.86 g yellow oil) was chromatographed on silica gel (0.05–0.20 mm) in pentane/ether (95:5, column 70×4.5 cm, control by GC) to yield 1.14 g (76%) of a 1:1 mixture of **17** and **22** as colorless solid, mp 34–36 °C. The data refer to the mixture. ^{1}H NMR (600 MHz, C_6D_6, C_6D_5H int): δ=1.265 (d, J=12.5 Hz, 1H), 1.275 (d, J=13 Hz, 1H), 1.33–1.70 (m, 26H), 1.90 (ddd, J=12.5, 7.5, 7.5 Hz, 1H), 1.96 (d, J=13 Hz, 1H), 2.00 (ddd, J=13, 7.5, 7.5 Hz, 1H), 2.05 (d, J=12.5 Hz, 1H); ^{13}C NMR (150.8 MHz, C_6D_6, C_6D_6 int): δ=24.67 (t), 24.71 (t), 24.96 (t), 24.97 (t), 37.09 (t), 37.14 (t), 37.66 (t), 37.82 (t), 39.33 (t), 39.36 (t), 39.44 (t), 39.60 (t), 39.90 (t), 39.90 (t), 50.17 (t), 50.42 (t), 51.80 (s), 51.84 (s), 55.57 (s), 55.60 (s), 225.33 (s), 225.49 (s). $C_{21}H_{32}O$ requires: C, 83.94; H, 10.73. Found: C, 84.11; H, 10.66.

3.13. (±)-Tetraspiro[4.1.1.1.4.2.2.2]heneicosane [(±)-10] and *meso*-tetraspiro[4.1.1.1.4.2.2.2]heneicosane (*meso*-23)

The 1:1 mixture of **17** and **22** (140 mg, 0.50 mmol) was reduced as described for **16** (see Section 3.7). According to GC [column A, 230 °C; retention times (min): 2.60 (**10**/**23**), 5.89 (**17**/**22**), 7.72 (hydrazones)], after 24 h at 140 °C the mixture contained >90% hydrazones, and after additional 48 h at 200 °C >90% **10** and **23**. Work up and chromatography yielded 93 mg (65%) of a 1:1 mixture of **10** and **23** as colorless liquid (purity 95% GC). The data refer to the mixture. ^{1}H NMR (600 MHz, $CDCl_3$, $CHCl_3$ int): δ=1.40–1.48 (m, 12H), 1.52–1.60 (m, 22H); ^{13}C NMR (150.8 MHz, $CDCl_3$, $CDCl_3$ int): δ=24.23 (t) (coincidence of two lines), 24.29 (t) (coincidence of two lines), 39.12 (t), 39.18 (t), 40.86 (t), 40.88 (t) (coincidence of two lines), 40.89 (t), 40.90 (t), 40.91 (t), 41.12 (t), 41.14 (t), 50.29 (s) (coincidence of two lines), 50.31 (s), 50.32 (s), 54.46 (t), 54.49 (t), 55.95 (t), 56.05 (t).

3.14. *rel*-(7*R*,8*R*,9*S*)-Tetraspiro[4.1.1.1.4.2.2.2]heneicosane-8-ol [*rel*-(7*R*,8*R*,9*S*)-24], *rel*-(7*R*,8*S*,9*S*)-tetraspiro[4.1.1.1.4.2.2.2]-heneicosane-8-ol [*rel*-(7*R*,8*S*,9*S*)-25], and *rel*-(7*R*,9*R*)-tetraspiro[4.1.1.1.4.2.2.2]heneicosane-8-ol [*rel*-(7*R*,9*R*)-26]

