125. Total Synthesis of β-Bulnesene and 1-Epi-β-bulnesene by Intramolecular Photoaddition[1])

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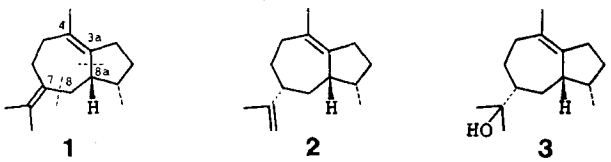
Summary

dl-β-Bulnesene (**1**) and *dl*-1-epi-β-bulnesene (**15**) have been synthesized starting from the bromide **4** (*Schemes 2* and *3*). In the key step **9** → **10** the bonds of the final product were formed by an intramolecular photoaddition. The synthesis was completed by the fragmentation **12** → **14** and the *Wittig* reaction **14** → **15** + **1**.

Introduction. – The hydroazulenic sesquiterpenes β-bulnesene, α-bulnesene and bulnesol have been assigned formulas **1**, **2** and **3** *(Scheme 1)* [1]. These compounds have been subject to considerable synthetic efforts[2]) involving rearrangements of bicyclo[4.4.0]decane [3] and bicyclo[4.3.1]decane derivatives [4] and more recently cyclization of a 1,6-dienal [5]. Another entry to the hydroazulene skeleton by an intermolecular photoaddition suffers from unsatisfactory regiochemical control [6]. We now report the total synthesis of β-bulnesene (**1**) and its C(1)-epimer **15** using a highly regioselective intramolecular photoaddition[3]) with formation of the bonds in a single step.

Scheme 1



1 β-Bulnesene — **2** α-Bulnesene — **3** Bulnesol

Preparation of the 3-acetoxy-2-alkenylcyclopentenone 9 *(Scheme 2)*. – To prepare the precursor **9** we chose the aldol-reaction/pinacol-rearrangement approach to 2-substituted-1,3-cyclopentanediones developed by *Kuwajima & Nakamura* [8].

[1]) Presented by *W.O.* at the The Chemical Society Second East Midlands Regional Symposium, Leicester, December 1979.

[2]) Review: [2].

[3]) For previous studies and synthetic applications of intramolecular *de Mayo* reactions see [7] and ref. therein.

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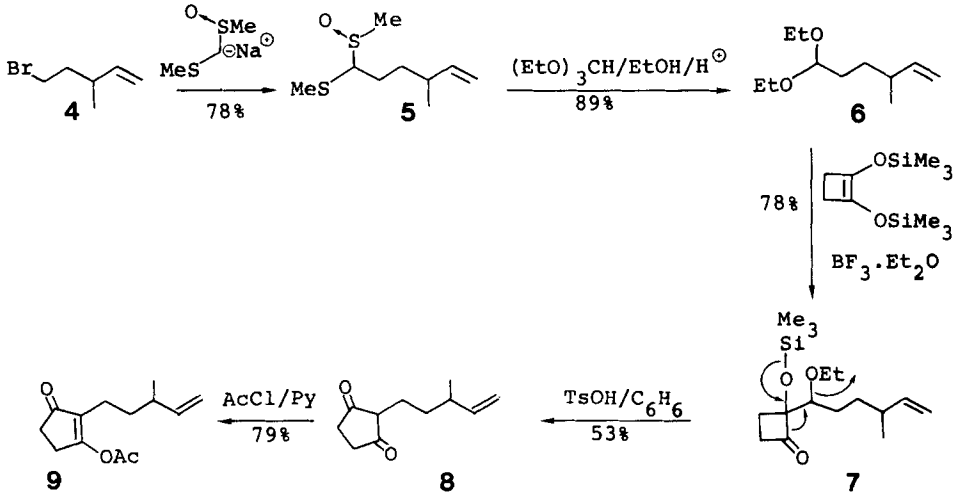
Scheme 2



Deprotonation of methyl methylthiomethyl sulfoxide with sodium hydride and subsequent alkylation with the bromide **4** [9] gave the sulfoxide **5** as a mixture of diastereoisomers (78%) which, with HCl in presence of an excess of triethyl orthoformate in dry ethanol at 25°, yielded the olefinic acetal **6** (89%)[4]). Aldol reaction of the acetal **6** with 1,2-bis(trimethylsilyloxy)cyclobutene [11] using boron trifluoride etherate at −78° gave the cyclobutanone **7** (78%) which rearranged on heating with *p*-toluenesulfonic acid in refluxing benzene giving the crystalline 1,3-cyclopentanedione **8** (53%). *O*-Acetylation of the dione **8** with acetyl chloride in pyridine at 0° afforded the enol acetate **9** (79%).

