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Synthesis and rearrangement of [1,1′-bicyclobutyl]-1-ols and spiro[3.4]octan-5-ols: a general access to bicyclo[3.3.0]octenes (hexahydropentalenes)☆

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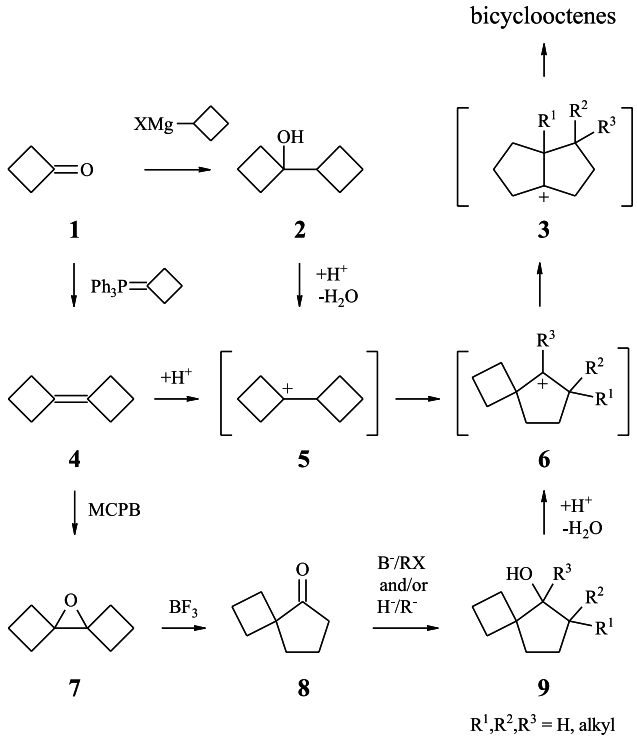
Abstract—Several new Grignard reagents based on substituted cyclobutanes have been generated and added to cyclobutanones to yield mono- to trimethylated [1,1′-bicyclobutyl]-1-ols. Mono- to trimethylated spiro[3.4]octan-5-ols have been prepared from the parent ketone via alkylation and/or addition reactions. Upon treatment with acid, all [1,1′-bicyclobutyl]-1-ols and spiro[3.4]octan-5-ols rearrange to yield a single bicyclo[3.3.0]octene.

1. Introduction

As shown for the parent compounds, the acid catalyzed rearrangement of [1,1′-bicyclobutyl]-1-ols and bicyclobutylidenes [**2**(**4**)–**5**–**6**–**3**)] is a potentially useful method for the construction of bicyclo[3.3.0]octenes.[2,3] However, any substituent to be established in the bicyclooctene must already be present in the cyclobutanone and/or the Wittig or Grignard reagent used for the synthesis of the educts required [**1**–**2**(**4**)] (Scheme 1). While cyclobutanones of greatest structural diversity are readily accessible,[4] Wittig and Grignard reagents based on substituted cyclobutanes are rare.[5,6] Therefore, substituents in that part of a bicyclooctene originating from such a reagent may be difficult to establish.

A possible resort from this dilemma is the synthesis and use of new Grignard reagents based on substituted cyclobutanes and/or a sequential transformation of a bicyclobutylidene to a bicyclooctene with intermediate introduction of substituents. In this last case the bicyclobutylidene must first be epoxidized and rearranged to give a cyclopentanone (**4**–**7**–**8**), and subsequently be modified via alkylation and/or addition reactions (**8**–**9**) such, that after a second rearrangement (**9**–**6**–**3**) the substitution pattern fits (Scheme 1). We herein report on both possibilities. In the first part, we describe the preparation of the new Grignard reagents **11a**,**b**, **12a**,**b** and **13** (Scheme 2), and their use, together with the previously described **10**,[6] for the synthesis of differently



Scheme 1.

☆ Cascade Rearrangements, Part 24. For Part 23, see Ref. 1.

Keywords: Grignard reagents; Cyclobutanes; Spiro compounds; Rearrangements; Bicyclic aliphatic compounds.

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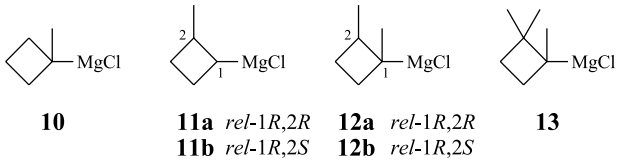


Scheme 2.

methylated [1,1′-bicyclobutyl]-1-ols. In the second part, we describe the introduction of up to three methyl groups to spiro[3.4]octan-5-one (**8**), and in the third part, we will show that acid catalyzed rearrangements of [1,1′-bicyclobutyl]-1-ols and spiro[3.4]octan-5-ols provide efficient entries to differently substituted bicyclo[3.3.0]octenes.

2. Results

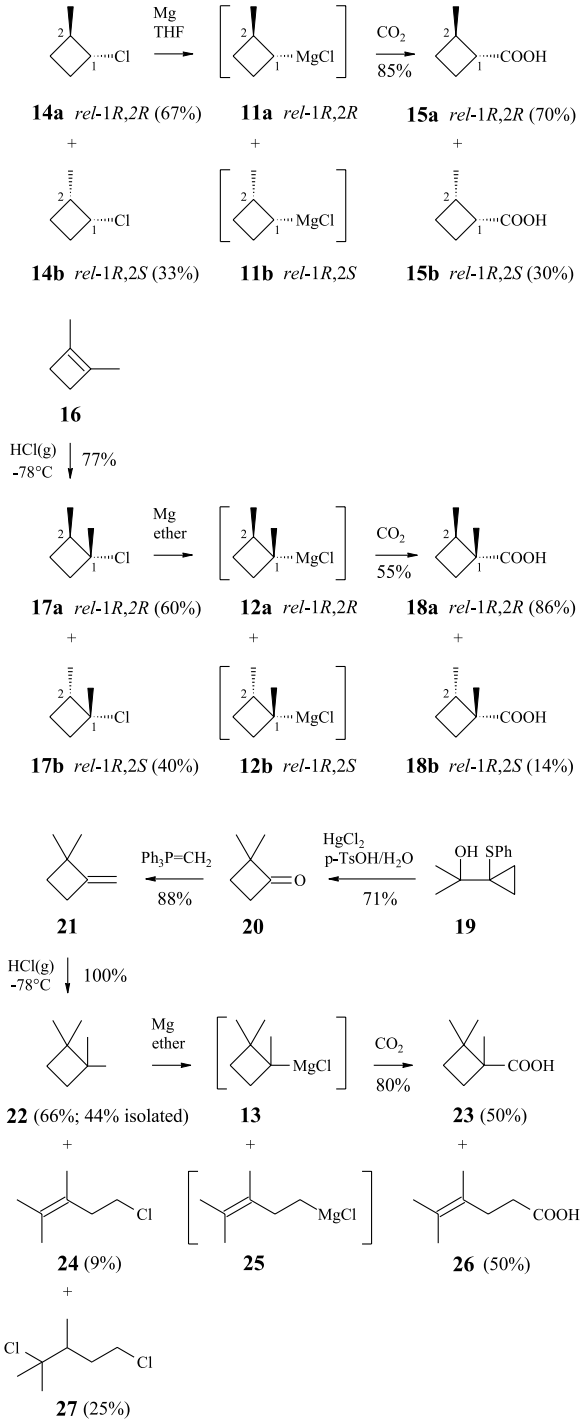
2.1. Synthesis of [1,1′-bicyclobutyl]-1-ols

For the preparation of the new Grignard reagents **11a**,**b**, **12a**,**b** and **13**, we needed the corresponding cyclobutyl chlorides **14a**,**b**, **17a**,**b** and **22**. Of these, **14a**,**b**[7] were prepared according to published procedures, while **17a**,**b**[8] and **22** were obtained by low temperature hydrochlorination of 1,2-dimethylcyclobutene (**16**)[9] and 1,1-dimethyl-2-methylene-cyclobutane (**21**), respectively. **21** was prepared by acid catalyzed rearrangement of the β-hydroxy sulfide **19**[10] to 2,2-dimethylcyclobutanone (**20**)[11] and subsequent methylenation.[12] Upon hydrochlorination, partial ring opening with formation of the homoallylic chloride **24**[13] and the dichloride **27**[14] was observed (Scheme 3).

