Chiral Allenes from D(+)-Camphor and Camphene

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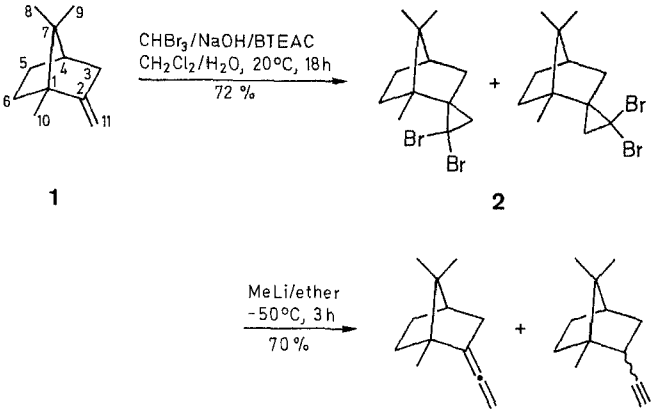
(−)-2-Ethenylidene-1,7,7-trimethylbicyclo[2.2.1]heptane (**3**), (+)- (**5**), and (−)-2,2-dimethyl-3-ethenylidenebicyclo[2.2.1]heptane (**6**) were synthesized in good yields starting with compounds from the chiral pool.

For our investigations of chiral induction in cycloadditions, we needed enantiomerically pure, sterically hindered allenes. There are many approaches for the synthesis of these compounds,[1] but only few which allow a scale-up to more than 50 mmols. Another disadvantage of some preparations of pure chiral allenes is the need of expensive or less easily available starting materials or reagents. Therefore we envisaged that chiral allenes could be prepared from chiral, naturally occuring ketones such as camphor or menthone.

Starting from compounds bearing an *exo*-methylene group, allenes have been prepared by the addition of a dihalocarbene to the double bond, followed by elimination of the halogen, and rearrangement of the carbenoid intermediate.[2] This reaction is by no means trivial, since *exo*-methylene compounds are often difficult to prepare from sterically hindered ketones and, moreover, the allenes formed tend to rearrange under these conditions.

The cyclopropanization of 1,7,7-trimethyl-2-methylenebicyclo[2.2.1]heptane [prepared from D(+)-camphor by Wittig reaction[3]] with dibromocarbene generated from bromoform under phase-transfer catalysis at room temperature, yields the addition products in 72% yield. By a ^{13}C-NMR investigation we found two isomers of 2',2'-dibromo-1,7,7-trimethylspiro[bicyclo[2.2.1]heptane-2,1'-cyclopropane] (**2a** and **2b**) in a 1:3 ratio. This mixture was treated with an ether solution containing an excess of methyllithium at − 50 °C for 3 h. After hydrolysis at room temperature (1*R*)-(−)-2-ethenylidene-1,7,7-trimethylbicyclo[2.2.1]heptane (**3**) was isolated in 70% yield. The product was contaminated with traces (up to 4%) of 2-ethynyl-1,7,7-trimethylbicyclo[2.2.1]heptane (**4**) (Scheme A).



1 **2** **3** 70 % **4** ~4%

Scheme A

Starting with (+)- and (−)-camphene two enantiomeric allenes were prepared. In the case of (+)-2,2-dimethyl-3-ethenylidenebicyclo[2.2.1]heptane **5** we could optimize the described yield[2] from 40% up to 79% by lowering reaction time and temperature in the second step; the (−)-enantiomer **6** was prepared in 70% yield by the same procedure.

A second approach to optical active allenic compounds starts with the transformation of optically pure, or optically enriched propargylic derivatives.[4,5] The alkynylation of D(+)-camphor

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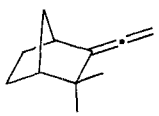
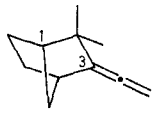
yields diastereomerically pure propargylic alcohols in yields up to 85% by reaction of the ketone with sodium acetylide in morpholine at room temperature[6] or with lithium alkynides in refluxing ether (Scheme **B**).