Irradiation of the enol acetate 9 and conversion of the photoadducts 10 to 1-epi-β-bulnesene (15) and β-bulnesene (1) *(Scheme 3).* – Irradiation of **9** in cyclohexane with a high pressure mercury lamp through Pyrex led regiospecifically to the photoadducts **10a** and **10b** (3.3:1, 76%)[5]) separated by preparative GC. Both products show in the IR. an unstrained cyclopentanone band (1735 to 1740 cm^{-1}) whereas in the ^1H-NMR. the secondary methyl doublet of the major adduct **10a** appears at higher field (0.78 ppm) than that of the minor isomer **10b** (0.88 ppm) in agreement with the depicted configurations. This assignment was confirmed by transformation of pure **10a** to the known ketone **14a** and by conversion of the mixture **10a** + **10b** to 1-epi-β-bulnesene (**15**) and β-bulnesene (**1**).

Treatment of the adduct mixture with 1.1 equiv. of methylmagnesium iodide in ether (−60°–+25°) yielded selectively the acetoxyalcohols **11** which on saponification with 4% KOH-solution in aq. dioxane at 100° gave the diols **12** (mixture of stereoisomers, 70%). The same diols were obtained more directly but in only 32% yield by reaction of **10** with 3.5 equiv. of methyllithium in ether/

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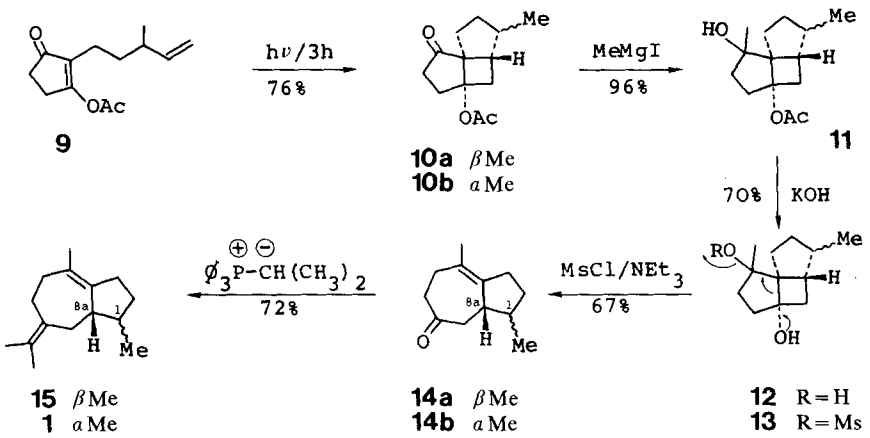
4) For elaboration of this approach to acetals see [10].

5) No major change of the product ratio was achieved on irradiation of **9** in acetonitrile at +25°, at −25° or in methylcyclohexane at −78°.

Scheme 3



hexane (−78°–+25°). Fragmentation of the tricyclo[5.3.0.0^{1,5}]decane skeleton was accomplished in one synthetic operation by reaction of **12** with methanesulfonyl chloride/triethylamine (−25°–+25°) without isolation of the presumed intermediate mesylates **13** yielding the azulenones **14** (67%, (3.3:1)-mixture of **14a** and **14b**). The configurational assignment of **14a** and **14b** agrees well with the ^{1}H-NMR. spectra which show the methyl doublet at 1.05 ppm, $J=5$ Hz for the major and 0.86 ppm, $J=7$ Hz for the minor isomer[6]). The analogous transformation of purified **10a** to pure **14a** (^{1}H-NMR. spectrum identical to that of independently derived **14a** [3b]) confirmed the assigned configurations of **10a** and **10b** and also the correspondence between the observed ratios **10a/10b** and **14a/14b**. *Wittig* reaction of the azulenone mixture **14** with the phosphorane (3 equiv. prepared from isopropyltriphenylphosphonium iodide and potassium *t*-butoxide in dimethyl sulfoxide/benzene at 60° [12]) gave a (3.3:1)-mixture (72%) of 1-epi-β-bulnesene (**15**) and β-bulnesene (**1**). After separation (GC.) the major isomer **15** shows in the ^{1}H-NMR. the H_3C–C(1) doublet at 1.05 ppm, $J=5$ Hz[6]) and in the ^{13}C-NMR. no signal upfield from 18.7 ppm, whereas the corresponding H_3C–C(1) signals of the minor isomer **1** appear at 0.88 ppm, $J=7$ Hz (^{1}H-NMR.) and at 14.9 ppm (^{13}C-NMR.). The minor isomer was identified as β-bulnesene (**1**) by comparison (GC. (coinjection), IR., ^{1}H-NMR., ^{13}C-NMR. and MS.) with an authentic sample obtained by dehydration of natural bulnesol [3c].