To generate the Grignard reagents **11a**,**b**, **12a**,**b** and **13**, the corresponding cyclobutyl chlorides were reacted with magnesium in tetrahydrofurane (**14a**,**b**) and ether (**17a**,**b** and **22**), respectively. Upon carboxylation, **11a**,**b** and **12a**,**b** yielded the cyclobutane carboxylic acids **15a**,**b**[15] and **18a**,**b**, respectively, while **13** partially ring opened to **25** to give a mixture of **23**[16] and **26**[17] (Scheme 3). While the configuration of **15a**,**b** was known,[15e] the configuration of **18a**,**b** was deduced from the known γ-*gauche* effect,[18] i.e. the upfield shift of the ^{13}C NMR resonances of 1,2-*cis* oriented substituents. This technique had formerly been applied to **17a**,**b**[8] and other methylated cyclobutanes[19] and was also used to determine the configuration of the [1,1′-bicyclobutyl]-1-ols **29a**,**b** and **30a**,**b** and the spiro[3.4]octan-5-ols **34a**,**b**[20] and **38a**,**b** described below.

In practice, we first identified the methyl groups as bound to tertiary and quaternary carbon atoms, respectively, and then used the ^{13}C chemical shifts of those methyl groups showing pure 1,2-*cis* or 1,2-*trans* relationships to other groups (CH_3, COOH, *c*-C_4H_6OH, OH) as stereochemical indicators (the corresponding shifts are given in bold). In all cases, and regardless of a geminal substituent eventually present, the shift differences between the stereoisomers proved large enough to allow an unambiguous assignment (Scheme 4).

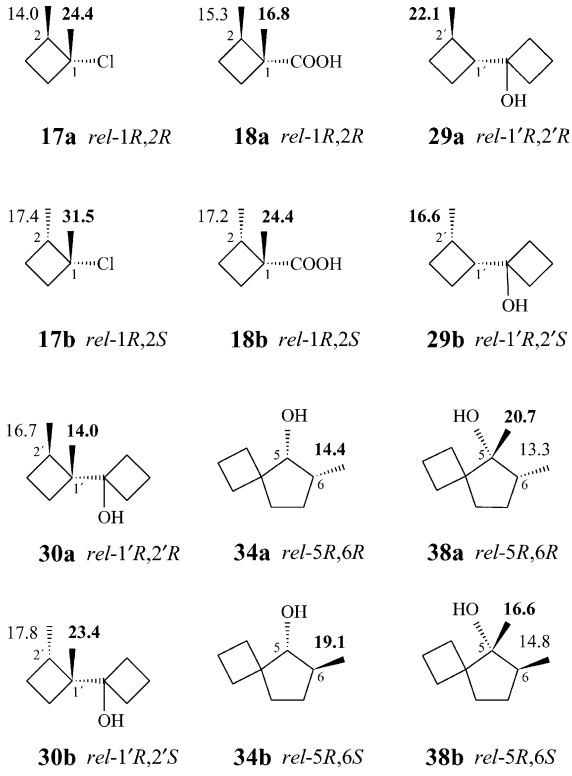
Having established the structures of the new Grignard reagents as **11a**,**b**, **12a**,**b** and **13**, we examined their usefulness for the synthesis of [1,1′-bicyclobutyl]-1-ols. This time, the Grignard reagent **10**[6] was included. Catalyzed



Scheme 3.

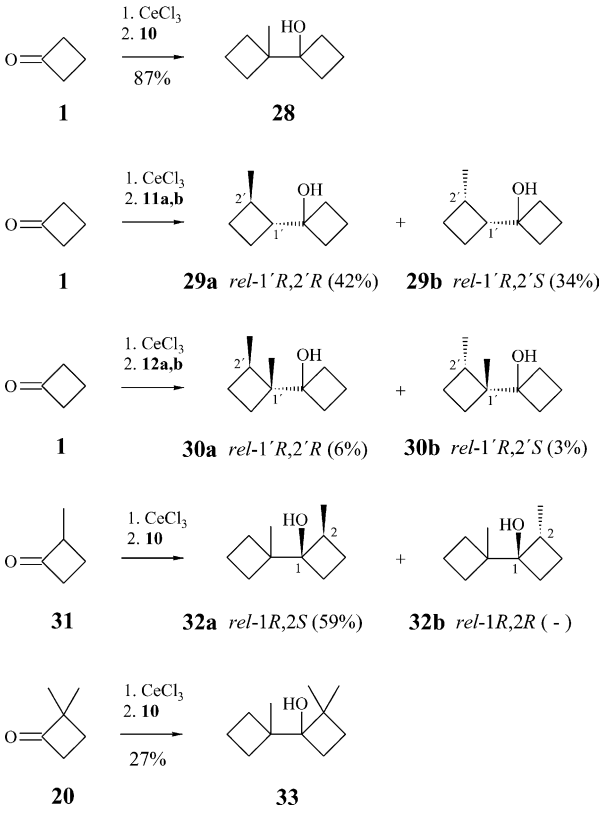
by anhydrous $CeCl_3$,[21] this reagent adds to cyclobutanone (**1**) with formation of the 1′-methyl-[1,1′-bicyclobutyl]-1-ol (**28**)[6] (Scheme 5).

Of the new Grignard reagents, **11a**,**b** and **12a**,**b** reacted with cyclobutanone (**1**) to yield the diastereoisomeric mono- and dimethylated [1,1′-bicyclobutyl]-1-ols **29a**,**b** and **30a**,**b**, respectively. On the contrary, attempted additions of **13** to **1**, and of **12a**,**b** to 2-methyl-cyclobutanone (**31**)[22] failed. However, **10**[6] reacted with **31** to give a single dimethylated [1,1′-bicyclobutyl]-1-ol, thought to be **32a**,[23] and with 2,2-dimethylcyclobutanone (**20**) to give the trimethylated



Scheme 4.

[1,1′-bicyclobutyl]-1-ol **33** (Scheme 5). The stereochemistry of **29a**,**b** and **30a**,**b** was determined as detailed above, and the results are given in Scheme 4. From a preparative point of view, the yields of **30a**,**b** and **33** are unsatisfactory.

