Selective Synthesis of Either Complex Aromatic Alkenes or (1,4-Cyclohexadienyl)alkenes by Tandem Arylation–Multistep Reduction of $\alpha,\beta,\gamma,\delta$-Unsaturated Ketones[1]

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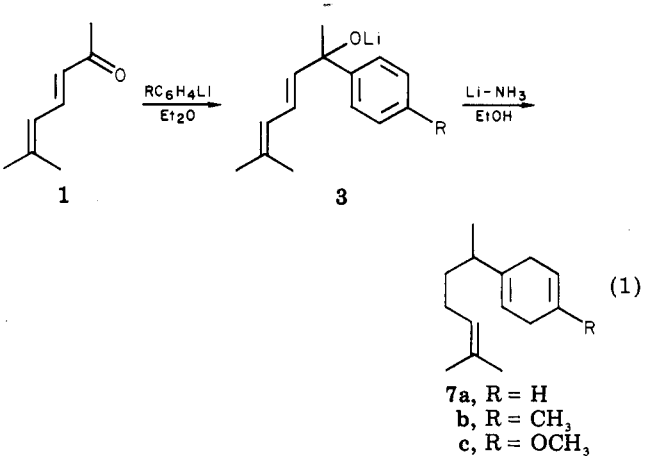
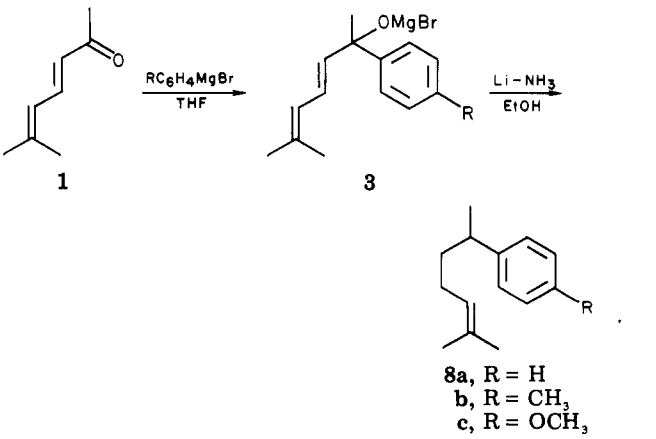
(1,4-Cyclohexadienyl)alkenes are conveniently prepared in excellent isolated yields from $\alpha,\beta,\gamma,\delta$-unsaturated ketones by tandem alkylation–multistep reductions. By this one-pot procedure, complex diene benzyl alkoxides, generated in situ by arylation of $\alpha,\beta,\gamma,\delta$-unsaturated ketones with organolithium reagents, are reduced by a multistep reduction process in lithium–ammonia–ethanol to the corresponding (1,4-cyclohexadienyl)alkenes. Examples include the synthesis of 2-methyl-6-(1,4-cyclohexadien-1-yl)-2-heptene (**7a**), (±)-β-curcumene (**7b**), 2-methyl-6-(4-methoxy-1,4-cyclohexadien-1-yl)-2-heptene (**7c**), 1-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-(1,4-cyclohexadien-1-yl)butane (**9a**), 1-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-(4-methyl-1,4-cyclohexadien-1-yl)butane (**9b**), and 1-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-(4-methoxy-1,4-cyclohexadien-1-yl)butane (**9c**) using phenyllithium, *p*-tolyllithium, and *p*-methoxyphenyllithium with 6-methyl-3,5-heptadien-2-one (**1**) and β-ionone (**2**), respectively. In contrast, use of the corresponding Grignard reagents prepared by the Rieke procedure results in the selective synthesis of the corresponding aromatic alkene. Examples include the synthesis of 2-methyl-6-phenyl-2-heptene (**8a**), (±)-α-curcumene (**8b**), 2-methyl-6-(*p*-methoxyphenyl)-2-heptene (**8c**), 1-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-phenylbutane (**10a**), 1-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-(4-tolyl)butane (**10b**), and 1-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-(*p*-methoxyphenyl)butane (**10c**) using phenylmagnesium bromide, *p*-tolylmagnesium bromide, and *p*-methoxyphenylmagnesium bromide with 6-methyl-3,5-heptadien-2-one (**1**) and β-ionone (**2**), respectively. The latter series of results suggest that some species, present in the Grignard sequence, is preventing the 1,4-reduction (Birch reduction) of the aromatic ring.

