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SYNTHESIS OF TRICYCLOPENTANOID SESQUITERPENES VIA REARRANGEMENT ROUTES: (±)-MODHEPHENE, (±)-EPIMODHEPHENE AND (±)-ISOCOMENE[1]

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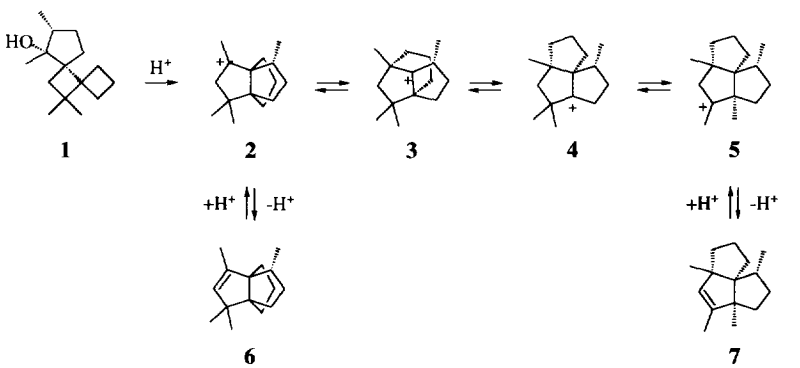
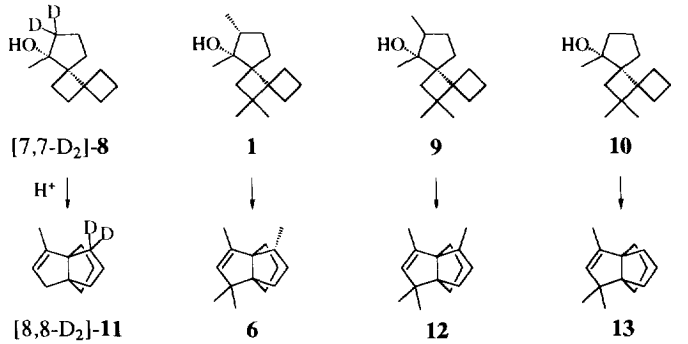
Abstract: Based on model studies with dispiroundecane **10**, dispiroundecane **1** has been synthesized and rearranged to (±)-modhephene **6** and (±)-isocomene **7**. The epimeric dispiroundecane **9** yields (±)-epimodhephene **12**. A total of thirteen rearrangement products (**6**, **7**, **12**, **37**, **38**, **39**, **42**, **43**, **44**, **55**, **57**, **64**, **67**) have been isolated from **1** and/or **9**, including six unnatural triquinanes. Two of these (**55**, **57**) are formed by unusual 1,3- and 1,4-shifts, respectively. A mechanistic rationale on the basis of force field calculations is given.

Introduction

Since their detection, (-)-modhephene **6**[2] and (-)-isocomene **7**[3] have been the subject of an increasing number of total syntheses. Within the strategies used,[2,3] rearrangements are rare and never comprise more than a single step. This is somewhat surprising since **6** and **7** are associated in nature[2a] and may formally be derived from each other by three consecutive 1,2-shifts (**6-2-3-4-5-7**).[2a] Despite of this fact, all syntheses of **6** and **7** are individual ones and no equilibration studies with **6** and/or **7** have become known. We now give a full account of our finding[2l] that the acid catalyzed rearrangement of dispiroundecane **1** is not only a well suited method for the synthesis of **6**, but also gives access to **7**, via **3** and **4**.



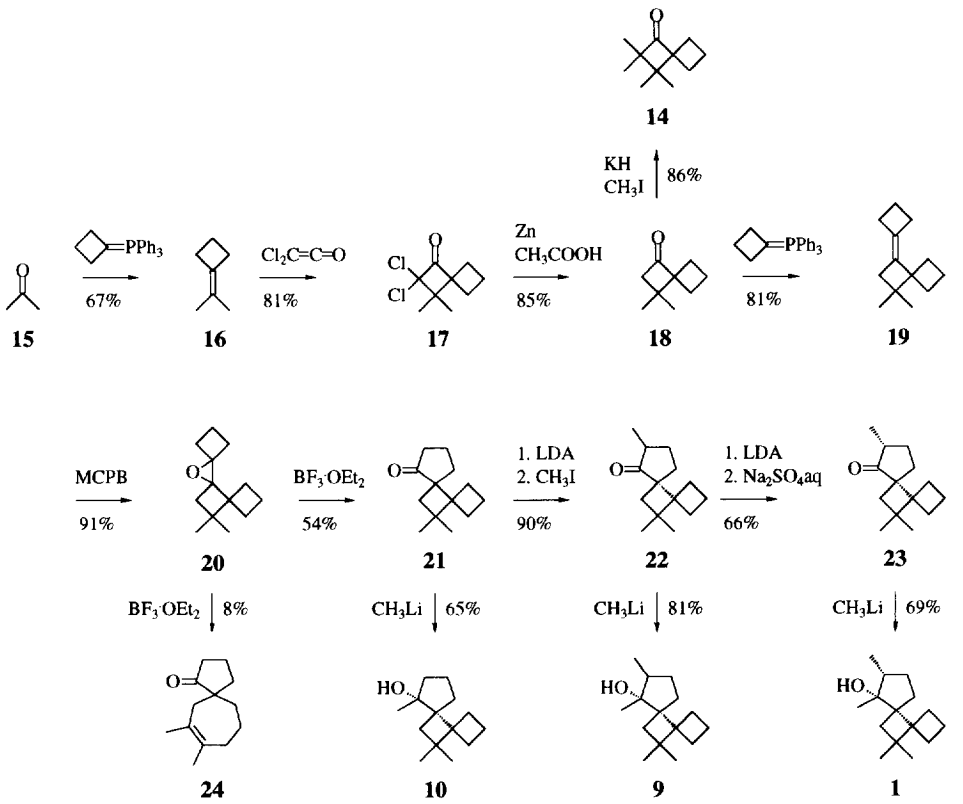
Based on the fact that on treatment with acids dispiroundecane [7,7-D_2]-**8** rearranges stereospecifically and without loss of deuterium to [8,8-D_2]-**11**,[4,5] we recently recognized dispiroundecane **1** being a promising candidate for a direct conversion to (±)-modhephene **6**. Assuming that the rearrangement of **1** proceeds analogously to the rearrangement of [7,7-D_2]-**8**, the methyl group at C-7 was thought to preserve its stereochemistry and to end up exclusively at C-8 of **6**. The same appeared to be true for dispiroundecane **9** as a potential precursor of (±)-epimodhephene **12**.[6] However, as an analogous rearrangement seemed endangered by the presence of a geminal dimethyl group at C-11, we first studied the rearrangement of dispirane **10** as a model before we rearranged dispiranes **1** and **9**.



Syntheses

The syntheses of dispiranes **10**, **9** and **1** are based on isopropylidenecyclobutane **16**,[7] itself obtained by cyclobutylidenation of acetone **15**. Addition of dichloroketene[8,9] and subsequent dechlorination[8] yielded a cyclobutanone, recognized as the desired regioisomer **18** through exhaustive methylation[10] with formation of the unsymmetrically tetramethylated cyclobutanone **14** (**16-17-18-14**). Cyclobutylidenation of **18** followed by epoxidation with m-chloroperbenzoic acid in dichloromethane and rearrangement of the resulting oxaspirohexane **20** with boron trifluoride etherate then yielded the desired dispiroketone **21**, albeit minor amounts of undesired spiroketone **24** were also formed [**18-19-20-21**(**24**)]. Obviously, the ring opening of **20** was regiospecific as anticipated, but the direct ring enlargement leading to **21** was accompanied by a ring enlargement of the spiroannulated ring followed by a 1,2-methyl shift and a transannular ring opening ultimately leading to **24**.

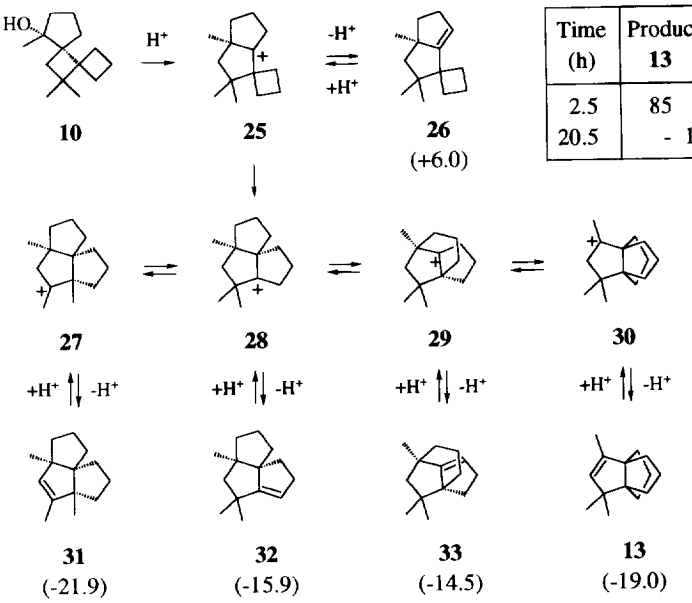
Stereospecific methylation of dispiroketone **21** with formation of **22** was observed during deprotonation with lithium diethylamide and subsequent treatment with methyl iodide, and inversion of the configuration with formation of **23** could be achieved by another deprotonation with lithium diethylamide followed by stereoselective reprotonation using saturated aqueous sodium sulfate.[11] The final addition of methyllithium to **21**, **22** and **23** proceeded stereospecifically and completed the synthesis of **10**, **9** and **1**.



Rearrangements

To learn about possible complications caused by the presence of a geminal dimethyl group in **1** and **9** we first rearranged **10**. When a 0.50 molar solution of **10** in benzene was heated with an equivalent amount (w/w) of Nafion-H[12] for 2.5 h to 70°C, complete conversion to a 85:15 mixture of [3.3.3]propellane **13** (**10-25-28-29-30-13**) and triquinane **31** (**10-25-28-27-31**) was observed. No bridgehead olefins (**26**, **32**, **33**) could be detected, and after 20.5 h at 70°C **31** was the only product (**13-30-29-28-27-31**). It thus turned out that **13** is formed under kinetic and **31** under thermodynamic control. Interestingly, this result corresponds with the calculated heats of formation (kcal/mol)[13] of **26**, **31**, **32**, **33** and **13**, which are given in brackets.

The structures of **13** and **31** were easily recognized by NMR. Ten resonance lines in the ^{13}C NMR together with a singlet for a geminal dimethyl group (δ = 0.99, 6H) and a quartet for a vinylic proton (δ = 4.82, J = 1.5 Hz, 1H) in the ^{1}H NMR established the structure of **13**. The second compound showed also a quartet for a vinylic proton (δ = 4.92, J = 1.3 Hz, 1H) which is only in accord with the structure **31**. Any confusion with a doublet of doublets to be expected for the vinylic protons of the bridgehead olefins **26**, **32** and **33** could be excluded.



