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SYNTHESIS AND REARRANGEMENT OF DISPIRO[3.1.3.2]-, DISPIRO[3.0.3.3]- AND DISPIRO[3.0.4.2]UNDECANES - NEW ENTRIES TO [3.3.3]PROPELLANES[1]

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Abstract: The dispiroketones **4-6** have been synthesized and rearranged by treatment with acids yielding the bicyclic enone **36** under kinetic control and the [3.3.3]propellane **37** under thermodynamic control. The corresponding alcohols **10-12** all yield the [3.3.3]propellane **41**. The rearrangement of [7,7-D_2]-**12** to [8,8-D_2]-**41** proceeds stereospecifically and points to dispirane **42** as potential precursor of (±)-modhephene **43**. Likewise, dispiranes **44** and **46** are potential precursors of (±)-isocomene **45**.

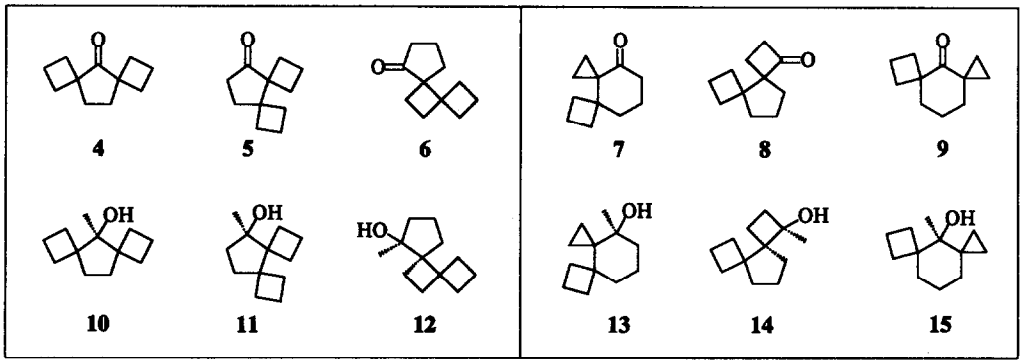
INTRODUCTION

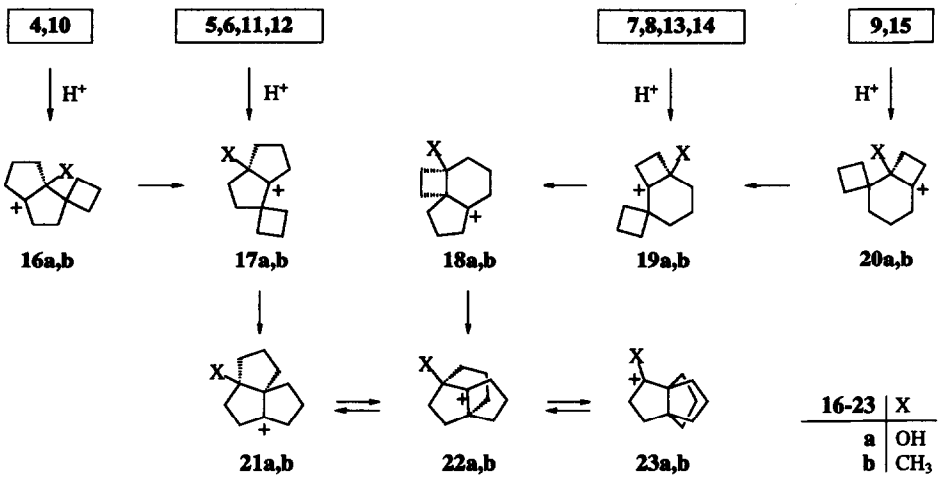
Naturally occurring sesquiterpenes based on tricycloundecanes **1**, **2** and **3** have been the focus of considerable interest.[2] Molecular mechanics calculations[3] predict **1** (ΔH_f = -26.7 kcal/mol) and **2** (ΔH_f = -25.7 kcal/mol) to be thermodynamically favoured over the vaste majority of their tricycloundecane congeners, but **3** (ΔH_f = -29.6 kcal/mol) is predicted to be the most stable of all. It therefore seemed particularly attractive to induce cascade rearrangements in suitable sized dispiroundecanes in order to enter the tricycloundecane energy surface specifically near **1** or **2** and to look whether derivatives of **1**, **2** and/or **3** would be obtained.

1 **2** **3**

Several features made ketones **4-6** and alcohols **10-12** especially well suited for an initial rearrangement to **21a,b** and hence the skeleton of **1**: first, the pronounced relief of strain associated with C_4-C_5 ring enlargements,[4] second, the well defined dihedral angle relationships favouring stereospecific rearrangements, and third, the possibility of rearrangements via energetically favourable tertiary carbenium ions[5] only.

Most of the arguments equally hold for ketones **7-9** and alcohols **13-15**, specifically devised for an initial rearrangement to **22a,b** and hence the skeleton of **2**. However, as the relief of strain associated with C_3-C_4 and C_5-C_6 ring enlargements is less pronounced[4], and the activation barrier for 1,2-shifts is higher in cyclobutanes than in cyclopentanes or cyclohexanes,[6] the outcome of the acid catalyzed rearrangements of **7-9** and **13-15** was less obvious. Nevertheless, we have studied all twelve dispiranes and herein describe the synthesis and rearrangement of **4-6** and **10-12**, and in a separate paper the synthesis of **7-9** and **13-15**, and the rearrangement of **9**, **13**, **14** and **15**.