To a suspension of lithium aluminum hydride (285 mg, 7.5 mmol) in ether (30 mL) was added under argon with stirring a solution of a 1:1 mixture of **17** and **22** (450 mg, 1.5 mmol) in ether (5 mL). After 1 h of reflux, the reaction was complete according to GC [column A, 230 °C; retention times (min): 5.45 (**24**/**25**/**26**), 5.89 (**17**/**22**)]. The mixture was treated with water (300 μL), 15% aqueous KOH (300 μL), and water (900 μL), the organic phase was decanted, and the residue was extracted with ether (3×20 mL). The combined organic phases were concentrated (bath temperature 60 °C/15 Torr) and the solid residue (438 mg) was chromatographed on silica gel (0.040–0.063 mm) in pentane/ether [97:3, column 100×2.5 cm, R_f=0.18 (**24**), 0.15 (**26**), 0.13 (**25**)] to yield 78 mg (17%) **24**, mp 92–94 °C, 89 mg (20%) **25**, mp 170–172 °C, and 147 mg (32%) **26**, mp 82–84 °C, as colorless solids. Compound **24**: ^{1}H NMR (600 MHz, C_6D_6, C_6D_5H int): δ=1.07 (br s, 1H), 1.23 (d, J=13 Hz, 2H), 1.46–1.56 (m, 14H), 1.56–1.72 (m, 14H), 2.06 (d, J=13 Hz, 2H), 3.32 (s, 1H); ^{13}C NMR (150.8 MHz, C_6D_6, C_6D_6 int): δ=24.53 (t, 2C), 24.90 (t, 2C), 38.42 (t, 2C), 39.06 (t, 2C), 39.70 (t, 2C), 40.60 (t, 2C), 40.95 (t, 2C), 46.43 (t, 2C), 50.79 (s, 2C), 53.43 (s, 2C), 86.15 (d); MS (EI): m/z=302 (11, M^+), 284 (10, M^+-H_2O), 67 (100); HRMS m/z (M^+) calcd 302.2620, obsd 302.2610. Compound **25**: ^{1}H NMR (600 MHz, C_6D_6, C_6D_5H int): δ=1.03 (br s, 1H), 1.23 (ddd, J=12, 6, 6 Hz, 2H), 1.41 (d, J=13 Hz, 2H), 1.45–1.54 (m, 14H), 1.57–1.64 (m, 10H), 1.66 (d, J=13 Hz, 2H), 1.96 (ddd, J=12, 8, 8 Hz, 2H), 3.33 (br s, 1H); ^{13}C NMR (150.8 MHz, C_6D_6, C_6D_6 int): δ=24.61 (t, 2C), 24.94 (t, 2C), 33.46 (t, 2C), 38.45 (t, 2C), 39.54 (t, 2C), 40.53 (t, 2C), 40.60 (t, 2C), 50.09 (s, 2C), 52.75 (s, 2C), 52.92 (t, 2C), 85.66 (d); MS (EI): m/z=302 (22, M^+), 284 (21, M^+-H_2O), 67 (100); HRMS m/z (M^+) calcd 302.2620, obsd 302.2610. Compound **26**: ^{1}H NMR (600 MHz, C_6D_6, C_6D_5H int): δ=1.14 (br s, 1H), 1.21 (d, J=13 Hz, 1H), 1.26 (ddd, J=12, 6, 6 Hz, 1H), 1.43 (d, J=13 Hz, 1H), 1.46–1.58 (m, 14H), 1.58–1.73 (m, 13H), 1.97 (ddd, J=12, 8, 8 Hz, 1H), 2.04 (d, J=13 Hz, 1H), 3.34 (s, 1H); ^{13}C NMR (150.8 MHz, C_6D_6, C_6D_6 int): δ=24.52 (t), 24.60 (t), 24.90 (t), 24.93 (t), 33.58 (t), 38.37 (t), 38.40 (t), 38.96 (t), 39.45 (t), 39.73 (t), 40.59 (t), 40.62 (t), 40.66 (t), 40.97 (t), 46.36 (t), 50.19 (s), 50.87 (s), 52.87 (t), 52.96 (s), 53.27 (s), 85.94 (d); MS (EI): m/z=302 (23, M^+), 284 (15, M^+-H_2O), 67 (100); HRMS m/z (M^+) calcd 302.2620, obsd 302.2610.

3.15. *rel*-(7*R*,9*R*)-Tetraspiro[4.1.1.1.4.2.2.2]heneicosan-8-one [*rel*-(7*R*,9*R*)-17]

