NMR data are collected in Tables II and III.

3-Bromo-2-phenyl-2*H*-indazole (2). During 3–5 h and at room temperature a solution of 1.7 g of bromine in 50 mL of acetic acid was added to a solution of 2 g of 1 in 50 mL of acetic acid. The resulting light yellow colored solution was stirred for an hour and the reaction mixture was allowed to stand at room temperature for another 20 h. The almost colorless mixture, containing colorless needles was treated with 10 mL of water and the so formed solution was gradually added to 500 mL of chilled water (ice–salt bath) under continuous stirring. Crystallization from the milky solutions was induced by seeding. After 3 h of stirring the colorless crystals were collected on a Hirsch funnel, washed with water, and vacuum dried over $CaCl_2$: yield 2.49 g (89%); mp 64–75 °C. Crystallization of 1 g of 2 from 12 mL of ethanol/water 2:1 gave crystals with mp 75.5–77 °C. Additional crystallization did not raise the melting point further. Anal. Calcd for $C_{13}BrH_9N_2$: C, 57.16; H, 3.32; Br, 29.26. Found: C, 56.91; H, 3.40; Br, 29.7.

Bromination of 1 and 2 at 65 and 120 °C. Analogous to the preparation of 2 at room temperature a 1–2 N solution of bromine in acetic acid was gradually dropped into a solution of 1 g of 1 or 2 in 25 mL of acetic acid. For the entire reaction time the reaction mixture was heated either at 65 or at 120 °C. See Table I for reaction times and yields. For the separation of products the short column chromatography technique of Hunt and Rigby[22] was used on silica gel 60 H (Merck) according to Stahl with toluene as solvent for elution.

3,5-Dibromo-2-phenyl-2*H*-indazole (3): white needles, mp 154–155 °C (from toluene/petroleum ether 80–100 and ethanol successively). Anal. Calcd for $C_{13}Br_2H_8N_2$: C, 44.35; H, 2.29; Br, 45.40. Found: C, 44.11; H, 2.31; Br, 45.7.

3,7-Dibromo-2-phenyl-2*H*-indazole (4): white crystals, mp 110.5–111.5 °C (from toluene/petroleum ether 40–60 and ethanol successively). Anal. Calcd for $C_{13}Br_2H_8N_2$: C, 44.35; H, 2.29; Br, 45.40. Found: C, 44.11; H, 2.40; Br, 46.0.

3,5,7-Tribromo-2-phenyl-2*H*-indazole (5): white crystals, mp 208–209 °C (from toluene and acetonitrile successively). Anal. Calcd for $C_{13}Br_3H_7N_2$: C, 36.23; H, 1.64; Br, 55.63. Found: C, 36.15; H, 1.74; Br, 56.1.

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Registry No. 1, 3682-71-1; 2, 91002-55-0; 3, 91002-56-1; 4, 91002-57-2; 5, 91002-58-3.

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New Synthetic Methods for γ-Geraniol, Boll Weevil Pheromone, and α-Damascone Employing 2-(Hydroxymethyl)-4-(phenylthio)-1-butene as a Building Block

