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SYNTHESIS AND REARRANGEMENT OF DISPIRO[2.0.3.4]-, DISPIRO-[3.0.3.3]- AND DISPIRO[2.1.3.3]UNDECANES - PREFERRED C_4-C_5 OVER C_3-C_4 AND C_4-C_3 OVER C_5-C_6 REARRANGEMENTS[1]

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Abstract: The dispiranes **10-12** have been synthesized and rearranged by treatment with acids. With **10**, an initial C_3-C_4 ring enlargement leads to [3.3.3]propellane **21**, with **11**, an initial C_4-C_3 ring contraction leads to pentalene **37**, and with **12**, an initial C_4-C_5 ring enlargement leads to **42**, **43**, **44** or **45**, depending on the reagent used. The structure of **43** has been determined by crystal structure analysis of the 3,5-dinitrobenzoate **46** derived therefrom. The rearrangement of **10** points to dispirane **47** as potential precursor of (±)-modhephene **48**.

INTRODUCTION

Acid catalyzed rearrangement of suitable sized dispiroundecanes is a new and effective way to [3.3.3]propellanes.[1] Thus, ketones **1-3** all rearrange to give the bicyclic enone **22** under kinetic control and the [3.3.3]-propellane **23** under thermodynamic control. The corresponding alcohols **7-9** all yield the [3.3.3]propellane **21**. The rearrangements are favoured by the large energy gain associated with the initial C_4-C_5 ring enlargements[2] and proceed via the tricyclic carbenium ions **18a** (**1-3**) and **18b** (**7-9**), respectively. In the case of **9**, the rearrangement proceeds stereospecifically with exclusive 1,2-shift of that cyclobutane bond having an antiperiplanar alignment with the leaving hydroxyl group. The potential value of this stereospecificy for the synthesis of (±)-modhephene has been recognized.[1]

The formation of [3.3.3]propellanes could also be imagined by rearrangement of ketones **4-6** and alcohols **10-12** via the tricyclic carbenium ions **19a** (**4-6**) and **19b** (**10-12**), respectively. However, the possibility of a concurrent C_4-C_5 vs. C_3-C_4 ring enlargement in the case of **6** and **12**, and a concurrent C_4-C_3 ring contraction vs. C_5-C_6 ring enlargement in the case of **5** and **11**, made the outcome in these cases less obvious.[2] We herein report on the synthesis of ketones **4-6** and alcohols **10-12**, and on the rearrangement of **6**, **10**, **11** and **12**.

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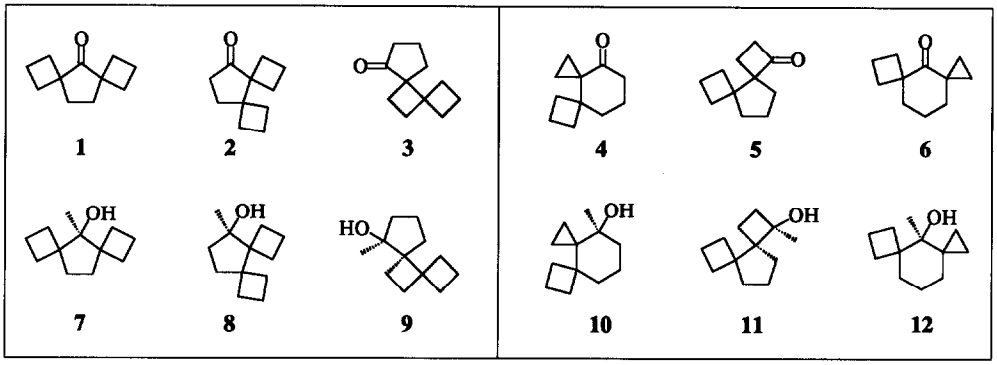
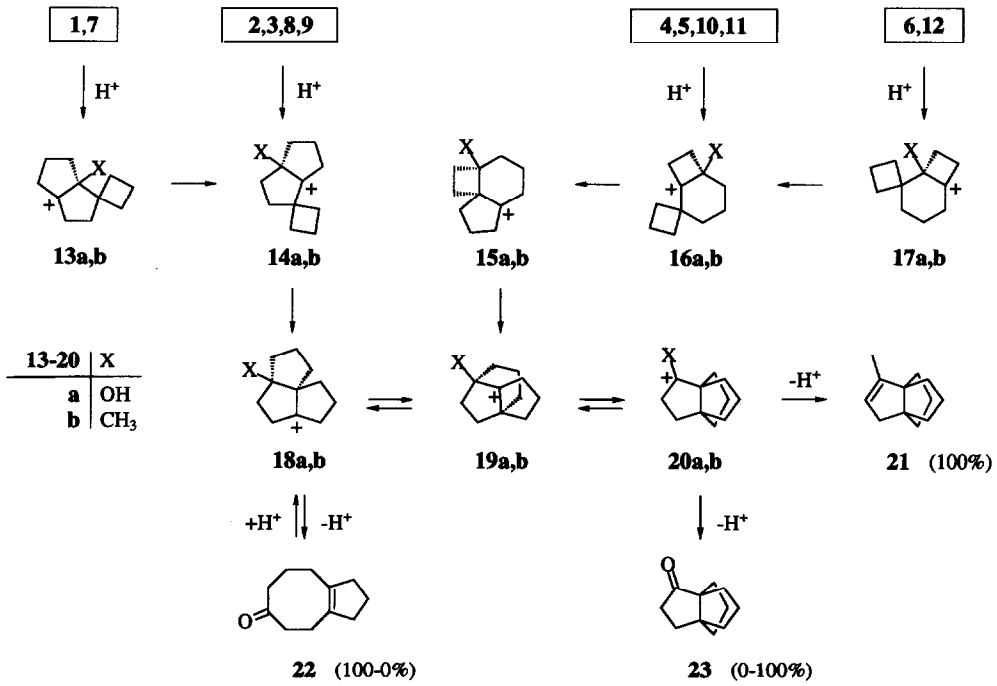


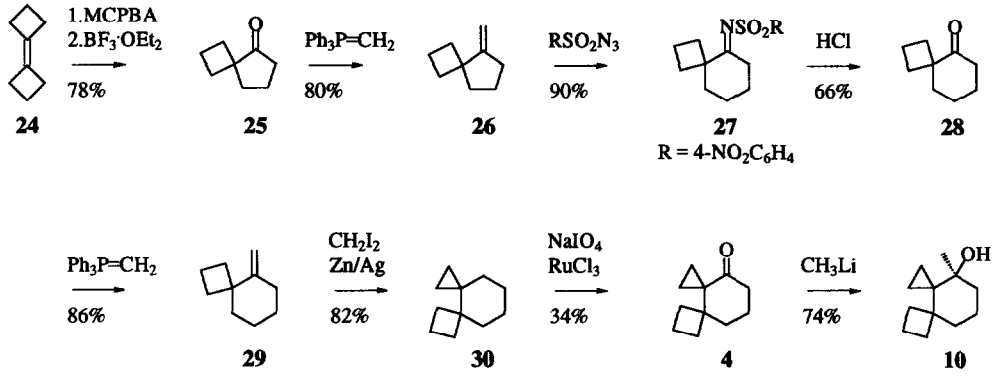


SYNTHESES

The syntheses of ketones **4-6** and alcohols **10-12** are based on the readily available bicyclobutylidene[3] **24** and take advantage of the fact, that ring enlargements via oxaspiropentanes,[4] oxaspirohexanes[5] and Δ^2-triazolines[6] are now well established.

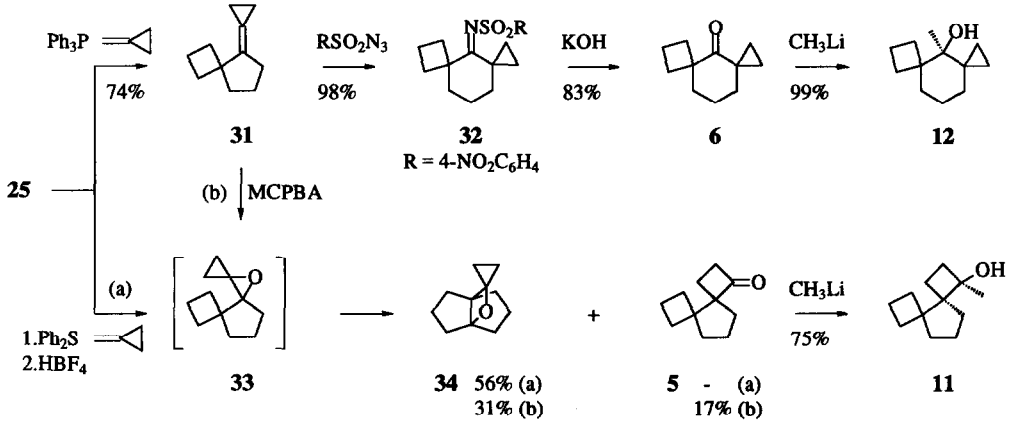
For the synthesis of **4** and **10**, we envisioned a selective oxidation of dispirane **30**. This compound was obtained as follows: epoxidation of bicyclobutylidene **24** and in situ rearrangement of the resulting oxaspirohexane with boron trifluoride etherate yielded spiro[3.4]octanone **25**,[7] which was first homologated to spiro[3.5]-nonanone **28** by a sequence of methylenation, reaction with p-nitrobenzenesulfonic acid azide and hydrolysis of

the resulting ring expanded imide, and then methylenated and cyclopropanated to give **30** (**24-25-26-27-28-29-30**). Of the remaining two steps, the selective oxidation of **30** proved difficult. Only 6% of the desired ketone **4** resulted from dry ozonization,[8] but 34% of **4** were obtained from oxidation with sodium periodate/ruthenium trichloride monohydrate.[9] No difficulties were encountered with the final addition of methyllithium to give **10**.