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[6]) In the ^{1}H-NMR.- spectra of several 1,2,3,5,6,7,8,8a-octahydro-1,4-dimethylazulene derivatives the *trans*-relation of H_3C–C(1) and H–C(8a) can be recognized by a doublet at 0.85 to 0.90 ppm, $J=7$ Hz, whereas the corresponding *cis*-isomers show this doublet at 1.02 to 1.05 ppm, $J=5$ Hz [3b, c] [4].

Experimental Part

General. Preparative chromatography was carried out on silica gel (*Merck* 0.063–0.2 mm). Gas chromatograms (GC.): 1 atm N_2; glass columns (3 mm ID × 3 m), stationary phases on chromosorb W (acid washed, 80/100 mesh): column A: 5% SE 30; column B; 5% OV 225; column C: 5% Carbowax unless otherwise specified; retention time in min (area %). Melting points (m.p.) are not corrected. IR. spectra: in $CHCl_3$ unless otherwise specified, $\tilde{\nu}_{max}$ in cm^{-1}. UV. spectra: λ_{max} in nm (log ε). NMR. spectra: in $CDCl_3$, internal standard tetramethylsilane ($\delta = 0$ ppm); abbreviations: *s* singlet, *d* doublet, *t* triplet, *qa* quartet, *m* multiplet, *J* spin-spin coupling constant (Hz), ^{1}H-NMR. at 100 MHz, ^{13}C-NMR. at 25.2 MHz. MS.: *m/z* (rel. %).

Preparation of the 3-acetoxy-2-alkenyl-cyclopentenone 9 *(Scheme 2). – Methyl 1-methylthio-4-methyl-5-hexenyl sulfoxides* (**5**). A mixture of methyl methylthiomethyl sulfoxide (*Fluka*, 19.8 g, 0.159 mol), sodium hydride (3.83 g, 0.159 mmol) and THF (70 ml) was heated at reflux under argon for 1 h. To this stirred solution the bromide **4** [9] (23.67 g, 0.145 mol) was added dropwise at 0°. The mixture was allowed to warm to RT., then stirred for 24 h, diluted with CH_2Cl_2 and filtered. Evaporation of the filtrate and distillation of the oily residue (72–75° (bath)/0.2 Torr) furnished the sulfoxide **5** as a mixture of diastereoisomers (23.28 g, 78%). – IR. (film): 1640*w*, 1050*s*, 920. – ^{1}H-NMR.: 0.97 (*d*, *J* = 7, 3 H); 1.1–1.8 (3 H); 1.9–2.4 (5 H); 2.48 (*s*, 1.5 H); 2.62 (*s*, 1.5 H); 3.37 (*m*, 1 H); 4.7–5.1 (2 H); 5.4–5.9 (1 H). – MS.: 207 ($C_9H_{18}OS_2^+ + 1$, 0.1), 142 (11), 127 (11), 95 (12), 87 (100).

4-Methyl-5-hexenal diethyl acetal (**6**). A mixture of the sulfoxide **5** (3.34 g, 16.5 mmol), triethyl orthoformate (6 ml), aq. conc. HCl-solution (10 drops) and dry ethanol (45 ml) was stirred at RT. for 64 h. Basification of the reaction mixture with 1N NaOH, extraction with ether, evaporation of the extracts and distillation of the oily residue at 89–91°/12 Torr gave the acetal **6** (2.65 g, 89%). – IR. (film): 1645*w*, 920. – ^{1}H-NMR.: 1.0 (*d*, *J* = 7, 3 H); 1.19 (*t*, *J* = 7, 6 H); 1.2–1.8 (4 H); 2.13 (*m*, 1 H); 3.56 (*m*, 4 H); 4.48 (*t*, *J* = 6, 1 H); 4.93 (*m*, 2 H); 5.71 (*m*, 1 H). – MS.: 185 ($C_{11}H_{21}O_2^+$, 0.5), 157 (0.3), 141 (1), 129 (2), 104 (4), 103 (100).