5

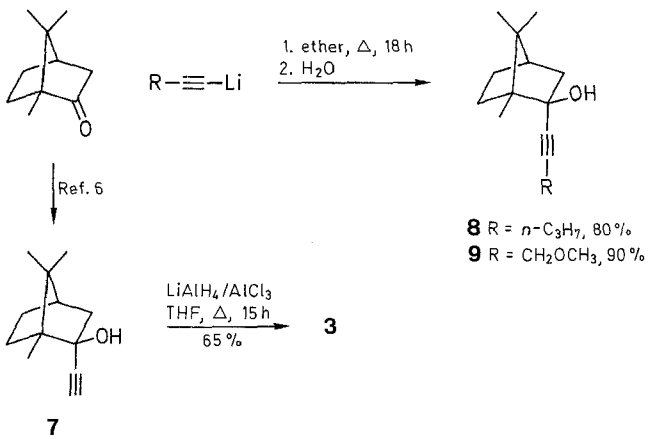


6

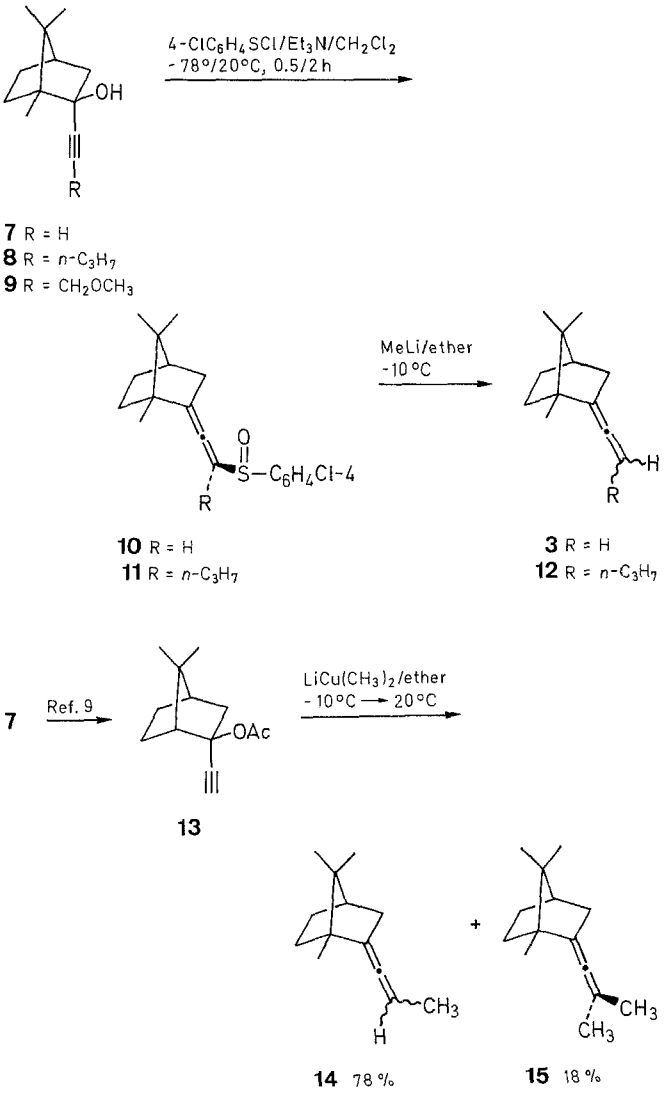
First we tried to reduce the (1*R*,2*S*,4*R*)-(+)-2-ethynyl-2-hydroxy-1,7,7-trimethylbicyclo[2.2.1]heptane **(7)** with two equivalents of lithium alanate/aluminum trichloride (ratio 3:1) in refluxing tetrahydrofuran.[7] After 15 h we isolated **3** in 65% yield by flash chromatography. Extending the reaction time decreases the yield, because of hydrogenation of **3**. Several attempts to prepare derivatives of the alcohol **7** by halogenation or mesylation failed. Therefore we applied the method of the *controlled formation of allenes with organocuprates*, which was reported by Crabbe[8] for simple cyclic and acyclic derivatives. However, the acetate[9] **13** did not show any reaction with lithium dimethylcopper up to −10 °C. Only at higher temperatures (0 °C–20 °C) **13** was converted to the diastereoisomeric methyl derivatives **14a/b** of **3** in a 1.1:1 ratio. GC-MS analysis showed that the crude product mixture contained 18% of the dimethylated allene **15**. If this reaction is carried out with five equivalents of lithium dimethylcopper and with a reaction time of several days, the part of **15** increases up to 45%, but attempts to isolate pure **15** or to transform **14** into **15** by treatment with *n*-butyllithium and methyl iodide[10] failed.