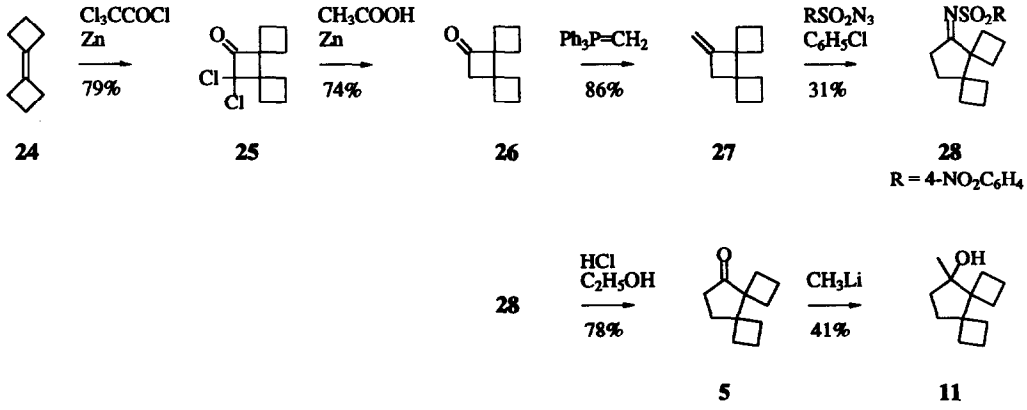




SYNTHESES

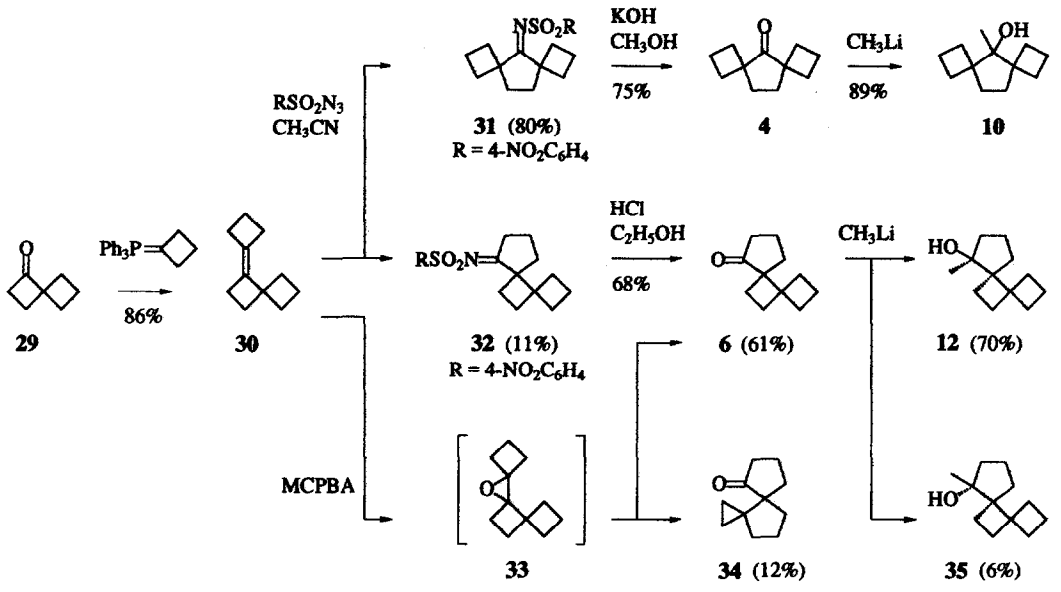
The syntheses of **4-6** and **10-12** are based on the readily available bicyclobutylidene[7] **24** and take advantage of the fact, that ring enlargements via Δ^2-triazolines[8] and 1-oxaspirohexanes[9] preferentially proceed via 1,2-shifts of the least and the most substituted carbon atom, respectively.

The synthesis of **5** and **11** was achieved as follows: addition of dichloroketene[10] to bicyclobutylidene **24** and dechlorination[10] of the resulting cyclobutanone **25** gave dispiroketone **26** which was then homologated to **5** by a sequence of methylenation, reaction with p-nitrobenzenesulfonic acid azide and hydrolysis of the resulting ring expanded imide (**26-27-28-5**). Addition of methyllithium yielded **11**, albeit extensive enolization led to the recovery of up to 50% of **5**. Out of the other reactions, only the reaction of **27** with p-nitrobenzenesulfonic acid azide proved difficult: it failed under the usual conditions [80°C in benzene[8a,b] or acetonitrile[8c]] and took 112 h at 100-110°C in chlorobenzene until imide **28** could be isolated in moderate yield (31%). This reflects a strong steric hindrance in the addition step which we have met with other 3-substituted methylenecyclobutanes, too.[11]



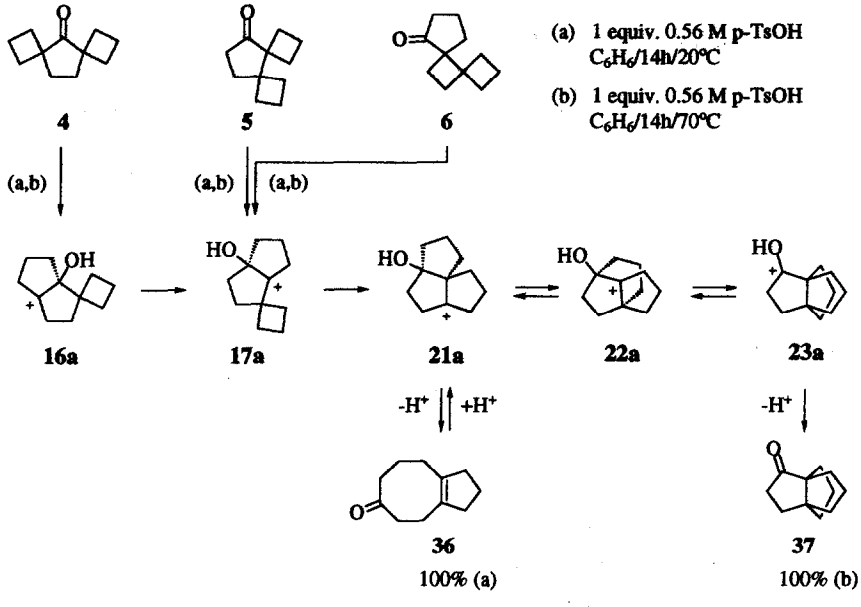
For the syntheses of **4**, **6**, **10** and **12**, bicyclobutylidene **24** was first transformed via cyclobutanone[7] to spiroheptanone **29**[12] and then cyclobutylidenated to cyclobutylidenespiroheptane **30**. This time the reaction with p-nitrobenzenesulfonic acid azide could be performed in acetonitrile and was complete within 42 h at 80°C. Formation of 80% of imide **31** and 11% of imide **32** indicated a pronounced regioselectivity in the addition step and a complete regiospecificy during the ring enlargement leading to **31**. Imides **31** and **32** were hydrolyzed to give dispiroketones **4** and **6**, respectively, and addition of methyllithium then yielded the desired alcohols **10** and **12**. Alcohol **12** was accompanied by minor amounts of its stereoisomer **35** but could easily be purified by column chromatography.

It became clear from above that the triazoline route was well suited for a synthesis of **4** but not for a synthesis of **6**. We therefore explored the possibility of a selective synthesis of **6** via rearrangement of 1-oxaspirohexane **33**. Indeed, treatment of bicyclobutylidene **30** with m-chloroperoxybenzoic acid in dichloromethane and in situ rearrangement of the resulting 1-oxaspirohexane **33** with catalytic amounts of borontrifluoride etherate in dichloromethane yielded 61% of the desired dispiroketone **6** and 12% of its skeletal isomer **34**. Obviously, the ring opening of **33** was regiospecific as anticipated, but the direct ring enlargement to **6** was accompanied by a ring enlargement of the spiroannulated ring followed by a C_4-C_3 ring contraction which ultimately led to the formation of **34**. Nevertheless, ketones **4-6** and alcohols **10-12** could now be prepared in quantities and allowed a detailed study of their behaviour under acidic conditions.