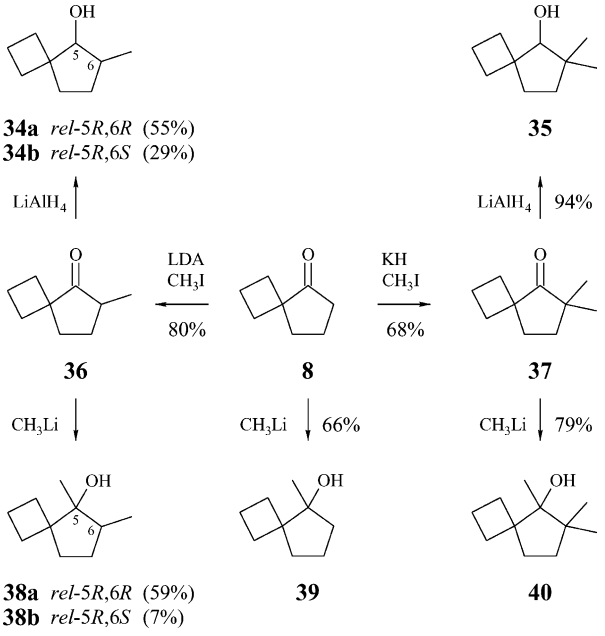


Scheme 5.

Obviously, steric hindrance in the Grignard reagent and/or the cyclobutanone employed is the principal factor that impedes or prevents an addition.

2.2. Synthesis of spiro[3.4]octan-5-ols

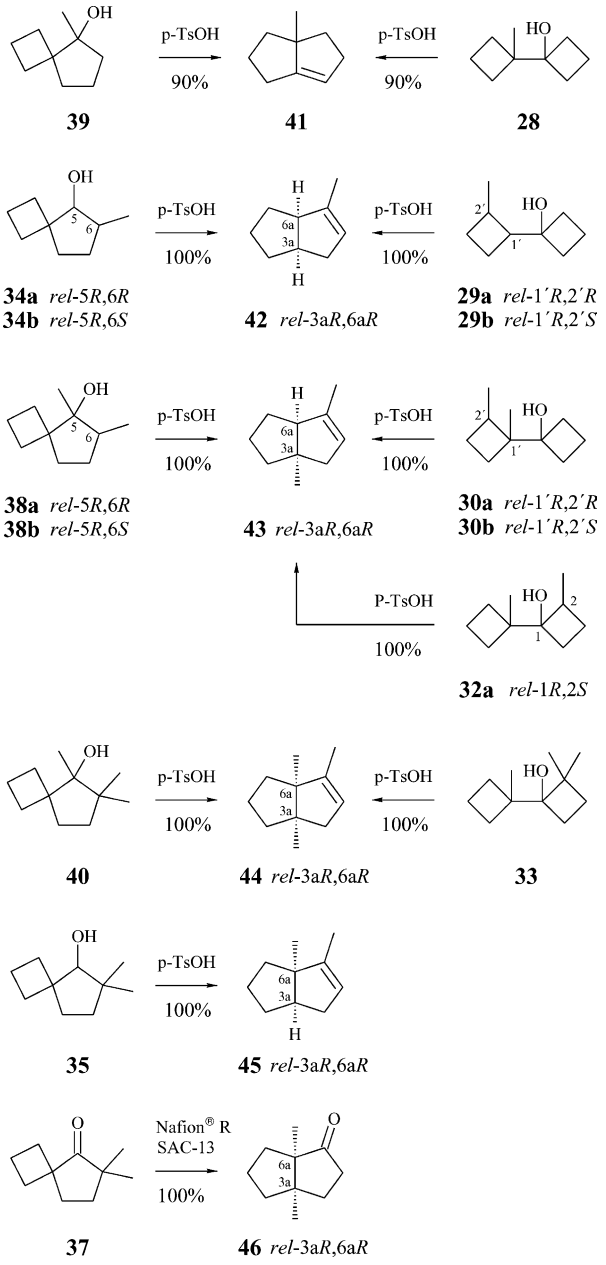
As described earlier,[24] epoxidation of bicyclobutylidene (**4**) and in situ rearrangement of the resulting oxaspirohexane **7** is a productive route to spiro[3.4]octan-5-one (**8**). In this case, the introduction of up to three methyl groups was easy to achieve: mono- and dimethylation, respectively, yielded the ketones **36** and **37**, and subsequent reduction with lithium aluminium hydride and addition of methyllithium, respectively, yielded the secondary alcohols **34a**,**b** and **35**, and the tertiary alcohols **38a**,**b** and **40**. The last reaction was also performed with **8** and yielded the tertiary alcohol **39** (Scheme 6). As with **18a**,**b**, **29a**,**b** and **30a**,**b**, the stereochemistry of **34a**,**b**[20] and **38a**,**b** resulted from an analysis of their ^{13}C methyl shifts (Scheme 4).



Scheme 6.

2.3. Rearrangements

Upon treatment with an equimolar amount of a 0.074 mol solution of anhydrous *p*-toluenesulfonic acid in benzene at 70 °C, all [1,1′-bicyclobutyl]-1-ols and all spiro[3.4]octan-5-ols underwent clear-cut rearrangements to yield a single bicyclo[3.3.0]octene. All stereoisomers were rearranged separately. The results were as follows: of the monomethylated alcohols, **39** rearranged to **41**, previously obtained from **28**,[6] and **34a** and **34b** rearranged to **42**,[25] which was also formed from **29a** and **29b**. Of the dimethylated alcohols, **35** rearranged to **45**, and **38a** and **38b** rearranged to **43**,[26] which was also formed from **30a**, **30b** and **32a**. The trimethylated alcohols **33** and **40** rearranged to **44**, and the dimethylated ketone **37** underwent a ketone to ketone rearrangement to yield **46**[27] (Scheme 7). Of the products formed, **41**,[6] **42**[25a–c,e] and **43**[26a,c] were identified by their known ^{1}H and/or ^{13}C NMR data, while the structures of **44**,

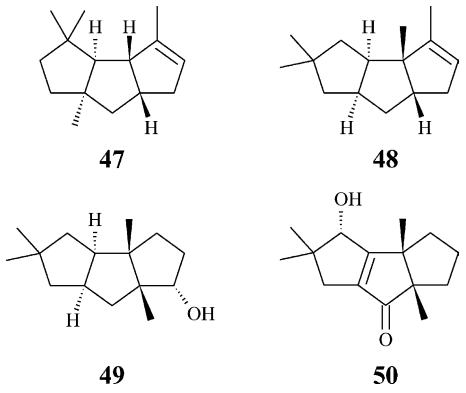


Scheme 7.

45 and **46** followed from their ^{1}H and ^{13}C NMR spectra together with APT, HETCOR and COSY measurements.

Mechanistically, all rearrangements benefit from the pronounced relief of strain associated with cyclobutylmethyl to cyclopentyl rearrangements.[28] Once a bicycloctyl cation has been formed, 1,2-methyl- and/or 1,2-hydride shifts with eventual intermediate deprotonations and reprotonations occur until the thermodynamically most stable bicyclooctene is formed. During this process, only energetically favoured tertiary cations are involved. For the mechanism of the rearrangement of **37**, we refer to a closely related example.[24]

From a synthetic point of view it is interesting to note that **42**, **45** and **46** represent partial structures of the linear triquinanes *endo*-hirsutene (**47**),[29] *endo*-capnellene (**48**)[30]



Scheme 8.

and both ceratopicanol (**49**)[31] and cucumin-H (**50**),[27,32] respectively (Scheme 8). While examples for successful syntheses of angular triquinanes via cyclobutylmethyl to cyclopentyl rearrangements are known,[33] their potential for a synthesis of linear triquinanes remains to be explored.