Another well established allene synthesis starts with the reaction of a propargylic alcohol with an arylsulfenyl chloride in the presence of excess base at low temperature, yielding initially a sulfenyl ester. In the course of warming the reaction mixture, a stereospecific [2,3]-sigmatropic rearrangement leads to the corresponding allenyl sulfoxide.[11] Here the reaction of **7** with *p*-chlorophenylsulfenyl chloride and triethylamine in ether at −78 °C seems to be diastereoselective. Though the sulfoxide function bears an additional asymmetric centre, the crude product shows a de > 88%, according to ^{13}C-NMR analysis. After recrystallization the (1*R*,2*R*,4*R*)-2-[(4′-chlorophenyl)sulfinylethenylidene]-1,7,7-trimethylbicyclo[2.2.1]heptane **(10)** was isolated in 72% yield (diastereoisomerically pure according to ^{13}C-NMR). Treatment of the sulfoxide **10** with five equivalents of methyllithium at −10 °C in ether gives pure **3** in 60% yield after filtration over silica gel.

In order to investigate the limitations of this synthetic approach we also used the substituted propargylic alcohols, 2-hydroxy-2-(1-pentynyl)-1,7,7-trimethylbicyclo[2.2.1]heptane **(8)** and 2-hydroxy-2-(3-methoxy-1-propynyl)-1,7,7-trimethylbicyclo-[2.2.1]heptane **(9)**. Only in the case of **8** we succeeded in synthesizing the sulfoxide **11**. We found no way to prepare more than traces of the sulfoxide from **9** using the procedure described above. The reaction of **11** with methyllithium in ether leads to a mixture of two diastereoisomeric products **12a** and **12b** in a temperature depending ratio (at −78 °C 1:3, at room temperature 1:1.6, according to GC and ^{13}C-NMR). This result is in contrast to the high stereoselectivity found for other examples of this reaction.[12,13] (Scheme **C**)



Scheme **B**



Scheme **C**

All reagents were of commercial quality from freshly opened containers. Ether and THF were dried over potassium hydroxide and distilled over $LiAlH_4$. Other solvents were purified by distillation. ^{1}H-NMR spectra were recorded on either a Varian EM 390 (90 MHz) or Varian VXR 300 (300 MHz) spectrometer and ^{13}C-NMR spectra were recorded on a Varian VXR 300 (75 MHz) using TMS as an internal standard. IR-spectra were recorded on a Perkin-Elmer 377 or Perkin-Elmer 1750 spectrophotometer. Observed rotations at the Na-D line were obtained

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at 25°C using a Perkin-Elmer 241 polarimeter. Mass spectra (70 eV) were recorded on a Varian Mat 212 instrument. Melting points were taken using a Büchi 510 apparatus and are uncorrected. Microanalyses were performed at Mikroanalytisches Labor der RWTH Aachen. GC-analyses were carried out on a Siemens Sichromat 3 with 25 m HP Ultra 2. Silica gel 60 (230–400 mesh) was purchased from Machery und Nagel. Analytical TLC plates Merck were used.

2′,2′-Dibromo-1,7,7-trimethylspiro[bicyclo[2.2.1]heptane-2,1′-cyclopropane] (2):

A solution of NaOH (50 g) in water is added slowly to a vigorously stirred mixture of 2-methylenebornane[3] (18 g, 120 mmol), $CHBr_3$ (57 g, 230 mmol), benzyltriethylammonium chloride (BTEAC; 0.5 g, 2.2 mmol, dissolved in 5 mL EtOH) and CH_2Cl_2 (100 mL) cooled in an ice bath. Stirring is continued at 0°C for 1 h and then for 18 h at room temperature. The mixture is diluted with ice-water (400 mL), and the water layer is extracted with pentane (200 mL) and ether (3 × 100 mL). The combined organic layer is washed with water (2 × 50 mL), dried ($MgSO_4$), and evaporated. The crude red oil is fractionally distilled *in vacuo*; yield 28 g (72%): bp 114–115°C/0.3 mbar.

$C_{12}H_{18}Br_2$ (322.1) calc. C 44.75 H 5.63; found 45.04 5.68

MS (70 eV) m/z = 243 ($C_{12}H_{18}{}^{81}Br$), 241 ($C_{12}H_{18}{}^{79}Br$).

IR (neat): ν = 2877, 2955, 2980 (CH); 1369, 1379, 1390 (*gem* CH_3); 680 cm^{-1} (CBr).