2-(1-Ethoxy-4-methyl-5-hexenyl)-2-trimethylsilyloxycyclobutanone (**7**). Boron trifluoride etherate (2.2 ml, 17.5 mmol) was added to a stirred mixture of the acetal **6** (3.26 g, 17.5 mmol), 1,2-bis-(trimethylsilyloxy)cyclobutene [11] (4.03 g, 17.5 mmol) and dry CH_2Cl_2 (50 ml) under argon at −78°. Stirring for 1 h, subsequent addition of further boron trifluoride etherate (1 ml), stirring for 1 h, quenching at −78° with aq. $NaHCO_3$-solution, extraction with CH_2Cl_2 and distillation of the dried and evaporated extracts gave the cyclobutanone **7**, oil, b.p. 75–85° (bath)/0.5 Torr (4.06 g, 78%). – IR. (film): 1795, 1255, 910*w*, 845. – ^{1}H-NMR.: 0.10 (*s*, 9 H); 0.97 (*d*, *J* = 6, 3 H); 1.06 (*t*, *J* = 6, 3 H); 1.1–2.9 (9 H); 3.2–3.7 (3 H); 4.95 (*m*, 2 H); 5.65 (*m*, 1 H). – MS.: 298 ($C_{16}H_{30}O_3Si^+$, 1), 283 (1), 270 (4), 256 (3), 229 (19), 111 (38), 95 (56), 73 (100).

2-(3-Methyl-4-pentenyl)-1,3-cyclopentanedione (**8**). A mixture of the cyclobutanone **7** (4.06 g, 13.6 mmol), *p*-toluenesulfonic acid monohydrate (6.5 g, 34 mmol) and benzene (200 ml) was heated under reflux for 4 h. Extraction of the solution with 1N NaOH (3×), acidification of the basic extracts to $p_H = 1$ and subsequent extraction with ether (3×), evaporation of the dried ether extracts and crystallization of the residue (toluene/hexane) gave the dione **8** as colorless crystals (m.p. 126–129°, 1.3 g, 53%). – UV. (MeOH): 254 (4.19). – IR.: 3500–2300br., 1600br., 1380, 1000*w*, 915*w*. – ^{1}H-NMR.: 1.02 (*d*, *J* = 7, 3 H); 1.1–1.8 (3 H); 1.9–2.4 (3 H); 2.58 (*s*, 4 H); 4.96 (*m*, 2 H); 5.77 (*m*, 1 H). – MS.: 180 ($C_{11}H_{16}O_2^+$, 40), 165 (8), 151 (32), 125 (28), 124 (32), 112 (100), 111 (68).

3-Acetoxy-2-(3-methyl-4-pentenyl)-2-cyclopenten-1-one (**9**). Acetyl chloride (384 mg, 4.9 mmol) was added to a stirred solution of the dione **8** (586 mg, 2.26 mmol) in dry pyridine (7 ml) at 0° under argon. The mixture was kept at RT. for 16 h, then shaken with aq. 2N HCl/ether and extracted with ether (3×). The ether extracts were washed successively with aq. 2N HCl, and H_2O, dried (Na_2SO_4) and evaporated. Chromatography (hexane/ether) or bulb distillation (115° (bath)/0.2 Torr) of the residue (1.20 g) gave the enol acetate **9** (574 mg, 79%). GC. (column A, 160°): 11.8. – UV. (cyclohexane): 255 (4.11), 300 (1.62). – IR.: 1775, 1705, 1660, 1175, 920*w*. – ^{1}H-NMR.: 1.0 (*d*, *J* = 7, 3 H); 1.4 (*m*, 2 H); 2.15 (*m*, 3 H); 2.28 (*s*, 3 H); 2.5 (*m*, 2 H); 2.84 (*m*, 2 H); 4.94 (*m*, 2 H); 5.71 (*m*, 1 H). – MS.: 222 ($C_{13}H_{18}O_3^+$, 2), 204 (1), 180 (28), 151 (17), 137 (4), 125 (12), 124 (14), 112 (45), 111 (21), 55 (14), 47 (100).