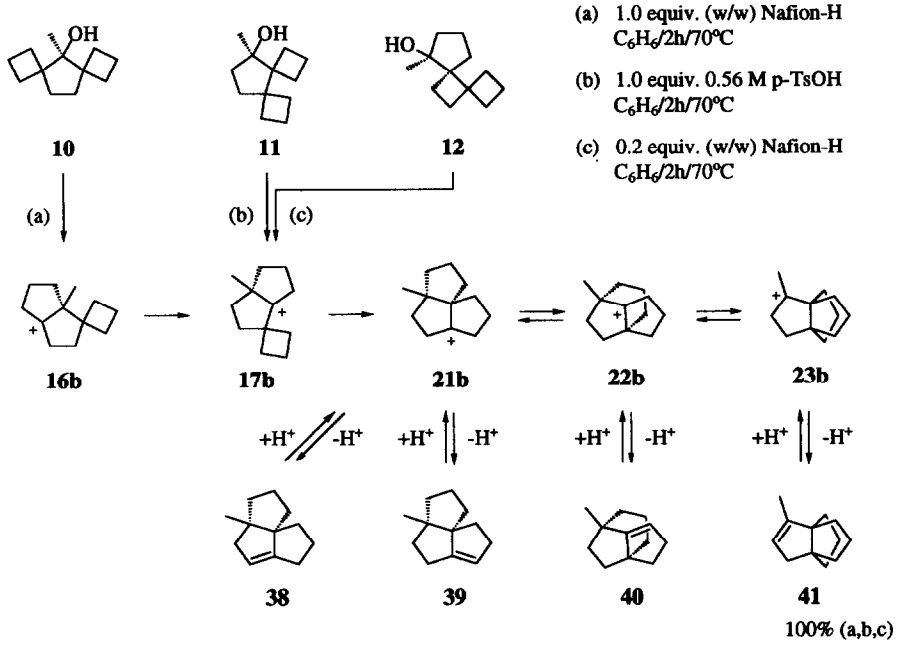
REARRANGEMENTS

When ketones **4**, **5** and **6** were treated with equimolar amounts of a 0.56 molar solution of anhydrous p-toluenesulfonic acid in benzene for 14 h at +20°C, quantitative conversion to the bicyclic enone **36**[13] was observed. The same conversion was complete within 10 min at +70°C, but after 14 h at +70°C, the propellane **37**[14] had formed instead.



We interprete these results as follows: protonation and two cyclobutylmethyl-cyclopentyl rearrangements, with an intermediate 1,2-hydroxyl shift in the case of **4** and - eventually - **6**, lead to the formation of the ß-hydroxycarbenium ion **21a** [**4-16a-17a-21a** and **5(6)-17a-21a**, respectively]. At this stage, a rapid but reversible ring opening to enone **36** occurs indicating that at least the first of the following two 1,2-shifts leading to propellane **37** is slow. It is thus obvious that the rearrangements of **4**, **5** and **6** to **36** and **37** are kinetically and thermodynamically controlled, respectively. Support comes from the fact that **37** (ΔH_f = -54.2 kcal/mol) is predicted[15] to be thermodynamically favoured over both **36** (ΔH_f = -43.2 kcal/mol) and **4** (ΔH_f = -12.7 kcal/mol), **5** (ΔH_f = -12.1 kcal/mol) and **6** (ΔH_f = -11.4 kcal/mol).

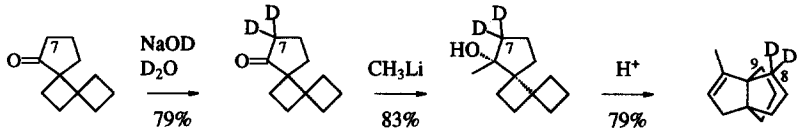
Having established the feasibility of acid catalyzed rearrangements of **4**, **5** and **6** to propellane **37**, we investigated the rearrangements of **10**, **11** and **12** next. Treatment of **10** with an equimolar amount of a 0.56 molar solution of anhydrous p-toluensulfonic acid in benzene for 2 h at +70°C resulted in a quantitative conversion to propellane **41**[16] and the same rearrangement was brought about when 0.28 molar solutions of **11** and **12** in benzene were treated with 1.0 (**11**) and 0.2 equivalents (w/w) of Nafion-H[17] (**12**), respectively, under otherwise unchanged conditions (2 h at +70°C). In no case any intermediate could be detected.



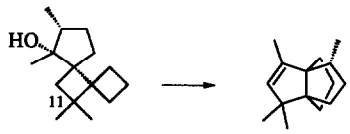
As in the case of **4-6**, the rearrangements of **10-12** must pass through an angular fused tricyclic carbenium ion **21b** as intermediate [**10-16b-17b-21b** and **11(12)-17b-21b**]. However, contrary to **21a**, **21b** is protected to ring opening by the presence of a methyl group instead of a hydroxyl group and hence the rearrangement proceeds further via **22b** and **23b** to **41** (ΔH_f = -10.2 kcal/mol). According to their calculated heats of formation[15], a formation of **38** (ΔH_f = -3.5 kcal/mol), **39** (ΔH_f = -3.2 kcal/mol) and/or **40** (ΔH_f = -4.0 kcal/mol) would have afforded kinetically favoured reaction paths. Under the rearrangement conditions choosen, these obviously do not exist.

LABELLING STUDIES

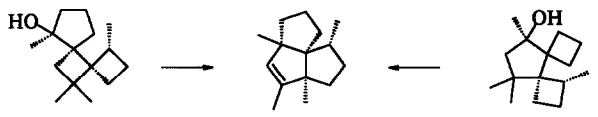
In view of the potential value of the rearrangement of **12** for a synthesis of (±)-modhephene **43** we studied its stereochemistry using specifically dideuterated [7,7-D_2]-**12**. We obtained [7,7-D_2]-**12** [3% D_1, 97% D_2 (MS)] by treatment of **6** with sodium deuteroxide and subsequent addition of methyllithium to [7,7-D_2]-**6** [3% D_1, 97% D_2 (MS)]. The rearrangement was achieved as described for **12** and resulted in a quantitative conversion to [8,8-D_2]-**41**. No loss of deuterium could be detected [4% D_1, 96% D_2 (MS)], and a ^{13}C-NMR analysis of [8,8-D_2]-**41** based on a ^{13}C-^{13}C connectivity study of **41** revealed that all resonance lines except that of C-8,9 [δ = 37.60 (s), 36.90 (quint, J = 19.5 Hz)] were free from any concomitant splitting due to the presence of mono- or dideuterated carbon atoms. Together with the fact that the resonance line of C-8,9 had lost approximately 50% of its intensity as compared to undeuterated **41**, this indicates that the rearrangement of [7,7-D_2]-**12** - and hence of **12** - had proceeded stereospecifically initiated by an exclusive 1,2-shift of that cyclobutane bond having an antiperiplanar alignment with the leaving hydroxyl group.



6 [7,7-D_2]-**6** [7,7-D_2]-**12** [8,8-D_2]-**41**



42 **43**



44 **45** **46**

It became clear from the above that a methyl group to be established at C-7 of **12** would preserve its stereochemistry and end up exclusively at C-8 of **41**. Assuming that a geminal dimethyl group at C-11 of **12** would not alter the rearrangement path, **42** could well rearrange directly to (±)-modhephene **43**. Moreover, anticipating the same stereospecificy as observed with **12**, dispiranes **44** and **46** could rearrange directly to (±)-isocomene **45**. Research with **42** has been successful,[18] research with **44** and **46** is in progress.

ACKNOWLEDGEMENT

Financial support of the Deutsche Forschungsgemeinschaft (project Fi 191/8-1) and the Fonds der Chemischen Industrie is gratefully acknowledged.

EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer 298 spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were measured on a Varian FT 80A, XL100, XL200 or VXR200 spectrometer. Mass spectra were obtained with a Varian MAT 731 operated at 70 eV. Analytical and preparative gas chromatography was carried out on a Intersmat IGC 16 or Carlo-Erba FTV 2450 instrument employing a thermal conductivity detector and hydrogen as carrier gas. Product ratios were not corrected for relative response. R_f-values are quoted for Macherey & Nagel Polygram SIL G/UV254 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.

10,10-Dichlorodispiro[3.0.3.2]decane-9-one (25): To a stirred suspension of activated zinc dust[10] (40.0 g) in anhydrous ether (1.0 l) under nitrogen was added bicyclobutylidene **24** (13.9 g, purity 94%, 120 mmol) and the mixture heated to reflux. A solution of trichloroacetyl chloride (22.7 g, 125 mmol) in anhydrous ether (1.0 l) was added over a period of 7 h and after additional 16 h of reflux the mixture was filtered. The filtrate was concentrated to 350 ml, diluted with pentane (500 ml), decanted from a brown oil, concentrated and fractionated through a microdistillation apparatus to give 20.8 g (79%) of **25** as a slightly yellow liquid, b.p. 81-83°C/0.3 torr, which turned violet on standing. According to glpc [3 m x 1/4" all glass system, 15% SE 30 on Chromosorb W AW/DMCS 60/80 mesh, 180°C; rel. retention times: 1.00, 1.47 (**25**)] the material was 94% pure. Analytically pure **25** was obtained by preparative glpc. - IR (film): 1800 cm^{-1} (C=O). - ^{1}H-NMR (200 MHz, $CDCl_3$, TMS int.): δ = 1.72-2.53 (m). - ^{13}C-NMR (20 MHz, $CDCl_3$, TMS int.): δ = 14.51, 16.01, 25.66, 27.82, 54.40, 65.54, 90.10, 199.68. - MS (70 eV): m/e = 218 (0.2%, M$^+$), 82 (100%). - Calculated for $C_{10}H_{12}Cl_2O$: 218.0265. Found: 218.0265 (MS).

Dispiro[3.0.3.2]decane-9-one (26): To a stirred suspension of zinc powder (55.0 g) in acetic acid (200 ml) was added over a period of 30 min a solution of **25** (36.6 g, purity 94%, 0.157 mol) in 50 ml of acetic acid. After 20 h of reflux the mixture was filtered, the filtrate diluted with water (150 ml) and extracted with pentane (1 x 250 ml, 7 x 75 ml). The combined extracts were washed with brine (2 x 40 ml), 1 M aqueous sodium hydroxide (4 x 30 ml) and dried ($CaCl_2$). The solvent was distilled off through a 30 cm Vigreux column and the residue fractionated through a microdistillation apparatus to yield 17.3 g (74%) of **26** as a colourless liquid, b.p. 86-88°C/8 torr. According to glpc [3 m x 1/4" all glass system, 15% OV 101 on Chromosorb W AW/DMCS 60/80 mesh, 170°C; rel retention times: 1.00, 1.16 (**26**), 1.42, 3.50 (**25**)] the material was 81% pure. Analytically pure **26** was obtained by preparative glpc. - IR (CCl_4): 1770 cm^{-1} (C=O). - ^{1}H-NMR (80 MHz, $CDCl_3$, TMS int.): δ = 1.55-2.40 (m, 12H), 2.90 (s, 2H). - ^{13}C-NMR (20 MHz, $CDCl_3$, TMS int.): δ = 15.68, 16.16, 26.00, 29.21, 39.51, 55.93, 66.92, 212.65. - MS (70 eV): m/e = 150 (1%, M$^+$), 79 (100%). - $C_{10}H_{14}O$ requires C, 79.96; H, 9.39. Found: C, 80.49; H, 9.53.

9-Methylenedispiro[3.0.3.2]decane (27): To a stirred suspension of potassium-t-butoxide (12.3 g, 0.110 mol) in anhydrous ether (200 ml) under nitrogen was added methyltriphenylphosphonium bromide (39.3 g, 0.110 mol) and the mixture heated to reflux. After 30 min, ether was distilled off under nitrogen until the temperature of the remaining slurry reached 40°C and **26** (16.0 g, purity 81%, 0.086 mol) was added (exothermic effect). According to glpc [3 m x 1/4" all glass system, 15% OV 101 on Chromosorb W AW/DMCS 60/80 mesh, 150°C; rel. retention times: 1.00 (**27**), 1.63 (**26**)] the reaction was complete within 1 h. Pentane (100 ml) and water (10 ml) were added with vigorous stirring, the organic layer was decanted, the heterogeneous residue extracted with pentane (4 x 50 ml) and the combined organic phases dried ($MgSO_4$). The solvent was distilled off through a 30 cm Vigreux column and the residue fractionated through a microdistillation apparatus to yield 11.1 g (86%) of **27** as a colourless liquid, b.p. 170-172°C, purity 82% (glpc). Analytically pure **27** was obtained by preparative glpc of the forerun. - IR (film): 1675 cm^{-1} (C=C). - ^{1}H-NMR (80 MHz, $CDCl_3$, TMS int.): δ = 1.50-2.35 (m, 12H), 2.50 (dd, ^{4}J = 2.1 Hz, ^{4}J = 2.5 Hz, 2H), 4.66 (t, ^{4}J = 2.1 Hz, 1H), 4.87 (t, ^{4}J = 2.5 Hz, 1H). - ^{13}C-NMR (20 MHz, $CDCl_3$, TMS int.): δ = 15.64, 15.99, 29.07, 29.44, 42.11, 45.10, 54.64, 101.52, 155.41. - MS (70 eV): m/e = 148 (2%, M$^+$), 91 (100%). - $C_{11}H_{16}$ requires C, 89.12; H, 10.88. Found: C, 89.11; H, 10.83.

9-(4-Nitrobenzenesulfonimido)dispiro[3.0.3.3]undecane (28): Protected from light, a solution of 4-nitrobenzenesulfonic acid azide (17.1 g, 75 mmol) and **27** (11.1 g, purity 82%, 61 mmol) in chlorobenzene (50 ml) was heated under nitrogen with stirring for 64 h to 100°C and 48 h to 110°C. After this time 92% of **27** had been consumed (^{1}H-NMR). The solvent was distilled off (bath temperature 100°C/40 torr) and the residual brown oil chromatographed through a short path of silica gel (0.2-0.5 mm) in dichloromethane (column 8 x 10 cm). The eluate was concentrated yielding first 7.6 g of crude **28** as yellow solid and then 9.0 g of a yellow oil. The oil was chromatographed on silica gel (0.032-0.063 mm) in dichloromethane (column 150 x 4.5 cm; control by tlc; R_f = 0.45) and gave a second crop of 1.9 g crude **28** as yellow solid. The solids were crystallized from 160 ml of methanol yielding 6.5 g (31%) of pure **28** as yellowish needles, m.p. 122°C. - IR (KBr): 1622 (C=N), 1525 cm^{-1} (N=O). - ^{1}H-NMR (80 MHz, $CDCl_3$, TMS int.): δ = 1.50-2.30 (m, 14H), 2.95 (t, J = 12 Hz, 2H), 8.26 (AA'BB',

4H). - ^{13}C-NMR (20 MHz, $CDCl_3$, $CDCl_3$ int.): δ = 13.63, 14.76, 25.39, 25.81, 31.03, 31.90, 48.12, 58.28, 123.71, 127.99, 146.23, 149.65, 203.15. - MS (70 eV): m/e = 348 (4%, M^+), 162 (100%). - $C_{17}H_{20}N_2O_4S$ requires C, 58.60; H, 5.59; N, 8.04; S, 9.20. Found: C, 58.42; H, 5.95; N, 8.02; S, 9.37.