24 **25** **26** **27** R = 4-$NO_2C_6H_4$ **28** **29** **30** **4** **10**

For the synthesis of **6** and **12**, spiro[3.4]octanone **25** was cyclopropylidenated with cyclopropylidene triphenylphosphorane and the resulting olefin **31** reacted with p-nitrobenzenesulfonic acid azide. A single ring expanded imide, **32**, arose, indicating the desired regiospecificy during addition and rearrangement. Base catalyzed hydrolysis and addition of methyllithium completed the synthesis of **6** and **12**.



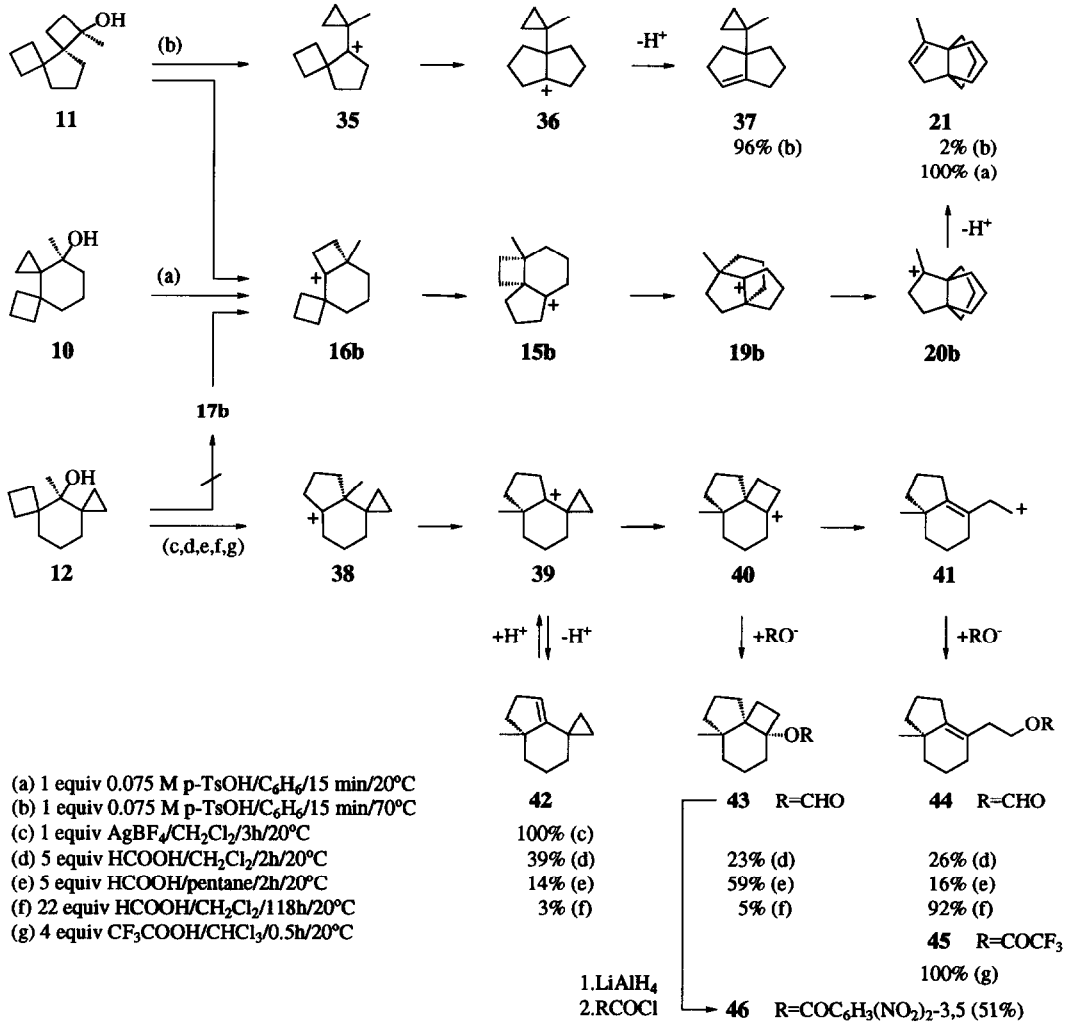
31 **32** R = 4-$NO_2C_6H_4$ **6** **12** **33** **34** 56% (a) 31% (b) **5** - (a) 17% (b) **11**

The outcome of the two spiroannelation procedures employed for the synthesis of **5** proved puzzling: when spiro[3.4]octanone **25** was treated with diphenylsulfonium cyclopropylide and the resulting oxaspiropentane **33** treated with aqueous tetrafluoroboric acid[10] (path a), an exclusive C_4-C_5 ring enlargement furnished propellane **34** (56%). On the other hand, when the same oxaspiropentane was generated by treatment of **31** with

m-chloroperoxybenzoic acid in dichloromethane[11] (path b), propellane **34** (31%) was still the main product, but a concurrent C_3-C_4 ring enlargement now also furnished ketone **5** (17%). The final addition of methyllithium to **5** proceeded stereospecifically and yielded **11**.

REARRANGEMENTS

When alcohol **10** was treated with an equimolar amount of a 0.075 molar solution of anhydrous p-toluenesulfonic acid in benzene for 15 min at 20°C (path a), quantitative conversion to [3.3.3]propellane **21**[1,12] was observed. Obviously, the desired initial C_3-C_4 ring enlargement had taken place, and with the following C_4-C_5 ring enlargement the rearrangement had entered the tricycloundecane energy surface specifically at **15b**. As previously shown,[1] this guaranteed the formation of **21** (**10-16b-15b-19b-20b-21**).

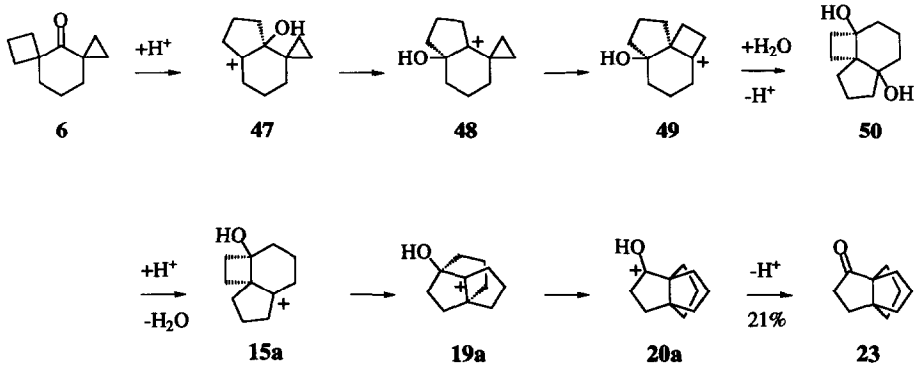


(a) 1 equiv 0.075 M p-TsOH/C_6H_6/15 min/20°C
(b) 1 equiv 0.075 M p-TsOH/C_6H_6/15 min/70°C
(c) 1 equiv $AgBF_4$/CH_2Cl_2/3h/20°C
(d) 5 equiv HCOOH/CH_2Cl_2/2h/20°C
(e) 5 equiv HCOOH/pentane/2h/20°C
(f) 22 equiv HCOOH/CH_2Cl_2/118h/20°C
(g) 4 equiv CF_3COOH/$CHCl_3$/0.5h/20°C

Only minor amounts of the desired [3.3.3]propellane **21** (2%) were formed from alcohol **11**. When this compound was treated with an equimolar amount of a 0.075 molar solution of anhydrous p-toluenesulfonic acid in benzene for 15 min at 70°C (path b), hexahydro-pentalene **37** (96%) was the major product. This indicates a large preference for an initial C_4-C_3 ring contraction leading to **37** (**11-35-36-37**) over the desired C_5-C_6 ring enlargement leading to **21** (**11-16b-15b-19b-20b-21**).

No [3.3.3]propellane **21** at all was formed from alcohol **12**. Treatment with silver tetrafluoroborate in dichloromethane (1 equiv/3h/20°C, path c) yielded hexahydro-indene **42**, treatment with formic acid in dichloromethane (5 equiv/2h/20°C, path d) a mixture of hexahydro-indene **42**, tricycloundecane **43** and hexahydro-indene **44**. Treatment with formic acid in pentane (5 equiv/2h/20°C, path e) favoured the formation of **43**, and use of a large excess of the same reagent in dichloromethane (22 equiv/118h/20°C, path f) the formation of **44**. Finally, treatment with trifluoroacetic acid in chloroform (4 equiv/0.5h/20°C, path g) yielded hexahydro-indene **45**. Clearly, in all cases a preferred C_4-C_5 over C_3-C_4 ring enlargement had taken place, and all products were derived from **38** [**12-38-39(42)-40(43)-41(44,45)**].