Recently we reported the regiospecific synthesis of 1,4-dienes by alkylation–reduction of $\alpha,\beta,\gamma,\delta$-unsaturated ketones with alkyl organolithium reagents.[3] Herein, we report a study extending this procedure to aromatic organolithium and organomagnesium bromide reagents that results in the selective synthesis of either (1,4-cyclohexadienyl)alkenes or aromatic alkenes, depending solely on the organometallic reagent used. The method involves the multistep reduction in lithium–ammonia–ethanol of the diene benzyl alkoxide that is generated in situ by the arylation of $\alpha,\beta,\gamma,\delta$-unsaturated ketones. The entire sequence is a consecutive one-pot procedure, and the isolated yield of the product is usually better than 90%.

When either dienone 6-methyl-3,5-heptadien-2-one (**1**) or β-ionone (**2**) was added to a cold (ca. −60 °C), ethereal solution of either phenyllithium, *p*-tolyllithium, or *p*-methoxyphenyllithium, generated in situ from the corresponding aryl bromide and lithium–sodium alloy[4] in a metal–ammonia reaction vessel, the intermediate lithium diene benzyl alkoxide is produced. Ammonia is then distilled into the vessel, followed by the addition of lithium and ethanol (eq 1). The latter are conditions that protonate the diene benzyl alkoxide and then reduce the resultant diene benzyl alcohol to the (1,4-cyclohexadienyl)alkene before all the excess lithium is destroyed.



In sharp contrast to the above results, when either dienone **1** or **2** was added to an arylmagnesium bromide, generated in situ in THF from the corresponding aryl bromide and a dark gray suspension of highly reactive magnesium metal, and then subjected to the lithium–ammonia–ethanol reducing conditions, only the aromatic alkene was produced (eq 2). The reactive magnesium metal is formed in the reaction vessel just prior to use by the Rieke procedure[5] and involves the potassium metal reduction of anhydrous magnesium chloride in refluxing THF.



(1) Part 12 in the series "Alkylation-Reduction of Carbonyl Systems". For part 11 see: Ryan Zilenovski, J. S.; Hall, S. S. *Synthesis* **1979**, 698–699.

(2) Taken in part from the Ph.D. Thesis of J.S.R.Z. that was submitted to the Graduate School, Rutgers University, Newark, NJ, Jan 1980; C. Sabat Graduate Award (Rutgers University), 1979.

(3) Ryan Zilenovski, J. S.; Hall, S. S. *J. Org. Chem.* **1979**, *44*, 1159–1161.

(4) Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. 1, pp 618–619 and the references cited therein.

(5) (a) Rieke, R. D.; Bales, S. E. *J. Am. Chem. Soc.* **1974**, *96*, 1775–1781. (b) *J. Chem. Soc., Chem. Commun.* **1973**, 879–880. (c) Rieke, R. D.; Hudnall, P. M. *J. Am. Chem. Soc.* **1972**, *94*, 7178–7179.

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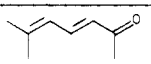
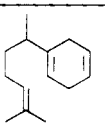
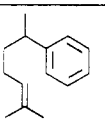
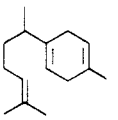
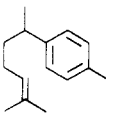
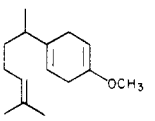
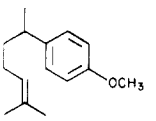
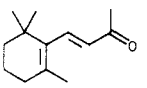
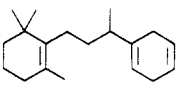
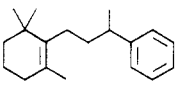
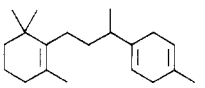
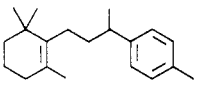
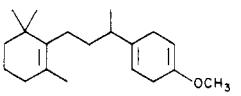
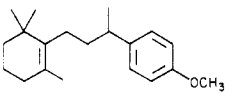
Table I. Arylation-Reduction of Conjugated Dienones[a]

