4-Alkenyl-1-methoxy-1,4-cyclohexadienes by Tandem Addition-Multistep Reduction of Alkenyl Aldehydes and Ketones. Synthesis of 4-Alkenyl-3-cyclohexen-1-ones by Subsequent Hydrolysis[1]

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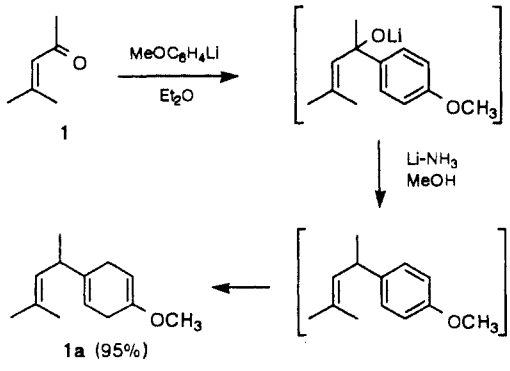
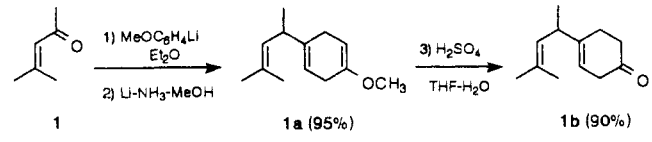
Abstract: A series of 4-alkenyl-1-methoxy-1,4-cyclohexadienes were prepared by a tandem addition-multistep reduction procedure. This one-pot process included the addition of 4-methoxyphenyllithium to alkenyl aldehydes and ketones, followed by multistep reduction of the intermediate benzyl alkoxides with lithium-ammonia-alcohol. Subsequent acid hydrolysis, selectively afforded the corresponding 4-alkenyl-3-cyclohexen-1-ones.

Regioselective synthesis of rather complex 4-alkenyl-1-methoxy-1,4-cyclohexadienes could be achieved by using one-pot tandem addition-multistep reduction techniques.[1] Because of the reactivity of the methyl vinyl ether functional group, these 4-alkenyl-1,4-cyclohexadien-1-yl methyl ethers could be preferentially manipulated and herein were selectively hydrolyzed to the corresponding 4-alkenyl-3-cyclohexen-1-ones.[3] For this study a series of alkenyl aldehydes and ketones were treated with 4-methoxyphenyllithium in ether. Subsequently, the benzyl alkoxides were sequentially reduced from benzyl alcohols to 4-alkenylanisoles to 4-alkenyl-1-methoxy-1,4-cyclohexadienes with lithium-ammonia-alcohol, *all in the same reaction vessel.*



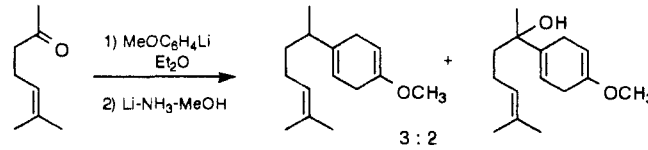
1 1a (95%)

The alkenyl aldehydes and ketones, compiled in Table I (entries 1-7), were subjected to 4-methoxyphenyllithium, and then the intermediate addition products were reduced with lithium-ammonia-methanol by using this procedure. The 4-alkenyl-1-methoxy-1,4-cyclohexadienes were in turn selectively hydrolyzed by refluxing for 2 h in dilute sulfuric acid (ca. 0.5% in THF-water) to yield the corresponding 4-alkenyl-3-cyclohexen-1-ones. The cyclohexenone isolated yields represent the entire addition-reduction-hydrolysis procedure, where the crude 4-alkenyl-1-methoxy-1,4-cyclohexadiene was immediately subjected to hydrolysis and then to purification by flash chromatography.[4]



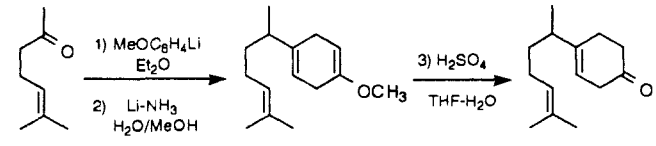
1 1a (95%) 1b (90%)

Using these reduction conditions (Li-NH_3-MeOH) for table entries 8-13 resulted in the formation of two products. The problem of the undesired side product could be rectified by minor modifications of the reduction conditions. For entries 8-10, using 6-methyl-5-hepten-2-one (**8**) as an example, a mixture of the expected addition-reduction product 1-(1,5-dimethyl-4-hexenyl)-4-methoxy-1,4-cyclohexadiene (**8a**), as well as the corresponding alcohol 1-(1-hydroxy-1,5-dimethyl-4-hexenyl)-4-methoxy-1,4-cyclohexadiene (**8c**), was formed after the tandem addition-reduction sequence. The presence of the alcohol side



8 8a 8c

product in these reactions suggested that the intermediate benzyl alkoxide was not efficiently protonated by methanol, which is essential for the reduction of the benzyl alcohol to the 4-alkenylanisole. Interjection of water (in THF), followed by methanol (in THF), as the added proton sources during the reduction solved this problem and afforded only the desired product (table entries 8-10). In the case of 6-methyl-5-hepten-2-one (**8**), the isolated yield of 1-(1,5-dimethyl-4-hexenyl)-4-methoxy-1,4-cyclohexadiene (**8a**) was 93% after this tandem addition-multistep reduction sequence and the isolated yield of 4-(1,5-dimethyl-4-hexenyl)-3-cyclohexen-1-one (**8b**) was 95% after the entire procedure, including the hydrolysis.



8 8a (93%) 8b (95%)

However, using this modified reduction procedure (Li-NH_3-H_2O-MeOH) for 2,4-dimethyl-4-penten-1-al (**10**) afforded a 3:2 mixture of the desired 1-alkenyl-4-methoxy-1,4-cyclohexadiene **10a**, as well as the 1-alkyl-4-methoxy-1,4-cyclohexadiene **10c** as a side product. Unfortunately, this problem of over-re-

(1) (a) Tandem Addition-Reduction. 22. Part 21: Weiberth, F. J.; Hall, S. S. *J. Org. Chem.* **1987**, *52*, 3901-3904. (b) Taken from the Ph.D. Thesis of J.R.F., Rutgers, The State University of New Jersey, October 1985; which received the Charles Sabat Thesis Award and the Rutgers University Graduate Student Government Thesis Award for Excellence in Research, May 1984. (c) Initially disclosed at the 189th National Meeting of the American Chemical Society, Miami Beach, FL, April 1985, paper ORGN 012, and at the 18th Middle Atlantic Regional Meeting of the American Chemical Society, Newark, NJ, May 1984, paper ORGN 248.

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(3) A parallel procedure provided a direct entry into the bisabolane sesquiterpene carbon skeleton by using more stringent hydrolysis conditions to afford 4-alkenyl-2-cyclohexen-1-ones. Flisak, J. R.; Hall, S. S. *Synth. Commun.* **1986**, *16*, 1217-1228.

(4) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2925.

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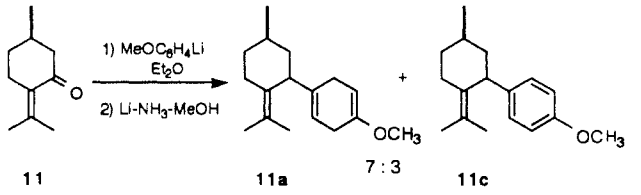
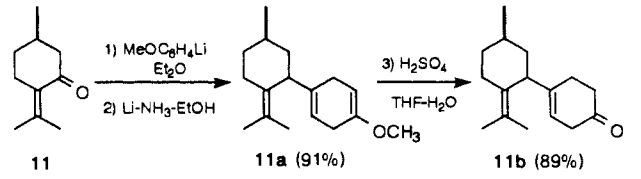
duction of the 1,1-disubstituted alkenyl side chain group could not be remedied in this case.

Using the original reduction conditions (Li-NH_3-MeOH) for the addition-multistep reduction of (*R*)-(+)-pulegone (**11**), β-cyclocitral (**12**), and β-ionone (**13**, table entries 11-13) also resulted in mixtures of two products. In addition to the expected 4-alkenyl-1-methoxy-1,4-cyclohexadienes (**11a-13a**), which were the major products in each case, substantial quantities of the corresponding 4-alkenylanisoles (**11c-13c**) were still present. The presence of the intermediate 4-alkenylanisoles indicated that the reduction of the aromatic ring was sluggish in these examples.



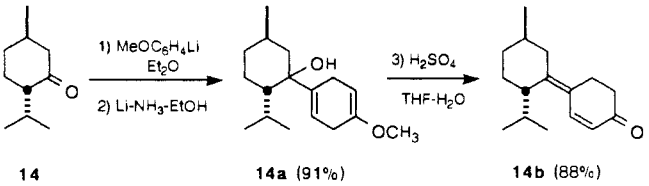
11 **11a** **11c**

When such a situation exists, the practical remedy is to prolong the time of the Birch reduction by either increasing the quantity of both reducing metal and alcohol or selecting a less acidic alcohol as proton source. For table entries 11-13, both tactics worked. Either increasing the quantity of lithium (from 45 to 75 mmol) and methanol (from 42 to 70 mmol) for a typical 5 mmol reaction or more conveniently by switching to ethanol (42 mmol) as the added proton source provided the desired products (**11a-13a**), exclusively. And in the entire addition-multistep reduction-hydrolysis sequence, using the latter modified reduction conditions (Li-NH_3-EtOH), the isolated yields of the corresponding 4-alkenyl-3-cyclohexen-1-ones (**11b-13b**) were excellent.



11 **11a** (91%) **11b** (89%)

The reduction problem associated with the last table entry (-)-menthone (**14**) was not surmountable, yet the results led to useful synthetic chemistry. Regardless of the added proton source for the reduction (MeOH, H_2O/MeOH, EtOH, H_2O/EtOH, or H_2O/*t*-BuOH), the hydroxy group of the benzyl alcohol was resistant to reduction and afforded 1-methoxy-4-[1-hydroxy-5-methyl-2-(1-methylethyl)cyclohexyl]-1,4-cyclohexadiene (**14a**). Subsequent hydrolysis furnished the corresponding α,β,γ,δ-unsaturated ketone **14b** in respectable isolated yield.