From the above, it seemed most likely that a rearrangement of ketone **6** would proceed by the same mechanism as for alcohol **12**. Formation of the hydroxycarbenium ion **49** could be anticipated but, contrary to **40**, this ion was thought to possibly avoid ring opening through a 1,3-transposition of its hydroxyl group (**49-50-15a**) under aqueous conditions. Indeed, treatment of ketone **6** with 50 % aqueous sulfuric acid in dichloromethane (1:1) for 16h at 20°C yielded the [3.3.3]propellane **23**[1,13], albeit in moderate yield (21%). No efforts were made to optimize this process.



6 **47** **48** **49** **50**

15a **19a** **20a** **23**

Of the new products formed, hexahydro-pentalene **37** and hexahydro-indenes **42**, **44** and **45** were easily recognized from their ^{1}H- and ^{13}C-NMR data. In the case of **42**, olefins derived from **38** could be ruled out by a $^2J,^3J$-^{13}C-^{1}H correlation. The tricyclic formiate **43** was identified by means of a crystal structure analysis of the 3,5-dinitrobenzoate **46** derived therefrom. To this purpose, **43** was reduced with lithium aluminium hydride and the resulting alcohol reacted with 3,5-dinitrobenzoyl chloride in pyridine (**43-46**).

CRYSTAL STRUCTURE

The 3,5-dinitrobenzoate **46** forms monoclinic crystals from methanol. The tricyclic system is all-cis configurated (Fig. 1). The central six-membered ring adopts a chair conformation. The chair is normally puckered in the unsubstituted part [C(5)-C(6)-C(7)-C(8) 59.8°, C(6)-C(7)-C(8)-C(9) -56.4°] and strongly flattened in the substituted part [C(9)-C(1)-C(5)-C(6) 33.4°, C(5)-C(1)-C(9)-C(8) -31.8°]. As a consequence, remarkably different bond lengths are observed [e.g. C(1)-C(9) 157.1 pm, C(7)-C(8) 144.4 pm]. The cyclopentane ring adopts an envelope conformation with C(5) out of plane [C(1)-C(2)-C(3)-C(4) 6.8°], and the cyclobutane ring is moderately puckered [C(1)-C(9)-C(10)-C(11) 19.2°]. Bond lengths, bond angles and torsion angles of the tricycloundecane part are given in Tables 1-3.

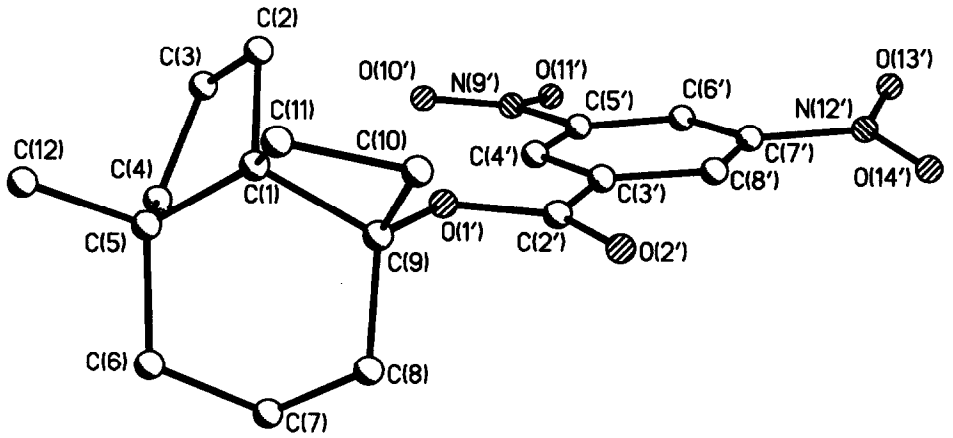


Fig.1. Molecular structure of **46** with the crystallographic atom numbering (hydrogen atoms omitted)

Table 1. Bond lengths (pm) for **46** with estimated standard deviations in parentheses

C(1)-C(2)	155.1(7)	C(2)-C(3)	154.0(9)	C(5)-C(12)	151.8(7)	C(8)-C(9)	151.3(6)
C(1)-C(5)	148.2(6)	C(3)-C(4)	145.6(10)	C(6)-C(7)	147.6(7)	C(9)-C(10)	153.4(6)
C(1)-C(9)	157.1(6)	C(4)-C(5)	153.8(7)	C(7)-C(8)	144.4(8)	C(10)-C(11)	152.1(7)
C(1)-C(11)	153.9(7)	C(5)-C(6)	158.2(8)				

Table 2. Bond angles (°) for **46** with estimated standard deviations in parentheses

C(1)-C(2)-C(3)	105.1(4)	C(2)-C(1)-C(9)	112.9(3)	C(5)-C(6)-C(7)	112.6(4)
C(1)-C(5)-C(4)	104.6(4)	C(2)-C(1)-C(11)	112.5(4)	C(6)-C(5)-C(12)	106.1(4)
C(1)-C(5)-C(6)	111.7(4)	C(2)-C(3)-C(4)	107.5(5)	C(6)-C(7)-C(8)	113.8(5)
C(1)-C(5)-C(12)	113.9(4)	C(3)-C(4)-C(5)	104.9(5)	C(7)-C(8)-C(9)	112.4(4)
C(1)-C(9)-C(8)	115.5(3)	C(4)-C(5)-C(6)	109.3(4)	C(8)-C(9)-C(10)	113.8(4)
C(1)-C(9)-C(10)	87.2(3)	C(4)-C(5)-C(12)	111.2(4)	C(9)-C(1)-C(11)	87.7(3)
C(1)-C(11)-C(10)	88.8(4)	C(5)-C(1)-C(9)	117.9(4)	C(9)-C(10)-C(11)	89.7(3)
C(2)-C(1)-C(5)	102.0(4)	C(5)-C(1)-C(11)	124.1(4)		

Table 3. Torsion angles (°) for **46** with estimated standard deviations in parentheses

C(1)-C(2)-C(3)-C(4)	6.8(6)	C(3)-C(4)-C(5)-C(12)	87.0(5)	C(9)-C(1)-C(5)-C(4)	-84.7(5)
C(1)-C(5)-C(6)-C(7)	-46.5(6)	C(4)-C(5)-C(6)-C(7)	68.7(6)	C(9)-C(1)-C(5)-C(6)	33.4(5)
C(1)-C(9)-C(10)-C(11)	19.2(4)	C(5)-C(1)-C(2)-C(3)	-28.7(5)	C(9)-C(1)-C(5)-C(12)	153.6(4)
C(2)-C(1)-C(5)-C(4)	39.5(5)	C(5)-C(1)-C(9)-C(8)	-31.8(6)	C(9)-C(1)-C(11)-C(10)	19.1(4)
C(2)-C(1)-C(5)-C(6)	157.6(4)	C(5)-C(1)-C(9)-C(10)	-146.9(4)	C(9)-C(10)-C(11)-C(1)	-19.6(4)
C(2)-C(1)-C(5)-C(12)	-82.1(5)	C(5)-C(1)-C(11)-C(10)	141.7(5)	C(11)-C(1)-C(5)-C(4)	167.6(5)
C(2)-C(1)-C(9)-C(8)	-150.4(4)	C(5)-C(6)-C(7)-C(8)	59.8(6)	C(11)-C(1)-C(5)-C(6)	-74.3(6)
C(2)-C(1)-C(9)-C(10)	94.5(4)	C(6)-C(7)-C(8)-C(9)	-56.4(6)	C(11)-C(1)-C(5)-C(12)	45.9(7)
C(2)-C(1)-C(11)-C(10)	-94.8(4)	C(7)-C(8)-C(9)-C(1)	41.1(6)	C(11)-C(1)-C(9)-C(8)	96.0(4)
C(2)-C(3)-C(4)-C(5)	17.3(6)	C(7)-C(8)-C(9)-C(10)	139.7(4)	C(11)-C(1)-C(9)-C(10)	-19.0(4)
C(3)-C(4)-C(5)-C(1)	-36.5(6)	C(8)-C(9)-C(10)-C(11)	-97.5(4)	C(12)-C(5)-C(6)-C(7)	-171.3(5)
C(3)-C(4)-C(5)-C(6)	-156.2(4)	C(9)-C(1)-C(2)-C(3)	98.8(4)		

SUMMARY

In an approach to the synthesis of naturally occurring triquinanes via rearrangement routes, dispiroundecanes **10**-**12** have been synthesized and rearranged by treatment with acids. Most interestingly, the rearrangements of **11** and **12** are regioselective to regiospecific, albeit in undesired sense. In the case of **11**, a large preference for an initial C_4-C_3 ring contraction over the desired C_5-C_6 ring enlargement leads to hexahydro-pentalene **37**, and in the case of **12**, an exclusive initial C_4-C_5 over the desired C_3-C_4 ring enlargement leads to products derived from the cyclopropylmethyl-cyclobutyl-homoallyl manifold **39**-**41**, i.e. hexahydro-indene **42**, tricycloundecane **43** and hexahydro-indenes **44** and **45**, respectively. In both cases, the initial 1,2-shift observed results from a more favourable dihedral angle relationship as compared to the 1,2-shift desired.[14]

47 **48**

It is only with **10** that no concurrent 1,2-shift could occur and the desired initial C_3-C_4 ring enlargement led to [3.3.3]propellane **21**. Therefore, a rearrangement of dispiroundecane **47** with an initial 1,2-shift of that cyclopropane bond having an antiperiplanar alignment with the leaving hydroxyl group could well lead to (±)-modhephene **48**. Albeit endangered by the propensity of substituted cyclopropylmethyl alcohols to rearrange to homoallylic alcohols, the prospect of a synthesis of **48** through rearrangement of **47** is highly attractive.