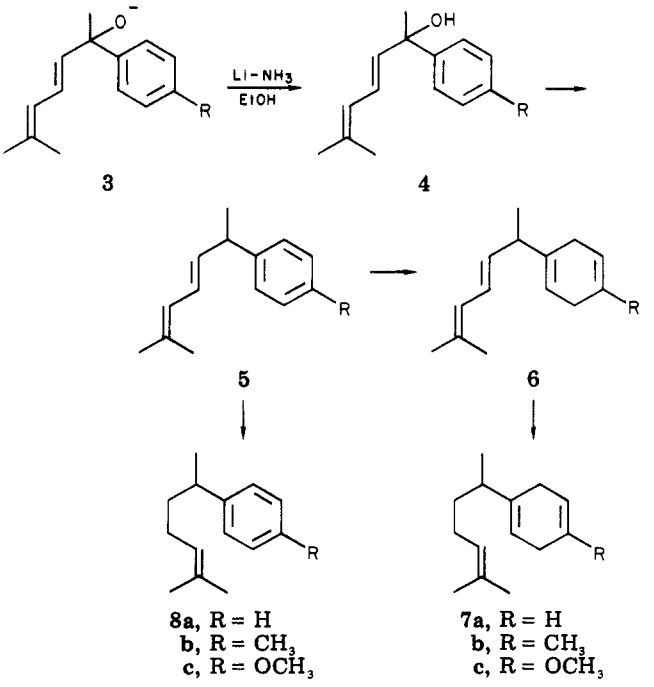
conjugated dienone	aryl group	product (yield, %)[b] with organolithium reagent[c]	product (yield, %)[b] with Grignard reagent[d]
 1	C_6H_5	 7a (95)	 8a (96)
	p-$CH_3C_6H_4$	 7b (94)	 8b (91)
	p-$CH_3OC_6H_4$	 7c (85)	 8c (92)[e]
 2	C_6H_5	 9a (90)	 10a (95)
	p-$CH_3C_6H_4$	 9b (98)	 10b (92)
	p-$CH_3OC_6H_4$	 9c (83)	 10c (90)[e]

[a] See the Experimental Section for details. [b] Pure, isolated yield after column chromatography. [c] Generated in situ from the corresponding aryl bromide and lithium-sodium alloy in Et_2O. [d] Generated in situ from the corresponding aryl bromide and reactive magnesium metal (Rieke procedure) in THF. [e] See footnote 11.

Table I is a listing of these results with the organolithium and organomagnesium bromide reagents with the two $\alpha,\beta,\gamma,\delta$-unsaturated ketones selected for this study. The reported yields are after isolation of pure material from column chromatography. In addition to the remarkable selectivity of these procedures, the other advantages are that the entire sequence is performed in one reaction vessel without isolation or purification of the intermediate products, and the yields are excellent. Two of the examples listed in Table I with p-tolylorgano reagents and dienone 1 represent extremely convenient methods for the total syntheses of the sesquiterpenes β-curcumene (**7b**)[1] and α-curcumene (**8b**).[6]

We have previously established,[1] using sodium benzoate (rather than EtOH) as the quenching agent, that the intermediate diene benzyl alkoxide **3** is stable to lithium–ammonia conditions and that no reduction occurs until the external proton source (EtOH) is introduced. In addition, limiting the amount of lithium in either the synthesis involving organolithium or the Grignard reagent during the reduction step produced mixtures of dienes **6** and **7** or aromatic alkenes **5** and **8**, respectively. These observations, we feel, can be accommodated by the reduction sequence outlined in Scheme I. After protonation of alkoxide **3**, the diene benzyl alcohol **4** is rapidly reduced to the diene aromatic hydrocarbon **5**. When an aryllithium is used for the alkylation, then 1,4-reduction (Birch reduction) of the aromatic ring produces **6**, which is then reduced to (1,4-cyclohexadienyl)alkene **7** in the last step. When an arylmagnesium bromide is used, some species present obviously prevents the Birch reduction (**5** to **6**),

Scheme I



(6) Hall, S. S.; McEnroe, F. J.; Shue, H.-J. *J. Org. Chem.* **1975**, *40*, 3306–3307 and the references cited therein.

and the diene aromatic reduces by the 1,2-addition to the less substituted double bond forming aromatic alkene 8. At this time we have been unable to determine what species present in the alkylation–reduction sequence, using the in situ generated Grignard reagent, is inhibiting the Birch reduction so effectively. Experiments designed to solve this problem are in progress in this laboratory.