14 **14a** (91%) **14b** (88%)

Experimental Section[5]

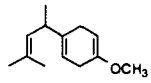
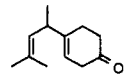
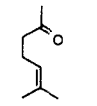
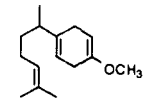
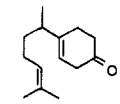
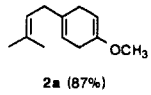
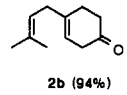
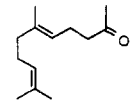
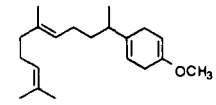
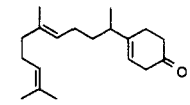
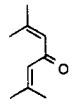
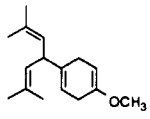
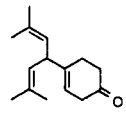
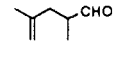
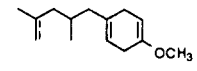
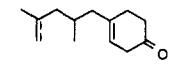
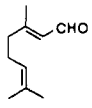
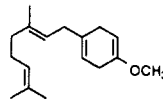
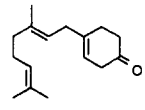
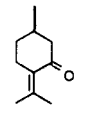
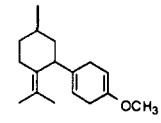
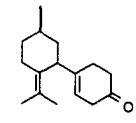
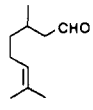
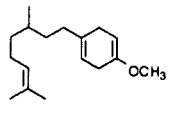
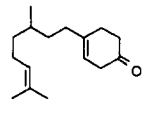
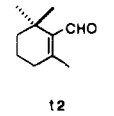
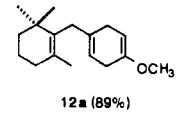
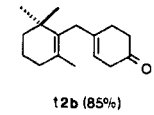
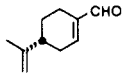
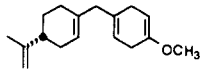
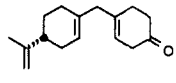
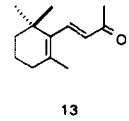
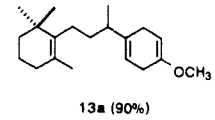
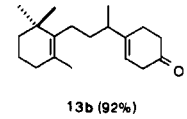
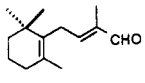
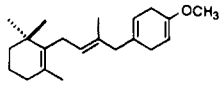
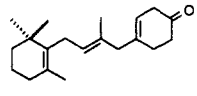
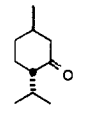
Heavy white paraffin oil (Saybolt viscosity 335/365) was from Fisher Scientific Co. Lithium wire for the alloy was from Foote Mineral Co. (3.2-mm diameter, high purity: 0.050% Na, 0.004% K, and 0.010% Ca) and the sodium metal was from Fisher Scientific Co. The preparation of the lithium-sodium alloy has been described.[6] The reaction assembly consisted of a large Dewar condenser mounted on a sealed 250-mL, three-necked, indented, round-bottom flask (Morton) containing a magnetic star-head Nalgene stir bar (17-mm diameter). All glassware was oven-dried, cooled to ambient temperature in a box desiccator, quickly assembled, and flushed with argon. The in situ generation of 4-methoxyphenyllithium and the subsequent addition sequence was performed under an inert argon atmosphere. When ammonia was to be introduced for the reduction phase, the inert gas source was disconnected and the reaction protected by attaching a soda-lime trap to the side arm of the Dewar condenser for the duration. Anhydrous ethyl ether (Reagent ACS, Fisher Scientific Co.) was used directly from freshly opened 500-g containers. Tetrahydrofuran (THF), which was filtered through an alumina column, was freshly distilled under a nitrogen atmosphere from a dark blue THF solution containing the sodium-benzophenone ketyl radical. The lithium-sodium alloy was rinsed in hexane, pounded to a thin foil, and cut into thin slivers directly into the reaction vessel with argon sweeping through the flask and out the temporarily opened side-arm joint. Freshly redistilled (104-105 °C, 20 Torr) 4-bromoanisole was from Aldrich Chemical Co. 4-Methyl-3-penten-2-one (**1**, redistilled, 35-37 °C, 20 Torr) was from Eastman Chemical Co. 4-Methyl-2-buten-1-al (**2**, redistilled, 35-36 °C, 16 Torr), C-14 Aldehyde 7 [2-methyl-4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-butenal, redistilled, 90-94 °C, 0.1 Torr], β-cyclocitral (**12**), and (-)-menthone [**14**, 20% of (-)-isomenthone] were from Hoffmann-La Roche Inc. 2,6-Dimethyl-2,5-heptadiene-4-one (**3**, redistilled, 92-94 °C, 21 Torr), citral (**4**, an *E*/*Z* mixture, geranial/neral, redistilled, 115-117 °C, 21 Torr), citronellal (**5**, redistilled, 86-90 °C, 14 Torr), geranyl acetone (**9**, an *E*/*Z* mixture, redistilled, 130-132 °C, 15 Torr), (*R*)-(+)-pulegone (**11**, redistilled, 103-104 °C, 15 Torr), β-ionone (**13**), and 2,4-dimethyl-4-penten-1-al (**10**, redistilled, 47-49 °C, 23 Torr) were from Givaudan Corp. (*S*)-(-)-Perillaldehyde (**6**) and 6-methyl-5-hepten-2-one (**8**, redistilled, 56 °C, 11 Torr) were from Aldrich Chemical Co. Anhydrous ammonia (Matheson) was passed through a tower of potassium hydroxide pellets and condensed directly into the reaction vessel. Lithium wire for the reduction sequence (Foote Mineral Co., 3.2-mm diameter, high purity: 0.020% Na, 0.002% K, 0.008% Ca, 0.037% N_2) was wiped free of oil, rinsed in hexane, and cut into 0.5-cm pieces just prior to use. Methanol (spectrophotometric grade, less than 0.05% water) was from Aldrich Chemical Co. Purification of the products by flash chromatography[4] was accomplished on silica gel 60 (230-240 mesh, E. Merck, Darmstadt) and eluted with EtOAc-hexane (2:98 for the cyclohexadienes, 1:9 for the cyclohexenones). Samples for microanalysis were obtained by bulb-to-bulb distillation on a Büchi Kugelrohr apparatus, and the boiling point temperature cited (uncorrected) was the oven temperature.

1-(1,3-Dimethyl-2-butenyl)-4-methoxy-1,4-cyclohexadiene (1a). To a vigorously stirred mixture of 104 mg (15.0 mmol) of lithium-sodium alloy[6] (rinsed in hexane, pounded to a foil, and cut into 40 thin slivers) in 15 mL of anhydrous Et_2O under an argon atmosphere was slowly added (ca. 1 min) 0.5 mL of a solution of 1.402 g (7.50 mmol) of 4-bromoanisole in 5 mL of Et_2O. During the subsequent 10-min induction period, the cut edges of the alloy slivers became very shiny and the solution turned cloudy gray (suspension). Then the remaining ethereal 4-bromoanisole solution was slowly added (ca. 5 min), and within ca. 20 min from the end of this addition all of the alloy slivers had been consumed and the suspension was dark gray. After the mixture was cooled to -75 °C (dry ice-acetone, Dewar bath), a solution of 491 mg (5.00 mmol) of 4-methyl-3-penten-2-one (**1**) in 6 mL of anhydrous Et_2O was slowly added (ca. 10 min). After 15 min, the cooling bath was removed and the stirred mixture allowed to return to ambient temperature (ca. 1 h) during which time the mixture turned a pale green color. After adding 50 mL of anhydrous THF and stirring for an additional 30 min, the reaction mixture became a yellow-orange solution. Anhydrous ammonia (ca. 100 mL) was condensed into the reaction vessel, producing a creamy flocculent precipitate, and then 313 mg (45.0 mmol, 18 pieces) of lithium wire was quickly added. Thirty minutes after the dark blue color of the mixture was established, 1.70 mL (1.34 g, 42 mmol) of MeOH in 5 mL of anhydrous THF was slowly added (ca. 10 min). When the dark blue color had faded and turned white, after ca. 10 min of vigorous stirring, excess ammonium chloride (ca. 5 g) was added to buffer the system, and then the ammonia was allowed to evaporate. The residue was partitioned between 50 mL of Et_2O and 75 mL of water. The separated aqueous layer was extracted once with a 50-mL portion and twice with 25-mL portions of Et_2O. The combined organic phase was

(5) Gas-liquid chromatographic (GLC) analyses were determined on a Hewlett-Packard Model 7610A (flame detector) chromatograph with a 1.8 m × 4 mm (i.d.) glass column packed with 3% silicon gum rubber OV-225 (25% cyanopropyl, 25% phenyl, 50% methyl) supported on 80-100 mesh Chromosorb W HP with a 40 mL/min carrier gas flow rate. The IR spectra were determined with a Beckman Model 4240 infrared spectrophotometer and the FT-IR spectra were determined with a Mattson Sirius Model 100 Fourier transform infrared spectrophotometer. The ^1H NMR spectra were determined at 200 MHz and the ^{13}C NMR spectra (broad-band proton-decoupled) were determined at 50 MHz on an IBM Instruments Model WP200SY Fourier transform spectrometer. All NMR spectra were determined in $CDCl_3$, and the chemical shifts are expressed in δ values (ppm) relative to a Me_4Si internal standard. The mass spectra were determined with a Varian Associates Model CH5 mass spectrometer at an ionizing voltage of 70 eV and an emission current of 300 μA.

(6) (a) Hall, S. S.; Farahat, S. E. *J. Heterocycl. Chem.* **1987**, *24*, 1205-1213. (b) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; Wiley: New York, 1967; Vol. 1, pp 618-619 and the references cited therein.

Table I. Tandem Addition–Multistep Reduction of Alkenyl Aldehydes and Ketones

aldehyde or ketone	1,4-cyclohexadiene (yield)	cyclohexenone (yield)	aldehyde or ketone	1,4-cyclohexadiene (yield)	cyclohexenone (yield)
 1	 1a (95%)	 1b (90%)	 8	 8a (93%)	 8b (95%)
 2	 2a (87%)	 2b (94%)	 9	 9a (93%)	 9b (91%)
 3	 3a (91%)	 3b (91%)	 10	 10a,c (91%)	 10b,d (90%)
 4	 4a (89%)	 4b (88%)	 11	 11a (91%)	 11b (89%)
 5	 5a (89%)	 5b (89%)	 12	 12a (89%)	 12b (85%)
 6	 6a (90%)	 6b (91%)	 13	 13a (90%)	 13b (92%)
 7	 7a (93%)	 7b (90%)	 14	14a (91%)	14b (88%)

washed with 100 mL of water, dried ($MgSO_4$), filtered, and concentrated in vacuo (water aspirator pressure) on a rotary evaporator. The resultant crude yellow oil exhibited one product peak (GLC), and following flash chromatography, 910 mg (4.73 mmol, 95%) of **1a** was obtained as a colorless oil: IR (film) 3090, 3040, 2990, 2960, 2920, 2900, 2870, 2820, 2720, 1690, 1660, 1445, 1385, 1375, 1240, 1215, 1170, 1080, 1050, 1025, 995, 980, 945, 845, 820, 780, 700 cm^{-1}; ^1H NMR δ 5.42 (1 H, septet, J = ca. 1.2 Hz), 4.98 (1 H, d of septets, J = 9.4, 1.4 Hz), 4.62 (1 H, br s, $W_{1/2}$ = 4.1 Hz), 3.54 (3 H, s), 2.95 (1 H, dq, J = 9.0, 7.1 Hz), 2.73 (4 H, apparent t, J = ca. 1.6 Hz), 1.69 (3 H, d, J = 1.2 Hz), 1.63 (3 H, d, J = 1.2 Hz), 1.06 (3 H, d, J = 6.9 Hz); ^{13}C NMR 153.12, 139.74, 130.73, 129.34, 115.58, 90.71, 53.80, 38.59, 29.23, 27.80, 25.78, 19.54, 17.85 ppm; mass spectrum, m/z (relative intensity) 194 (10), 193 (11), 192 (M^+, 78), 190 (8), 177 (100), 175 (21), 145 (29), 137 (56), 135 (36), 121 (90), 119 (36), 110 (32), 109 (80), 105 (36), 91 (38), 83 (22), 79 (32), 77 (37), 55 (47), 45 (20), 41 (65), 39 (36). Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.26; H, 10.14.