^{1}H-NMR (300 MHz, $CDCl_3$): Isomer A: δ = 0.86, 0.87, 0.92 (3 s, 9 H, 3 × CH_3); 1.30 (d, 1 H, J = 7.6 Hz); 1.40–1.56 (m, 2 H); 1.92 (d, 1 H, J = 7.6 Hz); 1.78–2.10 (m, 5 H). Isomer B: δ = 0.90, 0.92, 1.01 (3 s, 9 H, 3 × CH_3); 1.67 (d, 1 H, J = 7.6 Hz).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (A/B) = 12.95/14.23 (C-10); 19.91/19.64, 19.96/19.67 (C-8, C-9); 27.88/28.12 (C-5); 30.898/37.00 (C-6); 34.95/29.86 (C-11, ^1J = 164 Hz); 35.85/42.25 (quart. C); 40.95/41.06 (quart. C); 43.91/44.21 (C-3); 45.30/45.97 (C-4); 50.49/48.52 (quart. C); 52.57/53.16 (quart. C)

(1*R*)-(−)-2-Ethenylidene-1,7,7-trimethylbicyclo[2.2.1]heptane (3); Typical Procedure:

To a solution of the dibromocarbene adduct **2** (20.9 g, 65 mmol) in ether (150 mL), cooled to −50°C, a 1 M ethereal solution of MeLi (100 mL, 100 mmol) is added with stirring during 1 h under an argon atmosphere. Stirring is continued for 3 h, the cooling bath is removed and the excess MeLi is destroyed with water (20 mL). The organic layer is diluted with ether (250 mL) washed alkali free with water and dried ($MgSO_4$). After evaporation *in vacuo* (26 mbar) at room temperature, the crude, yellow product is fractionally distilled using a 30 cm Vigreux column. There is only a little forerun, but it is necessary to take two fractions, because the ethynyl derivative **4** is enriched in the first part of the distillate; yield: 7.4 g (70%); bp 70.5°C/12 mbar; $[\alpha]_D^{25}$ −50.9° (neat).

$C_{12}H_{18}$ (162.3) calc. C 88.82 H 11.18; found 88.80 11.10

MS (70 eV): m/z = 162 (M^+), 119 (100%).

IR (neat): ν = 3050 (=CH), 2950 (CH), 1925 (C=C=C), 848 cm^{-1} (C=C=CH_2).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.86, 0.89, 0.90 (3 s, 3 H each, 3 CH_3); 1.23 (m, 1 H, 6-H_{ax}); 1.46 (m, 1 H, 6-H_{eq}); 1.65 (m, 1 H, 5-H_{ax}); 1.73 (m, 1 H, 5-H_{eq}); 1.77 (m, 1 H, 4-H); 1.99 (dt, 1 H, J = 15.2/3.8 Hz, 3-H_{ax}); 2.52 (d quint, 1 H, J = 15.2/4 Hz, 3-H_{eq}); 4.66 (dddd, 1 H, J = 8.5, 5.0, 3.5, 1.2 Hz, =CH); 4.72 (dddd, 1 H, J = 8.5, 4.5, 4.0, 1.0 Hz, =CH).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 13.13 (C-10); 18.78, 19.75 (C-8, C-9); 27.91, 34.95, 35.26 (C-3, C-5, C-6); 45.01 (C-4); 47.84 (C-7); 50.77 (C-1); 77.23 (C-12); 110.35 (C-2); 201.12 (C-11).

(+)-2,2-Dimethyl-3-ethenylidenebicyclo[2.2.1]heptane **(5)**: Use of the above typical procedure to the dibromocarbene adduct of (+)-camphene[14] affords **5**; yield 79% (Lit.[2] 40%); bp 59°C/11 mbar (Lit.[2] bp 40–42°C/1.3 mbar); $[\alpha]_D^{25}$ +23.2° (neat) (Lit.[2] $[\alpha]_D^{25}$ +21.1° (neat)). The spectroscopic data are according to those of the (−)-enantiomer **6**.

(−)-2,2-Dimethyl-3-ethenylidenebicyclo[2.2.1]heptane **(6)**: (−)-Camphene (31 g, 230 mmol) and $CHBr_3$ (95 g, 375 mmol) are reacted according to the described procedure. Excess $CHBr_3$ and (−)-camphene are removed at room temperature *in vacuo* (0.15 mbar). The crude product, yield: 48 g (68%), is used without further purification in the next step. The dibromocarbene adduct (20 g, 65 mmol) is treated with MeLi as described in the typical procedure to give **6**; yield 6.7 g (70%). bp 59–60°C/11 mbar; $[\alpha]_D^{25}$ −24.1° (neat).