Experimental Section[7]

General Comments. The in situ generation of the aryl reagent and subsequent alkylation sequence is performed under an inert atmosphere by connecting an argon gas source to a T tube that is connected to the reaction assembly and to a soda lime drying trap. The latter is connected in series to an oil bubbler. Argon is swept through the system at a moderate flow rate. When ammonia is to be introduced, the inert gas source is disconnected and the reaction protected from moisture by attaching a soda lime drying tube to the side arm of the Dewar condenser for the duration of the reaction. All glassware was oven dried, cooled to room temperature in a box desiccator, and then quickly assembled. Anhydrous ether was used directly from freshly opened containers. Tetrahydrofuran (THF), which had been filtered through an alumina column, was freshly distilled under a nitrogen atmosphere from a dark blue THF solution containing the sodium–benzophenone ketyl radical. Lithium wire for the reduction sequence (0.32 cm, high purity, Foote Mineral Co.)[8] was wiped free of oil, rinsed in hexane, and cut into 0.5-cm pieces just prior to use. The sodium and potassium metals (Fisher Scientific Co.) were wiped free of oil, rinsed in hexane, and cut into small pieces just prior to use. The lithium–sodium alloy[9] 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 opened side-arm joint. Anhydrous magnesium chloride (Alfa Products) was quickly weighed in a dry capped vial and added to the reaction vessel to avoid uptake of moisture. Bromobenzene (Aldrich Chemical Co.), *p*-bromotoluene (Eastman Kodak Co.), and *p*-bromoanisole (Aldrich Chemical Co.) were redistilled. 6-Methyl-3,5-heptadien-2-one (K&K Life Science Division, ICN Pharmaceuticals, Inc.) and β-ionone (Hoffmann-La Roche Inc.) were used without further purification. Anhydrous ammonia was distilled, through a tower of potassium hydroxide pellets, directly into the reaction vessel. Gas–liquid chromatographic analyses were performed on 100 × 0.4 cm (i.d.) glass columns packed either with 5% silicone OV-225 (25% phenyl, 25% cyanopropyl, methyl) supported on 60–80-mesh Chromosorb W or with 3% silicone OV-17 (50% phenyl, methyl) supported on 100–120-mesh Chromosorb W. Purification of the products by column chromatography was accomplished on 100–200-mesh Floridin magnesium silicate (Florisil) by elution with hexane. Samples for microanalyses were obtained by evaporative distillation in a Kugelrohr oven. Boiling points are uncorrected. The assigned structure of each product is consistent with the spectral data. Satisfactory composition analyses (±0.4% for C and H) on all products were obtained. Two experiments, one using *p*-methoxyphenylmagnesium bromide and the other *p*-methoxyphenyllithium, are described in detail to illustrate the two procedures.