In summary, we describe the synthesis and rearrangement of mono- to trimethylated [1,1′-bicyclobutyl]-1-ols and spiro[3.4]octan-5-ols to yield a single bicyclo[3.3.0]octene in all cases. To note, that stereoisomeric educts yield the same product and hence mixtures of stereoisomers may be employed. With regard to the short and productive syntheses of the educts required, we recommend the route over spiro[3.4]octan-5-ols.

3. Experimental

3.1. General

IR spectra were obtained with a Perkin–Elmer 457 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR 200 or a Bruker AMX 300 spectrometer. For standards other than TMS 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 APT and/or DEPT measurements. Mass spectra were obtained with a Finnigan MAT 95 spectrometer (EI, CI and HREI) 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 101 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. Colourless substances were detected by oxidation with 3.5% alcoholic 12-molybdophosphoric acid (Merck) 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. For the preparation of anhydrous $CeCl_3$, finely powdered $CeCl_3 \cdot 7H_2O$ was heated at 140 °C/0.1 Torr to constant weight. Nafion® R SAC-13 was purchased from

Aldrich Chemical Company, Inc. Some of the stereoisomers could also have been described using the *cis*/*trans* convention. However, in view of a consistent notation, the *R*,*S* convention was used throughout.

3.1.1. *rel*-(1*R*,2*R*)-1-Chloro-1,2-dimethyl-cyclobutane (17a) and *rel*-(1*R*,2*S*)-1-chloro-1,2-dimethyl-cyclobutane (17b)

At −78 °C, hydrogen chloride was bubbled through a solution of 1,2-dimethyl-cyclobutene (**16**)[9] (5.88 g, 72 mmol) in pentane (2 ml) until GC analysis [column A, 7 min 50 °C, 20 °C/min to 140 °C; retention times: 2.69 (**16**), 8.21 (**17a**), 8.53 (**17b**)] indicated that the addition was complete (1.5 h). The solution was diluted with pentane (20 ml), washed with water (20 ml), saturated sodium bicarbonate (2×25 ml) and dried ($MgSO_4$). Fractional distillation yielded 5.91 g (77%) of a 60:40 mixture of **17a** and **17b** as colourless liquid, bp 73–76 °C/140 Torr. The ^1H and ^{13}C NMR data were in accord with literature data.[8]

3.1.2. 2,2-Dimethyl-cyclobutanone (20)

To a solution of the β-hydroxy sulfide **19**[10] (24.8 g, 120 mmol) in tetralin (40 ml) was added $HgCl_2$ (19.0 g, 70 mmol), water (2.48 g, 140 mmol) and *p*-toluenesulfonic acid monohydrate (2.51 g, 10 mmol) and the mixture heated to 70 °C. After 2 h, more water (3.72 g, 210 mmol) was added, the temperature was raised to 140 °C and the distillate collected. The phases were separated and the aqueous phase was saturated with sodium chloride and extracted with dichloromethane (2×10 ml). The combined organic phases were dried ($MgSO_4$) and fractionated over a 10 cm Vigreux column to yield 8.5 g (72%) of **20** as colourless liquid, bp 106–110 °C (lit.[11a] bp 108 °C). The ^1H[11b] and ^{13}C NMR data[34] were in accord with literature data.

3.1.3. 1,1-Dimethyl-2-methylene-cyclobutane (21)

To a suspension of methyltriphenylphosphonium bromide (37.5 g, 105 mmol) in dry xylene (100 ml) was added under nitrogen with stirring sodium hydride (2.52 g, 105 mmol) and the mixture heated to 90 °C. After 3.5 h, the mixture was cooled to 45 °C, 2,2-dimethyl-cyclobutanone (**20**) (8.5 g, 87 mmol) was added slowly, and after additional 3 h at 60 °C direct distillation over a 30 cm Vigreux column yielded 6.66 g (88%) of pure **21** as colourless liquid, bp 83–90 °C (lit.[12] bp 80–95 °C). The ^1H NMR data were in accord with literature data.[12] The ^{13}C NMR data have not yet been reported and were as follows: ^{13}C NMR (50 MHz, $CDCl_3$, $CDCl_3$ int): $\delta=26.62$ (t), 27.44 (q), 31.97 (t), 44.20 (s), 101.58 (t), 160.24 (s).

3.1.4. 1-Chloro-1,2,2-trimethyl-cyclobutane (22), 5-chloro-2,3-dimethyl-pent-2-ene (24) and 1,4-dichloro-3,4-dimethyl-pentane (27)

At −78 °C, hydrogen chloride was bubbled through a solution of 1,1-dimethyl-2-methylene-cyclobutane (**21**) (6.66 g, 69 mmol) in pentane (2 ml) until GC analysis [column A, 5 min 100 °C, 20 °C/min to 190 °C; retention times (min): 1.22 (**21**), 3.38 (**22**) (66%), 5.76 (**24**) (9%), 9.17 (**27**) (25%)] indicated that the addition was complete (3 h). The solution was diluted with pentane (20 ml), washed with water (2×20 ml), saturated sodium bicarbonate (3×20 ml) and dried ($MgSO_4$). Fractional distillation yielded 4.03 g (44%) of **22** as colourless liquid, bp 95–105 °C/180 Torr, which solidified on cooling; mp 27–30 °C. Preparative GC of the remaining material delivered pure samples of **24** and **27** as colourless liquids. **22**: ^1H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): $\delta=0.99$ (s, 3H), 1.24 (s, 3H), 1.60 (ddd, $J=10.5, 10.5, 9$ Hz, 1H), 1.61 (s, 3H), 1.73 (ddd, $J=10.5, 10.5, 3$ Hz, 1H), 2.08 (ddd, $J=12, 9, 3$ Hz, 1H), 2.44 (ddd, $J=12, 10.5, 10.5$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, $CDCl_3$ int): $\delta=23.36$ (q), 26.90 (q), 27.38 (q), 30.45 (t), 36.25 (t), 44.72 (s), 72.99 (s); MS (EI): $m/e=56$ (100). $C_7H_{13}Cl$ requires C, 63.39; H, 9.88. Found: C, 63.15; H, 9.84. **24**: ^1H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): $\delta=1.66$ (s, 6H), 1.68 (s, 3H), 2.48 (symm m, 2H), 3.46 (symm m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, $CDCl_3$ int): $\delta=18.35$ (q), 20.26 (q), 20.61 (q), 37.99 (t), 42.82 (t), 123.64 (s), 127.88 (s); MS (EI): $m/e=132$ (30, M^+), 83 (100). $C_7H_{13}Cl$ requires C, 63.39; H, 9.88. Found: 61.70; H, 9.62. **27**: The ^1H NMR data were in accord with literature data.[14] The ^{13}C NMR data have not yet been reported and were as follows: ^{13}C NMR (50 MHz, $CDCl_3$, $CDCl_3$ int): $\delta=14.50$ (q), 30.04 (q), 30.86 (q), 35.11 (t), 42.68 (d), 43.63 (t), 74.48 (s).