Dispiro[3.0.3.3]undecane-9-one (5): A mixture of **28** (7.17 g, 20.6 mmol), ethanol (100 ml) and 4N hydrochloric acid (100 ml) was heated to 60°C until **28** was completely consumed [18 h; control by tlc in ether; R_f = 0.38 (**5**), 0.57 (**28**)]. The mixture was diluted with water (200 ml), extracted with pentane (5 x 100 ml), the combined organic phases washed with water (2 x 100 ml) and dried over sodium carbonate. The solvent was distilled off through a 30 cm Vigreux column and the residue fractionated through a microdistillation apparatus to yield 2.65 g (78%) **5** as a colourless liquid, b.p. 103-108°C/8 torr. According to glpc [3 m x 1/4" all glass system, 15% OV 101 on Chromosorb W AW/DMCS 60/80 mesh, 180°C; rel. retention times: 1.00, 1.16 (**5**), 1.44, 2.05] the material was 93% pure. Analytically pure **5** was obtained by preparative glpc. - IR (film): 1735 cm^{-1} (C=O). - ^{1}H-NMR (80 MHz, $CDCl_3$, TMS int.): δ = 1.40-2.25 (m). - ^{13}C-NMR (20 MHz, $CDCl_3$, $CDCl_3$ int.): δ = 14.33, 14.94, 23.90, 26.46, 30.58, 33.66, 47.89, 56.77, 219.82. - MS (70 eV): m/e = 164 (17%, M^+), 108 (100%). - $C_{11}H_{16}O$ requires C, 80.44; H, 9.82. Found: C, 80.34; H, 9.79.

(9*R)-9-Methyldispiro[3.0.3.3]undecane-9-ol (11)**: A solution of **5** (2.65 g, purity 93%, 15.0 mmol) in anhydrous ether (2 ml) was cooled to 0°C under nitrogen with stirring. A 1.5 M solution of methyllithium in ether (11.0 ml, 16.5 mmol) was added dropwise. During addition the temperature rose to 20°C and a vigorous evolution of gas was observed. Glpc analysis [3 m x 1/4" all glass system, 15% OV 101 on Chromosorb W AW/DMCS 60/80 mesh, 180°C; rel. retention times: 1.00 (**5**), 1.24 (**11**)] indicated a 50% yield of **11** which remained unchanged upon addition of another 2 ml of 1.5 M methyllithium in ether. The mixture was hydrolyzed with a saturated solution of ammonium chloride (6 ml), the aqueous phase extracted with pentane (5 x 15 ml), the combined organic phases concentrated and the residue (2.75 g) chromatographed in two charges on silica gel (0.2-0.5 mm) in pentane/ether [7:3; column 80 x 3 cm, control by tlc; R_f = 0.38 (**5**), 0.22 (**11**)] to yield 1.11 g (41%) **11** and 0.99 g (40%) **5** as colourless oils. - IR (film): 3600 (OH), 3580-3200 cm^{-1} (OH_{ass}). - ^{1}H-NMR (200 MHz, $CDCl_3$, TMS int.): δ = 1.12 (s, 1H), 1.29 (s, 3H), 1.50-1.81 (m, 10H), 1.81-2.06 (m, 4H), 2.06-2.34 (m, 2H). - ^{13}C-NMR (20 MHz, $CDCl_3$, TMS int.): δ = 15.02, 15.96, 21.53, 24.16 (coincidence of two lines), 29.90, 31.08, 34.44, 36.83, 51.20, 55.87, 81.83. - MS (70 eV): m/e = 180 (0.2%, M^+), 43 (100). - $C_{12}H_{20}O$ requires C, 79.94; H, 11.18. Found: C, 79.98; H, 11.21.

1-Cyclobutylidenespiro[3.3]heptane (30): To a suspension of 4-bromotriphenylphosphonium bromide (46.9 g, 98 mmol) in dry benzene (150 ml) was added under argon with stirring potassium-t-butoxide (22.0 g, 196 mmol) and the mixture heated for 3 h to 50°C. Spiro[3.3]heptane-1-one (**29**) (7.7 g, 70 mmol) was added causing an exothermic effect and after additional 1.5 h at 50°C the reaction was complete according to glpc [3 m x 1/4" all glass system, 15% OV 210 on Chromosorb W AW/DMCS 60/80 mesh, 100°C; rel. retention times: 1.00 (**29**), 1.13 (**30**)]. The reaction mixture was diluted with pentane (50 ml), hydrolyzed with water (2 ml), the organic layer decanted, the heterogeneous residue extracted with pentane (3 x 20 ml), the combined organic phases distilled through a 20 cm Vigreux column and the residue fractionated through a microdistillation apparatus to yield 8.9 g (86%) of **30** as a colourless liquid, b.p. 48°C/0.01 torr. - ^{1}H-NMR (100 MHz, $CDCl_3$, TMS int.): δ = 1.5-2.2 (m). - ^{13}C-NMR (20 MHz, $CDCl_3$, TMS int.): δ = 16.32, 18.18, 23.98, 29.05, 29.71, 32.80, 33.84, 50.01, 129.36, 136.44. - MS (70 eV): m/e = 148 (13%, M^+), 91 (100%). - $C_{11}H_{16}$ requires C, 89.19; H, 10.81. Found: C, 89.15; H, 10.87.