ACKNOWLEDGEMENT

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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, VXR200, VXR500 or Bruker AMX300 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 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.

Spiro[3.4]octane-5-one (25): To a solution of **24** (22.3 g, purity 94%, 0.19 mol) in dichloromethane (500 ml) was added m-chloroperbenzoic acid (43.1 g, purity 80-90%, ca. 0.20 mol) in small portions with vigorous stirring. The reaction was monitored by glpc [3 m x 1/4" all glass system, 15% OV 101 on Chromosorb W AW/DMCS, 90°C; rel. retention times: 1.00 (**24**), 1.48 (epoxide)]. 30 min after the exothermic reaction had ceased the mixture was cooled to 0°C and a 0.24 M solution of borontrifluoride etherate in dichloromethane (4 ml, 0.96 mmol) added at such a rate that the temperature did not exceed 5°C. After additional 10 min of stirring the rearrangement was complete according to glpc [rel. retention times: 1.00 (epoxide), 1.54 (**25**)]. A 1 M solution of potassium hydroxide (200 ml) was added, the phases separated, the aqueous layer extracted with dichloromethane (100 ml), the combined organic layers dried over molecular sieves 4Å and the solvent distilled off through a 30 cm Vigreux column (bath temperature 80°C). The residue was fractionated in vacuo through a 30 cm Vigreux column yielding 18.9 g (78%) of pure **25** as a colourless liquid, b.p. 57°C/10 torr. The ^{1}H-NMR data were identical with literature data.[8]. ^{13}C-NMR (20 MHz, $CDCl_3$, $CDCl_3$ int.): δ = 15.23, 18.55, 29.34, 36.43, 36.54, 50.51, 220.54.

5-Methylenespiro[3.4]octane (26): To a stirred suspension of potassium-t-butoxide (13.4 g, 0.12 mol) in anhydrous ether (250 ml) under nitrogen was added methyltriphenylphosphonium bromide (42.8 g, 0.12 mol) and the mixture heated to reflux. After 30 min the heating was stopped and **25** (14.4 g, 0.116 mol) added within 15 min causing an exothermic effect. After additional 5 min of reflux the reaction was complete according to glpc [3 m x 1/4" all glass system, 15% OV 101 on Chromosorb W AW/DMCS 60/80 mesh, 115°C; rel. retention times: 1.00 (**26**), 1.71 (**25**)]. The mixture was diluted with pentane (250 ml), hydrolyzed with water (25 ml), the organic layer decanted and the heterogeneous residue extracted with pentane (3 x 60 ml). The combined organic layers were washed with water (3 x 60 ml), dried ($MgSO_4$), the solvents distilled off through a 30 cm Vigreux column (bath temperature 60°C) and the residue fractionated in vacuo yielding 11.3 g (80%) of pure **26** as a colourless liquid, b.p. 82-84°C/70 torr. - IR (film): 3080 (=CH_2), 1655 cm^{-1} (C=C). - ^{1}H-NMR (100 MHz, $CDCl_3$, TMS int.): δ = 1.4-2.3 (m, 12H), 4.85 (mc, 1H), 4.97 (mc, 1H). - ^{13}C-NMR (20 MHz, $CDCl_3$, TMS int.): δ = 15.83, 22.45, 32.58, 34.63, 40.79, 49.43, 103.07, 159.69. - MS (70 eV): m/e = 122 (< 1%, M^+), 79 (100%). - C_9H_{14} requires C, 88.45; H, 11.55. Found: C, 88.43; H, 11.60.

5-(4-Nitrobenzenesulfonimido)-spiro[3.5]octane (27): Protected from light, a stirred solution of 4-nitrobenzenesulfonic acid azide (23.0 g, 100 mmol) and **26** (10.6 g, 86 mmol) in anhydrous acetonitrile (100 ml) was heated under nitrogen for 21.5 h to reflux. After this time, the reaction was complete according to tlc [dichloromethane; R_f = 0.80 (**26**), 0.56 (**27**)]. The mixture was cooled to 0°C and filtered from 14.0 g (51%) of solid **27** which was washed with acetonitrile (2 x 10 ml). The filtrate was concentrated on a rotary evaporator (bath temperature 60°C/10 torr) and the residual brown oil (20.1 g) chromatographed on silica gel (70-130 mesh) in dichloromethane (column 30 x 5 cm) yielding a second crop of 10.8 g (39%) of **27** as a pale yellow oil which crystallized on standing. Recrystallization of a 500 mg sample from 5 ml acetonitrile yielded 445 mg analytically pure **27**, m.p. 131°C. IR (KBr): 1595 (C=N), 1535 cm^{-1} (C=C). - ^{1}H-NMR (100 MHz, $CDCl_3$, TMS int.): δ = 1.5-2.5 (m, 12H), 2.99 (mc, 2H), 8.26 (AA'BB', 4H). - ^{13}C-NMR (50.3 MHz, $CDCl_3$, TMS int.): δ = 14.59, 21.54, 27.62, 30.26, 33.12, 39.49, 50.55, 124.07, 128.27, 147.24, 149.94, 198.37.- MS (70 eV): m/e = 322 (2%, M^+), 136 (96%), 41 (100%). Calculated for $C_{15}H_{18}N_2O_4S$: 322.0987. Found: 322.0987 (MS).

Spiro[3.5]nonane-5-one (28): A mixture of **27** (24.8 g, 77 mmol), ethanol (200 ml) and hydrochloric acid (4 N, 200 ml) was heated for 16 h to 50°C. The liquid phase was decanted from a tarry residue, diluted with water (400 ml) and extracted with pentane (3 x 150 ml). The combined organic layers were washed with water (2 x 150 ml), dried (Na_2CO_3), concentrated on a rotary evaporator (bath temperature 60°C) and the remaining yellowish oil fractionated through a microdistillation apparatus yielding 7.0 g (66%) of pure **28** as colourless liquid, b.p. 78-83°C/10 torr. - IR (film): 1708 cm^{-1} (C=O). - ^{1}H-NMR (100 MHz, $CDCl_3$, TMS int.): δ = 1.5-2.2 (m, 10 H), 2.2-2.6 (m, 4H). - ^{13}C-NMR (50.3 MHz, $CDCl_3$, TMS int.): δ = 14.92, 21.15, 27.12, 28.96, 37.84, 38.83, 51.40, 213.18. - MS (70 eV): m/e = 138 (25%, M^+), 67 (100%). $C_9H_{14}O$ requires C, 78.21; H, 10.21. Found : C, 78.14; H, 10.14.

5-Methylenespiro[3.5]nonane (29): To a stirred suspension of potassium-t-butoxide (7.2 g, 64 mmol) in anhydrous ether (125 ml) under nitrogen was added methyltriphenylphosphonium bromide (22.9 g, 64 mmol) and the mixture heated to reflux. After 30 min the heating was stopped and **28** (5.84 g, 42 mmol) added within 8 min causing an exothermic effect. After additional 15 min of reflux the reaction was complete according to glpc [3 m x 1/4" all glass system, 15% OV 101 on Chromosorb W AW/DMCS 60/80 mesh, 138°C; rel. retention times: 1.00 (**29**), 1.68 (**28**)]. The mixture was diluted with pentane (135 ml), hydrolyzed with water (14 ml), the organic layer decanted and the heterogeneous residue extracted with pentane (3 x 30 ml). The combined organic layers were washed with water (3 x 30 ml), dried over molecular sieves 3Å, the solvents distilled off through a 20 cm Vigreux column (bath temperature 90°C) and the residue fractionated in vacuo yielding 4.89 g (86%) of **29** as a colourless liquid, b.p. 80-82°C/55 torr. Analytically pure **29** was obtained by preparative glpc. - IR (film): 3085 (=CH_2), 1648 cm^{-1} (C=C). - ^{1}H-NMR (100 MHz, $CDCl_3$, TMS int.): δ = 1.4-2.3 (m, 14H), 4.63 (mc, 1H), 4.67 (mc, 1H). - ^{13}C-NMR (20 MHz, $CDCl_3$, $CDCl_3$ int.): δ = 15.09, 22.90, 28.41, 30.93, 32.61, 39.58, 45.50, 103.37, 155.49. - MS (70 eV): m/e = 136 (20%, M^+), 93 (100%). - $C_{10}H_{16}$ requires C, 88.16, H; 11.84. Found: C, 88.27; H, 11.81.