Irradiation of the enol acetate 9 and conversion of the photoadducts 10 to 1-epi-β-bulnesene (15) and β-bulnesene (1) *Scheme 3).* – *5-Acetoxy-8-methyl-tricyclo[5.3.0.0^{1,5}]decan-2-ones* (**10**). A degassed solution of the enol acetate **9** (520 mg, 2.34 mmol) in cyclohexane (200 ml) was irradiated with a high pressure Hg-lamp (*Philips* HPK 125 W) through Pyrex for 3 h under argon. Evaporation of the solution and chromatography (hexane/ether) of the oily residue (560 mg) gave **10** (394 mg, 76%) as a (3.3:1)-mixture of diastereoisomers. – GC. (column B, 170°): 29.6 (75.5), 32.4 (22.6). – MS.: 222 ($C_{13}H_{18}O_3^+$, 2), 180 (57), 165 (7), 151 (3), 137 (18), 109 (39), 43 (75), 18 (100).

The mixture of **10a** and **10b** (130 mg) was separated by preparative GC. (column: 13 mm ID × 2 m, 10% OV225 on Chromosorb W, flow rate: 150 ml N_2/min, 175°) to give the major isomer **10a** (22 mg): GC. (column B, 170°): 29.6. – IR. (CCl_4): 1735. – ^{1}H-NMR.: 0.78 (*d*, *J* = 7, 3 H); 1.98 (*s*, 3 H); 1.2–2.8 (12 H). The minor isomer **10b** (5 mg) showed the following properties: GC. (column B, 170°): 32.4. – IR. (CCl_4): 1740. – ^{1}H-NMR.: 0.88 (*d*, *J* = 7, 3 H); 2.0 (*s*, 3 H); 1.4–2.8 (12 H).

5-Acetoxy-2,8-dimethyl-tricyclo[5.3.0.0^{1,5}]decan-2-ols (**11**). Methylmagnesium iodide in ether (1 M, 5 ml) was added to a solution of the adducts **10** (877 mg, 4.14 mmol) in dry ether (30 ml) at −60° under argon. The mixture was allowed to warm to RT. over 2.5 h. Treatment with aq. NH_4Cl, extraction with ether and evaporation of the extracts gave the alcohol **11** as a solid mixture of diastereoisomers (952 mg, 96%). – IR.: 3600–3100br., 1725. – ^{1}H-NMR.: 0.86 (*d*, *J* = 7, 2.3 H); 0.90 (*d*, *J* = 7, 0.7 H); 1.16 (*s*, 0.5 H); 1.18 (*s*, 2.5 H); 1.35 (br. *s*, 1 H); disappears on treatment with D_2O); 2.02 (*s*, 3 H); 1.4–2.2 (10 H); 2.44 (*m*, 2 H). – MS.: 238 ($C_{14}H_{22}O_3^+$, 1), 222 (5), 220 (2), 205 (5), 196 (5), 181 (50), 180 (50), 179 (100), 163 (50), 160 (73).

2,8-Dimethyl-tricyclo[5.3.0.0^{1,5}]decane-2,5-diols (**12**). a) The mixture of acetates **11** (952 mg, 4.0 mmol) was heated at 100° with 50 ml 4% KOH-solution in dioxane/water 1:1 for 30 min. Addition of NH_4Cl, extraction with ether and chromatography (toluene/ether) of the evaporated extracts gave the diols **12** as a mixture of diastereoisomers (550 mg, 70%). – IR.: 3580, 3500, 3100br. – ^{1}H-NMR.: 0.84 (*d*, *J* = 7, 2.4 H); 0.9 (*d*, *J* = 7, 0.6 H); 1.12 (*s*, 0.6 H); 1.15 (*s*, 2.4 H); 1.2–2.5 (14 H). – MS.: 196 ($C_{12}H_{20}O_2^+$, 0.4), 178 (3), 163 (2), 135 (2), 125 (6), 111 (5), 99 (10), 86 (43), 84 (70), 51 (30), 49 (100).

b) Methyllithium in hexane (1.75 N, 0.92 ml, 1.6 mmol) was added dropwise to a stirred solution of the adducts **10** (102 mg, 0.46 mmol) in dry ether (20 ml) at −78° under argon. The mixture was allowed to warm to RT. over 2 h. Addition of aq. NH_4Cl-solution, extraction with ether, evaporation of the dried extracts and chromatography (hexane/ether) of the residue (77 mg) gave the diols **12** (29 mg, 32%).