***p*-Methoxyphenylation–Reduction of 6-Methyl-3,5-heptadien-2-one (1). 2-Methyl-6-(*p*-methoxyphenyl)-2-heptene (8c).** A stirred mixture containing 952 mg (10.0 mmol) of magnesium chloride and 782 mg (20.0 mmol, 2 chunks) of potassium in 20 mL of THF was refluxed (oil bath, 80 °C) for 2 h. After the dark gray suspension was allowed to cool to ambient temperature (ca. 20 min), a solution of 1.31 g (7.0 mmol) of *p*-bromoanisole in 10 mL of THF was slowly added (ca. 5 min). After 45 min the stirred dark gray suspension was cooled to −60 °C (dry ice/2-propanol bath), and then a solution of 620 mg (5.0 mmol) of 6-methyl-3,5-heptadien-2-one (1) in 10 mL of THF was added dropwise (ca. 3 min). After 20 min the cooling bath was removed and the stirred mixture allowed to warm to ambient temperature (ca. 45 min). Ammonia (ca. 80 mL) was then distilled into the mixture and 375 mg (54 mmol, 20 pieces) of lithium wire was quickly added. Fifteen minutes after the dark blue-black color of the mixture was established, 2.84 g (3.60 mL, 62 mmol) of absolute ethanol was slowly added (ca. 5 min). When the dark blue-black color started to fade, after ca. 2–3 h of vigorous stirring, excess ammonium chloride (ca. 10 g) was added to completely discharge the blue color to gray (and buffer the system). After the ammonia was allowed to evaporate,[10] the residue was partitioned between ether and water. The organic phase was dried ($MgSO_4$), filtered, and concentrated at water aspirator pressure. The resultant crude yellow oil usually exhibited only one peak on GLC.[11] Following column chromatography, 1.00 g (92%) of 2-methyl-6-(*p*-methoxyphenyl)-2-heptene (8c) was obtained as a colorless oil: bp 113–115 °C (1.5 torr); IR (film) 3100, 3060, 3030, 2960, 2920, 2860, 2830, 1600, 1585, 1490, 1460, 1440, 1375, 1290, 1240, 1120, 1030, 750 cm^{-1}; NMR ($CDCl_3$) δ 7.14 (2 H, superficial t, J = 7.6 Hz, with further fine splitting), 6.88 (2 H, superficial t, J = 8.8 Hz, with further fine splitting), 5.11 (1 H, t, J = 6.6 Hz), 3.81 (3 H, s), 3.18 (1 H, sextet, J = 6.9 Hz), 1.88 (2 H, t, J = ca. 7 Hz), 1.67 (3 H, s) and 1.52 (3 H, s) superimposed on 1.74–1.38 (2 H, m), 1.19 (3 H, d, J = 7.1 Hz); mass spectrum, m/e (relative intensity) 218 (M^+, 13), 203 (1), 175 (1), 162 (3), 148 (35), 135 (100), 132 (30), 123 (13), 121 (25), 110 (17), 105 (20), 95 (26), 83 (16), 69 (16), 55 (22).

2-Methyl-6-(4-methoxy-1,4-cyclohexadien-1-yl)-2-heptene (7c). To a vigorously stirred mixture of 100 mg (14.3 mmol) of lithium–sodium alloy[9] (rinsed in hexane, pounded to a foil, and cut into 15 thin slivers) in 20 mL of anhydrous ether under an argon atmosphere was slowly added (ca. 5 min) 10% of a solution of 1.31 g (7.0 mmol) of freshly distilled *p*-bromoanisole [95 °C (14 torr)] in 10 mL of ether. During the subsequent 15-min induction period, the cut edges of the alloy slivers became very shinny, and the solution turned cloudy gray (suspension). The remaining ethereal *p*-bromoanisole solution was then slowly added (ca. 15 min). Within ca. 25 min from the end of this addition almost all of the alloy slivers had been consumed, and the suspension was now dark gray.[12] After the mixture was cooled to −60 °C (dry ice/2-propanol bath), a solution of 620 mg (5.0 mmol) of 6-methyl-3,5-heptadien-2-one (1) in 10 mL of anhydrous ether was added slowly (ca. 3 min). After 20 min, the cooling bath was removed and the stirred mixture allowed to return to ambient temperature (ca. 45 min) during which time the mixture turns yellow. Anhydrous ammonia (ca. 80 mL) was then distilled into the mixture, and 375 mg (54 mmol, 20 pieces) of lithium wire was

(7) GLC analyses were determined on a Hewlett-Packard Model 7610A (flame detector) chromatograph using a 40 mL/min carrier gas flow rate. The refractive index was determined with a Bausch and Lomb refractometer. The IR spectra were determined with a Beckman Model 4240 infrared spectrophotometer. The raman spectra were determined with a Jarrell-Ash Model 25-400 raman spectrophotometer equipped with a Spectra-Physics Model 164 AR^+ laser using ca. 150 mW of 4880-Å radiation for excitation. The samples for raman spectral analysis were sealed in 1-mm (i.d.) capillaries and examined in the transverse mode. The ^1H NMR spectra were determined at 100 MHz with a JEOL Model JNM-PS-FT-100 fast Fourier transform NMR spectrometer. The chemical shifts are expressed in δ values (parts per million) 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 ionizing current of 30 mA.

(8) This particular lot contained 0.01% Na, 0.01% Ca, and 0.008% K.

(9) The lithium–sodium alloy (2% Na) was prepared by heating a stirred mixture of the two metals in heavy oil at 190 °C in a stainless-steel beaker under an argon atmosphere tent for 1 h. The melt is then allowed to cool with slow stirring to control the size of the alloy shot, which are then stored under oil. See ref 4 as well.