4-(1,3-Dimethyl-2-butenyl)-3-cyclohexen-1-one (1b). Similar treatment of 492 mg (5.00 mmol) of 4-methyl-3-penten-2-one (**1**), as described for **1a** except that after extraction the combined organic phase was not dried, afforded a cloudy yellow oil after removal of solvent, which was diluted with a solution of 50 mL of THF and 5 mL of 5% H_2SO_4. After the resultant yellow solution had been refluxed with stirring for 2 h, the solution was diluted with 75 mL of water and extracted twice with 50-mL portions and twice with 25-mL portions of Et_2O. The combined organic phase was washed with 100 mL of water, dried ($MgSO_4$), filtered, and concentrated in vacuo (water aspirator pressure) on a rotary evaporator. The resultant 836 mg of yellow oil (one peak, GLC), after flash chromatography, afforded 805 mg (4.52 mmol, 90%) of **1b** as a pale yellow oil: bp 80–83 °C (0.1 Torr); IR (film) 3050, 3020, 2955, 2920, 2900, 2860, 2840, 1715, 1670, 1440, 1400, 1370, 1335, 1190, 1110, 1050, 990, 960, 885, 840, 815, 795 cm^{-1}; ^1H NMR δ 6.17 (1 H, td, J = 3.6, 1.1 Hz), 5.68 (1 H, d of septets, J = 9.3, 1.4 Hz), 3.73 (1 H, quintet, J = 7.4 Hz), 2.86 (2 H, apparent dd, J = 3.6, 1.4 Hz), 2.51–2.32 (4 H, two overlapping complex m), 1.70 (3 H, d, J = 1.3 Hz), 1.64 (3 H, d, J = 1.3 Hz), 1.08 (3 H, d, J = 6.8 Hz); ^{13}C NMR 174.13, 143.00, 131.51, 128.26, 116.03, 39.65, 38.94, 38.80, 26.91, 25.71, 19.39, 17.81 ppm; mass spectrum, m/z (relative intensity) 180 (6), 179 (5), 178 (M^+, 42), 163 (64), 137 (12), 136 (22), 135 (17), 122 (11), 121 (59), 119 (20), 110 (10), 109 (12), 108 (11), 107 (36), 105 (25), 94 (16), 93 (100), 91 (36), 83 (95), 81 (13), 79 (47), 77 (26), 67 (18), 65 (14), 55 (59), 53 (18), 43 (22), 41 (61), 39 (23). Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.38; H, 10.18.

1-Methoxy-4-(3-methyl-2-butenyl)-1,4-cyclohexadiene (2a). Similar treatment of 494 mg (5.88 mmol) of 4-methyl-2-buten-1-al (**2**), as described for **1a**, produced 1.080 g of a pale yellow oil that after flash chromatography afforded 900 mg (5.05 mmol, 87%) of **2a** as a colorless oil: IR (film) 3080, 3060, 3030, 2980, 2950, 2890, 2840, 2815, 2720, 1685, 1655, 1600, 1485, 1430, 1375, 1235, 1210, 1165, 1090, 1025, 1005, 945, 840, 775, 745, 710 cm^{-1}; ^1H NMR δ 5.38 (1 H, br s, $W_{1/2}$ = 4.5 Hz), 5.16 (1 H, t of quintets, J = 7.4, 1.4 Hz), 4.62 (1 H, br s, $W_{1/2}$ = 4.7 Hz), 3.55 (3 H, s), 2.72 (4 H, s) superimposed on 2.66 (2 H, d, J = 7.6 Hz), 1.72 (3 H, br s, $W_{1/2}$ = 4.3 Hz), 1.63 (3 H, br s, $W_{1/2}$ = 3.3 Hz); ^{13}C NMR 153.26, 135.06, 132.83, 122.06, 117.28, 90.62, 53.82, 35.43, 29.64, 29.28, 25.71, 17.64 ppm; mass spectrum, m/z (relative intensity) 180 (10), 179 (10), 178 (M^+, 70), 176 (12), 163 (19), 161 (18), 135 (12), 131 (11), 123 (60), 122 (67), 121 (51), 109 (100), 94 (22), 91 (44), 79 (26), 77 (40), 69 (30), 41 (87), 39 (30). Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.95; H, 9.94.

4-(3-Methyl-2-butenyl)-3-cyclohexen-1-one (2b). Similar treatment of 420 mg (5.00 mmol) of 4-methyl-2-buten-1-al (**2**), as described for **1b**, afforded 845 mg of a pale yellow oil that after flash chromatography afforded 770 mg (4.70 mmol, 94%) of **2b** as a colorless oil: bp 75–77 °C (0.1 Torr); IR (film) 3050, 3020, 2960, 2920, 2900, 2850, 1715, 1672, 1440, 1400, 1372, 1345, 1332, 1285, 1235, 1190, 1095, 1035, 980, 885, 845, 790 cm^{-1}; ^1H NMR δ 5.44 (1 H, t of quintets, J = 3.6, 1.3 Hz), 5.15

(1 H, t of septets, J = 7.3, 1.4 Hz), 2.85 (2 H, apparent septet, J = ca. 1.8 Hz), 2.73 (2 H, d, J = 7.3 Hz), 2.53–2.34 (4 H, two complex overlapping m), 1.73 (3 H, d, J = 1.0 Hz), 1.64 (3 H, s); ^{13}C NMR 174.38, 138.10, 133.51, 121.23, 117.75, 39.66, 38.64, 35.63, 28.75, 25.69, 17.64 ppm; mass spectrum, m/z (relative intensity) 166 (5), 165 (4), 164 (M^+, 43), 149 (11), 122 (21), 109 (12), 107 (22), 105 (10), 96 (11), 93 (23), 91 (22), 83 (20), 80 (23), 79 (100), 77 (19), 69 (28), 67 (16), 55 (13), 53 (13), 41 (54), 39 (18). Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.27; H, 10.01.

1-Methoxy-4-[3-methyl-1-(2-methyl-1-propenyl)-2-butenyl]-1,4-cyclohexadiene (3a). Similar treatment of 852 mg (6.16 mmol) of 2,6-dimethyl-2,5-heptadien-4-one (**3**), as described for **1a**, afforded 1.427 g of a pale yellow oil that after flash chromatography yielded 1.291 g (5.65 mmol, 91%) of **3a** as a colorless oil: bp 100–103 °C (0.1 Torr); IR (film) 3080, 3030, 2955, 2920, 2900, 2850, 2820, 2720, 1680, 1655, 1600, 1435, 1375, 1235, 1210, 1165, 1015, 1000, 945, 870, 835, 775, 725 cm^{-1}; ^{1}H NMR δ 5.42 (1 H, septet, J = ca. 1.4 Hz), 5.08 (2 H, d of septets, J = 9.3, 1.4 Hz), 4.61 (1 H, br s, $W_{1/2}$ = 4.1 Hz), 3.69 (1 H, t, J = 9.2 Hz), 3.54 (3 H, s), 2.73 (4 H, apparent t, J = ca. 0.8 Hz), 1.71 (6 H, d, J = 1.2 Hz), 1.65 (6 H, d, J = 1.2 Hz); ^{13}C NMR 153.11, 138.29, 131.06 (2 C), 126.71 (2 C), 116.55, 90.77, 53.79, 43.71, 29.30, 28.14, 25.86 (2 C), 18.05 (2 C) ppm; mass spectrum, m/z (relative intensity) 234 (9), 233 (10), 232 (M^+, 49), 217 (15), 189 (12), 177 (22), 176 (21), 175 (20), 161 (100), 150 (29), 123 (57), 121 (42), 109 (70), 105 (23), 91 (44), 81 (47), 79 (29), 77 (31), 69 (33), 67 (23), 55 (32), 53 (23), 43 (40), 41 (84), 39 (21). Anal. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.70; H, 10.25.

4-[3-Methyl-1-(2-methyl-1-propenyl)-2-butenyl]-3-cyclohexen-1-one (3b). Similar treatment of 691 mg (4.99 mmol) of 2,6-dimethyl-2,5-heptadien-4-one (**3**), as described for **1b**, yielded 1.088 g of a yellow oil that after flash chromatography yielded 989 mg (4.54 mmol, 91%) of **3b** as a pale orange oil: bp 85–87 °C (0.1 Torr); IR (film) 3050, 3020, 2960, 2920, 2900, 2870, 1715, 1667, 1502, 1440, 1398, 1378, 1370, 1345, 1328, 1237, 1180, 1105, 967, 870, 845, 800, 785 cm^{-1}; ^{1}H NMR δ 5.48 (1 H, tq, J = 3.6, 1.2 Hz), 5.06 (2 H, d of septets, J = 9.2, 1.4 Hz), 3.78 (1 H, t, J = ca. 9.2 Hz), 2.86 (2 H, dd, J = 3.6, 1.7 Hz), 2.51–2.34 (4 H, two overlapping complex m), 1.73 (6 H, d, J = 1.3 Hz), 1.66 (6 H, d, J = 1.2 Hz); ^{13}C NMR 211.09, 141.60, 131.93 (2 C), 126.10 (2 C), 117.22, 44.16, 39.96, 39.07, 27.47, 26.05 (2 C), 18.24 (2 C) ppm; mass spectrum, m/z (relative intensity) 219 (1), 218 (M^+, 7), 203 (12), 161 (14), 147 (15), 133 (20), 123 (20), 119 (40), 117 (12), 115 (13), 107 (15), 105 (42), 103 (10), 95 (10), 93 (23), 91 (79), 81 (28), 79 (43), 78 (19), 77 (57), 69 (19), 67 (29), 66 (16), 65 (35), 63 (12), 55 (36), 53 (56), 51 (27), 43 (31), 42 (100), 41 (100), 39 (100). Anal. Calcd for $C_{15}H_{22}O$: C, 82.52; H, 10.16. Found: C, 82.48; H, 10.11.