$C_{11}H_{16}$ (148.2) calc. C 89.12 H 10.88; found 89.07 11.09

MS (70 eV): m/z = 148 (M^+), 105 (100%).

IR (neat): ν = 3048 (=C–H); 2960, 2870 (C–H); 1955 (C=C=C); 847 cm^{-1} (C=C=CH_2).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.05, 1.07 (2 s, 3 H, each, CH_3); 1.23 (dt, 1 H, J = 9.8, 1.3 Hz, 6-H_{eq}); 1.39 (m, 1 H, 6-H_{ax}); 1.6–2.0 (m, 5 H); 2.76 (d, 1 H, J = 3.5 Hz, 4-H); 4.67 (s, 2 H, =C=CH_2).

^{13}C-NMR (75 MHz), $CDCl_3$): δ = 25.16, 28.50 (C-8, C-9); 23.86, 28.55, 38.14 (C-5, C-6, C-7); 41.86 (C-2); 44.31, 47.51 (C-1, C-4); 77.34 (C-11); 115.93 (C-3); 199.54 (C-10).

2-Hydroxy-2-(1-pentynyl)-1,7,7-trimethyl-2-bicyclo[2.2.1]heptane (8):

To a solution of 1-pentyne (6.8 g, 100 mmol) in ether (100 mL) at 0°C is added a 1 M solution of MeLi (90 mL, 90 mmol) under an argon atmosphere. The cooling bath is removed, and D(+)-camphor (10.2 g, 71 mmol) in ether (70 mL) is added to the colorless solution. The mixture is heated for 18 h under reflux and after cooling, treated with water (20 mL) to destroy the excess lithium pentynide. The organic layer is washed with sat. NH_4Cl solution (30 mL), dried ($MgSO_4$) and evaporated; yield: 11.8 g (80%); bp 120°C/27 mbar; $[\alpha]_D^{25}$ = 8.8° (c = 0.056, MeOH).

$C_{15}H_{24}O$ (220.4) calc. C 81.74 H 10.97; found 81.85 11.15

MS (70 eV): m/z = 220 (M^+), 95 (100%).

IR (neat): ν = 3500 (OH); 3010, 2960, 2935 (CH); 2738 cm^{-1} (C≡C).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.86, 0.93, 1.05 (3 s, 3 H, each, 3 CH_3); 0.98 (t, 3 H, J = 7.2 Hz, 15-CH_3); 1.14 (m, 1 H); 1.43 (m, 1 H); 1.52 (sext, 2 H, J = 7.2 Hz, 14-CH_2); 1.69 (m, 2 H); 1.8 (d, 1 H, J = 13.2 Hz); 1.90 (m, 1 H); 2.08 (br s, 1 H, OH); 2.18 (t, 2 H, J = 7.2 Hz, 13-CH_2); 2.21 (m, 1 H, 4-CH).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 10.32 (C-10); 13.48 (C-15); 20.73, 22.28 (C-13, C-14); 21.06, 21.46 (C-8, C-9); 26.95, 32.58 (C-5, C-6); 45.44 (C-4); 47.78 (C-7); 48.45 (C-3); 53.43 (C-1); 78.02, 83.50, 84.71 (C-2, C-11, C-12).

2-Hydroxy-2-(3-methoxy-1-propynyl)-1,7,7-trimethylbicyclo[2.2.1]heptane (9):

This alcohol is prepared according to the procedure mentioned above from 3-methoxypropyne[15] (5.6 g, 80 mmol), MeLi (80 mmol) and D(+)-camphor (9.1 g, 60 mmol). The product is purified by filtration over silica gel with cyclohexane as eluent; yield 12.1 g (90%); mp 31–32°C; $[\alpha]_D^{25}$ +18.0° (c = 0.11, MeOH).

$C_{14}H_{22}O_2$ (222.3) calc. C 75.63 H 9.97; found 75.93 10.05

MS: m/z = 175 (M^+ − OCH_3), 95 (100%).