(10) For small-scale reactions, we have occasionally, rather than waiting for the ammonia to evaporate, cautiously poured the reaction mixture into water and extracted with ether.

(11) With the anisole derivatives 8c and 10c there would sometimes be as much as 8–10% of a minor component (7c and 9c, respectively). On these occasions, the mixture was first treated with aqueous acid (10% HCl) overnight, extracted with ether, dried, and chromatographed to separate the desired aromatic alkene product from the minor resultant ketone.

(12) For the substituted aryllithium reagents, especially *p*-methoxyphenyllithium, we have found the generation of the organolithium reagent is not always reliable unless the aryl bromide is distilled, the lithium–sodium alloy is used, and the latter is pounded to a foil and cut into thin slivers while in an argon atmosphere. The most effective reaction vessel was a three-necked, indented, 250-mL, round-bottomed flask containing a magnetic star-head Nalgene stir bar (17 mm diameter).

quickly added. Fifteen minutes after the dark blue color of the mixture was established, 2.84 g (3.60 mL, 62 mmol) of absolute ethanol was slowly added (ca. 5 min). When the dark blue color started to fade, after ca. 1–2 h of vigorous stirring, excess ammonium chloride (ca. 10 g) was added to completely discharge the blue color to white (and buffer the system). After the ammonia evaporated,[10] the residue was partitioned between ether and water. The organic phase was dried ($MgSO_4$), filtered, and concentrated at water aspirator pressure. The resultant crude yellow oil exhibited one peak on GLC. Following column chromatography, 935 mg (85%) of 2-methyl-6-(4-methoxy-1,4-cyclohexadien-1-yl)-2-heptene (**7c**) was obtained as a colorless oil: bp 75–77 °C (1.3 torr); IR (film) 3030, 2990, 2960, 2930, 2830, 1690, 1665, 1655, 1490, 1450, 1385, 1220, 1165, 1030, 955, 890, 785, 750, 665 cm^{-1}; Raman (neat) 2878, 2806, 1861, 1688, 1668, 1459, 1307, 1043, 896, 820 cm^{-1}; NMR ($CDCl_3$) δ 5.69 (1 H, br s), 5.10 (1 H, t, J = 7.3 Hz), 4.63 (1 H, br s), 3.55 (3 H, s), 2.73 (4 H, perturbed d, J = 3.4 Hz), 2.32–1.76 (3 H, m), 1.68 (3 H, s), 1.59 (3 H, s), 1.4–1.1 (2 H, m), 1.00 (3 H, d, J = 6.8 Hz); mass spectrum, m/e (relative intensity) 220 (M^+, 1), 207 (3), 161 (2), 148 (26), 137 (13), 135 (30), 132 (100), 123 (50), 119 (17), 105 (17), 95 (23), 81 (33), 69 (17).

2-Methyl-6-phenyl-2-heptene (8a): bp 83–85 °C (1.3 torr); IR (film) 3080, 3020, 2950, 2920, 2860, 1600, 1510, 1490, 1450, 1370, 1110, 1015, 965, 810, 755, 715, 695 cm^{-1}; NMR ($CDCl_3$) δ 7.37–7.05 (5 H, m; two intense lines at 7.22 and 7.20), 5.09 (1 H, t, J = 6.8 Hz), 2.69 (1 H, sextet, J = 7.1 Hz), 1.85 (2 H, t, J = ca. 7 Hz), 1.74–1.39 (2 H, m), 1.66 (6 H, s), 1.51 (3 H, s), 1.23 (3 H, d, J = 6.9 Hz); mass spectrum, m/e (relative intensity) 188 (M^+, 1), 163 (1), 161 (3), 148 (18), 132 (100), 123 (44), 119 (22), 95 (17), 81 (19), 69 (12).