3.1.5. Carboxylation of the Grignard reagents 11a,b, 12a,b and 13 generated from 14a,b, 17a,b and 22

Mg turnings (304 mg, 12.5 mmol) were covered with ether (**14a**,**b**: THF) (1.5 ml), a solution of the appropriate cyclobutyl chloride(s) (10.0 mmol) in ether (**14a**,**b**: THF) (0.5 ml) and a drop of Br_2 were added under argon with stirring, and the reaction was started by gentle to strong heating until additional ether (**14a**,**b**: THF) (10 ml) was added and the mixture was heated to reflux. After 2 h (**14a**,**b**: 3 h), GC analysis on column A [retention times (min): 2.01 (**14b**) and 2.51 (**14a**) at 90 °C; 2.64 (**17b**) and 2.82 (**17a**) at 90 °C; 3.38 (**22**) at 100 °C] indicated that the cyclobutyl chloride(s) had been consumed. The solution was cooled to 0 °C and a stream of dry carbon dioxide was passed through. After 2 h, the mixture was hydrolyzed with 0.5 N HCl (20 ml), and the aqueous phase was adjusted to pH 1 and extracted with ether (7×20 ml). The combined organic phases were dried ($MgSO_4$), and most of the solvent was distilled off over a 20 cm Vigreux column. Final concentration on a rotary evaporator (bath temperature 20 °C/14 Torr) yielded the cyclobutanecarboxylic acids. Pure samples were obtained by preparative GC on column B.

3.1.5.1. *rel*-(1*R*,2*R*)-2-Methyl-cyclobutanecarboxylic acid (15a) and rel-(1*R*,2*S*)-2-methyl-cyclobutanecarboxylic acid (15b). Yield 970 mg (85%) of a 70:30 mixture of **15a** and **15b**. Pure samples were obtained by preparative GC [column B, 160 °C; retention times (min): 4.90 (**15b**), 5.70 (**15a**)]. Colourless liquids. The ^1H and ^{13}C NMR data were in accord with literature data.[15e]

3.1.5.2. *rel*-(1*R*,2*R*)-1,2-Dimethyl-cyclobutanecarboxylic acid (18a) and *rel*-(1*R*,2*S*)-1,2-dimethyl-cyclobutanecarboxylic acid (18b). Yield 705 mg (55%) of a 86:14 mixture of **18a** and **18b**. Pure samples were obtained by preparative

GC [column B, 175 °C; retention times (min): 3.08 (**18b**), 3.61 (**18a**)]. Colourless liquids. **18a**: ^{1}H NMR (200 MHz, $CDCl_3$, $CHCl_3$ int): $\delta=0.97$ (d, $J=7$ Hz, 3H), 1.27 (s, 3H), 1.45–1.70 (m, 2H), 1.85–2.05 (m, 1H), 2.24–2.45 (m, 1H), 2.72 (symm m, 1H), 10.7–11.7 (br s, 1H, COO*H*); ^{13}C NMR (50 MHz, $CDCl_3$, $CDCl_3$ int): $\delta=15.28$ (q), 16.83 (q), 23.92 (t), 28.63 (t), 35.86 (d), 45.39 (s), 184.49 (s); MS (EI): *m/e*=128 (7, M^+), 87 (100). $C_7H_{12}O_2$ requires C, 65.60; H, 9.44. Found: C, 65.56; H, 9.62. **18b**: ^{1}H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): $\delta=1.06$ (d, $J=7$ Hz, 3H), 1.38 (s, 3H), 1.50–1.72 (m, 2H), 2.00–2.15 (m, 1H), 2.20–2.37 (m, 1H), 2.45–2.58 (m, 1H), COO*H* not detected; ^{13}C NMR (75 MHz, $CDCl_3$, $CDCl_3$ int): $\delta=17.15$ (q), 23.66 (t), 24.39 (q), 27.36 (t), 40.68 (d), 47.55 (s), 182.66 (s); MS (EI): *m/e*=128 (8, M^+), 87 (100). $C_7H_{12}O_2$ requires C, 65.60; H, 9.44. Found: C, 65.25; H, 9.70.

3.1.5.3. 1,2,2-Trimethyl-cyclobutanecarboxylic acid (23) and 4,5-dimethyl-hex-4-enoic acid (26). Yield 1.14 g (80%) of a 1:1-mixture of **23** and **26**. Pure samples were obtained by preparative GC [column B, 6 min 180 °C, 20 °C/min to 220 °C; retention times (min): 4.68 (**23**), 8.85 (**26**)]. **23**: colourless solid, mp 115–117 °C. ^{1}H NMR (200 MHz, $CDCl_3$, $CHCl_3$ int): $\delta=1.03$ (s, 3H), 1.12 (s, 3H), 1.33 (s, 3H), 1.44–1.54 (m, 2H), 1.75 (ddd, $J=$ 10, 10, 9 Hz, 1H), 2.50 (ddd, $J=10$, 10, 9 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$, $CDCl_3$ int): $\delta=19.90$ (q), 23.85 (q), 25.40 (t), 25.53 (q), 30.07 (t), 40.51 (s), 48.58 (s), 182.83 (s); MS (EI): *m/e*=142 (4, M^+), 56 (100). $C_8H_{14}O_2$ requires C, 67.35; H, 9.92. Found: C, 67.35; H, 9.77. **26**: colourless liquid.[17] Spectral data have not yet been reported and were as follows: ^{1}H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): $\delta=$ 1.63 (s, 6H), 1.65 (s, 3H), 2.36 (s, 4H); ^{13}C NMR (50 MHz, $CDCl_3$, $CDCl_3$ int): $\delta=17.98$ (q), 20.08 (q), 20.63 (q), 29.60 (t), 32.87 (t), 125.34 (s), 125.94 (s), 180.14 (s); MS (EI): *m/e*=142 (98, M^+), 83 (100).

3.1.6. Synthesis of the [1,1′-bicyclobutyl]-1-ols 29a,b, 30a,b, 32a and 33

A suspension of finely powdered dry $CeCl_3$ (4.93 g, 20 mmol) in THF (85 ml) was stirred under argon overnight. After addition of the appropriate cyclobutanone (10 mmol), stirring was continued for 2 h until the mixture was cooled to −78 °C and the appropriate Grignard reagent (15 mmol) was added. After 15 min at −78 °C and 4 h at room temperature the mixture was hydrolyzed with 2 N HCl (50 ml). The aqueous phase was extracted with ether (4×40 ml), and the combined organic phases were washed with saturated sodium bicarbonate (60 ml), brine (60 ml) and dried ($MgSO_4$). The solvents were distilled off on a rotary evaporator (bath temperature 20 °C/14 Torr) and the residue was chromatographed on silica gel (0.05–0.20 mm) in pentane/ether 3:1 (**32a**) and 5:1 (**29a**,**b**, **30a**,**b**, **33**) respectively.