(*E*)- and (*Z*)-1-(3,7-Dimethyl-2,6-octadienyl)-4-methoxy-1,4-cyclohexadiene (4a). Similar treatment of 820 mg (5.38 mmol) of citral (**4**), as described for **1a**, afforded 1.275 g of a pale yellow oil that after flash chromatography yielded 1.175 g (4.77 mmol, 89%) of **4a** as a colorless oil: IR (film) 3080, 3030, 2990, 2960, 2920, 2900, 2850, 2820, 1690, 1660, 1440, 1380, 1235, 1210, 1170, 1105, 1065, 1015, 945, 780 cm^{-1}; ^{1}H NMR δ 5.38 (1 H, br s, $W_{1/2}$ = 4.6 Hz), two overlapping t with further fine splitting at 5.16 (1 H, J = 6.8 Hz) and 5.12 (1 H, J = 8.0 Hz), 4.62 (1 H, br s, $W_{1/2}$ = 4.9 Hz), 3.55 (3 H, s), 2.72 (4 H, s) superimposed on 2.67 (2 H, d, J = 7.8 Hz), 2.05 (4 H, br s, $W_{1/2}$ = 6 Hz), 1.72 (ca. 1.5 H, d, J = 1.1 Hz), 1.68 (3 H, s), 1.61 (ca. 4.5 H, d, J = 1.1 Hz); ^{13}C NMR 153.24, 136.64 and 136.56 (1 C), 135.16 and 135.02 (1 C), 131.52 and 131.35 (1 C), 124.46 and 124.40 (1 C), 122.69 and 121.96 (1 C), 117.40 and 117.26 (1 C), 90.67, 53.85, 39.83 and 31.92 (1 C), 35.29 and 35.15 (1 C), 29.74 and 29.67 and 29.30 (1 C), 26.73 and 26.68 (1 C), 25.69, 23.41, 17.68 and 17.64 (1 C), 15.96 ppm; mass spectrum, m/z (relative intensity) 248 (4), 247 (5), 246 (M^+, 27), 175 (12), 163 (16), 162 (17), 161 (100), 123 (42), 122 (33), 121 (52), 110 (14), 109 (48), 108 (15), 105 (10), 91 (18), 79 (11), 77 (14), 69 (40), 41 (38). Anal. Calcd for $C_{17}H_{26}O$: C, 82.87; H, 10.64. Found: C, 83.09; H, 10.51.

(*E*)- and (*Z*)-4-(3,7-Dimethyl-2,6-octadienyl)-3-cyclohexen-1-one (4b). Similar treatment of 761 mg (5.00 mmol) of citral (**4**), as described for **1b**, produced 1.174 g of a pale yellow oil that after flash chromatography yielded 1.021 g (4.39 mmol, 88%) of **4b** as a colorless oil: bp 127–129 °C (0.1 Torr); IR (film) 3040, 3020, 2950, 2900, 2840, 1710, 1670, 1435, 1370, 1330, 1185, 1100, 1030, 725 cm^{-1}; ^{1}H NMR δ 5.44 (1 H, br s, with fine splitting, $W_{1/2}$ = 8 Hz), 5.20–5.05 (2 H, two complex overlapping m), 2.85 (2 H, br s with fine splitting, $W_{1/2}$ = 8 Hz), 2.75 (2 H, d, J = 7.2 Hz), 2.54–2.35 (4 H, two complex overlapping m), 2.11–2.01 (4 H, m), 1.74 (ca. 1.5 H, d, J = 1.2 Hz), 1.68 (3 H, s), 1.62 (ca. 1.5 H, d, J = 1.2 Hz) on which is superimposed 1.61 (3 H, s); ^{13}C NMR 174.43 and 174.38 (1 C), 138.26 and 138.12 (1 C), 137.37 and 137.25 (1 C), 131.64 and 131.53 (1 C), 124.29 and 124.22 (1 C), 121.89 and 121.21 (1 C), 117.89 and 117.79 (1 C), 39.72, 38.71 and 31.92 (1 C), 35.54 and 35.39 (1 C), 28.86 and 28.81 (1 C), 26.65 and 26.62 (1 C), 25.69, 23.43, 17.69 and 17.64 (1 C), 15.97 ppm; mass spectrum, m/z (relative intensity) 234 (1), 233 (2), 232 (M^+, 6), 123 (20), 109 (13), 105 (15), 93 (9), 91 (10), 81 (10), 79 (13), 69 (100), 67 (10), 55 (17), 53 (18), 41 (70). Anal. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.41; H, 10.65.

1-(3,7-Dimethyl-6-octenyl)-4-methoxy-1,4-cyclohexadiene (5a). Similar treatment of 938 mg (6.08 mmol) of citronellal (**5**), as described for **1a**, afforded 1.488 g of a yellow oil that after flash chromatography yielded 1.332 g (5.36 mmol, 89%) of **5a** as a colorless oil: IR (film) 3090, 3030, 2990, 2960, 2920, 2900, 2840, 2820, 1690, 1665, 1490, 1450, 1385, 1375, 1240, 1215, 1170, 1015, 945, 780, 745 cm^{-1}; ^{1}H NMR δ 5.37 (1 H, apparent septet, J = ca. 1.2 Hz), 5.10 (1 H, t of apparent quintets, J = 7.1, 1.4 Hz), 4.63 (1 H, br s, $W_{1/2}$ = 4.4 Hz), 3.55 (3 H, s), 2.72 (4 H, superficial s, $W_{1/2}$ = 4 Hz), 2.03–1.93 (4 H, m), 1.68 (3 H, d, J = 1.0 Hz), 1.60 (3 H, s), 1.53–1.11 (5 H, m), 0.88 (3 H, d, J = 6.3 Hz); ^{13}C NMR 153.26, 135.99, 130.99, 125.09, 117.04, 90.60, 53.83, 37.09, 35.05, 34.25, 32.26, 29.52, 29.25, 25.71, 25.61, 19.58, 17.63 ppm; mass spectrum, m/z (relative intensity) 250 (2), 249 (5), 248 (M^+, 21), 163 (11), 123 (35), 122 (20), 121 (100), 109 (36), 91 (14), 69 (20), 55 (10), 41 (26). Anal. Calcd for $C_{17}H_{28}O$: C, 82.20; H, 11.36. Found: C, 82.39; H, 11.21.

4-(3,7-Dimethyl-6-octenyl)-3-cyclohexen-1-one (5b). Similar treatment of 771 mg (5.00 mmol) of citronellal (**5**), as described for **1b**, afforded 1.222 g of a yellow oil that after flash chromatography yielded 1.048 g (4.47 mmol, 89%) of **5b** as a colorless oil: bp 122–123 °C (0.1 Torr); IR (film) 3050, 3020, 2950, 2910, 2840, 1713, 1670, 1440, 1400, 1370, 1335, 1285, 1235, 1185, 1110, 1075, 1035, 1015, 975, 885, 820, 790 cm^{-1}; ^{1}H NMR δ 5.44 (1 H, apparent septet, J = 1.2 Hz), 5.10 (1 H, t of apparent septets, J = 7.1, 1.3 Hz), 2.85 (2 H, apparent t, J = 1.7 Hz), 2.53–2.35 (4 H, two overlapping complex m), 2.08–1.94 (4 H, two overlapping m), 1.69 (3 H, s), 1.61 (3 H, s), 1.53–1.06 (5 H, complex m), 0.89 (3 H, d, J = 6.2 Hz); ^{13}C NMR 174.31, 139.26, 131.09, 124.94 and 124.90 (1 C), 117.58, 39.66, 38.71, 36.99, 34.88, 34.62, 32.12, 28.67, 25.69, 25.54, 19.53, 17.64 ppm; mass spectrum, m/z (relative intensity) 236 (4), 235 (5), 234 (M^+, 29), 149 (17), 122 (16), 109 (65), 107 (25), 96 (12), 95 (14), 93 (14), 82 (17), 81 (41), 79 (18), 69 (85), 68 (18), 67 (29), 55 (37), 53 (15), 43 (15), 41 (100), 39 (10). Anal. Calcd for $C_{16}H_{26}O$: C, 81.99; H, 11.18. Found: C, 81.74; H, 11.10.

(*S*)-1-Methoxy-4-[[4-(1-methylethenyl)-1-cyclohexen-1-yl]methyl]-1,4-cyclohexadiene (6a). Similar treatment of 760 mg (5.06 mmol) of (*S*)-(−)-perillaldehyde (**6**), as described for **1a**, produced 1.444 g of a pale yellow oil that after flash chromatography yielded 1.112 g (4.56 mmol, 90%) of **6a** as a colorless oil: IR (film) 3070, 3030, 2980, 2950, 2920, 2890, 2820, 1689, 1657, 1637, 1502, 1455, 1442, 1428, 1380, 1360, 1238, 1210, 1165, 1145, 1065, 1035, 1015, 945, 905, 880, 775 cm^{-1}; ^{1}H NMR δ 5.46 (1 H, br m, $W_{1/2}$ = 9.7 Hz; apparent d with further splitting, J = ca. 3.1 Hz), 5.40 (1 H, br m, $W_{1/2}$ = 8.1 Hz; apparent septet, J = ca. 1.3 Hz), 4.71 (1 H, s), 4.70 (1 H, s), 4.62 (1 H, apparent t, J = ca. 2.7 Hz), 3.55 (3 H, s), 2.78–2.70 (2 H, m), 2.68–2.62 (4 H, m), 2.17–2.01 (2 H, m), 1.99–1.90 (3 H, m), 1.73 (3 H, t, J = 1.0 Hz), 1.53–1.36 (2 H, complex m); ^{13}C NMR 153.04, 150.03, 135.43, 133.78, 122.40, 118.91, 108.49, 90.62, 53.78, 45.53, 41.25, 30.90, 29.30, 29.03, 28.33, 27.98, 20.79 ppm; mass spectrum, m/z (relative intensity) 246 (7), 245 (12), 244 (M^+, 55), 175 (11), 161 (10), 159 (12), 147 (10), 136 (15), 129 (10), 123 (35), 122 (32), 121 (100), 110 (41), 109 (85), 108 (76), 94 (16), 93 (51), 92 (13), 91 (47), 81 (17), 80 (14), 79 (30), 78 (16), 77 (33), 67 (20), 65 (13), 55 (13), 53 (15), 41 (21), 39 (12). Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.49; H, 10.10.