1,2,3,5,6,7,8,8a-Octahydro-1,4-dimethyl-7-azulenones (**14**). a) Methanesulfonyl chloride (0.16 ml) was added to a solution of the diols **12** (74 mg, 0.38 mmol) and triethylamine (0.21 ml) in dry CH_2Cl_2 (10 ml) at −25° under argon. The mixture was allowed to warm to RT. over 1 h, stirred for 1 h at 25°, diluted with CH_2Cl_2 (30 ml), washed successively with 2 N aq. HCl, aq. $NaHCO_3$-solution, dried and evaporated to give after chromatography (hexane/toluene) the azulenone **14** as a mixture of 2 stereoisomers (45 mg, 67%). GC. (column A, 160°): 8.42 (77), 9.65 (23). – IR.: 1700, 820. – ^{1}H-NMR.: 0.86 (*d*, *J* = 7, 0.7 H); 1.05 (*d*, *J* = 5, 2.3 H); 2.68 (*s*, 3 H); 0.9–3.2 (12 H). – MS.: 178 ($C_{12}H_{18}O^+$, 61), 163 (11), 145 (11), 135 (11), 122 (100), 121 (50).

b) The separated major adduct **10a** (17 mg, 0.075 mmol) was treated successively with methylmagnesium iodide, KOH and methanesulfonyl chloride as described above for the mixture **10a** and **10b**, to give after chromatography (toluene/CH_2Cl_2) the azulenone **14a** (6 mg, 44% from **10a**). GC. (column A, 160°): 8.34. – ^{1}H-NMR.: 1.05 (*d*, *J* = 5, 3 H); 2.68 (*s*, 3 H); 0.9–3.1 (12 H).

dl-1-Epi-β-bulnesene (**15**) *and dl-β-bulnesene* (**1**). A solution of the ylid (4 ml, 3.15 mmol), prepared from isopropyltriphenylphosphonium iodide [12] (4.1 g, 9.5 mmol) and freshly sublimed *t*-BuOK (1.063 g, 9.5 mmol) in dry dimethyl sulfoxide (12 ml) was added to a solution of the ketones **14** (mixture of stereoisomers, 145 mg, 0.8 mmol) in dry benzene (4 ml) at −25° under argon. The mixture was then heated at 60° for 2.5 h. Treatment with aq. NH_4Cl-solution, extraction with pentane and chromatography of the evaporated extracts on SiO_2/5% $AgNO_3$ (pentane/toluene 95:5) gave a mixture of **15** and **1** (120 mg, 72%), oil. GC. (column A, 160°): 12.7 (76.7), 14.0 (22.3); (column C, 142°): 16.3, 18.6. The isomers were separated by preparative GC. (column: 13 mm ID × 2 m, 10% Carbowax on Chromosorb W, flow rate 100 ml N_2/min, 170°) to give the

major isomer **15**, oil. – GC. (column A, 160°): 12.7; (column C, 142°): 16.3. – IR. (CCl_4): 1455, 1440sh., 1380, 910*w*. – ^{1}H-NMR.: 1.05 (*d*, $J=5$, 3 H); 1.62 (*s*, 3 H); 1.69 (*s*, 6 H); 1.2–2.9 (12 H). – ^{13}C-NMR.: 140.2 (*s*), 133.2 (*s*), 126.2 (*s*), 121.7 (*s*), 49.6 (*d*), 42.8 (*d*), 37.1 (*t*), 36.8 (*t*), 33.9 (*t*), 31.5 (*t*), 29.6 (*t*), 21.9 (*qa*), 20.1 (*qa*), 18.7 (*qa*). – MS.: 204 ($C_{15}H_{24}^+$, 93), 189 (32), 175 (7), 161 (53), 133 (40), 121 (100), 107 (98).

The minor product *dl*-**1** showed properties identical to those of *β*-bulnesene from dehydration of bulnesol [3c]: GC. (column A, 160°): 14.1; (column C, 142°): 18.6. – IR. (CCl_4): 1455, 1440sh., 1380, 890*w*. – ^{1}H-NMR.: 0.88 (*d*, $J=7$, 3 H); 1.62 (*s*, 3 H); 1.67 (*s*, 6 H); 1.6–2.9 (12 H). – ^{13}C-NMR.: 139.1 (*s*), 133.1 (*s*), 126.9 (*s*), 121.9 (*s*), 44.6 (*d*), 38.9 (*d*), 36.2 (*t*), 33.5 (*t*), 32.2 (*t*), 30.8 (*t*), 29.6 (*t*), 22.1 (*qa*), 20.2 (*qa*), 14.9 (*qa*). – MS.: 204 ($C_{15}H_{24}^+$, 85), 189 (40), 175 (6), 161 (61), 147 (45), 133 (49), 121 (97), 107 (100).

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