2-Methyl-6-(1,4-cyclohexadien-1-yl)-2-heptene (7a): bp 85–87 °C (1.3 torr); IR (film) 3030, 2960, 2930, 2880, 2860, 2820, 1690, 1650, 1455, 1430, 1375, 1135, 1110, 960, 700, 665 cm^{-1}; Raman (neat) 3043, 2967, 2943, 2922, 2883, 2830, 1661, 1640, 1373, 1354, 1229, 1122, 1098, 965, 925, 817, 738 cm^{-1}; NMR ($CDCl_3$) δ 5.70 (2 H, s), 5.42 (1 H, br s), 5.09 (1 H, t, J = 7.1 Hz), 2.61 (4 H, superficial s with further fine splitting), 1.99 (1 H, sextet, J = 7.1 Hz), 1.87 (2 H, t, J = 7.8 Hz), 1.67 (3 H, s), 1.58 (3 H, s), 1.52–1.19 (2 H, m), 1.00 (3 H, d, J = 6.8 Hz); mass spectrum, m/e (relative intensity) 190 (M^+, 1), 188 (2), 147 (6), 132 (7), 118 (22), 105 (100), 91 (40), 82 (60), 79 (40), 69 (23), 67 (15), 55 (24).

(±)-α-Curcumene (8b): bp 125–126 °C (2.5 torr); n^{24}_D 1.4986; Raman (neat) 3065, 3031, 2978, 2930, 2880, 1678, 1620, 1462, 1388, 1308, 1218, 1208, 1192, 833, 813, 656 cm^{-1}; NMR ($CDCl_3$) δ 7.08 (4 H, s), 5.09 (1 H, t, J = 7.3 Hz), 2.65 (1 H, sextet, J = 7.0 Hz), 2.31 (3 H, s), 1.84 (2 H, superficial t, J = ca. 7 Hz), 1.7–1.4 (2 H, br m), 1.66 (3 H, s), 1.51 (3 H, s), 1.21 (3 H, d, J = 6.8 Hz); mass spectrum, m/e (relative intensity) 202 (M^+, 7), 145 (7), 132 (14), 120 (13), 119 (100), 105 (12), 91 (12), 55 (7), 41 (14); other data as previously cited.[6]

(±)-β-Curcumene (7b): bp 122–123 °C (2.5 torr); Raman (neat) 2980, 2940, 2900, 2826, 1705, 1682, 1454, 1442, 1397, 1316, 767, 587 cm^{-1}; other data as previously cited.[1]

1-(2,6,6-Trimethyl-1-cyclohexen-1-yl)-3-phenylbutane (10a): bp 115–117 °C (2.5 torr); IR (film) 3080, 3060, 3020, 2950, 2920, 2860, 1605, 1495, 1450, 1375, 1360, 955, 905, 750, 735, 695 cm^{-1}; NMR ($CDCl_3$) δ 7.38–7.06 (5 H, m; superficial s at 7.22), 2.66 (1 H, sextet, J = 6.8 Hz), 2.0–1.7 (4 H, m), 1.70–0.97 (6 H, m), 1.49 (3 H, s), 1.26 (3 H, d, J = 7.0 Hz), 0.92 (3 H, s), 0.90 (3 H, s); mass spectrum, m/e (relative intensity) 256 (M^+, 1), 241 (1), 151 (2), 131 (2), 123 (87), 118 (100), 105 (18), 95 (32), 69 (37).

1-(2,6,6-Trimethyl-1-cyclohexen-1-yl)-3-(1,4-cyclohexadien-1-yl)butane (9a): bp 119–120 °C (2.5 torr); IR (film) 3040, 2970, 2940, 2880, 2835, 1690, 1655, 1460, 1390, 1380, 1365, 960, 910, 740, 670 cm^{-1}; Raman (neat) 2967, 2943, 2882, 1698, 1660, 1457, 1046, 898, 823 cm^{-1}; NMR ($CDCl_3$) δ 5.71 (2 H, s), 5.44 (1 H, br s), 2.64 (4 H, br s), 2.10–1.75 (1 H, m), 1.90 (4 H, t, J = 7.1 Hz), 1.65–1.22 (6 H, m), 1.57 (3 H, s), 1.03 (3 H, d, J = 6.8 Hz), 0.97 (6 H, s); mass spectrum, m/e (relative intensity) 258 (M^+, 1), 256 (1), 151 (6), 150 (6), 135 (13), 131 (6), 123 (80), 120 (36), 118 (100), 107 (36), 105 (45), 95 (51), 81 (53), 69 (56).