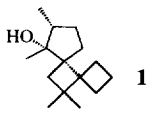
Time (h)	Products (%) 13	31
2.5	85	15
20.5	-	100

Having established the feasibility of a kinetically controlled rearrangement of dispirane **10** to [3.3.3]-propellane **13**, we rearranged dispiranes **1** and **9** next. Based on the results with **10**, we expected a kinetically controlled rearrangement of **1** to (±)-modhephene **6**, and a kinetically controlled rearrangement of **9** to (±)-epimodhephene **12**. The rearrangements were initiated by treatment with equivalent amounts of a 0.075 molar solution of anhydrous p-toluenesulfonic acid in benzene at 70°C monitoring the reaction progress by capillary gas chromatography. Products and yields are given in the scheme.

After 0.3 h, both **1** and **9** had been completely consumed. Analogously to the rearrangement of **10**, the first products from **1** were (±)-modhephene **6** (65%) (**1-35-36-2-6**) and triquinane **37** (34%) (**1-35-34-37**), and the first products from **9** were (±)-epimodhephene **12** (65%) (**9-48-49-50-12**) and triquinane **42** (35%) (**9-48-47-42**). After 6 h, the situation had changed dramatically: both **1** and **9** had rearranged to the same set of compounds, albeit in different yields. The following products were present: (±)-modhephene **6** (6%, 2%), (±)-isocomene **7** (24%, 18%), triquinane **37** (27%, 5%), triquinane **42** (18%, 68%), [3.3.3]propellane **55** (**2-54-55**) (8%, 5%) and triquinane **57** (7%, 2%) (**34-56-57**). Obviously, the desired isomerization of (±)-modhephene **6** to (±)-isocomene **7** (**6-2-3-4-5-7**) had taken place, but equilibration through epimerization (**3-40-51**) had begun. After 48 h, both mixtures were nearly identical, but the main products besides triquinane **42** (33%, 47%) were now three unknowns **U1** (10%, 8%), **U2** (10%, 8%) and **U3** (11%, 9%).

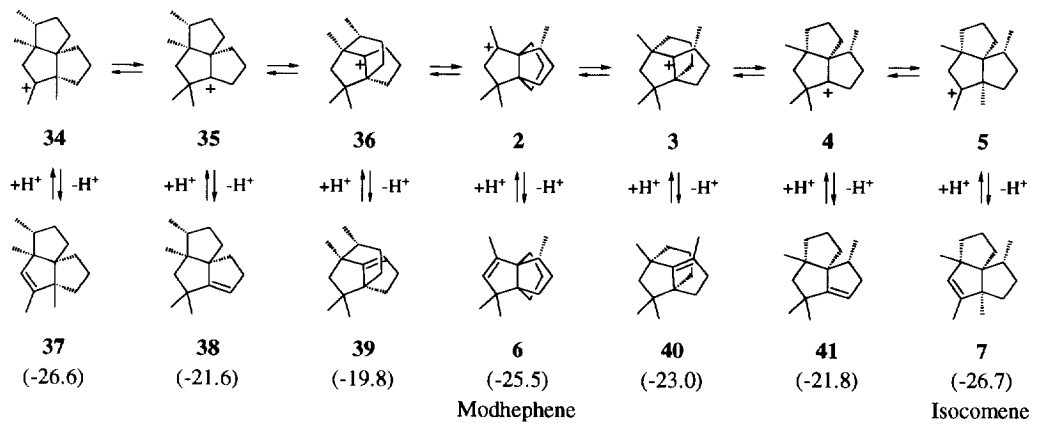
The mixtures obtained by rearrangement of **1** for 0.3, 6.0 and 48.0 h, and of **9** for 0.3 h were subjected to chromatography on silica gel impregnated with silver nitrate[14] giving pure samples of **6**, **7**, **12**, **37**, **42**, **55**, **57**, **U1**, **U2** and **U3**. (±)-Modhephene **6**,[2d,n] (±)-isocomene **7**[3b,e] and (±)-epimodhephene **12**[2b,n] were identified by means of their known ^{13}C NMR data. The same technique revealed that none of the remaining products was (±)-epiisocomene **46**.[15] The structural assignment for triquinanes **37** and **42** was thus straightforward: they were the

only remaining olefins which could exhibit the one proton quartets observed in the vinylic proton region [δ = 5.05, J = 1.3 Hz, (**37**) and δ = 4.90, J = 1.3 Hz, (**42**)].



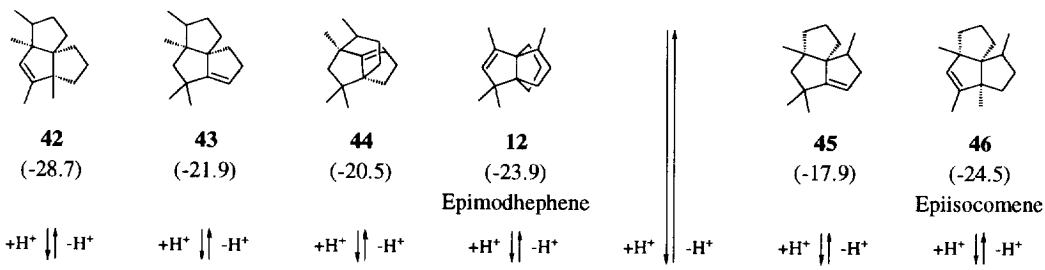
1

Time (h)	Products from **1** (%)									
	6	**7**	**12**	**37**	**42**	**55**	**57**	**U1**	**U2**	**U3**
0.3	65	-	-	34	-	-	-	-	-	-
6.0	6	24	-	27	18	8	7	-	-	-
48.0	-	1	-	-	33	-	-	10	10	11

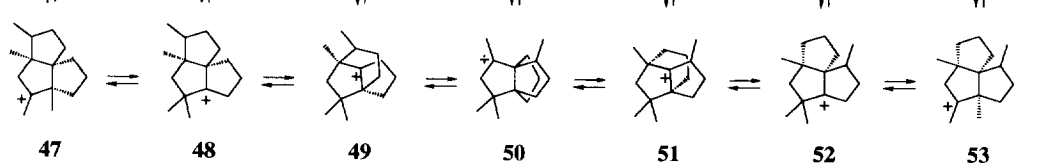


34 **35** **36** **2** **3** **4** **5**

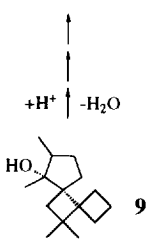
37 (-26.6) **38** (-21.6) **39** (-19.8) **6** (-25.5) Modhephene **40** (-23.0) **41** (-21.8) **7** (-26.7) Isocomene



42 (-28.7) **43** (-21.9) **44** (-20.5) **12** (-23.9) Epimodhephene **45** (-17.9) **46** (-24.5) Epiisocomene



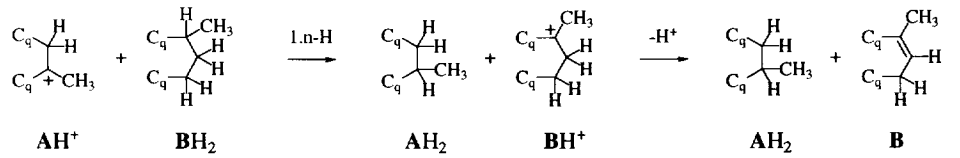
47 **48** **49** **50** **51** **52** **53**

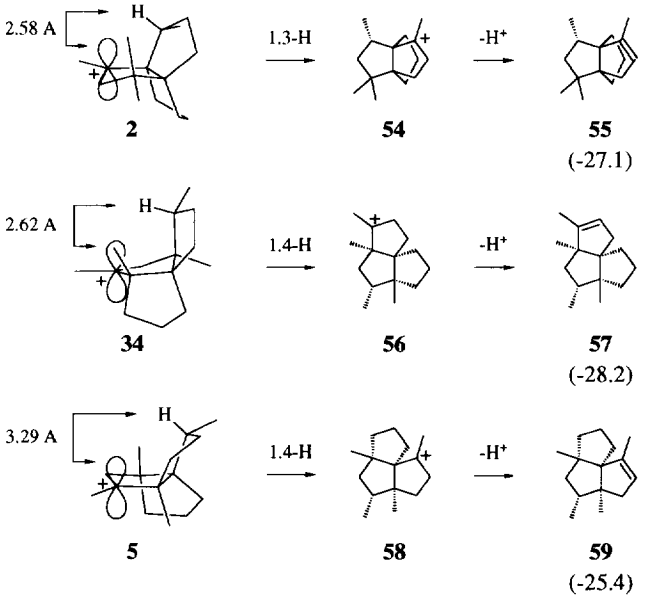


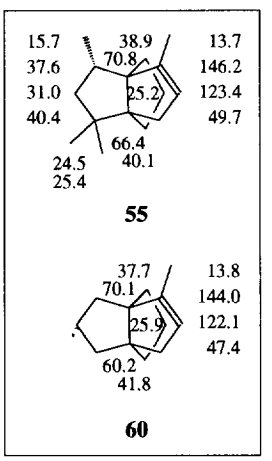
9

Time (h)	Products from **9** (%)									
	6	**7**	**12**	**37**	**42**	**55**	**57**	**U1**	**U2**	**U3**
0.3	-	-	65	-	35	-	-	-	-	-
6.0	2	18	-	5	68	5	4	-	-	-
48.0	-	1	-	-	47	-	-	8	8	9

The structural assignment of [3.3.3]propellane **55** and triquinane **57** was less obvious. Information from ^1H NMR was poor, and a ^1H-^1H correlation only confirmed, that in both compounds substructures AH_2 and **B** were present. However, anticipating that substructure **B** resulted from a deprotonation of BH^+, and BH^+ from an intramolecular 1,n-hydrogen shift from BH_2 to AH^+, only carbenium ions **2**, **5** and **34**, containing both AH^+ and BH_2, could account for the products observed. Because of an unfavourable stereochemistry for an intramolecular 1,n-hydrogen shift, the epimeric carbenium ions **47**, **50** and **53** could be excluded. In order to decide between three candidates for two products, we optimized the geometry of the carbenium ions **2**, **34** and **5**, and calculated the heats of formation of the olefins **55**, **57** and **59**, derived therefrom via a 1,3- (**55**) and 1,4-hydrogen shift (**57**, **59**), respectively.[13] Inspection of the geometry-optimized structures of **2**, **34** and **5** reveals the close proximity (d) of the methine hydrogen to the center of one lobe of the lone pair orbital[13] in **2** (d = 2.58 Å) and **34** (d = 2.62 Å) as compared to **5** (d = 3.29 Å) and hence a kinetic preference for a formation of **55** and **57**. Thermodynamically, **55** (ΔH_f = -27.1 kcal/mol) and **57** (ΔH_f = -28.2 kcal/mol) are also favoured over **59** (ΔH_f = -25.4 kcal/mol). We therefore believe that the structures of 55 and 57 are correct. Further evidence comes from the close fit of the ^{13}C NMR data of **55** and **60**.[5]