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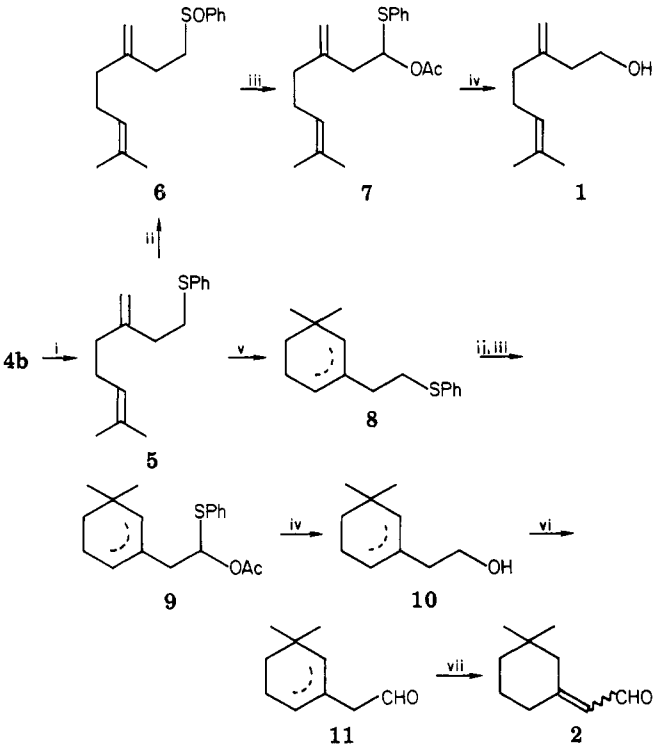
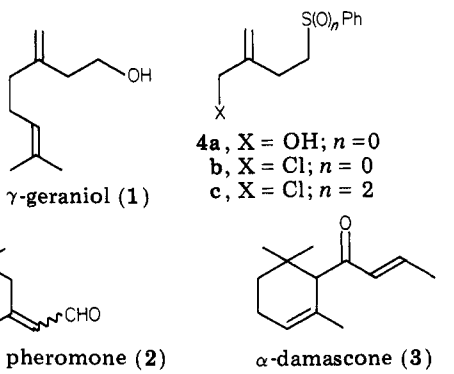
Previously, we have reported a convenient synthetic method for 2-(hydroxymethyl)-4-(phenylthio)-1-butene (**4a**) from ethyl acetoacetate and 2-(phenylthio)-1-bromoethane.[1] The versatility of the functionalities in **4a** has led us to novel syntheses of several terpenoids such as myrcene, citral, squalane, isophytol, β-ionone, irones, β-farnesene, β-sinensal, and dendrolasin.[2] Further, conjugated polyenes and methyl retinoate also have been successfully synthesized by employing **4a**.[3]

In this paper, we describe a new synthetic method for γ-geraniol (**1**), the cyclohexyl constituent of the boll weevil pheromone (**2**), and α-damascone (**3**). γ-Geraniol has been postulated as the biosynthetic precursor for grandisol and **2**,[4] while α-damascone is a black tea aroma constituent having a powerful fragrance.[5]

Scheme I[a]



[a] (i) $(CH_3)_2C{=}CHCH_2MgCl$, CuI, α,α′-dipyridyl, THF; (ii) H_2O_2, dioxane; (iii) Ac_2O catalyst $(CF_3CO)_2O$; (iv) $NaBH_4$–EtOH; (v) HCO_2H; (vi) PDC, CH_2Cl_2; (vii) MeONa–MeOH.



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The exo-methylenated structure of **1** is suggestive of the applicability of **4a** as an appropriate starting material. As shown in Scheme I, this is indeed the case. Grignard coupling[6] of the chloride **4b** with prenylmagnesium chloride afforded **5**, which then was converted to **6** by H_2O_2 oxidation. The resulting oxide **6** was then subjected to the Pummerer reaction which modified the method by Tanikaga et al.[7] This method, employing a large amount of trifluoroacetic acid and 2,6-lutidine, gave rise to an unsatisfactory yield probably due to an acid-sensitive exo-methylene group, but the use of a catalytic amount of trifluoroacetic acid proved feasible. It should be noted that our method needs no base such as 2,6-lutidine. Conversion of α-acetoxy sulfide **7** into **1** was successfully achieved by $NaBH_4$/EtOH which had been found to give homoallyl alcohols without double-bond migration.[2c]

Although **1** can be cyclized to give **2** as already mentioned, we established another route to **2** which involves cyclization of the exo-methylenated sulfide **5** into **8** with formic acid[4] (Scheme I). Conversion of **8** into **9** was conducted as described above. Since direct oxidation of **9** to **2** under alkaline conditions failed to give identifiable products, this difficulty was bypassed through intermediate formation of **10**.