1-(2,6,6-Trimethyl-1-cyclohexen-1-yl)-3-(4-tolyl)butane (10b): bp 113–115 °C (2 torr); IR (film) 3090, 3010, 2950, 2920, 2860, 1510, 1450, 1370, 1360, 810 cm^{-1}; NMR ($CDCl_3$) δ 7.09 (4 H, s), 2.60 (1 H, sextet, J = 6.9 Hz), 2.31 (3 H, s), 1.95–1.70 (4 H, m), 1.70–0.94 (6 H, complex m), 1.49 (3 H, s), 1.24 (3 H, d, J = 6.8 Hz), 0.92 (3 H, s), 0.90 (3 H, s); mass spectrum, m/e (relative intensity) 270 (M^+, 1), 255 (1), 145 (3), 132 (100), 123 (42), 119 (25), 95 (15), 81 (15), 69 (53).

1-(2,6,6-Trimethyl-1-cyclohexen-1-yl)-3-(4-methyl-1,4-cyclohexadien-1-yl)butane (9b): bp 105–107 °C (1.3 torr); IR (film) 3020, 2960, 2920, 2860, 1660, 1515, 1470, 1450, 1380, 1370, 1360, 945, 815, 780 cm^{-1}; Raman (neat) 2966, 2927, 2879, 2824, 1709, 1658, 1451, 1434, 1206, 763, 621 cm^{-1}; NMR ($CDCl_3$) δ 5.44 (2 H, br s), 2.59 (4 H, s), 1.96 (1 H, sextet, J = 6.6 Hz), 1.89 (4 H, t, J = 7.1 Hz), 1.67 (3 H, s), 1.56 (3 H, s), 1.7–1.2 (6 H, m), 1.02 (3 H, d, J = 6.9 Hz), 0.96 (6 H, s); mass spectrum, m/e (relative intensity) 272 (M^+, 2), 147 (6), 145 (8), 135 (29), 134 (54), 132 (92), 123 (44), 121 (100), 119 (69), 105 (28), 95 (31), 81 (28), 69 (26).

1-(2,6,6-Trimethyl-1-cyclohexen-1-yl)-3-(*p*-methoxyphenyl)butane (10c): bp 105–106 °C (2.6 torr); IR (film) 3020, 2950, 2920, 2900, 2860, 2820, 1685, 1660, 1650, 1610, 1580, 1510, 1450, 1380, 1360, 1245, 1215, 1175, 1160, 1035, 955, 890, 825, 785, 750, 670 cm^{-1}; NMR ($CDCl_3$) δ 7.12 (2 H, d, J = 8.8 Hz), 6.83 (2 H, d, J = 8.8 Hz), 3.81 (3 H, s), 2.08–1.73 (5 H, m), 1.73–1.28 (6 H, m), 1.52 (3 H, s), 1.22 (3 H, d, J = 6.7 Hz), 0.93 (6 H, s); mass spectrum, m/e (relative intensity) 286 (M^+, 1), 163 (2), 162 (2), 161 (7), 150 (11), 149 (14), 148 (100), 137 (29), 135 (50), 123 (29), 95 (13), 81 (14), 69 (7).

1-(2,6,6-Trimethyl-1-cyclohexen-1-yl)-3-(4-methoxy-1,4-cyclohexadien-1-yl)butane (9c): bp 115–117 °C (2.6 torr); IR (film) 3020, 2940, 2920, 2900, 2860, 2820, 1690, 1660, 1650, 1510, 1450, 1380, 1355, 1240, 1210, 1160, 1020, 950, 880, 820, 780, 750, 660 cm^{-1}; Raman (neat) 2878, 2806, 1613, 1588, 1562, 1434, 1287, 1159, 1055, 875, 799, 752, 638 cm^{-1}; NMR ($CDCl_3$) δ 5.68 (0.5 H, br s), 5.41 (0.5 H, s), 4.63 (1 H, br s), 3.55 (3 H, s), 2.73 (4 H, br s), 2.20–1.75 (1 H, m), 1.89 (4 H, t, J = 7.1 Hz), 1.65–1.18 (6 H, m), 1.57 (3 H, s), 1.03 (3 H, d, J = 6.8 Hz), 0.97 (6 H, s); mass spectrum, m/e (relative intensity) 288 (M^+, 1), 207 (4), 161 (7), 149 (16), 148 (100), 135 (80), 133 (31), 132 (27), 123 (100), 95 (38), 81 (47), 69 (22), 67 (18).

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