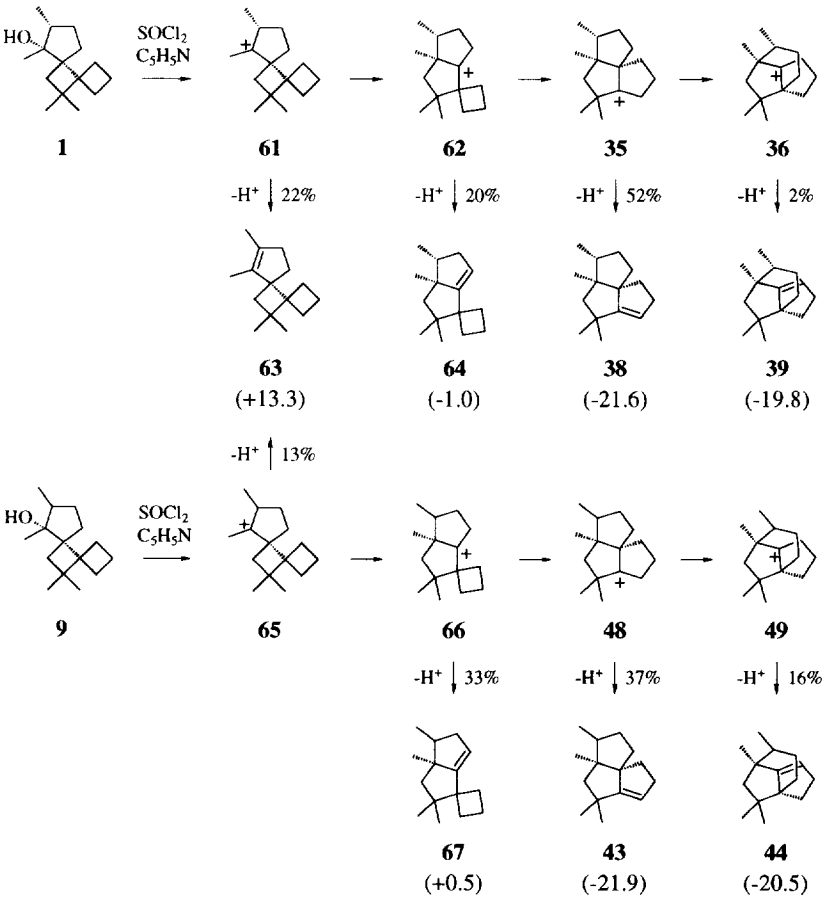




^{13}C NMR Data of **55** and **60**

The ^{1}H and ^{13}C NMR spectra of the remaining unknowns **U1**, **U2** and **U3** indicate that each of them is a tetrasubstituted olefin with three quarternary and a tertiary methyl group. However, albeit extensive ^{1}H-^{1}H and ^{1}J-^{13}C-^{1}H correlation studies were undertaken, none of the structures could be solved.

In a last experiment, we reacted dispiranes **1** and **9** with thionyl chloride in pyridine. Under these conditions reprotonation is impossible, and hence no equilibration can occur. In both cases four products were formed, indicating that rearrangements had taken place. As none of the products was identical with any of the products observed during the acid catalyzed rearrangements, they could only be derived from the very first carbenium ions formed, i.e. from **61**, **62**, **35** and **36** in the case of **1**, and **65**, **66**, **48** and **49** in the case of **9**. Indeed, ^{1}H and ^{13}C NMR spectra confirmed, that the products from **1** were **63**, **64**, **38** and **39**, and the products from **9** were **63**, **67**, **43** and **44**.



63, **64** and **67** could be distinguished from **38**, **39**, **48** and **49** through the presence of ^{13}C-resonances at δ = 17.05 (**63**), 16.16 (**64**) and 16.21 (**67**), characteristic for the peripheral methylene group of spirocyclobutanes. **63**

was easily recognized as tetrasubstituted olefin [δ = 132.57 (C_{quart}), 134.95 (C_{quart})] with two methyl groups at the double bond [δ = 1.53 (3H), 1.62 ppm (3H)], and **64** and **67** as trisubstituted olefins [δ = 115.72 (C_{tert}), 165.37 (C_{quart}) (**64**) and δ = 113.28 (C_{tert}), 161.93 (C_{quart}) (**67**)] with characteristic doublets of doublets for the methine proton [δ = 5.38, J = 3.5, 1.8 Hz (**64**) and δ = 5.26, J = 3.5, 1.8 Hz (**67**)]. Doublets of doublets were also observed for the methine protons of **38** and **43** [δ = 5.16, J = 3.0, 1.5 Hz (**38**) and δ = 5.12, J = 3.5, 1.8 Hz (**43**)], and **39** and **44** [δ = 4.92, J = 2.0, 2.0 Hz (**39**) and δ = 4.85, J = 2.0, 2.0 Hz (**44**)], and the similarity of the coupling constants in **38** and **43** with those in **64** and **67** was thought to be decisive for the structural assignments given.

Summary

Based on model studies with **10**, the epimeric dispiroundecanes **1** and **9** have been synthesized and rearranged by treatment with acids. Under kinetic control, **1** rearranges to (±)-modhephene **6** (65%) and triquinane **37** (34%), and **9** to (±)-epimodhephene **12** (65%) and triquinane **42** (35%). Under thermodynamic control, epimerization takes place and identical products are obtained from both **1** and **9**. These comprise (±)-isocomene **7**, the triquinanes **37**, **42** and **57**, and the propellane **55**. **55** and **57** are formed by unusual 1,3- and 1,4-hydrogen shifts, respectively. This finding was rationalized by force field calculations using MMP2. The early stage of the rearrangements was investigated by reacting **1** and **9** with thionyl chloride in pyridine. Under these conditions, the olefins **63**, **64**, **38**, **39**, and **63**, **67**, **43**, **44**, respectively, are formed. In summary, from a total of sixteen conceivable rearrangement products of **1** and **9** (**6**, **7**, **12**, **37**, **38**, **39**, **40**, **41**, **42**, **43**, **44**, **45**, **46**, **63**, **64**, **67**) twelve (**6**, **7**, **12**, **37**, **38**, **39**, **42**, **43**, **44**, **63**, **64**, **67**) have been isolated and identified. Moreover, an efficient entry to (±)-modhephene **6** has been established, and its rearrangement to (±)-isocomene **7** has been demonstrated for the first time. As optical activity established in **1** and **9** should be preserved throughout the whole rearrangements, enantiospecific syntheses of (-)-modhephene **6**, (-)-isocomene **7** and (-)-epimodhephene **12** should be feasible and their absolute configuration thus clarified. Work towards this end has been successful.[16] A full account will be given elsewhere.

EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer 298 spectrophotometer. ^1H and ^{13}C NMR spectra were measured on a Varian FT 80A, XL 100, XL 200, VXR 200, VXR 500 or a Bruker AMX 300 spectrometer. Mass spectra were obtained with a Varian MAT 311 A, 711 or Finnigan MAT 95 instrument operated at 70 eV. Preparative gas chromatography was carried out on an Intersmat IGC 16, Carlo-Erba FTV 2450 or Carlo-Erba GC 6000 Vega Series 2 instrument employing a thermal conductivity detector and hydrogen as carrier gas. Analytical gas chromatography was carried out on a Carlo-Erba GC 6000 Vega Series 2 instrument employing a split/splitless injector, a FID 40 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. Of the solvents used, ether ($LiAlH_4$), tetrahydrofuran ($LiAlH_4$), benzene (Na) and pyridine (KOH) were dried as indicated and distilled.

Isopropylidenecyclobutane (16): To a vigorously stirred suspension of 4-bromobutyltriphenylphosphonium bromide (360.0 g, 0.75 mol) in ether (1.5 l) under nitrogen were added three portions of potassium-t-butoxide (3 x 56.0 g, 1.50 mol) in 20 min intervals, and the mixture heated to reflux. After 3 h the heating was stopped and acetone (44.1 g, 0.75 mol) was added dropwise, causing a slight to gentle reflux. After an additional hour of reflux, pentane (750 ml) and water (75 ml) were added, the liquid layer decanted, the residue extracted with pentane (6 x 50 ml), and the combined organic layers dried ($MgSO_4$) and concentrated through a 30 cm Vigreux column. The remaining material (300 ml) was distilled to dryness (bath temperature 100°C/10 torr), the distillate washed with water (5 x 30 ml), dried ($MgSO_4$) and fractionated through a 30 cm Vigreux column, yielding 50.3 g (67%) of **16**, b.p. 107°C. - ^{1}H NMR (100 MHz, $CDCl_3$, TMS int.): δ = 1.44-1.54 (m, 6H), 1.60-2.12 (m, 2H), 2.44-2.72 (m, 4H). - ^{13}C NMR (20 MHz, $CDCl_3$, TMS int.): δ = 15.96, 18.10, 29.29, 121.87, 132.37. - MS (70 eV): m/e = 96 (42%, M^+), 41 (100%). - C_7H_{12} requires C, 87.42; H, 12.58: Found: C, 87.29; H, 12.60.

2,2-Dichloro-3,3-dimethylspiro[3.3]heptan-1-one (17): To a sonicated (35 Hz, 320 W) mixture of **16** (9.8 g, 0.10 mol) and zinc dust (13.0 g, 0.20 mol) in ether (500 ml) was added within 2 h at 15-20°C a solution of trichloroacetyl chloride (27.3 g, 0.15 mol) in ether (250 ml). After an additional 30 min the reaction was complete according to glpc [2 m x 1/4" all glass system, 15% SE 30 on Chromosorb W AW/DMCS 60/80 mesh, 3 min at 80°C, 20°C/min to 240°C; rel. retention times: 1.00 (**16**), 3.60 (**17**)]. The mixture was diluted with ether (250 ml) and then filtered over celite. The filtrate was washed with water (2 x 200 ml), saturated sodium bicarbonate (5 x 200 ml) and brine (200 ml), and dried ($MgSO_4$) and concentrated to 40 ml by distillation through a 30 cm Vigreux column. The remaining solvent was distilled off on a rotary evaporator (bath temperature 25°C/20 torr) yielding 19.6 g (95%, purity 85%) of **17** as colourless liquid. Analytically pure **17** was obtained by preparative glpc. - IR (film): 1795 cm^{-1} (C=O). - ^{1}H NMR (80 MHz, $CDCl_3$, $CHCl_3$ int.): δ = 1.25 (s, 6H), 1.60-2.40 (m, 6H). - ^{13}C NMR (50.3 MHz, $CDCl_3$, TMS int.): δ = 15.93, 20.90, 27.03, 46.96, 66.64, 91.82, 200.78. - MS (70 eV): m/e = 206 (1.5%, M^+), 82 (100%). - $C_9H_{12}Cl_2O$ requires C, 52.20; H, 5.84; Cl, 34.24: Found: C, 52.38; H, 5.74; Cl, 34.22.