(*S*)-4-[[4-(1-Methylethenyl)-1-cyclohexen-1-yl]methyl]-3-cyclohexen-1-one (6b). Similar treatment of 754 mg (5.02 mmol) of (*S*)-(−)-perillaldehyde (**6**), as described for **1b**, afforded 1.226 g of a yellow oil that after flash chromatography yielded 1.050 g (4.56 mmol, 91%) of **6b** as a colorless oil: bp 93–96 °C (0.1 Torr); IR (film) 3080, 3050, 3010, 2960, 2900, 2840, 1715, 1640, 1510, 1445, 1432, 1400, 1371, 1335, 1288, 1235, 1195, 1183, 1110, 1040, 1015, 985, 910, 880, 830, 790 cm^{-1}; ^{1}H NMR δ 5.48 (2 H, overlapping m, $W_{1/2}$ = 7.9 Hz), 4.71 (2 H, overlapping m, $W_{1/2}$ = 4.2 Hz), 2.88 (2 H, dt, J = 3.5, 1.8 Hz), 2.70 (2 H, br s), 2.52–2.44 (2 H, m), 2.37–2.29 (2 H, m), 2.19–2.03 (2 H, m), 2.02–1.90 (2 H, m), 1.86–1.76 (1 H, m), 1.74 (3 H, t, J = ca. 1.0 Hz), 1.55–1.40 (2 H, m); ^{13}C NMR 210.70, 149.79, 137.05, 134.81, 122.95, 119.47, 108.58, 45.66, 41.08, 39.69, 38.70, 30.82, 28.38, 28.02, 27.81, 20.80 ppm; mass spectrum, m/z (relative intensity) 232 (8), 231 (7), 230 (M^+, 36), 188 (26), 187 (27), 186 (24), 174 (10), 173 (11), 160 (9), 159 (10), 148 (9), 147 (10), 145 (22), 144 (11), 143 (9), 134 (16), 133 (17), 131 (19), 129 (20), 122 (21), 121 (93), 120 (35), 119 (37), 118 (24), 117 (28), 109 (68), 107 (37), 106 (35), 105 (93), 104 (24), 93 (90), 92 (42), 91 (95), 81 (64), 80 (30), 79 (100), 77 (43), 68 (29), 67 (59), 65 (18), 55 (34), 53 (33), 43 (16), 41 (62), 39 (25). Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.27; H, 9.76.

(*E*)-1-Methoxy-4-[2-methyl-4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-butenyl]-1,4-cyclohexadiene (7a). Similar treatment of 1.042 g (5,05 mmol) of C-14 Aldehyde **7**, as described for **1a**, afforded 1.530 g of a pale yellow oil that after flash chromatography yielded 1.410 g (4.70 mmol, 93%) of **7a** as a colorless oil: IR (film) 3090, 3070, 3040, 3020, 2990, 2960, 2910, 2860, 2820, 1690, 1660, 1460, 1445, 1435, 1380, 1355, 1215, 1170, 1030, 1015, 945, 780, 765 cm^{-1}; ^1H NMR δ 5.40 (1 H, m, $W_{1/2}$ = 7.5 Hz; apparent septet, J = 1.3 Hz), 5.04 (1 H, t of sextets, J = 6.1, 1.2 Hz), 4.61 (1 H, t, J = 3.3 Hz), 3.54 (3 H, s), 2.84–2.66 (4 H, m), 2.66–2.52 (4 H, m), 1.93 (2 H, t, J = 6.2 Hz), four singlets at 1.572, 1.566, 1.556, 1.552 (6 H) superimposed on 1.64–1.55 (2 H, m), 1.52–1.39 (2 H, m), 0.97 (6 H, s); ^{13}C NMR 153.06, 136.86, 134.12, 131.18, 127.94, 127.42, 118.79, 90.75, 53.80, 47.69, 39.95, 35.00, 32.94, 29.34, 28.95, 28.40 (2 C), 27.46, 19.77, 19.68, 15.43 ppm; mass spectrum, m/z (relative intensity) 302 (2), 301 (2), 300 (M^+, 9), 177 (10), 163 (19), 161 (12), 123 (33), 121 (40), 119 (13), 110 (17), 109 (62), 108 (29), 107 (26), 105 (28), 95 (24), 93 (54), 91 (61), 81 (97), 79 (61), 77 (50), 69 (21), 67 (28), 66 (18), 65 (25), 55 (50), 53 (44), 43 (26), 41 (100), 39 (46). Anal. Calcd for $C_{21}H_{32}O$: C, 83.94; H, 10.73. Found: C, 83.93; H, 10.63.

(*E*)-4-[2-Methyl-4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-butenyl]-3-cyclohexen-1-one (7b). Similar treatment of 1.036 g (5.02 mmol) of C-14 Aldehyde **7**, as described for **1b**, produced 1.566 g of a bright yellow oil that after flash chromatography yielded 1.295 g (4.53 mmol, 90%) of **7b** as a pale yellow oil: IR (film) 3050, 3020, 2960, 2910, 2860, 2850, 2830, 1723, 1675, 1507, 1465, 1438, 1400, 1380, 1357, 1335, 1290, 1240, 1198, 1182, 1115, 1075, 1040, 1015, 975, 885, 860, 790, 770 cm^{-1}; ^1H NMR δ 5.48 (1 H, overlapping t of quintets, J = 3.5, 1.1 Hz), 5.06 (1 H, tq, J = 5.1, 1.3 Hz), 2.88 (2 H, dt, J = 3.4, 1.7 Hz), 2.70 (4 H, br s), 2.45 (2 H, apparent t with further splitting, J = 6.1 Hz), 2.30 (2 H, apparent t, J = 6.6 Hz), 1.92 (2 H, t, J = 6.1 Hz), 1.59 (3 H, d, J = 1.1 Hz) and 1.54 (3 H, s) superimposed on 1.62–1.52 (2 H, m), 1.46–1.39 (2 H, m), 0.97 (6 H, s); ^{13}C NMR 210.83, 137.33, 136.60, 130.43, 128.43, 127.53, 119.38, 47.71, 39.81, 39.69, 38.71, 34.96, 32.87, 28.35 (2 C), 27.78, 27.41, 19.74, 19.59, 15.59 ppm; mass spectrum, m/z (relative intensity) 286 (M^+, 1), 123 (13), 122 (10), 121 (17), 119 (11), 108 (20), 107 (61), 105 (30), 93 (57), 91 (68), 81 (35), 79 (58), 77 (46), 67 (57), 66 (19), 65 (29), 55 (45), 53 (83), 43 (28), 42 (100), 41 (100), 39 (49). Anal. Calcd for $C_{20}H_{30}O$: C, 83.86; H, 10.56. Found: C, 83.79; H, 10.58.

1-(1,5-Dimethyl-4-hexenyl)-4-methoxy-1,4-cyclohexadiene (8a). Similar treatment of 635 mg (5.04 mmol) of 6-methyl-5-hepten-2-one (**8**), as described for **1a**, except that for the reduction 348 mg (50.0 mmol, 24 pieces) of lithium wire was used and for the quench 0.27 mL (15 mmol) of distilled H_2O in 5 mL of THF was initially added (ca. 5 min) and after 30 min 1.30 mL (32 mmol) of MeOH in 5 mL of THF was introduced (ca. 5 min) and the dark blue color turned white after 10 min, afforded 1.186 g of a yellow oil (one product peak, GLC) that after flash chromatography yielded 1.024 g (4.65 mmol, 93%) of **8a** as a colorless oil:[3,7] IR (film) 3080, 3035, 2980, 2945, 2900, 2860, 2840, 2820, 1698, 1656, 1500, 1445, 1430, 1383, 1367, 1240, 1210, 1165, 1035, 1100, 940, 820, 775, 760, 660 cm^{-1}; ^1H NMR δ 5.39 (1 H, m, $W_{1/2}$ = 4.6 Hz), 5.09 (1 H, t of apparent septets, J = 7.1, 1.4 Hz), 4.63 (1 H, br s, $W_{1/2}$ = 4.6 Hz), 3.55 (3 H, s), 2.71 (4 H, apparent d, J = 1.6 Hz), 2.12 (1 H, sextet, J = 6.9 Hz), 1.90 (2 H, q, J = 7.2 Hz), 1.68 (3 H, d, J = 1.1 Hz), 1.58 (3 H, s), 1.36 (2 H, two overlapping 8-line m, J = ca. 15, 7 Hz), 1.00 (3 H, d, J = 6.9 Hz); ^{13}C NMR 153.18, 139.60, 131.16 124.85 and 124.79 (1 C), 116.83 and 116.78 (1 C), 90.55 and 90.49 (1 C), 53.80, 40.00 and 39.94 (1 C), 35.36 and 35.31 (1 C), 29.20 and 29.14 (1 C), 26.14, 26.08, 25.72, 19.78, 17.68 ppm; mass spectrum, m/z (relative intensity) 222 (3), 221 (4), 220 (M^+, 24), 150 (11), 149 (10), 138 (17), 137 (100), 135 (46), 123 (12), 121 (11), 109 (23), 105 (19), 93 (12), 91 (16), 82 (61), 81 (31), 79 (25), 77 (20), 69 (23), 67 (34), 55 (24), 45 (14), 41 (47). Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.99; H, 10.99.

4-(1,5-Dimethyl-4-hexenyl)-3-cyclohexen-1-one (8b). Similar treatment of 634 mg (5.03 mmol) of 6-methyl-5-hepten-2-one (**8**), as described for **8a** except that after extraction the combined organic phase, which was not dried, afforded a cloudy yellow oil after removal of solvent, which was diluted with a solution of 50 mL of THF and 5 mL of 5% H_2SO_4. After the resultant yellow solution had been refluxed with stirring for 2 h, the solution was diluted with 75 mL of water and extracted twice with 50-mL portions and twice with 25-mL portions of Et_2O. The combined organic phase was washed with 100 mL of water, dried ($MgSO_4$), filtered, and concentrated in vacuo (water aspirator pressure) on a rotary evaporator. The resultant 1.185 g of bright yellow oil afforded after flash chromatography 985 mg (4.78 mmol, 95%) of **8b** as a pale yellow oil:[7b,8] IR (film) 3050, 3020, 2960, 2920, 2870, 2850, 1720, 1675, 1450, 1400, 1375, 1190, 1110, 1010, 965, 890, 825, 799 cm^{-1}; ^1H NMR δ 5.46 (1 H, td, J = 3.6, 0.8 Hz), 5.09 (1 H, t of septets, J = 7.1, 1.4 Hz), 2.87 (2 H, d with further splitting, J = 3.5 Hz), 2.51–2.44 (2 H, complex m), 2.39–2.30 (2 H, m), 2.22 (1 H, sextet, J = 7.0 Hz), 1.91 (2 H, q, J = 7.5 Hz), 1.68 (3 H, d, J = 1.0 Hz), 1.59 (3 H, s), 1.37 (2 H, two overlapping 8-line m, J = ca. 11.2, 6.9 Hz), 1.02 (3 H, d, J = 6.9 Hz); ^{13}C NMR 211.10, 143.27, 131.46, 124.49, 117.34, 40.34, 39.76, 38.89, 35.08, 26.15, 25.95 and 25.72 (1 C), 25.47 and 25.30 (1 C), 19.41, 17.70 ppm; mass spectrum, m/z (relative intensity) 91 (17), 81 (13), 79 (32), 77 (24), 69 (40), 68 (16), 67 (53), 66 (19), 65 (22), 55 (56), 53 (68), 51 (20), 43 (18), 42 (100), 41 (100), 40 (25), 39 (100). Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.22; H, 10.75.