IR (neat): ν = 3450 (OH); 2822, 2878, 2955 (CH); 1105 cm^{-1} (C–O).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.86, 0.94, 1.06 (3 s, 3 H each, 3 CH_3); 1.1–1.9 (m, 6 H); 2.22 (dt, 1 H, J = 13.4, 3.4 Hz, 4-H); 2.67 (br s, 1 H, OH); 3.37 (s, 3 H, OCH_3); 4.14 (s, 2 H, OCH_2).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 10.35 (C-10); 21.36, 21.0 (C-8, C-9); 26.90, 32.45 (C-5, C-6); 45.33 (C-4); 47.85 (C-7), 48.73 (C-3); 53.45 (C-1); 57.28 (C-14); 59.91 (C-13); 77.66, 78.79, 90.96 (C-2, C-11, C-12).

Reaction of 7 with Lithium Aluminum Hydride/Aluminum Chloride:

To a stirred suspension of $LiAlH_4$ (2.4 g, 63 mmol) and $AlCl_3$ (2.7 g, 20.7 mmol) in dry THF (200 mL) under argon, a solution of **5** (5.4 g, 30 mmol) in THF (100 mL) is added. After refluxing for 15 h, the mixture is cooled in an ice-bath and the excess of $LiAlH_4$ is decomposed by slow addition of water (10 mL) after which the precipitated $Al(OH)_3$ is separated and extracted with boiling hexane (100 mL). The combined organic layer is diluted with hexane (200 mL), washed with water until neutral, dried ($MgSO_4$), and evaporated *in vacuo*. The residue is purified by flash chromatography (silicagel, 0.15 bar, EtOAc/cyclohexane 3:97) to give **3**; yield 3.2 g (65%); spectroscopic data identical to **3**, obtained as above.

Reaction of 13 with Lithium Dimethylcuprate:

To a magnetically stirred ice-cold suspension of CuI (6.05 g, 32 mmol) in dry ether (120 mL) is added a 1 M ethereal solution of MeLi (64 mL, 64 mmol) under an argon atmosphere. The clear solution of the cuprate is cooled to −10°C and **13**[9] (6.4 g, 29 mmol) in ether (70 mL) is added. After stirring for 5 h at this temperature and for 15 h at room temperature, the mixture is treated with sat. NH_4Cl solution (60 mL). The aqueous layer is extracted with ether (3 × 50 mL), the combined organic

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layer is dried ($MgSO_4$) and evaporated *in vacuo*. The crude product (3.9 g) contains 78% of **14** and 18% of **15** according to GC-analysis. The product **14** is isolated by HPLC (Chromosorb Si60; EtOAc/cyclohexane, 3:97); yield 0.8 g (15%). The product **15** is detected only by GC-MS.

$C_{13}H_{20}$ calc. C 88.56 H 11.43
(176.3) found 87.62 11.24

MS: m/z = 176 (M^+), 105 (100%).

IR (neat): ν = 2965, 2938, 2870 (C–H); 1970 cm^{-1} (C=C=C).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.84, 0.86, 0.89 (3 s, 3 H each, $3CH_3$); 1.25 (m, 1 H); 1.44 (m, 1 H); 1.62, 1.64, 1.63 (2 d, 3 H combined, J = 7 Hz, $=CCH_3$); 1.6–1.8 (m, 2 H); 1.9–2.0 (m, 1 H, 3-H_{ax}); 2.4–2.5 (m, 1 H, 3-H_{eq}); 5.06, 5.15 (2 m, 1 H combined, C=C=CH).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (A/B) = 13.28/13.23 (C-10); 15.42/15.70 (C-13); 18.86/18.94, 19.82/19.75 (C-8, C-9); 28.01/27.99, 35.13/35.98, 35.12/35.09 (C-3, C-5, C-6); 45.09/45.05 (C-4); 47.63/47.55 (C-7); 51.06/50.58 (C-1); 88.22/88.20 (C-12); 111.11/111.01 (C-2); 196.65/196.93 (C-11).

15: MS: m/z = 190 (M^+ 100%); 175 ($M^+ - CH_3$).