To pyridinium chlorochromate (173 mg, 0.80 mmol) was added under argon with stirring a solution of **26** (121 mg, 0.40 mmol) in dichloromethane (2.0 mL). After 1 h at room temperature, the reaction was complete according to GC [column A, 230 °C; retention times (min): 5.33 (**26**), 5.88 (**17**)]. The mixture was diluted with ether (5 mL), the liquid phase was decanted, the residual black tar was extracted with ether (2×2 mL), and the combined organic phases were first filtrated over a short pad of silica gel (0.05–0.20 mm; column 7×2 cm) and then concentrated (bath temperature 60 °C/15 Torr) to yield 117 mg (97%) of **17** as colorless solid, mp 56–58 °C (purity >99%, GC). IR (KBr): 1720 cm^{-1} (C=O); ^{1}H NMR (600 MHz, C_6D_6, C_6D_5H int): δ=1.27 (d, J=12.5 Hz, 2H), 1.33–1.69 (m, 26H), 1.90 (ddd, J=12.5, 7.5, 7.5 Hz, 2H), 2.06 (d, J=12.5 Hz, 2H); ^{13}C NMR (150.8 MHz, C_6D_6, C_6D_6 int): δ=24.70 (t, 2C), 24.97 (t, 2C), 37.13 (t, 2C), 37.83 (t, 2C), 39.34 (t, 2C), 39.44 (t, 2C), 39.90 (t, 2C), 50.18 (t, 2C), 51.80 (s, 2C), 55.59 (s, 2C), 225.41 (s); MS (EI): m/z=300 (23, M^+), 205 (100); HRMS m/z (M^+) calcd 300.2453, obsd 300.2453.

3.16. *rel*-(7*R*,9*S*)-Tetraspiro[4.1.1.1.4.2.2.2]heneicosan-8-one [*rel*-(7*R*,9*S*)-22]

3.16.1. From *24*

Compound **24** (75 mg, 0.25 mmol) was oxidized as described for **26** (see Section 3.15) yielding 67 mg (89%) of **22** as colorless solid, mp 50–52 °C (purity >98%, GC) [column A, 230 °C, retention times (min): 5.11 (**24**), 5.89 (**22**)]. IR (KBr): 1720 cm^{-1} (C=O); ^{1}H NMR (600 MHz, C_6D_6, C_6D_5H int): δ=1.27 (d, J=13 Hz, 2H), 1.34–1.70 (m, 26H), 1.96 (d, J=13 Hz, 2H), 2.01 (ddd, J=13, 7.5, 7.5 Hz, 2H); ^{13}C NMR (150.8 MHz, C_6D_6, C_6D_6 int): δ=24.67 (t, 2C), 24.96 (t, 2C), 37.08 (t, 2C), 37.67 (t, 2C), 39.36 (t, 2C), 39.60 (t, 2C), 39.91 (t, 2C), 50.43 (t, 2C), 51.84 (s, 2C), 55.61 (s, 2C), 225.55 (s); MS (EI): m/z=300 (27, M^+), 205 (100); HRMS m/z (M^+) calcd 300.2453, obsd 300.2453.

3.16.2. From *25*

Compound **25** (75 mg, 0.25 mmol) was oxidized as described for **26** (see Section 3.15) yielding 70 mg (93%) of **22** as colorless solid, mp 50–52 °C (purity >98%, GC) [column A, 230 °C; retention times (min): 5.63 (**25**), 5.89 (**22**)]. The ^{1}H and ^{13}NMR data were identical with those of authentic material.

3.17. (±)-Tetraspiro[4.1.1.1.4.2.2.2]heneicosane [(±)-10]

Compound **17** (90 mg, 0.30 mmol) was reduced as described for **16** (see Section 3.7) and the mixture of **10** and **23** (see Section 3.13) yielding 43 mg (52%) of (±)-**10** as colorless liquid (purity >98% GC) [column A, 230 °C; retention times (min): 2.41 (**10**), 5.45 (**17**), 7.17 (hydrazone)]. ^{1}H NMR (600 MHz, $CDCl_3$, $CHCl_3$ int): δ=1.40–1.48 (m, 12H), 1.50–1.57 (m, 22H); ^{13}C NMR (150.8 MHz, $CDCl_3$, $CDCl_3$

int): δ=24.22 (t), 24.28 (t), 39.11 (t), 40.85 (t), 40.87 (t), 40.90 (t), 41.13 (t), 50.29 (s), 50.32 (s), 54.45 (t), 56.04 (t); MS (EI): *m*/*z*=286 (82, M^+), 95 (100); HRMS *m*/*z* (M^+) calcd 286.2661, obsd 286.2661.