3.1.6.1. *rel*-(1′*R*,2′*R*)-2′-Methyl-[1,1′-bicyclobutyl]-1-ol (29a) and *rel*-(1′*R*,2′*S*)-2′-methyl-[1,1′-bicyclobutyl]-1-ol (29b). Yield 297 mg (42%) **29a** and 237 mg (34%) **29b**; R_f 0.14 (**29a**) and 0.23 (**29b**). Colourless liquids. **29a**: ^{1}H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): $\delta=1.07$ (d, $J=7$ Hz, 3H), 1.30–1.55 (m, 2H), 1.60 (s, 1H, OH), 1.55–2.16 (m, 9H), 2.16–2.30 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$, $CDCl_3$ int): $\delta=11.96$ (t), 18.69 (t), 22.06 (q), 25.74 (t), 31.47 (d), 33.82 (t), 34.08 (t), 50.72 (d), 75.87 (s); MS (CI): *m/e*=140 (100, $M+NH_4-H_2O]^+$). $C_9H_{16}O$ requires C, 77.09; H, 11.50. Found: C, 77.15; H, 11.33. **29b**: ^{1}H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): $\delta=1.07$ (d, $J=7$ Hz, 3H), 1.40–1.60 (m, 2H), 1.72 (br s, 1H, OH), 1.70–1.85 (m, 1H), 1.85–2.06 (m, 6H), 2.06–2.18 (m, 1H), 2.46–2.52 (m, 2H); ^{13}C NMR (50 MHz, C_6D_6, C_6D_6 int): $\delta=12.85$ (t), 17.00 (q), 20.04 (t), 26.80 (t), 32.63 (d), 36.03 (t), 36.41 (t), 44.20 (d), 76.37 (s, hidden in $CDCl_3$); MS (CI): *m/e*=140 (93, $M+NH_4-H_2O]^+$), 123 (100). $C_9H_{16}O$ requires C, 77.09; H, 11.50. Found: C, 77.05; H, 11.29.

3.1.6.2. *rel*-(1′*R*,2′*R*)-1′,2′-Dimethyl-[1,1′-bicyclobutyl]-1-ol (30a) and *rel*-(1′*R*,2′*S*)-1′,2′-dimethyl-[1,1′-bicyclobutyl]-1-ol (30b). Yield 90 mg (6%) **30a** and 50 mg (3%) **30b**; R_f 0.22 (**30a**) and 0.29 (**30b**). Colourless liquids. **30a**: ^{1}H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): $\delta=0.92$ (d, $J=$ 7 Hz, 3H), 1.00 (s, 3H), 1.30–1.56 (m, 3H), 1.46 (s, 1H, OH), 1.76–1.94 (m, 5H), 2.16–2.42 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, $CDCl_3$ int): $\delta=12.37$ (t), 14.01 (q), 16.67 (q), 23.64 (t), 26.28 (t), 31.56 (t), 31.58 (t), 31.76 (d), 45.14 (s), 80.85 (s); MS (EI): *m/e*=154 (1, M^+), 84 (100). HRMS *m/e* (M^+) calcd 154.1358, obsd 154.1357. **30b**: ^{1}H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): $\delta=1.03$ (s, 3H), 1.04 (d, $J=$ 7 Hz, 3H), 1.30–1.45 (m, 1H), 1.50–1.85 (m, 5H), 1.90–2.20 (m, 5H), 2.55–2.67 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, $CDCl_3$ int): $\delta=14.78$ (t), 17.77 (q), 23.26 (q), 23.62 (t), 27.92 (t), 32.29 (t), 33.52 (t), 39.35 (d), 45.30 (s), 81.58 (s); MS (EI): *m/e*=154 (2, M^+), 84 (100). HRMS *m/z* (M^+) calcd 154.1358, obsd 154.1357.

3.1.6.3. *rel*-(1*R*,2*S*)-1′,2-Dimethyl-[1,1′-bicyclobutyl]-1-ol (32a). Yield 841 mg (59%); R_f 0.24. Colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): $\delta=1.00$ (d, $J=$ 7 Hz, 3H), 1.07 (s, 3H), 1.42 (br s, 1H, OH), 1.45–1.57 (m, 3H), 1.60–2.20 (m, 7H), 2.40 (symm m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, $CDCl_3$ int): $\delta=14.09$ (t), 15.37 (q), 21.36 (q), 22.40 (t), 28.27 (t), 28.43 (t), 28.47 (t), 33.57 (d), 43.76 (s), 80.99 (s); MS (EI): *m/e*=154 (60, M^+), 137 (100). $C_{10}H_{18}O$ requires C, 77.87; H, 11.76. Found: C, 78.15; H, 11.81.

3.1.6.4. 1′,2,2-Trimethyl-[1,1′-bicyclobutyl]-1-ol (33). Yield 460 mg (27%); R_f 0.32. Colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): $\delta=0.98$ (s, 3H), 1.02 (s, 3H), 1.19 (s, 3H), 1.40 (s, 1H, OH), 1.30–1.48 (m, 2H), 1.53–2.04 (m, 6H), 2.30 (symm m, 1H), 2.40 (symm m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$, $CDCl_3$ int): $\delta=15.32$ (t), 20.82 (q), 24.47 (q), 24.99 (q), 27.37 (t), 29.35 (t), 30.00 (t), 31.52 (t), 43.00 (s), 44.24 (s), 82.96 (s); MS (EI): *m/e*=168 (16, M^+), 151 (100). $C_{11}H_{20}O$ requires C, 78.77; H, 12.01. Found: C, 78.51; H, 11.98.

3.1.7. 6-Methyl-spiro[3.4]octan-5-one (36)

To a solution of diisopropylamine (8.1 g, 80 mmol) in THF (160 ml) was added at 5–10 °C under nitrogen with stirring a 1.6 M solution of n-butyllithium in hexane (50 ml, 80 mmol) followed by neat **8**[24] (9.9 g, 80 mmol). The mixture was stirred for 0.5 h at room temperature, until it was cooled to −78 °C and methyl iodide (56.8 g, 400 mmol) was added. Afterwards, the mixture was held

at −25 °C until GC analysis [column A, 110 °C; retention times (min): 9.19 (**8**) (8%), 11.94 (**36**) (89%), 12.93 (**37**) (3%)] indicated that the reaction was complete (2.5 h). The mixture was hydrolyzed with sat NH_4Cl (20 ml), the organic phase was decanted, the residue was extracted with pentane (3×75 ml), and the combined organic phases were concentrated by distillation over a 30 cm Vigreux column. The residue was diluted with pentane (20 ml) and extracted with 1 N HCl (10 ml). The organic phase was washed with water (2×10 ml), dried ($MgSO_4$) and distilled to yield 8.8 g (80%) of **36** as colourless liquid, bp 85–87 °C/30 Torr. IR (neat): 1730 cm^{-1} (C═O); ^1H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): $\delta=1.06$ (d, $J=7$ Hz, 3H), 1.25–1.40 (m, 1H), 1.70–1.85 (m, 3H), 1.85–2.00 (m, 2H), 2.00–2.20 (m, 4H), 2.30 (symm m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$, $CDCl_3$ int): $\delta=15.27$ (q), 15.78 (t), 27.97 (t), 28.66 (t), 32.11(t), 35.04 (t), 42.93 (d), 50.70 (s), 222.98 (s); MS (EI): $m/e=$ 138 (61, M^+), 67 (100). $C_9H_{14}O$ requires C, 78.21; H, 10.21. Found: C, 78.44; H, 10.48.