3,3-Dimethylspiro[3.3]heptan-1-one (18): To a stirred suspension of zinc dust (230.0 g, 3.52 mol) in acetic acid (460 ml) was added within 4 h a solution of **17** (117.8 g, purity 85%, 0.48 mol) in acetic acid (120 ml) and the mixture heated for 3 h to 60°C. After this time, the reaction was complete according to tlc in pentane/ether [9:1; R_f = 0.86 (**17**), 0.68 (**18**)]. The mixture was filtered, the residue extracted with pentane (5 x 200 ml) and the combined organic layers washed with water (500 ml). The aqueous layer was extracted with pentane (5 x 200 ml), the combined organic layers washed with a 1 N potassium hydroxide (2 x 100 ml) and saturated ammonium chloride (2 x 100 ml), dried ($CaCl_2$) and concentrated through a 30 cm Vigreux column. The residue was fractionated yielding 59.4 g (89%, purity 95%) of **18** as colourless liquid, b.p. 79-80°C/25 torr. Analytically pure **18** was obtained by preparative glpc (3 m x 1/4" all glass system, 15% OV 101 on Chromosorb W AW/DMCS 60/80 mesh, 120°C). - IR (film): 1770 cm^{-1} (C=O). - ^{1}H NMR (80 MHz, $CDCl_3$, TMS int.): δ = 1.15 (s, 6H), 1.55-2.20 (m, 6H), 2.65 (s, 2H). - ^{13}C NMR (20 MHz, $CDCl_3$, TMS int.): δ = 15.52, 24.10, 25.84, 30.51, 56.82, 68.11, 214.69. - MS (70 eV): m/e = 138 (3%, M^+), 96 (100%). - $C_9H_{14}O$ requires C, 78.21; H, 10.21. Found: C, 78.32; H, 10.18.

2,2,3,3-Tetramethylspiro[3.3]heptan-1-one (14): To a stirred suspension of potassium hydride (120 mg, 3.0 mmol) in tetrahydrofuran was added a solution of **18** (140 mg, 1.0 mmol) in the same solvent (1.0 ml). After the hydrogen evolution had ceased (5 min), methyliodide (468 mg, 3.3 mmol) was added, the mixture stirred for 2 h and then quenched with water (2.0 ml). The aqueous layer was extracted with ether (4 x 2.5 ml), the combined organic layers washed with brine (2 x 1 ml), dried over molecular sieves 4Å and concentrated to give

144 mg (86%) of crude **14**. Analytically pure **14** was obtained by preparative glpc [3 m x 1/4" all glass system, 15% OV 101 on Chromosorb W AW/DMCS 60/80 mesh, 120°C]. Colourless liquid. - IR (film): 1765 cm^{-1} (C=O). - ^1H NMR (80 MHz, $CDCl_3$, TMS int.): δ = 0.98 (s, 6H), 1.05 (s, 6H), 1.55-2.20 (m, 6H). - ^{13}C NMR (20 MHz, $CDCl_3$, TMS int.): δ = 16.01, 19.59, 20.13, 26.32, 36.62, 60.54, 66.83, 220.90. - MS (70 eV): m/e = 166 (6%, M^+), 84 (100%). - $C_{11}H_{18}O$ requires C, 79.47; H, 10.91. Found: C, 79.63; H, 10.80.

1-Cyclobutylidene-3,3-dimethylspiro[3.3]heptane (19): To a vigorously stirred suspension of 4-bromobutyltriphenylphosphonium bromide (305.0 g, 0.64 mol) in benzene (1.0 l) under nitrogen were added three portions of potassium-t-butoxide (3 x 48.0 g, 1.28 mol) in 20 min intervals and the mixture heated for 3 h to 50°C. **18** (59.0 g, purity 95%, 0.41 mol) was added over a period of 1 h and after additional 2 h at 70°C, the reaction was complete according to glpc [2 m x 1/4" all glass system, 15% SE 30 on Chromosorb W AW/DMCS 60/80 mesh, 150°C; rel. retention times: 1.00 (**18**), 1.25 (**19**)]. Pentane (700 ml) and water (45 ml) were added, the organic layer decanted, the residue extracted with pentane (3 x 200 ml) and the combined organic layers dried ($MgSO_4$) and concentrated through a 30 cm Vigreux column (bath temperature 120°C). The residue was fractionated in vacuo yielding 59.4 g (81%) of pure **19** as colourless liquid, b.p. 61-64°C/1.5 torr. - ^1H NMR (100 MHz, $CDCl_3$, $CHCl_3$ int.): δ = 0.96 (s, 6H), 1.20-2.20 (m, 10H), 2.40-2.98 (m, 4H). - ^{13}C NMR (20 MHz, $CDCl_3$, TMS int.): δ = 15.74, 17.95 (C_{sek}), 24.69 (C_{prim}), 28.27, 29.32, 29.68 (C_{sek}), 35.29 (C_{quart}), 39.75 (C_{sek}), 54.95, 129.41, 134.93 (C_{quart}). - MS (70 eV): m/e = 176 (53%, M^+), 91 (100%). - $C_{13}H_{20}$ requires C, 88.57; H, 11.43. Found: C, 88.68; H, 11.38.

(10*R)-12,12-Dimethyl-10-oxatrispiro[3.0.0.3.1.2]dodecane (20):** To a vigorously stirred mixture of **19** (29.6 g, 0.17 mol), dichloromethane (1750 ml) and a 0.5 M solution of sodium bicarbonate (550 ml) was added within 4 h a solution of m-chloroperbenzoic acid (55.0 g, 55% w/w, 0.18 mol) in dichloromethane (540 ml). After 1 h, the organic layer was washed with 1 N sodium hydroxide (4 x 400 ml), dried ($MgSO_4$) and concentrated on a rotary evaporator (bath temperature 25°C/15 torr) yielding 31.5 g (96%) of **20** as colourless liquid. The product was 95% pure according to glpc (2 m x 3/8" all glass system, 12% FFAP on Chromosorb W AW/DMCS 60/80 mesh, 150°C). Analytically pure **20** was obtained by preparative glpc. - ^1H NMR (100 MHz, $CDCl_3$, $CHCl_3$ int.): δ = 0.80-1.25 (m, 6H), 1.35-2.70 (m, 14H). - ^{13}C-NMR (20 MHz, $CDCl_3$, TMS int.): δ = 13.00, 16.42 (C_{sek}), 24.25 (C_{prim}), 24.35 (C_{sek}), 24.78 (C_{prim}), 25.25, 29.93, 30.37 (C_{sek}), 32.59 (C_{quart}), 39.91 (C_{sek}), 54.38, 68.27, 68.87 (C_{quart}). - MS (70 eV): m/e = 192 (3%, M^+), 149 (100%). - $C_{13}H_{20}O$ requires C, 81.20; H, 10.48. Found: C, 81.18; H, 10.46.

(5*R)-11,11-Dimethyldispiro[3.0.4.2]undecan-6-one (21) and (1R*)-7,8-Dimethylspiro[4.6]undec-7-en-1-one (24):** To a stirred solution of **20** (31.5 g, 0.16 mol) in ether (1.6 l) was added within 2 h at 0°C boron trifluoride etherate (33.9 g, 0.24 mol). After an additional 2 h, the mixture was washed with a solution of 10% (w/w) potassium bicarbonate (4 x 700 ml), the aqueous layers extracted with pentane (500 ml) and the combined organic layers dried ($MgSO_4$) and concentrated on a rotary evaporator (bath temperature 25°C/15 torr). The residue (30.1 g) was chromatographed on silica gel in pentane/ether [95:5; R_f = 0.41 (**20**), 0.30 (**21**), 0.21 (**24**)] yielding 17.0 g (54%) of **21** and 2.5 g (8%) of **24** as colourless liquids. Both compounds were 95% pure according to glpc [3 m x 1/4" all glass system, 15% OV 210 on Chromosorb W AW/DMCS 60/80 mesh, 3 min at 130°C, 20°C/min to 220°C; rel. retention times: 1.00 (**21**), 1.15 (**24**)]. Analytically pure **21** and **24** were obtained by preparative glpc. - **21:** IR (film): 1730 cm^{-1} (C=O). - ^1H NMR (100 MHz, $CDCl_3$, TMS int.): δ = 1.06 (s, 3H), 1.20-2.42 (m, 14H). - ^{13}C NMR (20 MHz, $CDCl_3$, TMS int.): δ = 16.05, 19.86 (C_{sek}), 25.23 (C_{prim}), 25.76 (C_{sek}), 26.76 (C_{prim}), 27.16 (C_{sek}), 33.72 (C_{quart}), 35.28, 37.61, 39.89 (C_{sek}), 51.45, 54.16, 220.71 (C_{quart}). - MS (70 eV): m/e = 192 (14%, M^+), 96 (100%). - $C_{13}H_{20}O$ requires C, 81.20; H, 10.48. Found: C, 81.26; H, 10.31. - **24:** IR (film): 1735 cm^{-1} (C=O). - ^1H NMR (200 MHz, $CDCl_3$, TMS int.): δ =

1.12-1.44 (m, 2H), 1.50-1.98 (m, 14H), 2.08-2.72 (m, 4H). - ^{13}C NMR (20 MHz, $CDCl_3$, TMS int.): δ = 19.11 (C_{sek}), 20.14 (coincidence of two lines, C_{prim}), 23.89, 29.82, 32.79, 33.21, 35.28, 37.83 (C_{sek}), 52.04, 123.69, 127.97, 222.68 (C_{quart}). - MS (70 eV): m/e = 192 (75%, M^+), 136 (100%). - $C_{13}H_{20}O$ requires C, 81.20; H, 10.48. Found: C, 81.29; H, 10.52.