(*E*)- and (*Z*)-1-(1,5,9-Trimethyl-4,8-decadienyl)-4-methoxy-1,4-cyclohexadiene (9a). Similar treatment of 1.071 g (5.52 mmol) of geranyl acetone (**9**), as described for **8a**, produced 1.732 g of a yellow oil that after flash chromatography yielded 1.482 g (5.15 mmol, 93%) of **9a** as a colorless oil: IR (film) 3090, 3040, 3030, 2960, 2930, 2900, 2870, 2850, 2830, 1692, 1661, 1510, 1445, 1388, 1372, 1245, 1215, 1170, 1105, 1035, 1010, 945, 825, 780 cm^{-1}; ^1H NMR δ 5.39 (1 H, br s with further fine splitting, $W_{1/2}$ = 5.7 Hz), 5.10 (2 H, two overlapping br s with further fine splitting, $W_{1/2}$ = 14.7 Hz), 4.64 (1 H, br s, $W_{1/2}$ = 5.1 Hz), 3.55 (3 H, s), 2.72 (4 H, br s, $W_{1/2}$ = 4.5 Hz), 2.14–1.86 (7 H, complex overlapping m), 1.68 (3 H, s), 1.60 (3 H, s), 1.58 (3 H, s), 1.47–1.23 (2 H, complex m), doublets at 1.01 and 0.96 (3 H, 7:3, J = 6.9 Hz); ^{13}C NMR 153.20, 139.60, 134.99, 134.82, 131.38, 131.16, 125.53, 124.73, 124.53, 116.85, 90.51, 53.78, 40.10, 39.95, 39.83, 35.68, 35.34, 32.06, 29.21, 26.83, 26.76, 26.12, 26.08, 26.00, 25.96, 25.71, 23.41, 19.79, 17.68, 17.59, 16.01 ppm; mass spectrum, m/z, (relative intensity) 288 (M^+, 2), 286 (1), 220 (9), 148 (18), 138 (41), 137 (64), 136 (22), 135 (52), 123 (41), 121 (20), 110 (36), 109 (86), 105 (18), 95 (17), 94 (34), 93 (14), 91 (43), 82 (26), 81 (25), 80 (11), 79 (57), 78 (18), 77 (61), 69 (43), 67 (34), 65 (26), 55 (23), 53 (16), 51 (11), 45 (48), 43 (20), 41 (100), 39 (36). Anal. Calcd for $C_{20}H_{32}O$: C, 83.27; H, 11.18. Found: C, 83.48; H, 11.01.

(*E*)- and (*Z*)-4-(1,5,9-Trimethyl-4,8-decadienyl)-3-cyclohexen-1-one (9b). Similar treatment of 978 mg (5.00 mmol) of geranyl acetone (**9**), as described for **8b**, yielded 1.250 g (4.56 mmol, 91%) of **9b** as a colorless oil: bp 115–120 °C (0.1 Torr); IR (film) 3050, 3030, 2960, 2920, 2850, 1721, 1670, 1450, 1375, 1190, 1110, 1030, 1015, 965, 890, 830, 800 cm^{-1}; ^1H NMR δ 5.46 (1 H, t, J = 3.6 Hz), 5.10 (2 H, m, $W_{1/2}$ = 13.3 Hz), 2.87 (2 H, d with further fine splitting, J = 2.8 Hz), 2.51–2.44 (2 H, m), 2.39–2.31 (2 H, m), 2.22 (1 H, sextet, J = 6.9 Hz), 2.11–1.92 (4 H, m), on which is superimposed 1.92 (2 H, q, J = 7.6 Hz), singlets at 1.68 and 1.60 and 1.58 (9 H), 1.51–1.17 (2 H, complex m), 1.02 (3 H, d, J = 6.9 Hz); ^{13}C NMR 210.76, 138.44, 138.26, 137.51, 137.40, 131.78, 131.57, 124.47, 124.39, 122.08, 121.40, 118.08, 117.96, 39.95, 39.89, 38.87, 35.73, 35.57, 32.09, 29.04, 28.98, 26.81, 25.88, 23.60, 17.86, 17.80, 16.14 ppm; mass spectrum, m/z (relative intensity) 276 (1), 275 (1), 274 (M^+, 4), 150 (8), 135 (10), 123 (17), 121 (13), 109 (13), 107 (16), 95 (20), 93 (13), 91 (10), 82 (19), 81 (29), 79 (16), 69 (100), 67 (20), 55 (19), 53 (14), 43 (27), 41 (68), 39 (13). Anal. Calcd for $C_{19}H_{30}O$: C, 83.15; H, 11.02. Found: C, 83.22; and H, 11.10.

1-(2,4-Dimethyl-4-pentenyl)-4-methoxy-1,4-cyclohexadiene (10a) and 1-(2,4-Dimethylpentyl)-4-methoxy-1,4-cyclohexadiene (10c). Similar treatment of 571 mg (5.09 mmol) of 2,4-dimethyl-4-penten-1-al (**10**), as described for **8a**, afforded 1.075 g of a yellow oil that after flash chromatography yielded 954 mg (4.63 mmol, 91%) of a colorless oil. Careful analysis (NMR, MS) of the oil indicated an inseparable ca. 3:2 mixture of **10a** and **10c**: IR (film) 3080, 3045, 3000, 2950, 2905, 2870, 2835, 1695, 1665, 1650, 1510, 1465, 1450, 1440, 1390, 1375, 1215, 1172, 1152, 1015, 950, 885, 780, 768, 720 cm^{-1}; ^1H NMR δ 5.36 (1 H, br m, $W_{1/2}$ = 7.3 Hz), 4.74 (0.6 H, br m, $W_{1/2}$ = 5.2 Hz), 4.66–4.63 (0.6 H, complex m), 4.62 (1 H, br s), 3.55 (3 H, s), 2.71 (4 H, d, J = 1.8 Hz), 2.06–1.91 (2 H, complex m), 1.80–1.74 (2 H, complex m), 1.69 (3 H, s), 1.03 (1 H, m, at least a 12-line pattern, J = ca. 6.7, 5.0 Hz), two overlapping d centered at 0.87 and 0.84 (3 H, J = 6.7 Hz); ^{13}C NMR 153.16, 144.65, 134.41, 134.24, 118.88, 118.66, 111.43, 90.57, 90.52, 53.80, 46.71, 45.38, 45.80, 44.75, 29.38, 29.23, 28.72, 28.38, 25.30, 23.50, 22.24, 22.15, 19.67, 19.43 ppm; mass spectrum, m/z (relative intensity) 208 (M^+, 5; **10c**), 207 (1), 206 (M^+, 7; **10a**), 124 (11), 123 (100), 121 (25), 109 (20), 91 (20), 77 (9), 45 (17), 41 (14). Anal. Calcd for a 3:2 mixture of $C_{14}H_{22}O$ and $C_{14}H_{24}O$: C, 81.18; H, 11.09. Found: C, 80.80; H, 10.87.

4-(2,4-Dimethyl-4-pentenyl)-3-cyclohexen-1-one (10b) and 4-(2,4-Dimethylpentyl)-3-cyclohexen-1-one (10d). Similar treatment of 563 mg (5.03 mmol) of 2,4-dimethyl-4-penten-1-al (**10**), as described for **8b**,

(7) (a) Zilenovski, J. S. R.; Hall, S. S. *J. Org. Chem.* **1981**, *46*, 4139–4142. (b) Birch, A. J.; Mukherji, S. M. *J. Chem. Soc.* **1949**, 2531–2536.

(8) Mukherji, S. M.; Bhattacharyya, N. K. *J. Am. Chem. Soc.* **1953**, *75*, 4698–4700.

produced 1.097 g of a yellow oil that after flash chromatography yielded 870 mg (4.53 mmol, 90%) of a colorless oil. Careful analysis (NMR, MS) of the oil indicated an inseparable ca. 3:2 mixture of **10b** and **10d**: IR (film) 3080, 3050, 2950, 2910, 2870, 2840, 1720, 1675, 1646, 1455, 1445, 1405, 1375, 1330, 1285, 1238, 1190, 1110, 1080, 1015, 970, 885, 785 cm^{-1}; ^1H NMR δ 5.44 (1 H, td, J = 3.4, 1.0 Hz), 4.76 (0.6 H, br s with further fine splitting, $W_{1/2}$ = 5.5 Hz), 4.67 (0.6 H, br s, $W_{1/2}$ = 5.5 Hz), 2.87 (2 H, br s, $W_{1/2}$ = 7.1 Hz), 2.53–2.44 (2 H, M), 2.42–2.32 (2 H, complex m), 2.11–1.97 (2 H, complex m), 1.89–1.72 (2 H, complex m), 1.70 (3 H, d, J = 0.9 Hz), 1.17–0.92 (1 H, m, at least a 16-line pattern), three overlapping d centered at 0.88, 0.84, and 0.82 (3 H, J = 6.7 Hz); ^{13}C NMR 210.91, 210.77, 144.33, 137.90, 137.74, 119.44, 119.25, 111.70, 111.55, 77.74, 77.11, 46.60, 45.78, 45.60, 44.96, 39.70, 39.52, 38.72, 28.84, 28.71, 28.52, 25.29, 23.50, 23.38, 22.25, 22.16, 19.74, 19.49 ppm; mass spectrum, m/z (relative intensity) 195 (3), 194 (M^+, 15; **10d**), 192 (M^+, 20; **10b**), 137 (16), 136 (43), 135 (10), 123 (15), 121 (12), 111 (24), 110 (23), 109 (41), 108 (13), 107 (18), 96 (16), 95 (36), 94 (37), 93 (30), 91 (17), 85 (25), 84 (34), 83 (65), 82 (37), 81 (32), 79 (58), 77 (19), 69 (31), 68 (26), 67 (65), 65 (12), 57 (22), 55 (72), 53 (28), 43 (100), 41 (76), 39 (29). Anal. Calcd for a 3:2 mixture of $C_{13}H_{20}O$ and $C_{13}H_{22}O$: C, 80.86; H, 10.85. Found: C, 80.28; H, 10.92.