3.18. *meso*-Tetraspiro[4.1.1.1.4.2.2.2]heneicosane (*meso*-23)

Compound **22** (90 mg, 0.30 mmol) was reduced as described for **16** (see Section 3.7) and the mixture of **10** and **23** (see Section 3.13) yielding 36 mg (42%) of *meso*-**23** as colorless liquid (purity >98% GC) [column A, 230 °C; retention times (min): 2.41 (**23**), 5.38 (**22**), 7.06 (hydrazone)]. ^{1}H NMR (600 MHz, $CDCl_3$, $CHCl_3$ int): δ=1.40–1.48 (m, 12H), 1.50–1.57 (m, 22H); ^{13}C NMR (150.8 MHz, $CDCl_3$, $CDCl_3$ int): δ=24.22 (t, 2C), 24.28 (t, 2C), 39.18 (t, 2C), 40.86 (t, 2C), 40.89 (t, 2×2C) (coincidence of two lines), 41.11 (t, 2C), 50.29 (s, 2C), 50.30 (s, 2C), 54.49 (t, 2C), 55.95 (t); MS (EI): *m*/*z*=286 (52, M^+), 81 (100); HRMS *m*/*z* (M^+) calcd 286.2661, obsd 286.2661.

3.19. 2-Methylene-spiro[4.4]nonane (27)

To a suspension of methyltriphenylphosphonium bromide (69.1 g, 193 mmol) in ether (200 mL) was added under argon with stirring potassium-*tert*-butoxide (21.7 g, 193 mmol) and the mixture heated to reflux. After 1 h, **13** (17.9 g, 129 mmol) was added and after additional 30 min, the reaction was complete. The mixture was hydrolyzed with water (50 mL), the organic phase was decanted, the residue was extracted with ether (3×100 mL), and the combined organic phases were washed with water (2×200 mL) and dried ($MgSO_4$). The solution was concentrated and the residue fractionated to yield 15.2 g (86%) of **27** as colorless liquid, bp 105 °C/80 Torr. IR (neat): 3080 (=C–H), 1660 cm^{-1} (C=C); ^{1}H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): δ=1.38–1.48 (m, 4H), 1.52–1.64 (m, 6H), 2.15 (m_c, 2H), 2.33 (m_c, 2H), 4.80 (m_c, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$, $CDCl_3$ int): δ=24.63 (t, 2C), 31.66 (t), 37.93 (t, 2C), 38.57 (t), 46.30 (t), 50.49 (s), 105.12 (t), 153.00 (s); MS (EI): *m*/*z*=136 (61, M^+), 121 (100). $C_{10}H_{16}$ requires: C, 88.16; H, 11.83. Found: C, 88.44; H, 11.61.

3.20. Dispiro[3.1.4.2]dodecan-2-one (29)

Compound **29** was prepared as described for **12** (see Section 3.2); 18.8 g (138 mmol) of **27** yielded 26.0 g of crude dichloroketone (purity 92% GC) [column B, 220 °C; retention time (min): 8.79], and, after dechlorination, 17.6 g (72%) of **29** as colorless liquid, bp 131 °C/17 Torr (purity 96% GC) [column B, 210 °C; retention time (min): 4.05]. An analytically pure sample was obtained by preparative GC. IR (neat): 1780 cm^{-1} (C=O); ^{1}H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): δ=1.40–1.50 (m, 4H), 1.50–1.62 (m, 6H), 1.80 (s, 2H), 1.85 (t, *J*=7.5 Hz, 2H), 2.92 (m_c, 4H); ^{13}C NMR (50.3 MHz, $CDCl_3$, $CDCl_3$ int): δ=24.03 (t, 2C), 36.25 (s), 38.92 (t), 39.60 (t), 40.29 (t, 2C), 50.85 (s), 52.28 (t), 58.71 (t, 2C), 208.88 (s); MS (EI): *m*/*z*=178 (10, M^+), 121 (100); $C_{12}H_{18}O$ requires: C, 80.85; H, 10.18. Found: C, 81.10; H, 9.92.