Dispiro[2.0.3.4]undecane (30): To a stirred suspension of freshly prepared zinc/silver couple[15] (15.4 g) in anhydrous ether (30 ml) under nitrogen was first added diiodomethane (15.6 g, 58 mmol), causing an exothermic effect, and then **29** (4.9 g, 36 mmol). After 5 h under reflux the reaction was complete according to glpc [3 m x 1/4" all glass system, 15% OV 101 on Chromosorb W AW/DMCS 60/80 mesh, 138°C; rel. retention times: 1.00 (**29**), 1.56 (**30**)]. The mixture was hydrolyzed with a saturated solution of ammonium chloride (40 ml), the liquid phase decanted and residue and aqueous layer extracted with ether (2 x 20 ml). The combined organic layers were washed with a saturated solution of ammonium chloride (10 ml), dried over molecular sieves 4Å and concentrated on a rotary evaporator (bath temperature 80°C) yielding 5.0 g (82%) of **30** as a colourless oil, purity 90% (glpc). Analytically pure **30** was obtained by preparative glpc. - IR (film): 3075 cm^{-1} (C-H). - ^{1}H-NMR (80 MHz, $CDCl_3$, TMS int.): δ = 0.30 (AA'BB', 4H), 1.0-1.9 (m, 14H). - ^{13}C-NMR (50.3 MHz, $CDCl_3$, TMS int.): δ = 8.21, 14.66, 23.01, 24.47, 25.51, 28.45, 33.01, 37.91, 42.12. - GC/MS (70 eV): m/e = 150 (<1%, M^+), 80 (100%). - $C_{11}H_{18}$ requires C, 87.93; H, 12.07. Found: C, 87.83; H, 11.99.

Dispiro[2.0.3.4]undecane-11-one (4): To a solution of **30** (957 mg, 6.37 mmol) in a mixture of acetonitrile (13 ml) and carbon tetrachloride (13 ml) was added phosphate buffer (17 ml, pH = 7), sodium periodate (4.13 g, 19.3 mmol) and ruthenium trichloride monohydrate (100 mg, 0.44 mmol) and the resulting mixture stirred for 21 h at 70°C . A second crop of sodium periodate (2.13 g, 10.0 mmol) and ruthenium trichloride monohydrate (50 mg, 0.22 mmol) was added and after additional 6 h at 70°C and 48 h at room temperature the reaction was nearly complete according to glpc [1.8 m x 1/4" all glass system, 15% FFAP on Chromosorb W AW/DMCS 60/80 mesh, 170°C; rel. retention times: 1.00 (**30**), 5.85 (**4**)]. The mixture was diluted with water (50 ml), extracted with chloroform (5 x 40 ml), the combined organic layers washed with a 1:1:1 mixture (60 ml) of saturated solutions of sodium chloride, sodium thiosulfate and sodium bicarbonate and dried ($MgSO_4$). The solvents were distilled off through a 30 cm Vigreux column (bath temperature 90°C) and the residue chromatographed on silica gel (0.05-0.20 mm) in pentane/ether [97:3; column 40 x 3 cm, control by tlc; R_f = 0.67 (**30**), 0.18, 0.11, 0.08 (**4**)] yielding 119 mg (12%) of **30** and 357 mg (34%) of **4**. - IR (film): 1700 cm^{-1} (C=O). - ^{1}H-NMR (100 MHz, $CDCl_3$, TMS int.): δ = 0.86 (AA'BB', 4H), 1.5-2.1 (m, 10H), 2.25-2.49 (m, 2H). - ^{13}C-NMR (50.3 MHz, $CDCl_3$, TMS int.): δ = 11.75, 15.09, 19.74, 28.58, 29.35, 35.18, 39.42, 42.56, 211.53. - GC/MS (70 eV): m/e = 164 (11%, M^+), 136 (100%).

(11*R)-11-Methyldispiro[2.0.3.4]undecane-11-ol (10):** To a stirred solution of **4** (450 mg, 2.74 mmol) in anhydrous ether (5 ml) under nitrogen were added at 0°C 6.5 ml (10.40 mmol) of a 1.6 M solution of methyllithium in ether. After 45 min at room temperature the reaction was complete according to tlc [pentane/ether 9:1; R_f = 0.21 (**4**), 0.09 (**10**)]. The mixture was hydrolyzed with a cold saturated solution of ammonium chloride (12 ml), the aqueous layer extracted with ether (4 x 25 ml), the combined organic layers dried over molecular sieves 3Å and concentrated on a rotary evaporator (bath temperature 20°C/20 torr). The residue (448 mg) was chromatographed on silica gel (0.05-0.20 mm) in pentane/ether (9:1; column 30 x 3 cm) yielding 101 mg (22%) of **4** and 367 mg (74%) of **10**. - IR (KBr): 3450 cm^{-1} (OH_{ass}). - ^{1}H-NMR (200 MHz, $CDCl_3$, $CHCl_3$ int.): δ = 0.12-0.24 (m, 1H), 0.30-0.45 (m, 2H), 0.50-0.61 (m, 1H), 0.75-1.90 (m, 13H), 1.00 (s, 3H). - ^{13}C-NMR (50.3 MHz, $CDCl_3$, $CDCl_3$ int.): δ = 4.32, 4.66, 15.32, 19.92, 26.13, 29.54, 30.29, 31.50, 36.44, 40.17, 42.86, 71.86. - MS (70 eV): m/e = 180 (18%, M^+), 109 (100%). - $C_{12}H_{20}O$ requires C, 79.94; H, 11.18. Found: C, 79.83; H, 11.30.

5-Cyclopropylidenespiro[3.4]octane (31): To a stirred suspension of potassium-t-butoxide (16.2 g, 145 mmol) in dry benzene (280 ml) under nitrogen was added cyclopropyltriphenylphosphonium bromide (55.6 g, 145 mmol) and the mixture heated for 1 h to 70-80°C. Spiro[3.4]octane-5-one (**25**) (6.60 g, 53 mmol) was added dropwise over 10 min causing an exothermic effect. After 1 h at reflux the reaction was complete according to glpc [3m x 1/4" all glass system, 15% OV 101 on Chromosorb W AW/DMCS 60/80 mesh, 140°C; rel. retention

times: 1.00 (**25**), 1.63 (**31**)]. The mixture was diluted with pentane (280 ml), hydrolyzed with water (28 ml), the organic layer decanted, the heterogeneous residue extracted with pentane (3 x 70 ml), the combined organic layers dried over molecular sieves 4Å, the solvents distilled off through a 30 cm Vigreux column and the residue fractionated yielding 5.89 g (75%) of **31** as colourless liquid, b.p. 30°C/0.01 torr, purity 85% (glpc). Analytically pure **31** was obtained by preparative glpc. - IR (film): 3040 cm^{-1} (CH). - ^{1}H-NMR (100 MHz, $CDCl_3$, TMS int.): δ = 1.20 (AA'BB', 4H), 1.5-2.2 (m, 8H), 2.5-2.9 (m, 4H). - ^{13}C-NMR (20 MHz, $CDCl_3$, TMS int.): δ = 0.83, 2.60, 17.50, 24.08, 33.31, 34.60, 42.26, 50.29, 110.37, 138.88. - MS (70 eV): m/e = 148 (4%, M^+), 91 (100%). - $C_{11}H_{16}$ requires C, 89.19; H, 10.81. Found: C, 89.00; H, 10.89.

4-(4-Nitrobenzenesulfonimido)-dispiro[2.1.3.3]undecane (32): Protected from light, a stirred solution of 4-nitrobenzenesulfonic acid azide (13.0 g, 60 mmol) and **31** (7.7 g, purity 91%, 47 mmol) in dry acetonitrile (100 ml) was heated under nitrogen for 20 h to reflux. After this time the reaction was complete according to tlc [dichloromethane; R_f = 0.73 (**31**), 0.39 (**32**)]. The mixture was concentrated on a rotary evaporator (bath temperature 50°C/20 torr), the remaining brown oil treated with pentane (100 ml), cooled to 0°C and filtered from 21.4 g (98%) of crude **32** as yellow solid, purity 75%. Recrystallization of a 2.00 g sample from 15 ml acetonitrile yielded 1.50 g analytically pure **32**, as yellowish crystals, m.p. 126°C. - IR (KBr): 1590 (C=N), 1534 cm^{-1} (C=C). - ^{1}H-NMR (100 MHz, $CDCl_3$, TMS int.): δ = 1.16 (AA'BB', 4H), 1.5-2.2 (m, 10H), 2.2-2.7 (m, 2H), 8.20 (AA'BB', 4H). - ^{13}C-NMR (20 MHz, $CDCl_3$, TMS int.): δ = 14.24, 15.16, 20.91, 27.84, 31.54, 38.75, 39.71, 53.00, 124.00, 127.93, 148.48, 149.69, 199.34.- $C_{17}H_{20}N_2O_4S$ requires C, 58.62; H, 5.75; N, 8.05; S, 9.20. Found: C, 58.56; H, 5.74; N, 8.10; S, 9.46.