1-Methoxy-4-[5-methyl-2-(1-methylethylidene)cyclohexyl]-1,4-cyclohexadiene (11a, a 7:3 Diastereomeric Pair). Similar treatment of 768 mg (5.05 mmol) of (*R*)-(+)-pulegone (**11**), as described for **1a**, except that for the quench 2.50 mL (1.935 g, 42 mmol) of absolute EtOH in 5 mL of anhydrous THF was slowly added (ca. 10 min) and the dark blue color turned white after ca. 40 min, afforded a pale orange oil that after flash chromatography yielded 1.132 g (4.60 mmol, 91%) of **11a** as a colorless oil: bp 108–113 °C (0.1 Torr); IR (film) 3090, 3040, 2990, 2940, 2910, 2860, 2820, 1690, 1660, 1460, 1450, 1435, 1385, 1360, 1215, 1170, 1015, 948, 781 cm^{-1}; ^1H NMR overlapping multiplets at δ 5.35–5.34 (0.3 H) and 5.32–5.30 (0.7 H), overlapping br s at 4.65 (0.3 H) and 4.63 (0.7 H), 3.55 (3 H, s), 3.28 (0.3 H, br s, $W_{1/2}$ = 11.0 Hz), 3.04 (0.7 H, dd, J = 8.3, 8.0 Hz), 2.74–2.70 (4 H, complex m) superimposed on 2.8–2.6 (1 H, m), 2.40 (1 H, ddd, J = 13.8, 7.1, 2.5 Hz), 2.03–1.85 (2 H, complex m), 1.71 (0.9 H, s), 1.69 (2.1 H, s), 1.65 (0.9 H, d, J = 1.7 Hz) and 1.54 (2.1 H, d, J = 1.6 Hz) superimposed on 1.65–1.53 (1 H, m), 1.43–1.02 (2 H, two complex overlapping m), 0.91 (2.1 H, d, J = 6.3 Hz), 0.84 (0.9 H, d, J = 6.3 Hz); ^{13}C NMR 153.06, 153.02, 137.95, 135.82, 132.37, 131.42, 125.00, 123.37, 117.57, 116.05, 90.84, 90.76, 53.76, 45.48, 42.40, 37.81, 36.91, 36.31, 32.11, 29.42, 29.25, 28.60, 28.18, 27.72, 27.44, 26.37, 24.40, 22.51, 22.08, 20.38, 20.30, 20.16 ppm; mass spectrum, m/z (relative intensity) 246 (M^+, 1), 128 (10), 121 (15), 119 (10), 117 (13), 115 (20), 110 (11), 109 (15), 108 (18), 107 (10), 105 (25), 103 (13), 95 (25), 93 (22), 91 (68), 81 (38), 79 (58), 78 (35), 77 (70), 69 (19), 67 (52), 66 (31), 65 (43), 56 (26), 55 (92), 53 (69), 51 (25), 43 (100), 42 (49), 41 (100), 40 (28), 39 (100). Anal. Calcd for $C_{17}H_{26}O$: C, 82.87; H, 10.64. Found: C, 82.90; H, 10.70.

4-[5-Methyl-2-(1-methylethylidene)cyclohexyl]-3-cyclohexen-1-one (11b, a 67:33 Diastereomeric Pair). Similar treatment of 758 mg (4.97 mmol) of (*R*)-(+)-pulegone (**11**), as described for **11a** except that after extraction the combined organic phase, which was not dried, afforded a cloudy yellow oil after removal of solvent, which was diluted with a solution of 50 mL of THF and 5 mL of 5% H_2SO_4. After the resultant, stirred yellow solution had been refluxed for 2 h, the solution was diluted with 75 mL of water and extracted twice with 50-mL portions and twice with 25-mL portions of Et_2O. The combined organic phase was washed with 100 mL of water, dried ($MgSO_4$), filtered, and concentrated in vacuo (water aspirator pressure) on a rotary evaporator. The resultant bright yellow oil afforded after flash chromatography 1.030 g (4.44 mmol, 89%) of **11b** as a colorless oil: IR (film) 3050, 2990, 2950, 2910, 2860, 1725, 1457, 1440, 1402, 1375, 1340, 1280, 1245, 1190, 1040, 1020, 975, 895, 805 cm^{-1}; ^1H NMR δ 5.44–5.40 (0.33 H, m), 5.40–5.35 (0.67 H, m, superficial t, J = ca. 3.6 Hz), 3.37 (0.33 H, br s, $W_{1/2}$ = 10.9 Hz), 3.12 (0.67 H, t, J = 7.8 Hz), 2.85 (2 H, br s with further fine splitting, $W_{1/2}$ = 9.8 Hz), 2.50–2.42 (4 H, m), 2.42–2.33 (2 H, m), 2.02–1.95 (1 H, m), 1.72–1.60 (2 H, m) on which is superimposed singlets at 1.72 and 1.70 (3 H) and doublets at 1.67 and 1.56 (3 H, J = 1.7 Hz), 1.40–1.04 (2 H, complex m), 0.93 (2 H, d, J = 6.4 Hz) and 0.85 (1 H, d, J = 6.4 Hz); ^{13}C NMR 211.38, 211.27, 141.78, 139.77, 131.90, 131.04, 125.74, 124.18, 118.38, 116.75, 45.72, 43.03, 39.99, 39.10, 37.85, 36.79, 36.44, 32.11, 28.24, 27.95, 27.86, 27.12, 26.62, 24.40, 22.64, 22.17, 20.58, 20.38 ppm; mass spectrum, m/z (relative intensity) 232 (M^+, 2), 119 (22), 117 (17), 115 (17), 107 (12), 105 (38), 103 (13), 95 (15), 93 (20), 91 (79), 81 (14), 79 (53), 78 (22), 77 (63), 69 (14), 67 (50), 66 (27), 65 (46), 63 (14), 56 (17), 55 (71), 54 (19), 53 (75), 52 (25), 51 (33), 43 (56), 42 (100), 41 (100), 40 (35), 39 (100). Anal. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.51; H, 10.51.

1-Methoxy-4-[(2,6,6-trimethyl-1-cyclohexen-1-yl)methyl]-1,4-cyclohexadiene (12a). Similar treatment of 772 mg (5.08 mmol) of β-cyclocitral (**12**), as described for **11a**, produced 1.345 g of a dark yellow oil that after flash chromatography yielded 1.112 g (4.52 mmol, 89%) of **12a** as a pale yellow oil: bp 95–99 °C (0.1 Torr); IR (film) 3085, 3060, 3035, 2980, 2950, 2900, 2850, 2820, 1689, 1659, 1605, 1460, 1432, 1382, 1354, 1235, 1210, 1165, 1035, 1010, 950, 780, 760 cm^{-1}; ^1H NMR δ 5.23 (1 H, apparent septet, J = ca. 1.5 Hz), 4.64 (1 H, br s, $W_{1/2}$ = 3.9 Hz), 3.55 (3 H, s), 2.71 (4 H, br s, $W_{1/2}$ = 4.6 Hz), 2.63 (2 H, br s, $W_{1/2}$ = 5.8 Hz), 1.97 (2 H, t, J = 6.2 Hz), 1.60 (2 H, tt, J = 11.4, 5.8 Hz), 1.50 (3 H, s) superimposed on 1.45 (2 H, dd, J = 11.3, 6.7 Hz), 0.94 (6 H, s); ^{13}C NMR 153.48, 133.83, 133.56, 129.34, 116.68, 90.75, 53.81, 39.91, 34.95, 34.86, 32.67, 30.59, 29.24, 28.45 (2 C), 20.43, 19.60 ppm; mass spectrum, m/z (relative intensity) 248 (1), 247 (3), 246 (M^+, 16), 244 (20), 229 (12), 135 (11), 123 (61), 122 (40), 121 (100), 110 (53), 109 (21), 108 (17), 95 (12), 93 (17), 91 (26), 81 (20), 79 (19), 77 (17), 69 (11), 67 (13), 55 (16), 41 (25). Anal. Calcd for $C_{17}H_{26}O$: C, 82.87; H, 10.64. Found: C, 82.79; H, 10.79.

4-[(2,6,6-Trimethyl-1-cyclohexen-1-yl)methyl]-3-cyclohexen-1-one (12b). Similar treatment of 774 mg (5.10 mmol) of β-cyclocitral (**12**), as described for **11b**, afforded 1.005 g (4.33 mmol, 85%) of **12b** as a pale yellow oil: bp 100–103 °C (0.1 Torr); IR (film) 3050, 3020, 2950, 2900, 2850, 1710, 1450, 1398, 1370, 1355, 1335, 1225, 1182, 1035, 1010, 970, 790, 755 cm^{-1}; ^1H NMR δ 5.32 (1 H, br s with further fine splitting, $W_{1/2}$ = 7.6 Hz), 2.85 (2 H, br s, $W_{1/2}$ = 8.4 Hz), 2.73 (2 H, br s, $W_{1/2}$ = 6.5 Hz), 2.54–2.40 (4 H, two overlapping m), 1.98 (2 H, t, J = 6.2 Hz), 1.68–1.56 (2 H, complex m), 1.51 (3 H, s) superimposed on 1.51–1.41 (2 H, complex m), 0.94 (6 H, s); ^{13}C NMR 211.34, 136.96, 133.57, 129.80, 117.31, 39.81, 39.69, 38.87, 35.32, 34.84, 32.62, 29.53, 28.44 (2 C), 20.44, 19.52 ppm; mass spectrum, m/z (relative intensity) 234 (2), 233 (12), 232 (M^+, 58), 218 (16), 217 (94), 175 (13), 161 (10), 159 (45), 157 (10), 147 (17), 145 (10), 133 (16), 131 (13), 124 (13), 123 (100), 121 (15), 119 (23), 117 (11), 109 (20), 107 (32), 105 (38), 95 (27), 93 (30), 91 (45), 81 (55), 79 (40), 77 (32), 69 (17), 67 (33), 65 (14), 55 (36), 53 (25), 41 (56), 39 (21). Anal. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.48; H, 10.01.

1-Methoxy-4-[1-methyl-3-(2,6,6-trimethyl-1-cyclohexen-1-yl)-propyl]-1,4-cyclohexadiene (13a). Similar treatment of 971 mg (5.05 mmol) of β-ionone (**13**), as described for **11a**, afforded 1.518 g of a pale yellow oil that after flash chromatography yielded 1.312 g (4.55 mmol, 90%) of **13a** as a colorless oil:[7a] bp 115–118 °C (0.1 Torr); IR (film) 3085, 3035, 3020, 2980, 2950, 2915, 2890, 2855, 2815, 1687, 1656, 1600, 1460, 1450, 1430, 1382, 1365, 1352, 1235, 1210, 1160, 940, 780 cm^{-1}; ^1H NMR δ 5.41 (1 H, br s, $W_{1/2}$ = 2.7 Hz), 4.64 (1 H, br s, $W_{1/2}$ = 2.6 Hz), 3.55 (3 H, s), 2.74 (4 H, br s, $W_{1/2}$ = 2.2 Hz), 2.08 (1 H, sextet, J = 6.9 Hz), 1.99–1.82 (4 H, two overlapping m), 1.56 (3 H, s) superimposed on 1.65–1.48 (2 H, m), 1.45–1.36 (4 H, complex m), 1.04 (3 H, d, J = 6.9 Hz), 0.97 (6 H, s); ^{13}C NMR 153.33, 139.91, 137.74, 126.57, 116.63, 90.64, 53.83, 41.46, 40.11, 36.01, 35.03, 32.91, 29.23, 28.74 (2 C), 27.10, 26.68, 19.84, 19.70, 19.55 ppm; mass spectrum, m/z (relative intensity) 290 (1), 289 (2), 288 (M^+, 7), 150 (25), 148 (14), 138 (13), 137 (100), 135 (44), 123 (20), 121 (11), 109 (17), 95 (15), 81 (18), 79 (12), 69 (15), 67 (12), 55 (17), 41 (23). Anal. Calcd for $C_{20}H_{32}O$: C, 83.27; H, 11.18. Found: C, 83.53; H, 11.16.