3.21. Dispiro[4.1.4.2]tridecan-2-one (28)

Compound **28** was prepared as described for **13** (see Section 3.3); 10.8 g (60 mmol) **29** yielded 7.8 g (67%) **28** as colorless liquid, bp 165 °C/18 Torr (purity 90% GC) [column B, 210 °C; retention times (min): 4.05 (**29**), 6.82 (**28**)]. An analytically pure sample was obtained by preparative GC. IR (neat): 1780 cm^{-1} (C=O); ^{1}H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): δ=1.40–1.50 (m, 4H), 1.50–1.66 (m, 10H), 1.88 (t, *J*=7.5 Hz, 2H), 2.16 (s, 2H), 2.22 (t, *J*=7.5 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$, $CDCl_3$ int): δ=24.19 (t), 24.24 (t), 36.72 (t), 37.99 (t), 38.44 (t), 38.67 (t), 40.47 (t), 40.66 (t), 47.32 (s), 50.52 (s), 51.84 (t), 52.91 (t), 220.07 (s); MS (EI): *m*/*z*=192 (100, M^+); $C_{13}H_{20}O$ requires: C, 81.19; H, 10.48. Found: C, 81.52; H, 10.28.

3.22. 2-Cyclobutyliden-dispiro[4.1.4.2]tridecan-2-one (30)

Compound **30** was prepared as described for **21** (see Section 3.4); 3.60 g (18.7 mmol) **28** yielded 3.67 g (85%) crude **30** as colorless liquid (purity 90% GC) [column B, 220 °C; retention times (min): 4.34 (**30**), 5.53 (**28**)]. This material was directly used in the next step. ^{1}H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): δ=1.40–1.62 (m, 16H), 1.94 (m_c, 2H), 2.00 (m_c, 2H), 2.07 (m_c, 2H), 2.54 (m_c, 4H); ^{13}C NMR (125.7 MHz, $CDCl_3$, $CDCl_3$ int): δ=17.13 (t), 24.32 (t), 24.37 (t), 28.02 (t), 29.85 (t), 30.06 (t), 38.30 (t), 39.03 (t), 40.24 (t), 40.53 (t), 40.61 (t), 43.83 (t), 50.29 (s), 50.61 (s), 51.72 (t), 129.62 (s), 132.47 (s); MS (EI): *m*/*z*=230 (69, M^+), 201 (100). HRMS *m*/*z* (M^+) calcd 230.2035, obsd 230.2035.

3.23. *rel*-(5*R*,7*R*)-Trispiro[4.1.1.4.2.2]heptadecan-1-one [*rel*-(5*R*,7*R*)-31] and *rel*-(5*R*,7*S*)-Trispiro[4.1.1.4.2.2]heptadecan-1-one [*rel*-(5*R*,7*S*)-33]

Compound **30** (3.80 g, 16.5 mmol) was epoxidized and rearranged as described for **15** (see Section 3.5). The reactions were monitored by GC [column B, 220 °C; retention times (min): 4.35 (**30**), 13.45 (**31**/**33**), 14.82 (epoxide), 16.10 (epoxide)] and the ketones formed chromatographed on silica gel (0.05–0.20 mm) in pentane/ether [8:2, column 3.5×80 cm, R_f=0.54 (**31**/**33**)] to yield 1.53 g (38%) of a 1:1 mixture of **31** and **33** as colorless oil. The data account for the mixture. IR (neat): 1735 cm^{-1} (C=O); ^{1}H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): δ=1.35–1.70 (m, 36H), 1.70–1.90 (m, 12H), 2.05–2.30 (m, 4H); ^{13}C NMR (125.7 MHz, $CDCl_3$, $CDCl_3$ int): δ=19.48 (t), 19.50 (t), 24.25 (t), 24.27 (t), 24.31 (t), 24.34 (t), 36.35 (t), 36.44 (t), 36.83 (t), 36.93 (t), 38.92 (t), 39.16 (t), 39.22 (t), 39.49 (t), 39.57 (t), 39.68 (t), 40.46 (t), 40.47 (t), 40.64 (t) 40.65 (t) (coincidence of two lines), 40.69 (t), 50.10 (t), 50.12 (s), 50.33 (t), 50.66 (s), 51.30 (s), 51.34 (s), 52.36 (t), 53.19 (t), 55.98 (s), 56.09 (s), 223.77 (s), 223.81 (s); MS (EI): *m*/*z*=246 (26, M^+), 150 (100). HRMS *m*/*z* (M^+) calcd 246.1984, obsd 246.1984.

Supplementary data

^{1}H and ^{13}C NMR spectra of **9**, **10**, **14**–**17**, **19**–**30**, and **31**/**33**. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.12.025.

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