(5*R,6*S**)-6,11,11-Trimethyldispiro[3.0.4.2]undecan-6-ol (10):** To a 0.5 M solution of methyllithium in ether (7.5 ml, 3.75 mmol) was added under nitrogen with stirring within 10 min at 0°C a solution of **21** (250 mg, purity 95%, 1.23 mmol) in ether (3.0 ml). After 1 h at 0°C, the mixture was hydrolyzed with saturated ammonium chloride (2.0 ml), the aqueous phase extracted with ether (4 x 2 ml), the combined organic phases dried over molecular sieves 4Å and concentrated on a rotary evaporator (bath temperature 25°C/15 torr). The residue (214 mg) was chromatographed on silica gel (70-130 mesh) in pentane/ether [4:1; column 35 x 2 cm, control by tlc, R_f = 0.42 (**21**), 0.29 (**10**), 0.20] yielding 171 mg (67%) of **10** and 23 mg (10%) of **21** as colourless liquids. **10** was 97% pure according to glpc (3 m x 3/8" all glass system, 12% FFAP on Chromosorb W AW/DMCS 60/80 mesh, 160°C). Analytically pure **10** was obtained by preparative glpc. - IR (film): 3620 (OH), 3600-3300 cm^{-1} (OH_{ass}). - ^1H NMR (100 MHz, $CDCl_3$, $CHCl_3$ int.): δ = 1.07 (s, 3H), 1.11 (s, 3H), 1.24 (s, 1H, OH), 1.28 (s, 3H), 1.36-1.76 (m, 8H), 1.80-2.62 (m, 6H). - ^{13}C NMR (20 MHz, $CDCl_3$, $CDCl_3$ int.): δ = 17.47, 18.20 (C_{sek}), 23.57, 26.71 (C_{prim}), 27.54 (C_{sek}), 27.61 (C_{prim}), 28.11 (C_{sek}), 32.85 (C_{quart}), 35.09, 39.68, 42.46 (C_{sek}), 49.51, 51.42, 82.79 (C_{quart}). - MS (70 eV): m/e = 175 (3%, M^+-33), 81 (100%). - $C_{14}H_{24}O$ requires C, 80.71; H, 11.61. Found: C, 80.68; H, 11.53.

(5*R,7*R**)-7,11,11-Trimethyldispiro[3.0.4.2]undecan-6-one (22):** To a solution of diisopropylamine (30.0 g, 0.30 mol) in ether (300 ml) was added at -78°C under nitrogen with stirring a 1.6 M solution of n-butyllithium in hexane (140 ml, 0.22 mol). After 30 min at 0°C, a solution of **21** (29.6 g, purity 95%, 0.15 mol) in ether (75 ml) was added. After an additional 30 min at 0°C the mixture was cooled to -78°C, methyl iodide (81.7 g, 0.58 mol) was added slowly and the mixture allowed to warm up again. Pentane (200 ml) was added, the mixture hydrolyzed with saturated ammonium chloride (200 ml), the aqueous phase extracted with pentane (2 x 150 ml), the combined organic layers dried ($MgSO_4$) and concentrated on a rotary evaporator (bath temperature 25°C/15 torr). The residue (32.7 g) was 85% pure and contained 27.9 g (90%) of **22**. Analytically pure **22** was obtained by preparative glpc [3 m x 3/8" all glass system, 12% FFAP on Chromosorb W AW/DMCS 60/80 mesh, 180°C; rel. retention times: 0.84, 1.00 (**22**)]. Colourless liquid. - IR (film): 1730 cm^{-1} (C=O). - ^1H NMR (100 MHz, $CDCl_3$, TMS int.): δ = 0.99 (s, 3H), 1.02 (s, 3H), 1.04 (d, J = 6 Hz, 3H), 1.10-2.27 (m, 13H). - ^{13}C NMR (20 MHz, $CDCl_3$, $CDCl_3$ int.): δ = 15.15 (C_{prim}), 16.11 (C_{sek}), 24.94 (C_{prim}), 25.94 (Csek), 26.74 (C_{prim}), 27.04, 27.83, 32.90 (C_{sek}), 33.88 (C_{quart}), 42.33 (C_{sek}), 43.46 (C_{tert}), 51.18, 53.31, 222.10 (C_{quart}). - MS (70 eV): m/e = 206 (18%, M^+), 96 (100%). - $C_{14}H_{22}O$ requires C, 81.50; H, 10.75. Found: C, 81.76; H, 10.89.

(5*R,6*S**,7*R**)-6,7,11,11-Tetramethyldispiro[3.0.4.2]undecan-6-ol (9):** To a 0.75 M solution of methyllithium in ether (10 ml, 7.50 mmol) was added at 0°C under nitrogen with stirring a solution of analytically pure **22** (420 mg, 2.04 mmol) in ether (5.0 ml). The mixture was stirred for 30 min at 0°C and 30 min at room temperature. Saturated ammonium chloride (5 ml) was added, the aqueous layer extracted with ether (2 x 5 ml) and the combined organic layers dried over molecular sieves 3Å and concentrated on a rotary evaporator (bath temperature 25°C/15 torr). The residue was chromatographed on silica gel (70-130 mesh) in pentane/ether [95:5; column 40 x 3 cm, control by tlc, R_f = 0.19 (**9**), 0.11] yielding 368 mg (81%) of pure **9** as colourless liquid. - IR (KBr): 3630 (OH), 3600-3300 cm^{-1} (OH_{ass}). - ^1H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int.): δ = 0.87 (d, J = 7 Hz, 3H), 0.90 (s, 3H), 1.08 (s, 3H), 1.11 (s, 3H), 1.28 (d, J = 12 Hz, 1H), 1.30-1.65 (m, 5H), 1.74 (d, J = 12 Hz, 1H), 1.78-2.15 (m, 6H), 2.41 (q, J = 7 Hz, 1H). - ^{13}C NMR (20 MHz, $CDCl_3$, $CDCl_3$ int.):

δ = 15.63 (C_{prim}), 17.51 (C_{sek}), 18.73, 26.99, 27.69 (C_{prim}), 28.08, 28.70, 29.39 (C_{sek}), 32.80 (C_{quart}), 33.16, 40.63 (C_{sek}), 43.08 (C_{tert}) 49.56, 53.00, 83.43 (C_{quart}). - MS (70 eV): m/e = 204 (0.7%, M^+-18), 96 (100%). - $C_{15}H_{26}O$ requires C, 81.02; H, 11.78. Found: C, 81.10; H, 11.64.

(5*R,7*S**)-7,11,11-Trimethyldispiro[3.0.4.2]undecan-6-one (23):** To a solution of diisopropylamine (25.2 g, 0.25 mol) in tetrahydrofuran (600 ml) was added at -78°C under nitrogen with stirring a 1.5 M solution of n-butyllithium in hexane (110 ml, 0.17 mol). After 30 min at 0°C, a solution of **22** (20.0 g, purity 85%, 82 mmol) in tetrahydrofuran (100 ml) was added. After an additional 30 min at 0°C, the mixture was cooled to -100°C and saturated sodium sulfate (75 ml) was added. After 12 h, more saturated sodium sulfate (75 ml) was added, the mixture warmed up, the layers separated, the aqueous layer extracted with ether (3 x 125 ml), the combined organic layers dried ($MgSO_4$) and concentrated. The residue was chromatographed twice on silica gel (70-130 mesh) in pentane/ether [96:4; control by tlc, R_f = 0.35 (**22**), 0.28 (**23**)], yielding 11.9 g (70%, purity 94%) of **23** as colourless liquid. Analytically pure **23** was obtained by preparative glpc (3 m x 1/4" all glass system, 15% OV 210 on Chromosorb W AW/DMCS 60/80 mesh, 160°C). - IR (film): 1730 cm^{-1} (C=O). - ^1H NMR (500 MHz, $CDCl_3$, $CHCl_3$ int.): δ = 1.04 (s, 6H), 1.10 (d, J = 7 Hz, 3H), 1.31 (d, J = 12 Hz, 1H), 1.32-1.60 (m, 5H), 1.83-1.90 (m, 1H), 1.91-1.98 (m, 1H), 1.99-2.08 (m, 2H), 2.01 (d, J = 12 Hz, 1H), 2.10-2.16 (m, 1H), 2.33 (dd, J = 13, 7 Hz, 1H). - ^{13}C NMR (20 MHz, $CDCl_3$, $CDCl_3$ int.): δ = 14.22 (C_{prim}), 15.51 (C_{sek}), 25.06 (C_{prim}), 25.28 (C_{sek}), 26.59 (C_{prim}), 27.53, 29.57, 33.36 (C_{sek}), 33.51 (C_{quart}), 39.92 (C_{sek}), 42.78 (C_{tert}), 51.33, 54.40, 222.14 (C_{quart}). - MS (70 eV): m/e = 206 (25%, M^+), 96 (100%). - $C_{14}H_{22}O$ requires C, 81.50; H, 10.75. Found: C, 81.41; H, 10.62.

(5*R,6*S**,7*S**)-6,7,11,11-Tetramethyldispiro[3.0.4.2]undecan-6-ol (1):** To a 0.5 M solution of methyllithium in ether (30 ml, 15 mmol) was added at 0°C under nitrogen with stirring a solution of **23** (1.05 g, purity 94%, 4.8 mmol) in ether (10 ml). The mixture was stirred for 45 min at 0°C and 30 min at room temperature. Saturated ammonium chloride (10 ml) was added, the aqueous layer extracted with pentane (2 x 20 ml), the combined organic layers dried ($MgSO_4$) and concentrated on a rotary evaporator (bath temperature 25° C/15 torr). The residue was chromatographed on silica gel in pentane/ether [95:5; R_f = 0.36 (**23**), 0.24 (**1**)] yielding 95 mg (10%) of **23** and 735 mg (69%) of **1**. Colourless liquid. - IR (film): 3620 (OH), 3600-3350 cm^{-1} (OH_{ass}). - ^1H NMR (500 MHz, $CDCl_3$, $CHCl_3$ int.): δ = 0.87 (d, J = 7 Hz, 3H), 0.99 (s, 1H, OH), 1.10 (s, 3H), 1.12 (s, 3H), 1.21 (s, 3H), 1.27 (d, J = 12 Hz, 1H), 1.45-1.56 (m, 4H), 1.59 (d, J = 12 Hz, 1H), 1.64-1.71 (m, 1H), 1.73-1.81 (m, 1H), 1.87-1.99 (m, 2H), 2.02-2.15 (m, 2H), 2.51-2.57 (m, 1H). - ^{13}C NMR (20 MHz, $CDCl_3$, $CDCl_3$ int.): δ = 12.20 (C_{prim}), 17.69 (C_{sek}), 21.34, 26.85 (C_{prim}), 27.48 (C_{sek}), 27.62 (C_{prim}), 27.96, 28.25 (C_{sek}), 33.26 (C_{quart}), 33.69 (C_{sek}), 41.68 (C_{tert}), 44.19 (C_{sek}), 50.47, 51.75, 83.21 (C_{quart}). - MS (70 eV): m/e = 222 (< 1%, M^+), 96 (100%). - $C_{15}H_{26}O$ requires C, 81.02; H, 11.78. Found: C, 80.94; H, 11.83.