5-(4-Nitrobenzenesulfonimido)dispiro[3.1.3.2]undecane (31) and **(5*R**)-6-(4-Nitrobenzenesulfonimido)-dispiro[3.0.4.2]undecane (32)**: Protected from light, a solution of 4-nitrobenzenesulfonic acid azide (6.3 g, 28 mmol) and **30** (4.0 g, 27 mmol) in dry acetonitrile (70 ml) was heated under nitrogen with stirring for 42 h to reflux. After this time the reaction was complete according to tlc in dichloromethane [R_f = 0.67 (**30**), 0.57 (**31**), 0.51 (**32**)]. The mixture was concentrated to 30 ml, cooled to 0°C, filtered from 5.3 g (56%) of solid **31**, the filtrate further concentrated (bath temperature 60°C/10 torr) and the residual brown oil (9.0 g) chromatographed on silica gel (70-130 mesh) in dichloromethane/pentane [3:1, column 35 x 5 cm; R_f = 0.41 (**31**), 0.33 (**32**)] yielding a second crop of 2.2 g (24%) of **31** and 1.0 g (11%) of **32**, both as solids. Crystallization from acetonitrile yielded pure **31**, m.p. 139°C and pure **32**, m.p. 96°C, respectively. - **31**: IR (KBr): 1608 (C=N), 1532 cm^{-1} (N=O). - ^{1}H-NMR (100 MHz, $CDCl_3$, $CHCl_3$ int.): δ = 1.6-2.3 (m, 12H), 2.4-2.9 (m, 4H), 8.28 (AA'BB', 4H). - ^{13}C-NMR (20 MHz, $CDCl_3$, $CDCl_3$ int.): δ = 15.32, 32.25, 35.22, 52.91, 123.92, 127.89, 148.09, 149.65, 205.38. - MS (70 eV): m/e = 348 (2%, M^+), 134 (100%). - $C_{17}H_{20}N_2O_4S$ requires C, 58.62; H, 5.75; N, 8.05; S, 9.20. Found: C, 58.35; H, 5.76; N, 8.03; S, 9.20. - **32**: IR (KBr): 1612 (C=N), 1531 cm^{-1} (N=O). - ^{1}H-NMR (100 MHz, $CDCl_3$, $CHCl_3$ int.): δ = 1.2-2.5 (m, 16H), 3.00 (mc, 2H), 8.25 (AA'BB', 4H). - ^{13}C-NMR (20 MHz, $CDCl_3$, $CDCl_3$ int.): δ = 14.93, 21.73, 25.73, 31.11, 31.46, 32.41, 33.17, 35.40, 50.66, 58.38, 124.10, 128.38, 146.94, 150.10, 203.84. - MS (70 eV): m/e = 348 (2%, M^+), 49 (100%). - $C_{17}H_{20}N_2O_4S$ requires C, 58.62; H, 5.75; N, 8.05; S, 9.20. Found: C, 58.11; H, 5.83; N, 8.37; S, 9.16.

Dispiro[3.1.3.2]undecane-5-one (4): A methanolic solution of potassium hydroxide (5% w/w, 40 g) and **31** (5.50 g, 15.8 mmol) was heated to reflux until **31** had been completely consumed [1 h; control by tlc in pentane/ether 3:1; R_f = 0.40 (**4**), 0.56 (**31**)]. The mixture was poured into water (200 ml), extracted with ether (3 x 100 ml) and the combined organic phases dried ($MgSO_4$). The solvent was distilled off through a 20 cm vigreux column and the residue fractionated through a microdistillation apparatus to yield 1.95 g (75%) of **4** as colourless liquid, b.p. 44°C/0.35 torr. - IR (film): 1730 cm^{-1} (C=O). - ^{1}H-NMR (100 MHz, $CDCl_3$, TMS int.): δ = 1.4-2.4 ppm (m). - ^{13}C-NMR (20 MHz, $CDCl_3$, TMS int.): δ = 15.98, 30.60, 33.59, 50.41, 222.21. - MS (70 eV): m/e = 164 (34%, M^+), 136 (100%). - $C_{11}H_{16}O$ requires C, 80.49; H, 9.76. Found: C, 80.65; H, 9.86.

(5*R)-Dispiro[3.0.4.2]undecane-6-one (6)**: A mixture of **32** (770 mg, 2.2 mmol), ethanol (8 ml) and 4 N hydrochloric acid (8 ml) was heated to reflux until **32** had completely disappeared [4 h; control by tlc in pentane/ether 3:1; R_f = 0.52 (**32**), 0.59 (**6**)]. The mixture was diluted with water (16 ml), extracted with pentane (5 x 10 ml), the combined organic phases dried ($MgSO_4$), concentrated on a rotary evaporator (bath temperature 50°C/80 torr) and the residue chromatographed on silica gel (70-130 mesh) in pentane/ether 5:1 (column 25 x 1.6 cm; control by tlc) to yield 250 mg (68%) of **6** as colourless liquid. According to glpc [3 m x 1/4" all glass system, 15% FFAP on Chromosorb W AW/DMCS 60/80 mesh, 6 min 140°C, 20°C/min to 240°C; rel. retention times: 1.00 (**6**), 1.04] the material was 94% pure. Analytically pure **6** was obtained by preparative glpc. - IR (film): 1732 cm^{-1} (C=O). - ^{1}H-NMR (200 MHz, C_6D_6, TMS int.): δ = 1.10-2.03 (m, 14H), 2.04-2.50 (m, 2H). - ^{13}C-NMR (50.3 MHz, $CDCl_3$, $CDCl_3$ int.): δ = 15.32, 19.47, 24.44, 31.11, 31.37, 32.29, 32.95, 37.95, 48.44, 56.05, 220.94. - MS (70 eV): m/e = 164 (14%, M^+), 136 (100%). - $C_{11}H_{16}O$ requires C, 80.49; H, 9.76. Found: C, 80.69; H, 9.79.

(5*R)-Dispiro[3.0.4.2]undecane-6-one (6) and (4*R**)-Dispiro[2.0.4.3]undecane-5-one (34)**: To a stirred solution of **30** (8.7 g, 59 mmol) in dichloromethane (650 ml) was added a solution of m-chloroperoxybenzoic acid (20.1 g, 80% w/w, 93 mmol) in dichloromethane (150 ml) within 1 h under nitrogen at 0°C. The reaction was monitored by tlc in pentane/ether 9:1 [R_f = 0.70 (**30**), 0.39 (**33**), 0.25 (**6**,**34**)] and the mixture allowed to warm up after **30** had been completely consumed (30 min). A 0.24 M solution of borontrifluoride etherate in dichloromethane (4.0 ml) was added at such a rate that the reaction temperature did not exceed 25°C (15 min), and after additional 15 min the rearrangement was complete. The mixture was hydrolyzed with 0.5 M sodium bicarbonate (20 ml; exothermic effect), the organic phase washed with the same reagent (2 x 20 ml) and dried over magnesium sulfate with addition of sodium carbonate. The solvent was distilled off through a 20 cm Vigreux column and the residue fractionated through a microdistillation apparatus to yield 7.1 g (73%) of a colourless liquid, b.p. 54-67°C/0.3 torr. According to glpc (3 m x 1/4" all glass system, 15% FFAP on Chromosorb W AW/DMCS 60/80 mesh; 6 min 140°C, 20°C/min to 240°C; rel. retention times: 1.00 (**6**), 1.04 (**34**)] this material consisted of 83% of **6** and 17% of **34**. Pure samples were obtained by preparative glpc. **6** was identical (IR, ^{1}H-NMR) with the compound obtained by saponification of **32**. **34**: IR (film): 1732 cm^{-1} (C=O). - ^{1}H-NMR (100 MHz, $CDCl_3$, TMS int.): δ = 0.2-0.6 (m, 4H), 1.3-2.5 (m, 12H). - ^{13}C-NMR (20 MHz, $CDCl_3$, $CDCl_3$ int.): δ = 8.60, 10.33, 19.36, 22.76, 27.68, 34.35, 36.98, 37.83, 38.29, 57.05, 222.52. - MS (70 eV): m/e = 164 (44%, M^+), 108 (100%). - $C_{11}H_{16}O$ requires C, 80.49; H, 9.76. Found: C, 80.60; H, 9.70.