Our route to α-damascone (**3**) employing **4c** is based on both the facile allylation at an α-sulfonyl carbon and the ketone equivalence of the phenylsulfonyl group (Scheme II). The sulfone **12** was easily lithiated by *n*-BuLi at −78 °C in THF, affording a wine-red solution. Successive addition of HMPA and allyl bromide to this solution at this temperature resulted in a smooth reaction to give **13** in 88% yield. Then, **13** was oxidized to the ketone **14** with LDA/Mo–Py–HMPA complex (MoOPH).[8] Treatment of **14** with MeONa gave the methoxylated α,β-enone **15**, which was cyclized to **16** with $SnCl_4$.[5b] Finally, *p*-toluenesulfonic acid effected demethoxylation to give the desired compounds **3**.

In conclusion, **4** proved to be a suitable building block for exo-methylenated compounds, and cyclic compounds are available by acid-promoted cyclization of derivatives of **4**. Judging from readily available reagents employed and simple experimental operations, the present method seems promising for large-scale preparations of **1** and **2**.

Experimental Section

Reactions requiring anhydrous conditions were carried out under a nitrogen atmosphere. Commercially available reagents were distilled before use. Solvents were purified by standard methods. ^{1}H NMR spectra were recorded in CCl_4 on a Hitachi R-24B spectrometer (60 MHz) with Me_4Si as an internal standard. IR spectra were obtained as neat films on a JASCO IRA-1 spectrometer. GLC was performed on Hitachi 163 gas chromatograph using a 3 mm × 3 m Silcone OV-17 column.

2-(Chloromethyl)-4-(phenylthio)-1-butene (4b). A mixed solution of **4a** (5 g, 25.8 mmol) and triphenylphosphine (10.14 g, 38.7 mmol) in carbon tetrachloride (50 mL) was heated under reflux for 8 h under a nitrogen atmosphere. The brown reaction mixture was cooled to 0 °C, diluted with hexane (150 mL), and filtered to remove triphenylphosphine oxide. After concentration of the filtrate, the residual oil was again diluted with hexane (150 mL). Heating the hexane solution at 50–60 °C precipitated a small amount of triphenylphosphine oxide and triphenylphosphine that were removed by filtration. The filtrate was concentrated in vacuo to give the chloride **4b**[1] (5.20 g, 95%) which was used in the next step without further purification: IR 1640, 1580, 1480, 1430, 1250, 900 cm^{-1}; NMR δ 2.48 (t, 2 H, J = 7 Hz), 2.98 (t, 2 H, J = 7 Hz), 3.96 (s, 2 H), 4.93 (s, 1 H), 5.10 (s, 1 H), 6.93–7.28 (m, 5 H).

Preparation of 5. The Grignard reagent of prenyl chloride was generated from prenyl chloride (3.14 g, 30 mmol) and magnesium turnings (1.22 g, 50 mmol) in THF (30 mL) at 0 °C. The resulting Grignard reagent (20 mL) was added over a period of 15 min to a stirred red brown mixture of the chloride **4b** (3.31 g, 15.6 mmol), cuprous iodide (571 mg, 3 mmol), and α,α'-dipyridyl (469 mg, 3 mmol) in THF (10 mL) at 0 °C. After being stirred at 0 °C for 15 min, the reaction mixture was poured into ice-cooled 1 N HCl and extracted with hexane (100 mL). The extract was successively washed with 1 N HCl twice, saturated sodium bicarbonate solution, and water, dried ($MgSO_4$), and evaporated. The residual yellow oil was purified by column chromatography (silica gel, 150:1 hexane–ether) to give the sulfide **5** (2.66 g, 74%): IR 1650, 1590 cm^{-1}; NMR δ 1.58 (s, 3 H), 1.66 (s, 3 H), 1.80–2.10 (m, 4 H), 2.26 (t, 2 H, J = 8 Hz), 2.94 (t, 2 H, J = 8 Hz), 4.71 (s, 2 H), 4.81–5.19 (m, 1 H), 6.90–7.30 (m, 5 H).