2,4,4-Trimethyltricyclo[3.3.3.0^{1,5}]undec-2-ene (13) and (3a*S,5a*S**,8a*R**)-3a,4,5a-Trimethyl-1,2,3,3a,5a,6,7,8-octahydrocyclopenta[c]pentalene (31):** A mixture of **10** (128 mg, purity 97%, 0.60 mmol), benzene (1.25 ml) and Nafion-H (125 mg) was heated for 2.5 h to 70°C. After this time, **10** had been completely consumed according to tlc in pentane/ether [9:1; R_f = 0.69 (**13**, **31**), 0.43 (**10**)] and the mixture contained 85% **13** and 15% **31** according to capillary glpc [50 m x 0.25 mm FS WCOT, 0.2 µm SE 52, 150°C; rel. retention times: 1.00 (**31**), 1.01 (**13**)]. Separation by preparative glpc [2 m x 1/4" all glass system, 20% OV 17 on Chromosorb W-HP 80/100 mesh; rel retention times: 1.00 (**13**, **31**)] proved impossible but was achieved by thick layer chromatography on plates impregnated with silver nitrate in dichloromethane [SIL G-100 UV254, 20 x 20 x 0.1 cm; R_f = 0.69 (**31**), 0.63 (**13**)] to give 10 mg (9%) of **31** as colourless solid, m.p. 49°C, and 57 mg (50%) of **13** as colourless liquid. In a second experiment, a mixture of **10** (128 mg, purity 97%, 0.60 mmol), benzene (1.25 ml) and Nafion-H (125 mg) was heated for 20 h to 70°C. Quantitative rearrangement to **31** was observed

and preparative glpc yielded 57 mg (50%) of **31**. **13:** ^{1}H NMR (200 MHz, $CDCl_3$, TMS int.): δ = 0.99 (s, 6H), 1.15-1.72 (m, 13H), 1.82-1.96 (m, 2H), 4.82 (q, J = 1.5 Hz, 1H). - ^{13}C NMR (50.3 MHz, $CDCl_3$, TMS int.): δ = 13.52 (C_{prim}), 27.20 (C_{sek}), 27.65 (C_{prim}), 37.45, 38.07 (C_{sek}), 46.21, 64.84, 72.15 (C_{quart}), 135.15 (C_{tert}), 140.02 (C_{quart}). - MS (70 eV): m/e = 190 (26%, M^+), 175 (100%). **31:** ^{1}H NMR (200 MHz, $CDCl_3$, $CHCl_3$ int.): δ = 1.00 (s, 3H), 1.02 (s, 3H), 1.06-1.84 (m, 12H), 1.55 (d, J = 1.3 Hz, 3H), 4.92 (q, J = 1.3 Hz, 1H). - ^{13}C NMR (20 MHz, $CDCl_3$, $CDCl_3$ int.): δ = 12.98, 22.43, 23.93 (C_{prim}), 24.42, 24.63, 37.14, 37.39, 39.93, 42.67 (C_{sek}), 55.78, 59.33, 61.30, 133.46 (C_{tert}), 142.64 (C_{quart}). - MS (70 eV): m/e = 190 (15%, M^+), 148 (100%). - $C_{14}H_{22}$ requires C, 88.35; H, 11.65. Found: C, 88.19; H, 11.53.

(3a*R,4*R**,6a*S**)-5,6-dihydro-1,1,3,4-tetramethyl-1*H*,4*H*-3a,6a-propanopentalene (Modhephene) (6) and (3*R**,3a*R**,5a*R**,8a*R**)-3,3a,5,5a-Tetramethyl-1,2,3,3a,5a,6,7,8-octahydrocyclopenta[c]pentalene (37):** To a 0.075 M solution of anhydrous p-toluenesulfonic acid in benzene (8.85 ml, 0.65 mmol) was added **1** (145 mg, 0.65 mmol) and the resulting mixture stirred for 20 min at 70°C. After this time, the mixture consisted of 65% **6** and 34% **37** according to capillary glpc [30 m x 0.32 mm i.D. fused silicacapillary column coated with 0.25 µm DB FFAP, 90°C; retention times (min): 6.71 (**6**), 6.91 (**37**)]. A 0.5 M solution of sodium bicarbonate (2.0 ml) was added, the layers separated, the aqueous layer extracted with pentane (2 x 5 ml) and the combined organic layers dried over molecular sieves 4Å and concentrated on a rotary evaporator (bath temperature 25°C/15 torr). The residue was chromatographed on silica gel (70-130 mesh) impregnated with 20% (w/w) silver nitrate in pentane/dichloromethane [(95:5); column 70 x 2 cm , R_f = 0.3 (**6**), 0.5 (**37**)] yielding 45 mg (34%) of pure **6** and 25 mg (19%) of pure **37** as colourless liquids. - **6:** ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$ int.): δ = 1.01 (s, 6H), 1.02 (d, J = 7 Hz, 2H), 1.06-2.20 (m, 12H), 1.65 (d, J = 1.3 Hz, 3H), 4.85 (q, J = 1.3 Hz, 1H). - ^{13}C NMR (50.3 MHz, $CDCl_3$, TMS int.): δ = 13.77, 15.60, 26.29 (C_{prim}), 27.14 (C_{sek}), 29.34 (C_{prim}), 29.82, 34.32, 35.77, 38.72 (C_{sek}), 43.90 (C_{tert}), 45.83, 66.00, 73.05 (C_{quart}), 135.42 (C_{tert}), 140.87 (C_{quart}). - MS (70 eV): m/e = 204 (21%, M^+). 189 (100%). - Calculated for $C_{15}H_{24}$: 204.1878. Found: 204.1878 (MS). - **37:** ^{1}H NMR (200 MHz, $CDCl_3$, $CHCl_3$ int.): δ = 0.90 (d, J = 7 Hz, 3H), 0.95 (s, 3H), 1.07 (s, 3H), 1.08-2.00 (m, 11H), 1.61 (d, J = 1.3 Hz, 3H), 5.05 (q, J = 1.3 Hz, 1H). - ^{13}C NMR (50.3 MHz, $CDCl_3$, TMS int.): δ = 13.00, 15.99, 17.59, 23.24 (C_{prim}), 24.87, 32.87, 34.97, 38.70, 39.61 (C_{sek}), 45.55 (C_{tert}), 57.97, 59.49, 63.03 (C_{quart}), 133.96 (C_{tert}), 141.67 (C_{quart}). - MS (70 eV): m/e = 204 (32%, M^+), 148 (100%). - Calculated for $C_{15}H_{24}$: 204.1878. Found: 204.1878 (MS).

(1*R,3a*S**,5a*S**,8a*R**)-1,3a,4,5a-Tetramethyl-1,2,3,3a,5a,6,7,8-octahydrocyclopenta[c]pentalene (Isocomene) (7), (3*R**,3a*R**,5a*R**,8a*R**)-3,3a,5,5a-Tetramethyl-1,2,3,3a,5a,6,7,8-octahydrocyclopenta[c]-pentalene (37), (3*S**,3a*R**,5a*R**,8a*R**)-3,3a,5,5a-Tetramethyl-1,2,3,3a,5a,6,7,8-octahydrocyclopenta[c]-pentalene (42), (1*S**,5*S**,8*S**)-2,6,6,8-Tetramethyltricyclo[3.3.3.0^{1,5}]undec-2-ene (55) and (3a*R**,4*R**,5a*S**,8a*S**)-3a,4,5a,6-Tetramethyl-1,2,3,3a,4,5,5a,8-octahydrocyclopenta[c]pentalene (57):** To a 0.075 M solution of anhydrous p-toluenesulfonic acid in benzene (18.0 ml, 1.35 mmol) was added **1** (300 mg, 1.35 mmol) and the resulting mixture stirred for 6 h at 70°C. After this time, the mixture consisted of 24% **7**, 27% **37**, 18% **42**, 8% **55** and 13% **6** + **57** according to capillary glpc [30 m x 0.32 mm i.d. fused silica capillary column coated with 0.25 µm DB FFAP, 90°C, retention times (min): 5.67 (**42**), 6.10 (**55**), 6.71 (**6** + **57**), 6.91 (**37**), 7.15 (**7**)]. A 0.5 M solution of sodium bicarbonate (10 ml) was added, the layers separated, the aqueous layer extracted with pentane (2 x 50 ml) and the combined organic layers dried over molecular sieves 4Å and concentrated on a rotary evaporator (bath temperature 25°C/15 torr). 100 mg of the residue were chromatographed on silica gel (60-200 mesh) impregnated with 20% (w/w) silver nitrate in pentane (column 150 x 2 cm) yielding 16 mg (6%) of **42**, 6 mg (2%) of **55**, 33 mg (12%) of a 3.8:1-mixture of **7** and **57**, and 20 mg (7%) of **37** as colurless liquids. The separation of **7** and **57** was achieved by twofold chromatography on silica gel impregnated with 20% (w/w)

silver nitrate in pentane and yielded 2.0 mg (1%) of **7** and 2.0 mg (1%) of **57**. The spectral data of **7** and **37** were identical with those of authentic material. - **42:** ^{1}H NMR (300 MHz, $CDCl_3$, $CHCl_3$ int.): δ = 0.84 ppm (d, J = 7 Hz, 3H), 0.98 (s, 3H), 1.00 (s, 3H), 1.04-1.90 (m, 11H), 1.57 (d, J = 1.3 Hz, 3H), 4.90 (q, J = 1.3 Hz, 1H). - ^{13}C NMR (50.3 MHz, $CDCl_3$, $CDCl_3$ int.): δ = 13.17, 14.96, 22.25, 22.43, 24.56, 33.34, 35.29, 37.64, 39.83, 47.10, 58.01, 59.53, 62.05, 129.60, 143.67. - MS (70 eV): m/e = 204 (18%, M^+), 148 (100%). - Calculated for $C_{15}H_{24}$: 204.1878. Found: 204.1878 (MS). - **55:** ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$ int.): δ = 0.92 (s, 3H), 0.94 (s, 3H), 0.95 (d, J = 7Hz, 3H), 1.20-1.30 (m, 1H), 1.32-1.40 (m, 5H), 1.44-1.48 (m, 1H), 1.56-1.62 (m, 1H), 1.60 (ddq, J = 16.5, 2.0, 2.0 Hz, 1H), 1.64 (mc, 3H), 1.94 (ddq, J = 13, 7, 6 Hz, 1H), 2.41 (ddq, J = 16.5, 2.0, 2.0 Hz, 1H), 5.06 (ddq, J = 2.0 Hz). - ^{13}C NMR (125.7 MHz, $CDCl_3$, $CDCl_3$ int.): δ = 13.66, 15.69, 24.35 (C_{prim}), 25.11 (C_{sek}), 25.43 (C_{prim}), 31.00 (C_{sek}), 37.61 (C_{tert}), 38.93, 40.06 (C_{sek}), 40.37 (C_{quart}), 49.68 (C_{sek}), 66.37, 70.80 (C_{quart}), 123.42 (C_{tert}), 146.21 (C_{quart}). - MS (70 eV): m/e = 204 (51%, M^+), 189 (100%). - Calculated for $C_{15}H_{24}$: 204.1878. Found: 204.1878 (MS). - **57:** ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$ int.): δ = 0.74 ppm (d, J = 7 Hz, 3H), 0.82 (s, 3H), 0.99 (s, 3H), 1.01 (dd, J = 13, 7 Hz, 1H), 1.20 (d, J = 14 Hz, 1H), 1.29 (dd, J = 14, 7 Hz, 1H), 1.40-1.70 (m, 6H), 1.59 (mc, 3H), 1.77 (ddq, J = 15.5, 2.5, 1.5 Hz, 1H), 1.91 (ddq, J = 15.5, 3.0, 1.5 Hz, 1H), 4.95 (ddq, J = 3.0, 1.5, 1.5 Hz, 1H). - Calculated for $C_{15}H_{24}$: 204.1878. Found: 204.1878 (MS)