(5*R)-5-Methyldispiro[3.1.3.2]undecane-5-ol (10)**: To a stirred solution of **4** (0.82 g, 5.0 mmol) in dry ether (2 ml) under nitrogen was added within 5 min a 1.5 M solution of methyllithium in ether (4.4 ml, 6.6 mmol). According to glpc [3 m x 1/4" all glass system, 15% FFAP on Chromosorb W AW/DMCS 60/80 mesh, 6 min 140°C, 20°C/min to 240°C; rel retention times: 1.00 (**4**), 1.23 (**10**)] the reaction was complete after additional 30 min. The mixture was hydrolyzed with saturated ammonium chloride (10 ml), the aqueous phase extracted with ether (4 x 10 ml), the combined organic phases dried over molecular sieves 4Å, concentrated on a rotary evaporator (bath temperature 50°C/50 torr) and the residue chromatographed on silica gel (70-130 mesh) in pentane/ether 9:1 [column 30 x 2.8 cm, control by tlc; R_f = 0.16) to yield 0.81 g (90%) of **10** as a colourless liquid, purity 95% (glpc). Analytically pure **10** was obtained by preparative glpc. - IR (film): 3610 (OH), 3600-3200 cm^{-1} (OH_{ass}). - ^{1}H-NMR (100 MHz, $CDCl_3$, $CHCl_3$ int.): δ = 1.00 (s, 3H), 1.36 (s, 1H), 1.2-2.3 (m, 16H). - ^{13}C-NMR (20 MHz, $CDCl_3$, $CDCl_3$ int.): δ = 15.61, 17.85, 29.09, 29.65, 35.10, 51.60, 80.12. - MS (70 eV): m/e = 180 (1%, M^+), 48 (100%). - $C_{12}H_{20}O$ requires C, 79.95; H, 11.18. Found: C, 80.09; H, 11.26.

(5*R,6*S**)-6-Methyldispiro[3.0.4.2]undecane-6-ol (12) and (5*R**,6*R**)-6-Methyldispiro[3.0.4.2]undecane-6-ol (35)**: To a 0.5 M solution of methyllithium in ether (22.0 ml, 11.0 mmol), cooled with stirring under nitrogen to 0°C, a solution of **6** (625 mg, 3.8 mmol, purified by glpc) in dry ether (10 ml) was added over 30 min. According to glpc [3 m x 1/4" all glass system, 15% FFAP on Chromosorb W AW/DMCS 60/80 mesh, 6 min 140°C, 20°C/min to 240°C; rel. retention times: 1.00 (**6**), 1.27 (**12**), 1.38 (**35**)] **6** had been completely consumed. The mixture was hydrolyzed with saturated ammonium chloride (10 ml), the aqueous phase extracted with ether (4 x 10 ml), the combined organic phases dried over molecular sieves 4Å, concentrated on a rotary evaporator (bath temperature 50°C/50 torr) and the residue chromatographed on silica gel (70-130 mesh) in pentane/ether 9:1 [column 50 x 2.8 cm; control by tlc; R_f = 0.16 (**12**), 0.12 (**35**)] to yield 480 mg (70%) of **12** (purity 98%)

and 35 mg (5%) of **35** (purity 95%) as colourless liquids. - **12**: IR (film): 3620 (OH), 3600-3200 cm^{-1} (OH_{ass}). - ^{1}H-NMR (100 MHz, $CDCl_3$, $CHCl_3$ int.): δ = 0.88 (s, 1H), 1.22 (s, 3H), 1.14-2.33 (m, 15H), 2.55-2.90 (m, 1H). - ^{13}C-NMR (50.3 MHz, $CDCl_3$, $CDCl_3$ int.): δ = 16.49, 18.63, 23.71, 26.93, 32.04, 32.18, 32.99, 33.13, 39.94, 47.15, 54.15, 82.66. - MS (70 eV): m/e = 180 (1%, M^+), 43 (100%). - $C_{12}H_{20}O$ requires C, 79.95; H, 11.18. Found: C, 80.14; H, 11.29. - **35**: IR (film): 3610 (OH), 3600-3200 cm^{-1} (OH_{ass}). - ^{1}H-NMR (100 MHz, $CDCl_3$, $CHCl_3$ int.): δ = 1.29 (s, 3H), 1.19-2.42 (m, 17H). - ^{13}C-NMR (50.3 MHz, $CDCl_3$, $CDCl_3$ int.): δ = 15.46, 18.23, 22.47, 22.99, 31.61, 32.03, 32.13, 32.52, 38.94, 47.29, 55.06, 80.68. - MS (70 eV): m/e = 180 (2%, M^+), 94 (100%). - $C_{12}H_{20}O$ requires C, 79.95; H, 11.18. Found: C, 79.89; H, 11.24.

2-Methyltricyclo[3.3.3.0^{1,5}]undec-2-ene (41):

From 11: To a 0.56 M solution of anhydrous p-toluenesulfonic acid in benzene (3.00 ml, 1.68 mmol) was added **11** (150 mg, purity 80%, 0.66 mmol) and the resulting solution stirred for 2 h at 70°C. After this time the rearrangement to **41** was complete according to glpc [3 m x 1/4" all glass system, 15% OV 101 on Chromosorb W AW/DMCS 60/80 mesh, 170°C; rel. retention times: 1.00 (**41**), 2.16 (**11**)]. The mixture was washed with water (1.5 ml), dried over sodium bicarbonate and **41** isolated by preparative glpc. Colourless liquid. - ^{1}H-NMR (80 MHz, $CDCl_3$, TMS int.): δ = 1.32-1.55 (m, 12H), 1.60 (dt, ^4J = 1.45 Hz, ^5J = 2.3 Hz, 3H), 2.15 (dq, ^3J = 2.3 Hz, ^5J = 2.3 Hz, 2H), 4.95-5.05 (m, 1H). - ^{13}C-NMR (50 MHz, $CDCl_3$, $CDCl_3$ int.): δ = 13.83, 25.93, 37.67, 41.78, 47.41, 60.23, 70.10, 122.05, 144.04. - MS (70 eV): m/e = 162 (75%, M^+), 133 (100%). - $C_{12}H_{18}$ requires C, 88.82; H, 11.18. Found: C, 88.78; H, 11.22.

From 12: To a solution of **12** (300 mg, 1.66 mmol) in dry benzene (4.0 ml) was added Nafion-H (50 mg) and the resulting mixture stirred for 2 h at 70°C. After this time the rearrangement to **41** was complete according to glpc [3 m x 1/4" all glass system, 15% FFAP on Chromosorb W AW/DMCS 60/80 mesh, 6 min at 140°C, 20°C/min to 240°C; rel. retention times: 1.00 (**41**), 4.68 (**12**)]. The mixture was filtered, the filtrate concentrated on a rotary evaporator (bath temp. 50°C/50 torr) and the residue chromatographed over silica gel (70-130 mesh) in pentane/ether (9:1; column 25 x 1.6 cm, R_f = 0.73) yielding 240 mg (89%) of pure **41** as colourless liquid. This material was used in a ^{13}C-^{13}C connectivity study (50.3 MHz, CD_2Cl_2, CD_2Cl_2 int.): δ = 14.29 (CH_3), 26.60 (C-7, C-10), 38.36 (C-8, C-9), 42.47 (C-6, C-11), 48.10 (C-4), 60.92 (C-5), 70.78 (C-1), 122.72 (C-3), 144.61 (C-2).