Preparation of 6. To a dioxane solution (20 mL) of the sulfide **5** (492 mg, 2.0 mmol) was added 30% H_2O_2 (ca. 5 mL) at 0 °C. The homogeneous mixture was stirred overnight at room temperature, then poured into ice-cooled saturated sodium sulfite solution (100 mL), and extracted with benzene (100 mL). The extract was washed with saturated sodium bicarbonate solution, dried ($MgSO_4$), and evaporated. The residue was purified by column chromatography (silica gel, 10:1 hexane–ethyl acetate) to afford the sulfoxide **6** (435 mg, 88%): IR 1640, 1440, 1080, 1040, 880 cm^{-1}; NMR δ 1.55 (s, 3 H), 1.62 (s, 3 H), 1.92–2.12 (m, 4 H), 2.32 (t, 2 H, J = 6 Hz), 2.72 (t, 2 H, J = 6 Hz), 4.67 (s, 2 H), 4.77–5.08 (m, 1 H), 7.17–7.57 (m, 5 H).

Preparation of 7. A mixed solution of acetic anhydride (10 mL) and freshly distilled trifluoroacetic anhydride (0.498 mmol, 0.07 mL) was stirred at room temperature for 3 h. After addition of sulfoxide **6** (435 mg, 1.66 mmol) in acetic anhydride (3 mL), the mixture was stirred at room temperature for 72 h. The reaction mixture was diluted with benzene (100 mL), poured into water (100 mL), and neutralized by sodium bicarbonate. The organic layer was separated, washed with water, dried ($MgSO_4$), and evaporated. The residual oil was purified by column chromatography (silica gel, 50:1 hexane–ether) to afford α-acetoxy sulfide **7** (280 mg, 55%): IR 1740, 1640, 1590, 1210 cm^{-1}; NMR δ 1.57 (s, 3 H), 1.65 (s, 3 H), 1.91 (s, 3 H), 1.97–2.15 (m, 4 H), 2.45 (d, 2 H, J = 7 Hz), 4.73 (br s, 2 H), 4.82–5.17 (m, 1 H), 6.11 (t, 1 H, J = 7 Hz), 7.12–7.52 (m, 5 H). Anal. Calcd for $C_{18}H_{24}O_2S$: C, 71.01; H, 7.95. Found: C, 70.89; H, 8.05.

Preparation of 1. To a solution of α-acetoxy sulfide **7** (256 mg, 0.85 mmol) in wet ethanol (5 mL of ethanol and 0.1 mL of water) was added an excess amount of sodium borohydride (380 mg, 10 mmol). After being stirred at room temperature for 12 h, the reaction mixture was poured into cold water and extracted with ether (50 mL). The extract was washed with water twice, dried ($MgSO_4$), and evaporated to give a crude oil that was purified by column chromatography (silica gel, 8:1 hexane–ethyl acetate) to afford γ-geraniol (**1**)[4] (109 mg, 84%): IR 3320, 1640, 1040 cm^{-1}; NMR δ 1.60 (s, 3 H), 1.66 (s, 3 H), 1.87–2.15 (m, 4 H), 2.20 (t, 2 H, J = 7 Hz), 3.14 (s, 1 H), 3.56 (t, 2 H, J = 7 Hz), 4.71 (br s, 2 H), 4.80 (m, 1 H).