U1, U2 and U3: To a 0.075 M solution of anhydrous p-toluenesulfonic acid in benzene (9.0 ml, 0.68 mmol) was added **1** (150 mg, 0.68 mmol) and the resulting mixture stirred for 48 h at 70°C. According to capillary glpc [30 m x 0.32 mm i.d. fused silica capillary column coated with 0.25 µm DB FFAP, 90°C; retention times (min): 3.92 (**U1** + **U2**), 4.36 (**U3**), 5.67 (**42**)], the main products after this time were **42** (33%) and three unknown compounds **U1** + **U2** (20%) and **U3** (11%). Preparative glpc [3 m x 1/4" all glass system, 15% FFAP on Chromosorb W-HP 80-100 mesh, 150°C; rel. retention times: 1.00 (**U1** + **U2**), 1.10 (**U3**)] yielded 24 mg of a 1:1-mixture of **U1** and **U2**, and 10 mg of **U3** (purity 90%). The mixture of **U1** and **U2**, and **U3** were chromatographed on silica gel (60-200 mesh) impregnated with 20% (w/w) of silver nitrate in pentane (column 40 x 2 cm) yielding 8 mg (6%) **U1**, 7 mg (5%) **U2** and 8 mg (6%) **U3** as colourless liquids. - **U1:** ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$ int.): δ = 0.84 (d, J = 7 Hz, 3H), 0.92 (s, 3H), 0.99 (s, 3H), 1.03 (s, 3H), 1.05 (dd, J = 11, 4 Hz, 1H), 1.40 (dbr, J = 11 Hz, 1H), 1.40-1.45 (m, 2H), 1.54-1.62 (m, 3H), 1.73 (qbr, J = 7 Hz, 1H), 1.70-1.78 (m, 1H), 1.90 (ddd, J = 15, 8, 5 Hz, 1H), 2.26 (ddd, J = 15, 8, 7 Hz, 1H), 2.31 (dd, J = 4.5 Hz, 1H). - ^{13}C NMR (125.7 MHz, $CDCl_3$, TMS int.): δ = 15.35 ppm, 25.40, 26.97, 27.25 (C_{prim}), 30.70 (C_{sek}), 34.94 (C_{tert}), 36.11, 39.35, 39.61, 39.91 (C_{sek}), 41.87, 45.56 (C_{quart}), 45.84 (C_{tert}), 134.65, 148.02 (C_{quart}). - MS (70 eV): m/e = 204 (13%, M^+), 190 (100%). - Calculated for $C_{15}H_{24}$: 204.1878. Found: 204.1878 (MS). - **U2:** ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$ int.): δ = 0.78 (d, J = 7 Hz, 3H), 0.84 (s, 3H), 0.87 (s, 3H), 0.96 (s, 3H), 1.27-1.38 (m, 1H), 1.39-1.46 (m, 1H), 1.48-1.57 (m, 3H), 1.59 (dbr, J = 16 Hz, 1H), 1.60 (q, J = 7 Hz, 1H), 1.79 (ddd, J = 17, 11, 5.5 Hz, 1H), 1.88 (d, J = 6 Hz, 1H), 1.91 (dbr, J = 16 Hz, 1H), 1.99-2.06 (m, 1H), 2.12-2.22 (m, 1H). - ^{13}C NMR (125.7 MHz, $CDCl_3$, TMS int.): δ = 15.14, 24.11, 26.07, 26.65 (C_{prim}), 31.38, 32.06, 35.58, 39.84, 41.41 (C_{sek}), 41.57 (C_{quart}), 44.22 (C_{tert}), 44.68 (C_{quart}), 46.00 (C_{tert}), 138.40, 141.75 (C_{quart}). - MS (70 eV): m/e = 204 (4%, M^+). - Calculated for $C_{15}H_{24}$: 204.1878. Found: 204.1878 (MS). - **U3:** ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$ int.): δ = 0.89 (d, J = 7 Hz, 3H), 0.93 (s, 3H), 0.97 (s, 3H), 1.08 (s, 3H), 1.10 (m, 1H), 1.43 (dd, J = 10, 4 Hz, 1H), 1.48 (dbr, J = 10 Hz, 1H), 1.50-1.52 (m, 1H), 1.55-1.64 (m, 2H), 1.69-1.78 (m, 2H), 1.93 (ddd, J = 16, 8, 7 Hz, 1H), 2.10-2.20 (m, 2H), 2.27 (dd, J = 4.5 Hz, 1H). - ^{13}C NMR (125.7 MHz, $CDCl_3$, TMS int.): δ = 12.05, 25.92, 26.90, 27.42 (C_{prim}), 29.77, 29.82 (C_{sek}), 33.90 (C_{tert}), 34.73, 39.97 (C_{sek}), 43.09 (C_{quart}), 44.02 (C_{tert}), 45.65 (C_{quart}), 47.48 (C_{sek}), 133.83, 148.42 (C_{quart}). - Calculated for $C_{15}H_{24}$: 204.1878. Found: 204.1878 (MS).

(3a*R,4*S**,6a*S**)-5,6-Dihydro-1,1,3,4-tetramethyl-1*H*,4*H*-3a,6a-propanopentalene (Epimodhephene) (12) and (3*S**,3a*R**,5a*R**,8a*R**)-3,3a,5,5a-Tetramethyl-1,2,3,3a,5a,6,7,8-octahydrocyclopenta[c]pentalene (42):** To a 0.075 M solution of anhydrous p-toluenesulfonic acid in benzene (4.9 ml, 0.37 mmol) was added **9** (82 mg, 0.37 mmol) and the resulting mixture stirred for 20 min at 70°C. After this time, the solution contained 65% of **12** and 35% of **42** according to capillary glpc [30 m x 0.32 mm i.d. fused silica capillary column coated with 0.25 µm DB FFAP, 90°C, retention times (min): 5.67 (**42**), 6.80 (**12**)]. A 0.5 M solution of sodium bicarbonate (1 ml) was added, the aqueous layer extracted with pentane (2 x 1 ml) and the combined organic layers dried over molecular sieves 4Å and concentrated on a rotary evaporator (bath temperature 25°C/15 torr). The residue (75 mg) was chromatographed on silica gel (60-200 mesh) impregnated with 20% (w/w) of silver nitrate in pentane [column 40 x 2 cm, R_f = 0.75 (**42**) and 0.55 (**12**) on impregnated tlc sheets] yielding 36 mg (48%) of epimodhephene (**12**) and 16 mg (21%) of **42** as colourless liquids. The spectral data of **42** were identical with those of authentic material. - **12:** ^{1}H NMR (200 MHz, $CDCl_3$, $CHCl_3$ int.): δ = 0.88 ppm (d, J = 7 Hz, 3H), 0.98 (s, 3H), 1.01 (s, 3H), 1.00-2.00 (m, 11H), 1.60 (d, J = 1.3 Hz, 3H), 4.97 (q, J = 1.3 Hz, 1H). - ^{13}C NMR (20 MHz, $CDCl_3$, $CDCl_3$ int.): δ = 14.94, 16.73 (C_{prim}), 26.64 (C_{sek}), 27.04, 27.68 (C_{prim}), 34.45, 35.40, 38.42, 38.64 (C_{sek}), 42.91 (C_{tert}), 45.79, 65.09, 75.07, 137.42 (C_{quart}), 138.39 (C_{tert}). - MS (70 eV): m/e = 204 (27%, M^+), 189 (100%). - Calculated for $C_{15}H_{24}$: 204.1878. Found: 204.1878 (MS).

When **9** was rearranged for longer times under otherwise unchanged conditions, the composition according to capillary glpc [30 m x 0.32 mm i.d. fused silica capillary column coated with 0.25 µm DB FFAP, 90°C, retention times (min): 3.92 (**U1** + **U2**), 4.36 (**U3**), 5.67 (**42**), 6.10 (**55**), 6.71 (**6** + **57**), 6.91 (**37**), 7.15 (**7**)] was 18% **7**, 5% **37**, 68% **42**, 5% **55** and 4% **6** + **57** after 6 h, and 47% **42**, 16% **U1** + **U2** and 9% **U3** after 48 h.