From 10: To a solution of **10** (50 mg, 0.28 mmol) in dry benzene (1.0 ml) was added Nafion-H (50 mg) and the resulting mixture stirred for 2 h at 70°C. After this time the rearrangement to **41** was complete according to glpc [3 m x 1/4" all glass system, 15% FFAP on Chromosorb W AW/DMCS 60/80 mesh, 6 min at 140°C, 20°C/min to 240°C; rel. retention times: 1.00 (**41**), 4.53 (**10**)]. The mixture was filtered and **41** isolated by preparative glpc. The material was identical with that from **12** (^{1}H-NMR).

Bicyclo[6.3.0]undec-1(8)-ene-4-one (36):

From 5: To a 0.56 M solution of anhydrous p-toluenesulfonic acid in benzene (1.60 ml, 0.90 mmol) was added **5** (161 mg, purity 93%, 0.90 mmol) and the resulting solution stirred for 12 h at room temperature. After this time the rearrangement to **36** was complete according to glpc [2 m x 1/4" all glass system, 15% FFAP on Chromosorb W AW/DMCS 60/80 mesh, 150°C; rel. retention times: 1.00 (**5**), 1.85 (**36**)]. The mixture was washed with water (1.0 ml), dried over potassium bicarbonate and **36** isolated by preparative glpc. Colourless liquid. - IR (film): 1705 cm^{-1} (C=O). - ^{1}H-NMR (200 MHz, $CDCl_3$, TMS int.): δ = 1.56-1.83 (m, 4H), 2.12-2.58 (m, 12H). - ^{13}C-NMR (20 MHz, C_6D_6, C_6D_6 int.): δ = 22.26, 23.17, 24.75, 28.24, 36.12, 37.28, 40.43, 45.85, 136.51, 137.21, 211.50. - MS (70 eV): m/e = 164 (65%, M^+), 79 (100%). - $C_{11}H_{16}O$ requires C, 80.44; H, 9.82. Found: C, 80.41; H, 9.76. **From 4 and 6:** Under the same conditions, quantitative rearrangements to **36** were also observed for **4** and **6** (^{1}H-NMR).

Tricyclo[3.3.3.0^{1,5}]undecane-2-one (37):

From 5: To a 0.56 M solution of anhydrous p-toluenesulfonic acid in benzene (3.00 ml, 1.68 mmol) was added **5** (150 mg, purity 93%, 0.84 mmol) and the resulting mixture stirred for 12 h at 70°C. After this time the rearrangement to **37** was complete according to glpc [2 m x 1/4" all glass system, 15% FFAP on Chromosorb W AW/DMCS 60/80 mesh, 150°C; rel. retention times: 1.00 (**5**), 1.23 (**37**), 1.85 (**36**)]. The mixture was washed with water (1.5 ml), dried over potassium bicarbonate and **37** isolated by preparative glpc. Colourless solid, m.p. 125-127°C (capillary). - IR (KBr): 1735 cm^{-1} (C=O). - ^{1}H-NMR (200 MHz, $CDCl_3$, TMS int.): δ = 1.40-1.94 (m, 14H), 2.38 (t, J = 8Hz, 2H). - ^{13}C-NMR (20 MHz, C_6D_6, C_6D_6 int.): δ = 26.49, 31.62, 37.38, 37.68, 41.00, 58.89, 65.97, 220.10. - MS (70 eV): m/e = 164 (58%, M^+), 80 (100%). $C_{11}H_{16}O$ requires C, 80.44; H, 9.82. Found: C, 80.29; H, 9.72. **From 4 and 6:** Under the same conditions, quantitative rearrangements to **37** were also observed for **4** and **6** (^{1}H-NMR).

(5*R)-[7,7-D_2]-Dispiro[3.0.4.2]undecane-7-one ([7,7-D_2]-6):** To a stirred solution of sodium deuteroxide prepared by dissolving sodium (250 mg) in a solution of deuterium oxide (22.5 ml, 99.75% D_2) and dioxane (22.5 ml) under nitrogen was added **6** (450 mg, 2.74 mmol) and the mixture heated for 30 min to 70°C. The dioxane was distilled off in a rotary evaporator (bath temperature 50°C/50 torr) and the residue extracted with ether (3 x 15 ml). The extract was dried over molecular sieves 4Å, the solvent evaporated (bath temperature 50°C/50 torr) and the remaining material (410 mg) subjected to a second deuteration yielding 360 mg (79%) [7,7-D_2]-**6** as a colourless liquid [3% D_1, 97%D_2 (MS)]. - ^{13}C-NMR (50.3 MHz, C_6D_6, TMS int.): δ = 15.75, 19.44, 24.95, 31.27, 31.73, 32.62, 32.94, 37.09 (quint, J = 19.8 Hz), 48.53, 55.81, 218.04.

(5*R,6*S**)-[7,7-D_2]-6-Methyldispiro[3.0.4.2]undecane-6-ol ([7,7-D_2]-12):** [7,7-D_2]-**6** (131 mg, 0.79 mmol) was dissolved in dry ether (5 ml) under nitrogen and reacted with a 0.35 M solution of methyllithium in ether (6.4 ml, 2.2 mmol) as described for **6**. Chromatographic purification yielded 120 mg (83%) [7,7-D_2]-**12** as a colourless liquid [3% D_1, 97% D_2 (MS)]. - ^{13}C-NMR (50.3 MHz, $CDCl_3$, $CDCl_3$ int.): δ = 16.50, 18.41, 23.66, 26.90, 32.03, 32.18, 32.98, 33.13, 39.17 (quint, J = 19.6 Hz), 47.15, 54.75, 82.58.

(1*R,5*R**)-[8,8-D_2]-2-Methyltricyclo[3.3.3.$0^{1,5}$]undec-2-en ([8,8-D_2]-41):** To a stirred solution of [7,7-D_2]-**12** (120 mg, 0.66 mmol) in dry benzene (2.0 ml) under nitrogen was added Nafion-H (100 mg) and the mixture heated for 2 h to 70°C. After this time the rearrangement to [8,8-D_2]-**41** was complete according to glpc [3 m x 1/4" all glass system, 15% FFAP on Chromosorb W AW/DMCS 60/80 mesh, 6 min 140°C, 20°C/min to 240°C; rel. retention times: 1.00 ([8,8-D_2]-**41**), 4.68 ([7,7-D_2]-**12**)]. After filtration, 86 mg (79%) [8,8-D_2]-**41** were isolated by preperative glpc. Colourless liquid [4% D_1, 96% D_2 (MS)]. - ^{13}C-NMR (50.3 MHz, $CDCl_3$, $CDCl_3$ int.): δ = 13.84 (CH_3), 25.70, 25.91 (C-7,10), 36.90 (quint, J = 19.5 Hz, C-8), 37.60 (C-9), 41.73 (C-6,11), 47.37 (C-4), 60.20 (C-5), 79.91 (C-1), 121.99 (C-3), 144.15 (C-2).

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Dedicated to Professor Christoph Rüchardt on the occasion of his 65th birthday

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