3.1.8. 6,6-Dimethyl-spiro[3.4]octan-5-one (37)

To a suspension of potassium hydride (3.48 g, 87 mmol) in ether (100 ml) was added at 0 °C under argon **8**[24] (3.61 g, 29 mmol). After the hydrogen evolution had ceased (30 min), methyl iodide (12.4 g, 87 mol) was added and the reaction progress monitored by GC [column A, 130 °C; retention times (min): 4.97 (**8**), 6.08 (**36**), 6.62 (**37**)]. After 45 min at 0 °C the reaction was complete. The mixture was hydrolyzed with sat NH_4Cl (5 ml), the organic phase was decanted, the residue was extracted with ether (2×20 ml), and the combined organic phases were dried ($MgSO_4$) and distilled to yield 3.00 g (68%) of **37** as colourless liquid, bp 55 °C/5 Torr. IR (neat): 1730 cm^{-1} (C═O); ^1H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): $\delta=0.97$ (s, 6H), 1.64 (t, $J=$ 7 Hz, 2H), 1.72–1.85 (m, 2H), 1.85–2.00 (m, 2H) 1.95 (t, $J=7$ Hz, 2H), 2.17–2.30 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$, $CDCl_3$ int): $\delta=15.86$ (t), 24.61 (q), 30.58 (t), 33.42 (t), 34.73 (t), 44.45 (s), 50.75 (s), 224.44 (s); MS (EI): $m/e=$ 152 (68, M^+), 68 (100). $C_{10}H_{16}O$ requires C, 78.89; H, 10.59. Found: C, 79.16; H, 10.59.

3.1.9. Addition of methyllithium to 8, 36 and 37

To a 0.5 M solution of methyllithium in ether were added at 0 °C under argon with stirring within 10 min 0.5 equiv of a 0.5 M solution of the selected ketone in ether. After additional 15 min at 0 °C, GC analysis indicated that the reaction was complete. The mixture was hydrolyzed with sat NH_4Cl, and the organic phase was separated and dried ($MgSO_4$). The solvent was distilled off on a rotary evaporator (bath temperature 20 °C/15 Torr), and the residue was chromatographed on silica gel (0.05–0.20 mm) in pentane/ether (8:2; column 30×3.5 cm).

3.1.9.1. *rel*-(5*R*,6*R*)-5,6-Dimethyl-spiro[3.4]octan-5-ol (38a) and *rel*-(5*R*,6*S*)-5,6-dimethyl-spiro[3.4]octan-5-ol (38b). From **36** (490 mg, 3.5 mmol); retention times (min): 4.59 (**36**), 8.25 (**38a**), 9.81 (**38b**) at 140 °C on column B; $R_f=0.79$ (**36**), 0.33 (**38a**), 0.28 (**38b**). Yield: 317 mg (59%) of pure **38a**, 137 mg (25%) of a 4:1 mixture of **38a** and **38b**, and 37 mg (7%) of pure **38b**. Colourless liquids. **38a**: ^1H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): $\delta=0.91$ (d, $J=7$ Hz, 3H), 1.18 (s, 3H), 1.20–1.30 (m, 1H), 1.50–1.95 (m, 10H), 2.10 (symm m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$, $CDCl_3$ int): $\delta=13.26$ (q), 15.18 (t), 20.70 (q), 26.34 (t), 28.63 (t), 31.77 (t), 36.57 (t), 40.86 (d), 52.79 (s), 81.19 (s); MS (EI): $m/e=154$ (18, M^+), 111 (100). $C_{10}H_{18}O$ requires C, 77.87; H, 11.76. Found: C, 76.97; H, 11.76. **38b**: ^1H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): $\delta=0.88$ (d, $J=7$ Hz, 3H), 0.90 (s, 3H), 1.05 (symm m, 1H), 1.22 (br s, 1H), 1.45–2.20 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$, $CDCl_3$ int): $\delta=14.79$ (q), 15.19 (t), 16.60 (q), 27.45 (t), 27.55 (t), 28.47 (t), 34.68 (t), 41.25 (d), 52.23 (s), 80.37 (s); MS (EI): $m/e=154$ (13, M^+), 111 (100). $C_{10}H_{18}O$ requires C, 77.87; H, 11.76. Found: C, 77.72; H, 11.77.

3.1.9.2. 5-Methyl-spiro[3.4]octan-5-ol (39). From **8**[24] (1.00 g, 8.05 mmol); retention times (min): 1.95 (**8**), 2.33 (**39**) at 150 °C on column A; $R_f=0.21$ (**39**). Yield: 740 mg (66%) of pure **39** as colourless liquid. ^1H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): $\delta=1.21$ (s, 3H), 1.36 (br s, 1H), 1.45–2.30 (m, 12H); ^{13}C NMR (50 MHz, $CDCl_3$, $CDCl_3$ int): $\delta=$ 14.98 (t), 16.72 (t), 22.59 (q), 26.18 (t), 29.10 (t), 37.00 (t), 37.66 (t), 52.03 (s), 80.31 (s); MS (EI): $m/e=140$ (6, M^+), 97 (100). $C_9H_{16}O$ requires C, 77.09; H, 11.50. Found: C, 76.95; H, 11.37.

3.1.9.3. 5,6,6-Trimethyl-spiro[3.4]octan-5-ol (40). From **37** (460 mg, 3.0 mmol); retention times (min): 2.38 (**37**), 4.16 (**40**) at 150 °C on column A; $R_f=0.35$ (**40**). Yield: 399 mg (79%) of pure **40** as colourless oil. ^1H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): $\delta=0.78$ (s, 3H), 0.92 (s, 3H), 1.06 (s, 3H), 1.14 (s, 1H), 1.40 (symm m, 1H), 1.50–1.70 (m, 4H), 1.82–2.07 (m, 3H), 2.07–2.22 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$, $CDCl_3$ int): $\delta=15.75$ (t), 18.23 (q), 23.46 (q), 26.09 (q), 29.89 (t), 33.90 (t), 36.70 (t), 37.10 (t), 44.84 (s), 52.92 (s), 83.08 (s); MS (EI): $m/e=168$ (7, M^+), 97 (100). $C_{11}H_{20}O$ requires C, 78.75; H, 11.98. Found: C, 78.76; H, 11.89.

3.1.10. Reduction of 36 and 37

To a suspension of $LiAlH_4$ (607 mg, 16.0 mmol) in ether (32 ml) was added under argon with stirring a solution of the selected ketone (8.0 mmol) in ether (8 ml) and the mixture heated to reflux until GC analysis indicated that the reaction was complete (1 h). Water (0.6 ml), 15% aqueous NaOH (0.6 ml) and water (1.8 ml) were added, the liquid was decanted and the residue was extracted with ether (2×20 ml). The combined organic layers were concentrated on a rotary evaporator (bath temperature 20 °C/15 Torr) and the residue chromatographed on silica gel (0.05–0.20 mm) in pentane/ether (8:2; column 60×2 cm).

3.1.10.1. *rel*-(5*R*,6*R*)-6-Methyl-spiro[3.4]octan-5-ol (34a) and *rel*-(5*R*,6*S*)-6-methyl-spiro[3.4]octan-5-ol (34b). From **36** (1.11 g, 8.0 mmol); retention times (min) 6.90 (**36**), 7.78 (**34a**,**b**) at 130 °C on column A; $R_f=0.34$ (**34a**), 0.25 (**34b**). Yield 620 mg (55%) of pure **34a**, 100 mg (9%) of a 1:1 mixture of **34a** and **34b**, and 320 mg (29%) of pure **34b** as colourless liquids. **34a**: ^1H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): $\delta=0.98$ (d, $J=7$ Hz, 3H), 1.18–1.36 (m, 2H), 1.65–1.90 (m, 8H), 1.98 (symm m, 1H), 2.10–2.20 (m, 1H), 3.65 (d, $J=4$ Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$, $CDCl_3$ int): $\delta=14.39$ (q), 15.80 (t), 26.97 (t), 29.20 (t), 33.99 (t),

36.00 (t), 36.19 (d), 50.75 (s), 82.19 (d); MS (EI): $m/e=140$ (3, M^+), 97 (100). $C_9H_{16}O$ requires C, 77.09; H, 11.50. Found: C, 76.99; H, 11.40. **34b**: ^1H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): $\delta=1.00$ (d, $J=7$ Hz, 3H), 1.02–1.10 (m, 1H), 1.55–2.00 (m, 10H), 2.08–2.20 (m, 1H), 3.22 (d, $J=6$ Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$, $CDCl_3$ int): $\delta=16.44$ (t), 19.08 (q), 27.12 (t), 28.62 (t), 30.61 (t), 35.41 (t), 40.12 (d), 49.31 (s), 85.33 (d); MS (EI): $m/e=140$ (3, M^+), 97 (100). $C_9H_{16}O$ requires C, 77.09; H, 11.50. Found: C, 76.87; H, 11.47.