(3*S,3a*R**,8a*R**)-3,3a,5,5-Tetramethyl-1,2,3,3a,4,5,7,8-octahydrocyclopenta[c]pentalene (38), (1*R**,6*R**,7*S**)-6,7,10,10-Tetramethyltricyclo[4.3.2.0^{1,5}]undec-4-ene (39), (5*R**)-6,7,11,11-Tetramethyldispiro-[3.0.4.2]undec-6-ene (63) and (4*R**,5*S**)-4,5,7,7-Tetramethylbicyclo[3.3.0]oct-1-ene-8-spirocyclobutane (64):** To a stirred solution of **1** (200 mg, 0.90 mmol) in pyridine (6.0 ml) was added at 0°C over a period of 5 min a solution of thionyl chloride (430 mg, 3.61 mmol) in the same solvent (1.2 ml). After 10 min, the mixture consisted of 54% of **38** + **39**, 22% **63** and 20% **64** according to capillary glpc [30 m x 0.32 mm i.d. fused silica capillary column coated with 0.25 µm DB FFAP, 90°C; retention times (min): 5.25 (**64**), 5.45 (**38** + **39**), 6.45 (**63**)]. The solution was treated with water (5 ml), extracted with pentane (2 x 10 ml) and the combined organic phases washed with water (5 ml), dried over molecular sieves 4Å and concentrated (bath temperature 25°C/15 torr). The residue was chromatographed on silica gel (70-130 mesh) impregnated with 20% (w/w) of silver nitrate in pentane (column 60 x 2 cm) yielding 45 mg (24%) of **38**, 4 mg (2%) of **39**, 20 mg (11%) of **63** and 18 mg (10%) of **64** as colourless liquids. The purity of all compounds was >95% according to capillary glpc. **38:** ^{1}H NMR (200 MHz, $CDCl_3$, $CHCl_3$ int.): δ = 0.85 (s, 3H), 0.85 (d, J = 7 Hz, 3H), 1.10 (s, 3H), 1.16 (s, 3H), 1.20-1.30 (m, 2H), 1.42 (m, 1H), 1.60 (d, J = 14 Hz, 1H), 1.80-2.04 (m, 4H), 1.90 (d, J = 14 Hz, 1H), 2.33 (dddd, J = 15, 8.5, 3, 1Hz, 1H), 2.60 (dddd, J = 15, 10, 6, 1.5 Hz, 1H), 5.16 (dd, J = 3, 1.5 Hz, 1H). - ^{13}C NMR (20 MHz, $CDCl_3$, TMS int.): δ = 17.61, 20.64, 31.34, 31.55 (C_{prim}), 33.36, 35.20 (C_{sek}), 36.10 (C_{quart}), 36.58, 38.43 (C_{sek}), 44.38 (C_{tert}), 50.79 (C_{quart}), 61.50 (C_{sek}), 69.08 (C_{quart}),115.65 (C_{tert}), 166.99 (C_{quart}). - MS (70 eV): m/e = 204 (9%, M^+), 69 (100%). - Calculated for $C_{15}H_{24}$: 204.1878. Found: 204.1878 (MS). - **39:** ^{1}H NMR (200 MHz, $CDCl_3$, $CHCl_3$ int.): δ = 0.77 ppm (s, 3H), 0.84 (d, J = 7 Hz, 3H), 0.97 (s, 3H), 1.01 (s, 3H), 1.10-1.26 (m, 2H), 1.32 (d, J = 13 Hz, 1H), 1.48-2.08 (m, 5H), 1.83 (d, J = 13 Hz, 1H), 2.35 (dddd, J = 16, 10, 4.5, 2 Hz, 1H), 2.57 (dddd, J = 16, 10, 5.5, 2 Hz, 1H), 4.92 (dd, J = 2 Hz, 1H). - MS (70 eV): m/e = 204 (4%, M^+), 133 (100%). - Calculated for $C_{15}H_{24}$: 204.1878. Found: 204.1878 (MS). **63:** ^{1}H NMR (80 MHz, $CDCl_3$, $CHCl_3$ int.): δ = 1.05 ppm (s, 3H), 1.11 (s, 3H), 1.17-2.38 (m, 12H), 1.53 (mc, 3H), 1.64 (mc, 3H). - ^{13}C NMR

(125.7 MHz, $CDCl_3$, TMS int.): δ = 12.39, 14.53 (C_{prim}), 17.05 (C_{sek}), 26.39, 27.51 (C_{prim}), 27.89, 28.43 (C_{sek}), 33.34 (C_{quart}), 36.57, 37.13, 43.18 (C_{sek}), 53.68, 55.57, 132.57, 134.95 (C_{quart}). - MS (70 eV): m/e = 204 (1%, M^+), 108 (100%). - Calculated for $C_{15}H_{24}$: 204.1878. Found: 204.1878 (MS). **64:** ^1H NMR (200 MHz, $CDCl_3$, $CHCl_3$ int.): δ = 0.65 ppm (s, 3H), 0.88 (s, 3H), 0.91 (d, J = 7 Hz, 3H), 1.03 (s, 3H), 1.20 (dd, J = 13.5, 0.7 Hz, 1H), 1.33 (d, J = 13.5 Hz, 1H), 1.60-1.68 (m, 1H), 1.70-1.76 (m, 1H), 1.79-1.93 (m, 3H), 1.96-2.05 (m, 1H), 2.18-2.26 (m, 2H), 2.32 (ddd, J = 15, 7, 3.5 Hz, 1H), 5.38 (dd, J = 3.5, 1.8 Hz, 1H). - ^{13}C NMR (50.3 MHz, $CDCl_3$, TMS int.): δ = 13.89 (C_{prim}), 16.16 (C_{sek}), 20.94, 25.39 (C_{prim}), 26.12 (C_{sek}), 26.37 (C_{prim}), 29.17, 40.75 (C_{sek}), 43.96 (C_{quart}), 49.87 (C_{tert}), 50.66 (C_{sek}), 52.31, 52.39 (C_{quart}), 115.72 (Ctert), 165.37 (C_{quart}). - MS (70 eV): m/e = 204 (9%, M^+), 161 (100%). - Calculated for $C_{15}H_{24}$: 204.1878. Found: 204.1878 (MS).

(3*R,3a*R**,8a*R**)-3,3a,5,5-Tetramethyl-1,2,3,3a,4,5,7,8-octahydrocyclopenta[c]pentalene (43), (1*R**, 6*R**,7*R**)-6,7,10,10-Tetramethyltricyclo[4.3.2.0^{1,5}]undec-4-ene (44), (5*R**)-6,7,11,11-Tetramethyldispiro-[3.0.4.2]undec-6-ene (63) and (4*R**,5*R**)-4,5,7,7-Tetramethylbicyclo[3.3.0]oct-1-ene-8-spirocyclobutane (67):** To a stirred solution of **9** (100 mg, 0.45 mmol) in pyridine (3.0 ml) was added at 0°C over a period of 5 min a solution of thionyl chloride (215 mg, 1.8 mmol) in the same solvent (0.6 ml). After 10 min, the mixture consisted of 37% **43**, 16% **44**, 13% **63** and 33% **67** according to capillary glpc [30 m x 0.32 mm i.d. fused silica capillary column coated with 0.25 µm DB FFAP, 90°C; retention times (min): 4.79 (**43**), 5.75 (**44**), 5.99 (**67**), 6.34 (**63**)]. The solution was treated with water (3 ml), extracted with pentane (3 x 5 ml) and the combined organic layers washed with water (5 ml), dried over molecular sieves 4Å and concentrated (bath temperature 25°C/15 torr). The residue was chromatographed on silica gel (70-130 mesh) impregnated with 20% (w/w) silver nitrate in pentane (column 60 x 2 cm) yielding 8.0 mg (9%) of **63** (purity 100%), 16.5 mg (18%) of a mixture of **43** and **67**, and 14.0 mg (15%) of **44** (purity 95%). **43** and **67** were separated by preparative glpc [3 m x 1/4" all glass system, 15% FFAP on Chromosorb W AW/DMCS 60-80 mesh; rel. retention times: 1.00 (**43**), 1.12 (**67**)] yielding 6 mg of pure **43** and 5 mg of pure **67**. The ^1H NMR data of **63** were identical with those of authentic material obtained from the rearrangement of **1**. **43:** .^1H NMR (200 MHz, $CDCl_3$, $CHCl_3$ int.): δ = 0.84 (d, J = 7 Hz, 3H), 0.86 (s, 3H), 1.13 (s, 3H), 1.15 (s, 3H), 1.31 (d, J = 14 Hz, 1H), 1.30-1.44 (m, 2H), 1.48-1.70 (m, 2H), 1.70-1.84 (m, 3H), 1.93 (d, J = 14 Hz, 1H), 2.32 (dddd, J = 15, 8.5, 3.5, 1 Hz, 1H), 2.59 (dddd, J = 15, 10, 6.5, 1.8 Hz, 1H), 5.12 (dd, J = 3.5, 1.8 Hz, 1H). - ^{13}C NMR (125.7 MHz, $CDCl_3$, TMS int.): δ = 14.60, 22.98 (C_{prim}), 31.32 (C_{sek}), 31.91, 32.11 (C_{prim}), 35.15 (C_{sek}), 35.33 (C_{quart}), 35.94, 37.03 (C_{sek}), 44.63 (C_{tert}), 51.27 (C_{quart}), 52.63 (C_{sek}), 70.31 (C_{quart}), 115.08 (C_{tert}), 167.00 (C_{quart}). - MS (70 eV): m/z = 204 (40%, M^+), 91 (100%). - Calculated for $C_{15}H_{24}$: 204.1878. Found: 204.1878 (MS). **44:** ^1H NMR (80 MHz, $CDCl_3$, $CHCl_3$ int.): δ = 0.75 (d, J = 7 Hz, 3H), 0.85 (s, 3H), 1.00 (s, 3H), 1.05 (s, 3H), 1.10-2.55 (m, 11H), 4.85 (dd, J = 2, 2 Hz, 1H). - ^{13}C NMR (50.3 MHz, $CDCl_3$, TMS int.): δ = 15.87, 21.20, 22.55 (C_{prim}), 29.07 (C_{sek}), 30.42 (C_{quart}), 30.60, 35.45, 37.09 (C_{sek}), 38.01, 40.88 (C_{quart}), 41.61 (C_{tert}), 48.93 (C_{sek}), 61.38 (C_{quart}), 108.91 (C_{tert}), 163.13 (C_{quart}). - MS (70 eV): m/e = 204 (5%, M^+), 133 (100%). - Calculated for $C_{15}H_{24}$: 204.1878. Found: 204.1878 (MS). **67:** ^1H NMR (200 MHz, $CDCl_3$, $CHCl_3$ int.): δ = 0.65 (s, 3H), 0.78 (d, J = 7 Hz, 3H), 1.06 (s, 3H), 1.08 (d, J = 14 Hz, 1H), 1.09 (s, 3H), 1.65 (d, J = 14 Hz, 1H), 1.55-2.00 (m, 7H), 2.16-2.32 (m, 1H), 2.91 (ddd, J = 15.5, 6.5, 1.5 Hz, 1H), 5.26 (dd, J = 3.5, 1.5 Hz, 1H). - ^{13}C NMR (50.3 MHz, $CDCl_3$, TMS int.): δ = 16.21 (C_{sek}), 18.63, 26.44, 26.64 (C_{prim}), 26.92 (C_{sek}), 29.40 (C_{prim}), 29.90, 41.95 (C_{sek}), 43.75 (C_{quart}), 44.71 (C_{tert}), 45.70 (C_{sek}), 51.43, 54.87 (C_{quart}), 113.28 (C_{tert}), 161.93 (C_{quart}). - MS (70 eV): m/e = 204 (12%; M^+), 161 (100%).

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