Dispiro[2.1.3.3]undecane-4-one (6): To a solution of 5% (w/w) potassium hydroxide in methanol (124 g) was added under nitrogen **32** (20.1 g, purity 75%, 43 mmol) and the resulting mixture heated for 2 h to reflux. The mixture was poured into water (670 ml) and extracted with ether (200, 2 x 150 and 100 ml). The combined organic layers were washed with water (2 x 100 ml), dried over molecular sieves 4Å, concentrated on a rotary evaporator (bath temperature 50°C/20 torr) and the residue fractionated yielding 6.0 g (83%) of **6** as a colourless oil, b.p. 50° C/0.15 torr, purity 98%. - IR (film): 1690 cm^{-1} (C=O). - ^{1}H-NMR (100 MHz, $CDCl_3$, TMS int.): δ = 0.81 (AA'BB', 4H), 1.5-2.2 (m, 10H), 2.2-2.8 (m, 2H). - ^{13}C-NMR (20 MHz, $CDCl_3$, TMS int.): δ = 15.23, 16.60, 20.31, 26.70, 30.90, 34.46, 36.99, 50.50, 213.37. - MS (70 eV): m/e = 164 (62%, M^+), 79 (100%). - $C_{11}H_{16}O$ requires C, 80.49; H, 9.76. Found C, 80.39; H, 9.83.

(4*R)-4-Methyldispiro[2.1.3.3]undecane-4-ol (12):** To a stirred solution of **6** (1.0 g, 6.1 mmol) in anhydrous ether (2 ml) under nitrogen was added dropwise a 1.5 M solution of methyllithium in ether (6.0 ml, 9.0 mmol). After 15 min the reaction was complete according to glpc [3 m x 1/4" all glass system, 15% OV 101 on Chromosorb W AW/DMCS 60/80 mesh, 160°C; rel. retention times: 1.00 (**6**), 1.41 (**12**)]. The mixture was hydrolyzed with a saturated solution of ammonium chloride (20 ml), the aqueous layer extracted with ether (3 x 10 ml), the combined organic layers dried over molecular sieves 4Å and the solvent distilled off on a rotary evaporator (bath temperature 50°C/10 torr) yielding 1.1 g (99%) of **12** as a colourless liquid, purity 99% (glpc). - IR (film): 3613 (OH), 3600-3400 cm^{-1} (OH_{ass}). - ^{1}H-NMR (100 MHz, $CDCl_3$, TMS int.): δ = 0.10-0.92 (m, 4H), 0.94-1.15 (m, 1H, OH), 1.11 (s, 3H), 1.15-2.50 (m, 12H). - ^{13}C-NMR (50.3 MHz, $CDCl_3$, TMS int.): δ = 5.38, 8.45, 15.10, 20.22, 20.91, 24.21, 25.64, 27.68, 34.92, 35.47, 47.80, 72.44. - MS (70 eV): m/e = 162 (1%, M^+-H_2O), 43 (100%). - $C_{12}H_{20}O$ requires C, 79.95; H, 11.18. Found: C, 79.98; H, 11.13.

9-Oxatricyclo[3.3.2.0^{1,5}]decane-10-spiro-1'-cyclopropane (34): To a solution of cyclopropyldiphenylsulfonium tetrafluoroborate (3.92 g, 13.5 mmol) and **25** (1.30 g, 10.5 mmol) in dimethylsulfoxide (30 ml) was added powdered potassium hydroxide (1.12 g, 20.0 mmol) and the solution stirred for 22 h at 20°C. After this time, **25** had been completely consumed according to tlc [dichloromethane; R_f = 0.30 (**25**), 0.23 (**34**)]. The reaction mixture was poured onto cold 1 M aqueous tetrafluoroboric acid (30 ml), extracted with ether (3 x 50 ml), the combined extracts washed with water (50 ml) and dried over molecular sieves 4 Å. The solvent was distilled off and the residue fractionated through a microdistillation apparatus yielding 1.28 g (74%) of crude **34** as colourless liquid, b.p. 104-108°C/12 torr. According to glpc [3 m x 1/4" all glass system, 15% OV101 on Chromosorb W AW/DMCS 60/80 mesh, 150°C, rel. retention times: 1.00 (**25**), 2.17 (**34**), 3.02, 3.31] this material was 76% pure. Analytically pure **34** was isolated by preparative glpc. Colourless liquid. IR (film): 3080 cm^{-1} (CH). - ^{1}H-NMR (100 MHz, $CDCl_3$, TMS int.): δ = 0.61 (AA'BB', 4H), 1.05-2.90 (m, 12H). - ^{13}C-NMR (50.3 MHz, $CDCl_3$, $CDCl_3$ int.): δ = 8.67, 31.25, 33.32, 35.95 (C_{sek}), 58.08, 69.87, 102.61 (C_{quart}). - MS (70 eV): m/e = 123 (30%, M^+-41), 80 (100%). - $C_{11}H_{16}O$ requires C, 80.44; H, 9.82. Found: C, 80.14; H, 9.63.

(4*R)-Dispiro[3.0.3.3]undecane-3-one (5):** To a vigorously stirred two-phase system consisting of a solution of **31** (3.41 g, 23 mmol) in dichloromethane (100 ml) and a 0.5 M aqueous solution of sodium bicarbonate (33 ml) was added m-chloroperoxybenzoic acid (5.68 g, purity 70%, 23 mmol) in small portions. After 1.5 h, tlc [pentane/ether 95:5; R_f = 0.65 (**31**), 0.24 (**5**), 0.14 (**34**)] indicated that the reaction was incomplete and more m-chloroperbenzoic acid (1.0 g, purity 70%, 4 mmol) was added. After additional 0.5 h the layers were separated,

the aqueous layer extracted with dichloromethane (2 x 40 ml), the combined organic layers washed with a 1 M solution of sodium hydroxide (2 x 40 ml) and water (40 ml) and dried ($MgSO_4$). The solvent was evaporated in vacuo (bath temperature 20°C/20 torr) and the residue (5.01 g) chromatographed on silica gel (0.05-0.20 mm) in pentane/ether (95:5; column 35 x 4 cm) yielding 154 mg (5%) of unchanged **31**, 639 mg (17%) of **5**, 100 mg of a mixture of **5** and **34** and 1.17 g (31%) of **34** as colourless liquids. The ^{1}H-NMR data of **34** were identical with those of a sample obtained from **25**. **5**: IR (KBr): 1760 cm^{-1} (C=O). - ^{1}H-NMR (200 MHz, $CDCl_3$, $CHCl_3$ int.): δ = 1.50-2.16 (m, 14H), 2.76 (ddd, J = 15, 10, 7 Hz, 1H), 2.91 (ddd, J = 15, 10, 7 Hz, 1H). - ^{13}C-NMR (20 MHz, $CDCl_3$, $CDCl_3$ int.): δ = 15.47, 19.86, 19.98, 27.66, 28.65, 32.56, 37.29, 42.69, 50.32, 75.40, 214.96. - MS (70 eV): m/e = 164 (4%, M^+), 79 (100%). - $C_{11}H_{16}O$ requires C, 80.44; H, 9.82. Found: C, 80.59; H, 9.86.

(1*R,4*R**)-1-Methyldispiro[3.0.3.3]undecane-1-ol (11):** To a 0.35 M solution of methyllithium in ether (75 ml, 26.3 mmol) was added at 0°C within 20 min under nitrogen with stirring a solution of **5** (676 mg, 4.12 mmol) in anhydrous ether (30 ml). After 1.5 h at 0°C the reaction was nearly complete according to tlc [pentane/ether 9:1; R_f = 0.36 (**5**), 0.18 (**11**), 0.08]. The mixture was hydrolized with a saturated solution of ammonium chloride (24 ml), the aqueous layer extracted with ether (60 ml), the combined organic layers dried over molecular sieves 3Å and the solvent evaporated. The residue was chromatographed on silica gel (0.05-0.20 mm) in pentane/ether (9:1; column 60 x 4 cm) yielding 93 mg (14%) of unreacted **5** and 555 mg (75%) of **11** as a colourless oil. - IR (KBr): 3625 (OH), 3600-3400 cm^{-1} (OH_{ass}). - ^{1}H-NMR (200 MHz, $CDCl_3$, $CHCl_3$ int.): δ = 1.12-1.60 (m, 7H), 1.21 (s, 3H), 1.61-2.14 (m, 9H), 2.28-2.45 (m, 1H). - ^{13}C-NMR (50.3 MHz, $CDCl_3$, $CDCl_3$ int.): δ = 16.10, 18.89, 20.30 (C_{sek}), 25.58 (C_{prim}), 28.74, 29.87, 31.79, 34.49, 36.74 (C_{sek}), 49.87, 57.18, 77.53 (C_{quart}). - MS (70 eV): m/e = 180 (< 1%, M^+), 94 (100%). - $C_{12}H_{20}O$ requires C, 79.94; H, 11.18. Found: C, 79.81; H, 11.10.