3.1.10.2. 6,6-Dimethyl-spiro[3.4]octan-5-ol (35). From **37** (1.22 g, 8.0 mmol); retention times (min) 2.38 (**37**), 3.52 (**35**) at 150 °C on column A; $R_f=0.30$ (**35**). Yield 1.17 g (94%) of pure **35** as colourless liquid. ^1H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): $\delta=0.82$ (s, 3H), 0.96 (s, 3H), 1.30–1.61 (m, 4H), 1.65–1.80 (m, 3H), 1.80–1.97 (m, 2H), 2.01–2.13 (m, 1H), 2.26 (symm m, 1H), 3.26 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$, $CDCl_3$ int): $\delta=16.72$ (t), 22.62 (q), 28.46 (q), 29.03 (t), 33.13 (t), 35.74 (t), 36.79 (t), 41.23 (s), 49.34 (s), 86.66 (d); MS (EI): $m/e=154$ (6, M^+), 139 (100). $C_{10}H_{18}O$ requires C, 77.87; H, 11.76. Found: C, 77.72; H, 11.77.

3.1.11. Rearrangement of 29a, 29b, 30a, 30b, 32a, 33, 34a, 34b, 35, 38a, 38b, 39 and 40

The selected bicyclobutyl-1-ol or spiro[3.4]octane-5-ol (1.0 mmol; **30a**, **30b**, **38b**: 0.2 mmol) was heated with an equimolar amount (13.5 ml; **30a**, **30b**, **38b**: 1.35 ml) of a 0.074 M solution of anhydrous *p*-toluenesulfonic acid in benzene to 70 °C. After 3 h, the mixture was diluted with pentane, washed with saturated sodium carbonate, dried over molecular sieves 3 Å and concentrated by distillation over a 20 cm Vigreux column (bath temperature 100°). According to GC on column A, the residue contained a single product in all cases. Analytically pure samples were isolated by preparative GC.

3.1.11.1. 3a-Methyl-1,2,3,3a,4,5-hexahydro-pentalen (41). From **39**; retention time (min): 2.42 at 120 °C. Colourless liquid. The ^1H[6] and ^{13}C NMR data[6] were in accord with literature data.

3.1.11.2. *rel*-(3a*R*,6a*R*)-6-Methyl-1,2,3,3a,4,6a-hexahydro-pentalene (42). From **29a**, **29b**, **34a** and **34b**; retention time (min): 2.81 at 130 °C. Colourless liquid. The ^1H[25b,c,e] and ^{13}C NMR data[25a,e] were in accord with literature data.

3.1.11.3. *rel*-(3a*R*,6a*R*)-3a,6-Dimethyl-1,2,3,3a,4,6a-hexahydro-pentalene (43). From **30a**, **30b**, **32a**, **38a** and **38b**; retention time (min): 3.09 at 120 °C. Colourless liquid. The ^{13}C NMR data[26a,c] were in accord with literature data. The ^1H NMR data have not yet been reported and were as follows: ^1H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): $\delta=1.12$ (s, 3H), 1.32–1.72 (m, 6H), 1.62 (br s, 3H), 2.15 (symm m, 2H), 2.34 (m_c, 1H), 5.10 (br s, 1H).

3.1.11.4. *rel*-(3a*R*,6a*R*)-3a,6,6a-Trimethyl-1,2,3,3a,4,6a-hexahydro-pentalene (44). From **33** and **40**; retention time (min): 5.22 at 120 °C. Colourless liquid. ^1H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): $\delta=0.91$ (s, 3H), 0.98 (s, 3H), 1.15–1.50 (m, 4H), 1.50–1.75 (m, 2H), 1.56 (br s, 3H), 2.11 (symm m, 2H), 5.13 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, $CDCl_3$ int): $\delta=13.03$ (q), 20.86 (q), 23.68 (t), 24.80 (q), 37.96 (t), 44.05 (t), 47.38 (t), 49.57 (s), 58.16 (s), 121.81 (d), 145.44 (s); MS (CI): $m/e=168$ (100, $M+NH_4]^+$). $C_{11}H_{18}$ requires C, 87.92; H, 12.08. Found: C, 88.10; H, 12.00.

3.1.11.5. *rel*-(3a*R*,6a*R*)-6,6a-Dimethyl-1,2,3,3a,4,6-hexahydro-pentalene (45). From **35**; retention time (min): 1.60 at 150 °C. Colourless liquid. ^1H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): $\delta=1.05$ (s, 3H), 1.18–1.55 (m, 5H), 1.57 (symm m, 3H), 1.74–1.88 (m, 2H), 2.12 (symm m, 1H), 2.52 (symm m, 1H), 5.10 (br s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$, $CDCl_3$ int): $\delta=12.69$ (q), 25.84 (q), 26.00 (t), 36.05 (t), 37.98 (t), 38.51 (t), 49.11 (d), 58.18 (s), 122.30 (d), 145.33 (s); MS (EI): $m/e=136$ (26, M^+), 107 (100). $C_{10}H_{16}$ requires C, 88.16; H, 11.84. Found: C, 88.18; H, 11.65.

3.1.12. *rel*-(3a*R*,6a*R*)-3a,6a-Dimethyl-hexahydro-pentalen-1-one (46)

To a suspension of Nafion® R SAC-13 (100 mg) in dry benzene (1.5 ml) was added under argon with stirring **37** (76 mg, 0.50 mmol). Afterwards, the mixture was heated to 70 °C until GC analysis [column B, 140 °C, retention times (min): 4.00 (**37**), 8.97 (**46**)] indicated, that the rearrangement was complete (45 h). The mixture was filtered, the residue was washed with ether (2×2.5 ml) and the combined organic phases were concentrated. An analytically pure sample was isolated by preparative GC. Colourless solid, m.p. 96 °C. IR (KBr): 1735 cm^{-1} (C=O); ^1H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int): $\delta=0.88$ (s, 3H), 1.00 (s, 3H), 1.48 (m_c, 2H), 1.54–1.70 (m, 4H), 1.80 (symm m, 1H), 1.98 (symm m, 1H), 2.30 (symm m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, $CDCl_3$ int): $\delta=17.33$ (q), 22.52 (q), 22.72 (t), 31.92 (t), 35.61 (t), 37.05 (t), 39.82 (t), 49.63 (s), 58.69 (s), 224.96 (s); MS (EI): $m/e=152$ (38, M^+), 95 (100). HRMS m/z (M^+) calcd 152.1201, obsd 152.1201.

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