(1*R*,2*R*,4*R*)-2-[(4-Chlorophenyl)sulfinylethenylidene]-1,7,7-trimethylbicyclo[2.2.1]heptane (10):

A solution of **7** (6.1 g, 34 mmol) and Et_3N (10.4 mL, 78 mmol, dried over KOH) in dry CH_2Cl_2 (100 mL) is cooled to –78°C. 4-Chlorophenylsulfenyl chloride[16] (6.1 g, 34 mmol) in CH_2Cl_2 (40 mL) is added carefully making sure that the reaction mixture does not acquire an orange color. After removal of the cooling bath, stirring is continued for 2 h at room temperature, then water (100 mL) is added, and the aqueous layer is extracted with CH_2Cl_2 (2 × 30 mL). The combined organic layer is washed with dil. HCl (20 mL) and sat. K_2CO_3 solution (30 mL), dried ($MgSO_4$), and evaporated *in vacuo*. The dark colored residue is purified by chromatography (silica gel, EtOAc/*n*-hexane 1:3) or crystallized from pentane/ether (9:1) at –20°C; (colorless needles); yield 7.5 g (72%); mp 100°C; $[\alpha]_D^{25}$ = –52.8° (c = 0.036, MeOH).

$C_{18}H_{21}ClOS$ calc. C 67.38 H 6.59
(320.9) found 67.57 6.73

MS: m/z = 320 (M^+), 161 ($M^+ - C_6H_4ClSO$), 105 (100%).

IR (KBr): ν = 3080 (=C–H); 2950 (C–H); 1950 (C=C=C); 1040 cm^{-1} (S=O).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.86, 0.91, 0.91 (3 s, 3 H each, $3CH_3$); 1.25 (m, 1 H, 5-H_{ax}); 1.43 (m, 1 H, 5-H_{eq}); 1.65–1.85 (m, 3 H, 4-H, 6-H_{eq}, 6-H_{ax}); 2.15 (dd, 1 H, J = 16.3, 3 Hz, 3-H_{ax}); 2.69 (d quart, 1 H, J = 16.3, 3.5 Hz, 3-H_{eq}); 6.05 (td, 1 H, J = 3.5, 0.9 Hz, 12-H); 7.47, 7.59 (2 m, 4 H_{arom}).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 13.39 (C-10); 18.53, 19.65 (C-8, C-9); 27.49, 34.68, 36.38 (C-3, C-5, C-6); 44.80 (C-4); 48.66 (C-7); 53.47 (C-1); 104.57 (C-12); 120.95 (C-2); 125.74, 129.33 (=CH_{arom}); 136.86, 143.69 (=C_{arom}); 197.50 (C-11).

Reaction of 10 with Methyllithium:

To a solution of **10** (1 g, 3.3 mmol) in ether (40 mL) is added a 1 M ethereal solution of MeLi (15 mL) with stirring at –10°C. The mixture is warmed to room temperature, treated with water (40 mL), and the aqueous layer is extracted with ether (50 mL). The combined organic layer is washed with brine, dried ($MgSO_4$) and evaporated *in vacuo*. The residue is chromatographed over silica gel (50 g) with pentane; yield 0.4 g (74%); spectroscopic data identical to **3** as described.

2-(2-Pentenylidene)-1,7,7-trimethylbicyclo[2.2.1]heptane (12):

Analogous to the conversion of **7** to **3** via **10** 2-hydroxy-2-(1-pentynyl)bornane (**8**; 1.7 g, 7.6 mmol) is treated with Et_3N (2.2 mL, 15.2 mmol) and 4-chlorophenylsulfenyl chloride. The crude sulfoxide **11** obtained is reacted with a 1 M ethereal solution of MeLi (50 mL, 50 mmol) at –78°C for 2 h. The **12** is isolated by flash chromatography (silica gel, *n*-hexane); yield 0.5 g (32%). According to GC-analysis two isomers in a 3:1 ratio.

$C_{15}H_{24}$ calc. C 88.16 H 11.84
(204.4) found 88.19 11.95

MS: m/z = 204 (M^+), 105 (100%).

IR (neat): ν = 2960, 2930, 2875 (CH); 1970 cm^{-1} (C=C=C).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.85–0.95 (m, 12 H, $4CH_3$); 1.26, 1.70, 1.95, 2.47 (4 m, 9 H); 1.41 (sext, 2 H, J = 7 Hz, 14-H); 5.12, 5.20 (2 m, 1 H combined, =CH).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (A/B) = 13.41/13.29 (C-10); 13.80/14.15 (C-15); 18.89/18.91, 19.78/19.84 (C-8, C-9); 22.34/22.51 (C-14); 32.06/31.85 (C-13); 28.03/28.05, 35.24/35.29, 35.23/35.91 (C-3, C-5, C-6); 45.09/45.14 (C-4); 47.69/47.63 (C-7); 51.02/50.88 (C-1); 93.80/93.73 (C-12); 111.69/111.73 (C-2); 195.99/195.93 (C-11).

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