2-Methyltricyclo[3.3.3.0^{1,5}]undec-2-ene (21), path a: To a 0.075 M solution of anhydrous p-toluenesulfonic acid in benzene (3.70 ml, 0.28 mmol) was added **10** (50 mg, 0.28 mmol) and the resulting mixture stirred under nitrogen for 15 min at 20°C. After this time, **10** had been completely rearranged to **21** according to glpc [1.8 m x 1/4" all glass system, 15% FFAP on Chromosorb W AW/DMCS 60/80 mesh, 130°C; rel. retention times: 1.00 (**21**), 2.40 (**10**)]. The mixture was washed with water (1.5 ml), dried over molecular sieves 3Å and sodium bicarbonate, and **21** isolated by preparative glpc. The ^{1}H-NMR data were identical with those of authentic material[1].

(3a*R)-3a-(1-Methylcyclopropyl)-1,2,3,3a,4,5-hexahydro-pentalene (37), path b:** To a 0.075 M solution of anhydrous p-toluenesulfonic acid in benzene (3.70 ml, 0.28 mmol) was added **11** (50 mg, 0.28 mmol) and the resulting mixture stirred under nitrogen for 15 min at 70°C. After this time, **11** had been completely rearranged to **21** (2%) and **37** (98%) according to glpc [1.8 m x 1/4" all glass system, 15% FFAP on Chromosorb W AW/DMCS 60/80 mesh, 140°C; rel. retention times: 1.00 (**21**), 1.29 (**37**), 3.72 (**11**)]. The mixture was washed with water (1.5 ml), dried over molecular sieves 3Å and sodium bicarbonate, and **21** and **37** isolated by preparative glpc. The ^{1}H-NMR data of **21** were identical with those of authentic material.[1] **37**: Colourless liquid. - IR (KBr): 3080 cm^{-1} (CH). - ^{1}H-NMR (300 MHz, $CDCl_3$, $CHCl_3$ int.): δ = 0.00-0.12 (m, 2H), 0.20-0.28 (m, 1H), 0.38-0.46 (m, 1H), 1.01 (s, 3H), 1.12-1.24 (m, 1H), 1.60 (ddd, 1H), 1.74-2.13 (m, 5H), 2.17 (ddd, 1H), 2.26-2.40 (m, 1H), 2.51-2.66 (m, 1H), 5.27 (mc, 1H). - ^{13}C-NMR (126 MHz, $CDCl_3$, $CDCl_3$ int.): δ = 9.68, 10.39 (C_{sek}), 18.57 (C_{quart}), 22.38 (C_{prim}), 25.08, 26.64, 35.46, 36.71, 38.79 (C_{sek}), 61.80 (C_{quart}), 120.86 (C_{tert}), 154.39 (C_{quart}). - MS (70 eV): m/e = 162 (< 1, M^+), 43 (100%). Calculated for $C_{12}H_{18}$: 162.1408. Found: 162.1409 (MS).

7a*R)-7a-Methyl-2,4,5,6,7,7a-hexahydro-1*H*-inden-4-spiro-1´-cyclopropane (42), path c:** To a solution of **12** (15 mg, 0.08 mmol) in dichloromethane (200 µl) was added silver tetrafluoroborate (20 mg, 0.10 mmol) and the resulting mixture stirred for 3 h at 20°C. After this time, **12** had been completely rearranged to **42** according to glpc [3 m x 1/4" all glass system, 15% OV 101 on Chromosorb W AW/DMCS 60/80 mesh, 160°C; rel. retention times: 1.00 (**42**), 1.80 (**12**)]. The mixture was washed with water (200 µl), the organic layer dried over molecular sieves 4 Å and **42** isolated by preparative glpc. The ^{1}H-NMR data were identical with those of an authentic sample obtained via path d.

(7a*R)-7a-Methyl-2,4,5,6,7,7a-hexahydro-1*H*-inden-4-spiro-1´-cyclopropane (42), formic acid (2a*S**, 5a*S**,8a*R**)-5a-methyl-octahydro-cyclobuta[d]inden-2a-yl ester (43) and formic acid (7a*R**)-2-(7a-methyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-4-yl)-ethyl ester (44), path d:** To a solution of **12** (2.0 g, 11 mmol) in dichloromethane (5 ml) was added formic acid (2 ml, 53 mmol) and the resulting mixture stirred for 2 h at 20°C. After this time, the reaction mixture consisted of 39% **42**, 23% **43**, 26% **44** and 12% **12** according to glpc [3 m x 1/4" all glass system, 15% OV 101 on Chromosorb W AW/DMCS 60/80 mesh, 160°C; rel. retention times: 1.00 (**42**), 1.80 (**12**), 2.89 (**43**) and 3.29 (**44**)]. Water (5 ml) was added, the aqueous layer extracted with dichloromethane (2 x 5 ml) and the combined organic layers dried over molecular sieves 4 Å. The solvent was evaporated and the residue chromatographed on silica gel (0.05-0.20 mm) in hexane/ether [10:1; column 30 x 2

cm, control by tlc; R_f = 0.94 (**42**), 0.48 (**43** and **44**)] yielding 0.5 g (29%) of **42** and 0.94 g (47%) of a 1:1-mixture of **43** and **44**. Analytically pure **43** and **44** was obtained by preparative glpc.

42: Colourless liquid. - ^{1}H-NMR (100 MHz, $CDCl_3$, TMS int.): δ = 0.2-0.9 (m, 4H), 1.15 (s, 3H), 0.9-2.4 (m, 10H), 4.99 (t, 1H). - ^{13}C-NMR (50.3 MHz, $CDCl_3$, TMS int.): δ = 8.25, 17.43 (C_{sek}), 18.24 (C_{quart}), 21.86 (C_{sek}), 23.37 (C_{prim}), 28.81, 36.85, 41.26, 41.87 (C_{sek}), 46.61 (C_{quart}), 116.11 (C_{tert}), 153.52 (C_{quart}). - MS (70 eV): m/e = 162 (46%, M^+), 147 (41%, $M^+ - CH_3$), 134 (100%, $M^+ - C_2H_4$). - $C_{12}H_{18}$ requires C, 88.82; H, 11.18. Found: C, 88.99; H, 11.25.

43: Colourless liquid. - IR (film): 1740 cm^{-1} (C=O). - ^{1}H-NMR (80 MHz, $CDCl_3$, TMS int.): δ = 0.82 (s, 3H), 1.1-2.5 (m, 16H), 7.93 (s, 1H). - ^{13}C-NMR (20 MHz, $CDCl_3$, TMS int.): δ = 16.74, 20.92, 22.97 (C_{sek}), 24.58 (C_{prim}), 33.07, 33.44, 33.86, 33.92, 36.20 (C_{sek}), 40.15, 55.16, 81.04 (C_{quart}), 160.35 (C_{tert}). - MS (70 eV): m/e = 180 (5%, $M^+ - C_2H_4$), 163 (7%, $M^+ - CO_2H$), 95 (100%). - Calculated for $C_{13}H_{20}O_2 - C_2H_4$: 180.1150. Found: 180.1150 (MS).

44: Colourless liquid. - IR (film): 1758 cm^{-1} (C=O). - ^{1}H-NMR (100 MHz, $CDCl_3$, TMS int.): δ = 0.90 (s, 3H), 0.9-2.5 (m, 14H), 4.15 (t, J = 7 Hz, 2H), 8.00 (s, 1H). - ^{13}C-NMR (20 MHz, $CDCl_3$, $CDCl_3$ int.): δ = 19.34, 20.69 (C_{sek}), 24.27 (C_{prim}), 26.63, 28.49, 33.00, 36.00 (C_{sek}), 40.91 (C_{quart}), 41.55, 62.46 (C_{sek}), 121.66, 144.26 (C_{quart}), 161.07 (C_{tert}). - MS (70 eV): m/e = 208 (7%, M^+), 163 (6%, $M^+ - CO_2H$), 47 (100%). - $C_{13}H_{20}O_2$ requires C, 74.96; H, 9.68: Found: C, 74.92; H, 9.66.

Formic acid (2a*S,5a*S**,8a*R**)-5a-methyl-octahydro-cyclobuta[d]inden-2a-yl ester (43), path e**: To a solution of **12** (20 mg, 0.11 mmol) in pentane (200 µl) was added formic acid (20 µl, 0.53 mml) and the resulting mixture stirred for 2 h at room temperature. After this time, the reaction mixture contained 14% **42**, 59% **43**, 16% **44** and 3% **12** according to glpc [3 m x 1/4" all glass system, 15% OV 101 on Chromosorb W AW/DMCS 60/80 mesh, 160°C; rel. retention times: 1.00 (**42**), 1.80 (**12**), 2.89 (**43**) and 3.29 (**44**)]. The retention times of all products were identical with those of authentic samples obtained via path d (glpc).