4-[1-Methyl-3-(2,6,6-trimethyl-1-cyclohexen-1-yl)propyl]-3-cyclohexen-1-one (13b). Similar treatment of 963 mg (5.02 mmol) of β-ionone (**13**), as described for **11b**, produced 1.326 g (4.84 mmol, 92%) of **13b** as a colorless oil: bp 115–119 °C (0.1 Torr); IR (film) 3050, 3020, 2960, 2930, 2900, 2865, 2850, 2825, 1720, 1470, 1455, 1440, 1375, 1358, 1315, 1190, 1115, 1012, 968, 800 cm^{-1}; ^1H NMR δ 5.49 (1 H, t, J = 3.4 Hz), 2.88 (2 H, br s with fine splitting, $W_{1/2}$ = 6.9 Hz), 2.53–2.36 (4 H, two overlapping m), 2.18 (1 H, sextet, J = 6.9 Hz), 1.90 (4 H, t, J = 6.9 Hz), 1.57 (3 H, s) superimposed on 1.62–1.46 (2 H, m), 1.45–1.33 (4 H, m), 1.05 (3 H, d, J = 6.9 Hz), 0.97 (6 H, s); ^{13}C NMR 211.28, 143.33, 137.45, 126.93, 117.46, 41.94, 40.05, 39.87, 39.05, 35.62, 35.14, 32.96, 28.87 (2 C), 27.22, 25.56, 20.01, 19.76, 19.42 ppm; mass spectrum, m/z (relative intensity) 275 (2), 274 (M^+, 6), 150 (25), 137 (29), 136 (71), 135 (28), 124 (18), 123 (100), 121 (13), 109 (13), 107 (14), 95 (51), 94 (18), 93 (16), 81 (55), 79 (28), 69 (33), 67 (28), 57 (12), 55 (27), 53 (14), 43 (13), 41 (36). Anal. Calcd for $C_{19}H_{30}O$: C, 83.15; H, 11.02. Found: C, 83.21; H, 10.92.

1-Methoxy-4-[1-hydroxy-5-methyl-2-(1-methylethyl)cyclohexyl]-1,4-cyclohexadiene (14a, Four Diastereomeric Pairs). Similar treatment of 780 mg (5.06 mmol) of (–)-menthone (**14**), as described for **11a**, produced 1.214 g (4.60 mmol, 91%) of **14a** as a colorless oil: bp 110–115 °C (0.1 Torr); IR (film) 3640–3420 (br), 3080, 3060, 3040, 2980, 2950, 2920, 2900, 2855, 2840, 2820, 1685, 1653, 1444, 1380, 1360, 1295, 1210, 1160, 1010, 940, 780 cm^{-1}; ^1H NMR br overlapping singlets at δ 5.85 and 5.84 (1 H), br overlapping singlets at 4.63 and 4.62 (1 H), 3.56 (3 H, s), 2.83–2.70 (4 H, complex m), 1.86–1.68 (3 H, m), 1.59 (0.46 H, s, exchanges in D_2O) and 1.28 (0.54 H, s, exchanges in D_2O) superimposed on 1.63–1.41 (6 H, complex overlapping m), at least three over-

lapping doublets centered at ca. 0.90 and 0.86 and 0.84 (9 H, J = ca. 6.8 Hz); ^{13}C NMR 153.09, 153.01, 143.29, 141.86, 141.14, 119.35, 117.14, 116.56, 90.38, 90.29, 79.42, 78.52, 53.83, 48.03, 46.98, 46.69, 35.27, 32.02, 29.20, 29.11, 28.09, 27.78, 26.72, 26.66, 26.35, 26.13, 25.22, 24.11, 23.87, 22.61, 22.34, 20.84, 18.85, 18.46, 16.62 ppm; mass spectrum, m/z (relative intensity) 265 (1), 264 (M^+, 7), 263 (3), 262 (3), 248 (10), 247 (8), 246 (35), 236 (10), 203 (16), 179 (58), 177 (26), 175 (9), 163 (11), 161 (38), 155 (38), 152 (19), 151 (100), 147 (22), 139 (22), 137 (30), 135 (23), 121 (38), 111 (15), 110 (38), 109 (42), 95 (43), 91 (29), 81 (67), 79 (27), 77 (28), 69 (48), 67 (26), 55 (57), 53 (21), 43 (36), 41 (78), 39 (25). Anal. Calcd for $C_{17}H_{28}O_2$: C, 77.22; H, 10.67. Found: C, 77.40; H, 10.53.

(*E*)- and (*Z*)-4-[5-Methyl-2-(1-methylethyl)cyclohexylidene]-2-cyclohexen-1-one (14b, Each as Four Diastereomeric Pairs). Similar treatment of 778 mg (5.04 mmol) of (-)-menthone (**14**), as described for **11b**, yielded 1.029 g (4.44 mmol, 88%) of **14b** as a colorless oil: bp 105-110 °C (0.1 Torr); IR (film) 3040, 2950, 2925, 2900, 2880, 2860, 1665, 1650, 1600, 1565, 1450, 1400, 1280, 1240, 1205, 1155, 1100, 1010, 960, 815 cm^{-1}; ^{1}H NMR δ 7.59 (1 H, dd, J = 10.2, 4.5 Hz), 5.85 (1 H, dd, J = 10.2, 3.1 Hz). 2.75 (2 H, m, apparent quintet, J = ca. 6.3 Hz), 2.47 (3 H, m, $W_{1/2}$ = 1.7 Hz), 2.30-2.23 (1 H, m), 2.04-1.85 (2 H, m), 1.82-1.08 (5 H, complex m), doublets centered at 0.99 and 0.92 (6 H, J = 6.8 Hz), three overlapping doublets centered at 0.77 and 0.74 and 0.72 (3 H, J = ca. 6.4 Hz); ^{13}C NMR 196.82, 147.17, 146.96, 144.98, 140.25, 140.10, 139.86, 123.59, 121.49, 121.41, 121.26, 41.85, 41.01, 34.11, 33.96, 32.16, 31.86, 31.81, 31.38, 29.32, 27.34, 26.03, 25.80, 25.67, 23.94, 23.79, 23.30, 22.45, 22.31, 22.02, 20.86, 19.37, 19.29, 17.74, 17.45, 17.31, 14.66 ppm; mass spectrum, m/z (relative intensity) 233 (8), 232 (M^+, 40), 189 (100), 188 (10), 161 (12), 147 (33), 145 (40), 133 (17), 131 (10), 121 (12), 119 (16), 117 (15), 115 (12), 109 (19), 107 (17), 105 (28), 95 (52), 93 (30), 91 (51), 81 (30), 79 (21), 77 (28), 69 (12), 67 (22), 65 (18), 55 (19), 53 (17), 51 (10), 43 (20), 41 (50), 39 (25). Anal. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.48; H, 10.21.

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Bimanes. 23. The Synthesis and Properties of Vinyl-9,10-dioxabimanes

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Abstract: Syntheses and useful reactions of *syn*-vinylbimanes are reported. The precursors are *syn*-(ethyl,methyl)bimane (4,6-diethyl-3,7-dimethyl-1,5-diazabicyclo[3.3.0]octa-3,6-diene-2,8-dione) (*syn*-(CH_3CH_2,CH_3)B) (**2**) and *syn*-(ethyl,chloro)bimane (4,6-diethyl-3,7-dichloro-1,5-diazabicyclo[3.3.0]octa-3,6-diene-2,8-dione) (*syn*-(CH_3CH_2,Cl)B) (**4**). Bromination of **2** yields the 1-bromoethyl derivative (*syn*-(CH_3CHBr,CH_3)(CH_3CH_2,CH_3)B) and both diastereomers of the bis-1-bromoethyl derivative (*syn*-(CH_3CHBr,CH_3)B) (Radkowsky; Kosower; Eisenberg; Goldberg *J. Am. Chem. Soc.* **1986**, *108*, 4532-4541). Elimination of HBr (Et_3N/CH_3CN) leads to monovinylbimane (*syn*-(CH_2=CH,CH_3)(CH_3CH_2,CH_3)B) and divinylbimane (*syn*-(CH_2=CH,CH_3)B), respectively. *syn*-(CH_3CH_2,CH_3)(CH_3,CH_3)B may be converted to *syn*-(CH_2=CH,CH_3)(CH_3,CH_3)B. Vinylbimanes can also be prepared via 2-hydroxyethylbimanes from paraformaldehyde and the anion of *syn*-(CH_3,CH_3)B. The novel reaction of pure bromine with *syn*-(ethyl,chloro)bimane (**4**) or *syn*-(methyl,chloro)bimane (**13**) yields monobromo or dibromo derivatives in high yields. The (1-bromoethyl,chloro)bimanes are converted into (vinyl,chloro)bimanes via phenyl thioethers, oxidation to sulfoxides, and thermal elimination. The synthesis of bimane precursors, chloropyrazolinones, is improved through removal of HCl with *t*-BuOH and dry $MgSO_4$. Vinylbimanes are stable, with UV absorption maxima similar to those of the corresponding ethylbimanes; the fluorescence maxima are at longer wavelengths, showing that excited state interaction of vinyl groups with the bimane ring is greater than in the ground state. Nucleophiles (water, chloride, amines, and bisulfite ion) add to give good yields of 2-adducts. The sulfonate (sulfite adduct) and Vilsmeier reagent ($(CH_3)_2N^+$=CHCl,Cl^-) react to form the sulfonyl chloride. The latter reacts with amines to yield fluorescent derivatives useful for identification. Tricyclic bimanes with an eight-membered ring, are readily obtained by bis addition of bifunctional nucleophiles (CH_3NH_2,S^{2-}). Dialkyl malonate anions yield both tricyclic monoadducts and bisadducts. The crystal structure of μ-(2-thiatrimethylene)-*syn*-(methylene,methyl)-9,10-dioxabimane is reported.

Introduction

9,10-Dioxabimanes ("bimanes") are stable, small heterocyclic systems, readily synthesized,[1-3] and converted via halogen derivatives into many other compounds.[4,5] The syn isomers are usually strongly fluorescent. Vinylbimanes are of interest as reactive intermediates, as potential biological thiol labeling agents,[6-25] and for analyzing the photophysics of conjugated 9,10-dioxabimanes.[26-31] We now report syntheses of monovinyl- and divinylbimanes, which are of interest in all these respects, along with some novel derivatives.

The effectiveness of bromobimanes as biological thiol labeling agents stimulated us to study bimanesulfonyl chlorides as protein labeling agents targeted at amino groups. Such agents might be useful in analysis of picomole quantities of amines, as is the case for thiols.[8,11,12,23]

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