Formic acid (7a*R)-2-(7a-methyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-4-yl)-ethyl ester (44), path f:** To a solution of **12** (100 mg, 0.55 mmol) in dichloromethane (1.0 ml) was added formic acid (150 µl, 4.0 mmol) and the mixture stirred at 20°C. The same amount of reagent (150 µl, 4.0 mmol) was added after 48 and 68 h, and after 118 h the rearrangement was complete according to glpc [3 m x 1/4" all glass system, 15% OV 101 on Chromosorb W AW/DMCS 60/80 mesh, 160°C; rel. retention times: 1.00 (**42**), 1.80 (**12**), 2.89 (**43**) and 3.29 (**44**)]. At this time, the reaction mixture contained 3% **42**, 5% **43** and 92% **44**. The retention times of all products were identical with those of authentic samples obtained via path d (glpc).

Trifluoro-acetic acid (7a*R)-2-(7a-methyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-4-yl)-ethyl ester (45), path g:** To a solution of **12** (500 mg, 2.8 mmol) in chloroform (2.5 ml) was added trifluoro-acetic acid (750 µl, 10.1 mmol) and the mixture stirred for 30 min at 20°C. After this time, **12** had been completely rearranged to **45** according to glpc [3 m x 1/4" all glass system, 15% OV 101 on Chromosorb W AW/DMCS 60/80 mesh, 160°C; rel. retention times: 1.00 (**12**), 1.56 (**47**)]. The mixture was washed with water (2 ml), the organic layer dried over molecular sieves 4 Å and the solvent evaporated (bath temperature 90°C) yielding 713 mg (84%) of **47** as a colourless liquid (purity 90%). Analytically pure **47** was obtained by preparative glpc. - IR (film): 1788 cm^{-1} (C=O). - ^{1}H-NMR (80 MHz, $CDCl_3$, TMS int.): δ = 0.83 (s, 3H), 1.0-2.6 (m, 14H), 4.37 (t, J = 7 Hz, 2H). - ^{13}C-NMR (50.3 MHz, $CDCl_3$, TMS int.): δ = 19.32, 20.70, 24.16, 26.16, 28.29, 32.73, 35.96, 41.07, 41.52, 66.34, 113.59 (q, $^1J_{C-F}$ = 286 Hz), 120.66, 145.44, 157.47 (q, $^2J_{C-F}$ = 39 Hz). - MS (70 eV): m/e = 276 (13%, M^+), 163 (5%, $M^+ - C_2F_3O_2$), 147 (100%). - $C_{14}H_{19}F_3O_2$ requires C, 60.86; H, 6.93. Found: C, 60.69; H, 6.85.

3,5-Dinitro-benzoic acid (2a*S,5a*S**,8a*R**)-5a-methyl-octahydro-cyclobuta[d]inden-2a-yl ester (46):** To a suspension of lithium aluminium hydride (200 mg, 5.3 mmol) in tetrahydrofuran (20 ml) under nitrogen was added **43** as 1:1-mixture with **44** (0.94 g, purity 50%, 2.2 mmol) and the resulting mixture stirred for 1 h at 0°C. After this time, the reaction was complete according to glpc [3 m x 1/4" all glass system, 15% OV 101 on Chromosorb W AW/DMCS 60/80 mesh, 160°C; rel. retention times: 1.00 (alcohol), 1.50 (**42**), 1.70 (**44**)]. Water (200 µl), a solution of 15% (w/w) potassium hydroxide in water (200 µl) and water (600 µl) were added dropwise. The mixture was filtered, the solid residue washed with ether (50 ml), the combined organic phases dried over molecular sieves 4 Å and concentrated (bath temperature 60°C). The residue was chromatographed on silica gel (0.032-0.063 mm) in hexane/ether [10:1; column 80 x 3.6 cm, 2-2.5 bar, control by tlc; R_f = 0.63 (alcohol), 0.43 (**43**)] yielding 286 mg (72%) of the alcohol derived from **43** as colourless solid, m.p. 33°C. To a solution of this material (55 mg, 0.3 mmol) in dry pyridine (1.5 ml) was added 3,5-dinitrobenzoyl chloride (139 mg, 0.6 mmol) and the mixture stirred for 14 h. After this time, the reaction was complete according to tlc in dichloromethane [R_f = 0.73 (**46**), 0.27 (alcohol)]. Water (10 ml) was added and the aqueous layer extracted with ether (4 x 10 ml). The combined organic layers were washed with 1 N sulfuric acid (10 ml) and water (2 x 20

ml), dried over molecular sieves 4 Å and concentrated on a rotary evaporator (bath temperature 80°C/100 torr). The residue was chromatographed on silica gel (0.032-0.063 mm) in dichloromethane [column 80 x 3.6 cm, 2-2.5 bar, control by tlc] yielding 102 mg of crude solid **46**. 76 mg of this material were crystallized from methanol (4.0 ml) yielding 58 mg (73%) of pure **46** as yellowish crystals, m.p. 152°C. - IR (film): 1740 cm-1 (C=O). - ^{1}H-NMR (80 MHz, $CDCl_3$, TMS int.): δ = 1.03 (s, 3H), 1.3-2.8 (m, 16H), 9.08 (m, 2H), 9.19 (m, 1H). - ^{13}C-NMR (50.3 MHz, $CDCl_3$, TMS int.): δ = 16.91, 21.26, 22.82 (C_{sek}), 24.38 (C_{prim}), 32.96, 33.10, 33.67, 34.06, 36.24 (C_{sek}), 40.30, 55.64, 83.39 (C_{quart}), 122.04, 129.17 (C_{tert}), 135.09, 148.66, 161.20 (C_{quart}). - MS (70 eV): m/e = 374 (< 1%, M^+), 163 (9%, $M^+ - C_7H_3N_2O_6$), 134 (100%). - Calculated for $C_{19}H_{27}N_2O_6$: 374.1478. Found: 374.1478 (MS).

Crystal structure analysis of 46: **46** (molecular formula $C_{19}H_{22}N_2O_6$, M = 374.1) formed monoclinic crystals from methanol, space group $P2_1/n$, a = 801.3(2), b = 760.2(1), c = 3081.5(9) pm, β = 95.80(2)°, V = 1.867 nm^3, Z = 4, D_c = 1.331 g·cm^{-3}. 3257 symmetry-independent reflections with $2\Theta_{max}$ = 50° were measured on a Stoe four-circle diffractometer using graphite-monochromated Mo-K_α radiation; of these, 2209 with $|F| > 3\sigma(F)$ were used for the structure determination and refinement. The structure was solved by direct methods. The anisotropic refinement with geometrically positioned H atoms (riding model: C-H = 96 pm, ∠ HCH = 109.5°) converged at R = 0.092 [R_w = 0.096; $w^{-1} = \sigma(F)^2 + 0.0007 \cdot F^2$]. Atomic parameters are listed in Table 4.[16] All calculations were performed with the program SHELXTL.

Table 4. Atomic coordinates (·10^4) and equivalent isotropic displacement parameters (pm^2·10^{-1}) for **46** with estimated standard deviations in parentheses

	x	*y*	*z*	*U**		*x*	*y*	*z*	*U**
C(1)	2639(5)	6410(6)	769(1)	63(2)	O(2')	5950(4)	4778(5)	1835(1)	78(1)
C(2)	1254(6)	7218(8)	1024(2)	91(2)	C(3')	5288(4)	7354(5)	2216(1)	46(1)
C(3)	1402(9)	9220(8)	962(2)	128(3)	C(4')	4660(5)	9044(6)	2194(1)	52(1)
C(4)	2623(9)	9516(7)	650(2)	108(3)	C(5')	4713(5)	10050(6)	2567(1)	53(2)
C(5)	2780(7)	7735(6)	421(1)	72(2)	C(6')	5329(5)	9400(6)	2967(1)	55(2)
C(6)	4539(6)	7633(8)	231(2)	89(2)	C(7')	5922(5)	7695(6)	2983(1)	53(2)
C(7)	5954(7)	7526(8)	576(2)	96(2)	C(8')	5943(5)	6674(6)	2615(2)	54(1)
C(8)	5890(6)	6011(7)	857(2)	77(2)	N(9')	4051(5)	11860(5)	2535(1)	69(2)
C(9)	4272(5)	5921(6)	1070(1)	54(1)	O(10')	3282(5)	12312(5)	2197(1)	94(2)
C(10)	3553(7)	4057(6)	1092(2)	79(2)	O(11')	4309(5)	12790(5)	2859(1)	102(2)
C(11)	2377(7)	4430(6)	683(2)	91(2)	N(12')	6597(4)	6980(5)	3409(1)	70(1)
C(12)	1465(7)	7545(8)	34(2)	99(2)	O(13')	6316(4)	7741(5)	3737(1)	87(1)
O(1')	4432(3)	6926(3)	1476(1)	50(1)	O(14')	7414(5)	5622(5)	3403(1)	105(2)
C(2')	5282(5)	6201(7)	1824(1)	55(2)					

* equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

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Dedicated to Professor Wolfgang Lüttke on the occasion of his 75th birthday

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