Preparation of 8. A solution of the sulfide **5** (492 mg, 2.0 mmol) in formic acid (4 mL) was heated under reflux for 0.5 h under a nitrogen atmosphere. The reaction mixture was poured into cold 1 N NaOH solution (100 mL) and extracted with hexane (50 mL). The extract was washed with water, dried ($MgSO_4$), and evaporated. Purification of the residual oil by column chromatography (silica gel, hexane) afforded the sulfide **8** (350 mg, 70%): IR 1590 cm^{-1}; NMR δ 0.86, 0.91 (s, 6 H), 1.02–2.36 (m, 8 H), 2.87 (t, 2 H, J = 7 Hz), 5.03 (br s, 0.36 H), 5.12–5.37 (m, 0.64 H), 6.72–7.27 (m, 5 H).

Preparation of 9. Sulfide **8** was converted into **9** by an analogous procedure described for **7**: IR 1740, 1220 cm^{-1}; NMR δ 0.90, 0.94 (s, 6 H), 1.09–2.19 (m, 8 H), 1.91 (s, 3 H), 2.34 (d, 2 H), 5.09 (br s, 0.36 H), 5.24–5.44 (m, 0.64 H), 6.10 (t, 1 H, J = 7 Hz), 7.07–7.49 (m, 5 H). Anal. Calcd for $C_{18}H_{24}O_2S$: C, 71.01; H, 7.95. Found: C, 71.01; H, 8.17.

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Preparation of 10. Acetate **9** was treated with sodium borohydride as described for **1** to give **10**: yield 66%; IR 3320, 1040 cm^{-1}; NMR δ 0.91, 0.96 (s, 6 H), 1.16–2.33 (m, 8 H), 1.92 (s, 1 H), 3.57 (t, 2 H, J = 7 Hz), 5.15 (br s, 0.36 H), 5.28–5.52 (m, 0.64 H).

Preparation of 11. To a stirred suspension of pyridinium dichromate (PDC) (1.88 g, 5.0 mmol) in dry dichloromethane (15 mL) was added the alcohol **10** (308 mg, 2.0 mmol) in dry dichloromethane (5 mL) at 0 °C. After being stirred at room temperature for 30 h, the mixture was diluted with ether (100 mL) and filtered. The filtrate was concentrated under reduced pressure, and the residue was subjected to column chromatography (100:1 pentane–ether) to afford the aldehyde **11** (229 mg, 75%): IR 2700, 1725, 1695, 1360, 1260, 1030 cm^{-1}; NMR δ 0.86, 0.91 (s, 6 H), 1.00–2.20 (m, 6 H), 2.79 (br s, 2 H), 5.15 (br s, 0.36 H), 5.25–5.52 (m, 0.64 H), 9.33 (t, 1 H, J = 2 Hz).

Preparation of 2. To a solution of sodium methoxide (4.5 mmol) in methanol (10 mL) was added the aldehyde **11** (229 mg, 1.5 mmol) in dry methanol (5 mL) at 0 °C. The resulting pale yellow mixture was stirred at 0 °C for 5 h, poured into ice-cooled 1 N HCl, and extracted with ether (30 mL). The organic layer was washed with saturated sodium bicarbonate solution and water, dried ($MgSO_4$), and evaporated to give a mixture of **11** and **2**. GLC analysis (120 °C: He pressure 1.4 kg/cm^2) revealed that the ratio of **11** (t_R 11.5 and 12.0 min) and **2** (t_R 5.3 and 5.7 min) was 1:1. The mixture was purified by column chromatography (silica gel, 20:1 pentane–ether) to afford the aldehyde **2**[4] (105 mg, 46%) and **11** recovered (100 mg, 44%): IR 1680, 1630, 1450, 1360, 1200, 1160, 1110 cm^{-1}; NMR δ 0.94, 0.98 (s, 6 H), 1.15–2.00 (m, 4 H), 2.05 (s, 2 H), 2.22 (t, 2 H, J = 5 Hz), 2.49 (s, 2 H), 2.64 (t, 2 H, J = 5 Hz), 5.70 (d, 1 H, J = 8 Hz), 5.85 (d, 1 H, J = 8 Hz), 9.86 (d, 1 H, J = 8 Hz), 9.90 (d, 1 H, J = 8 Hz).

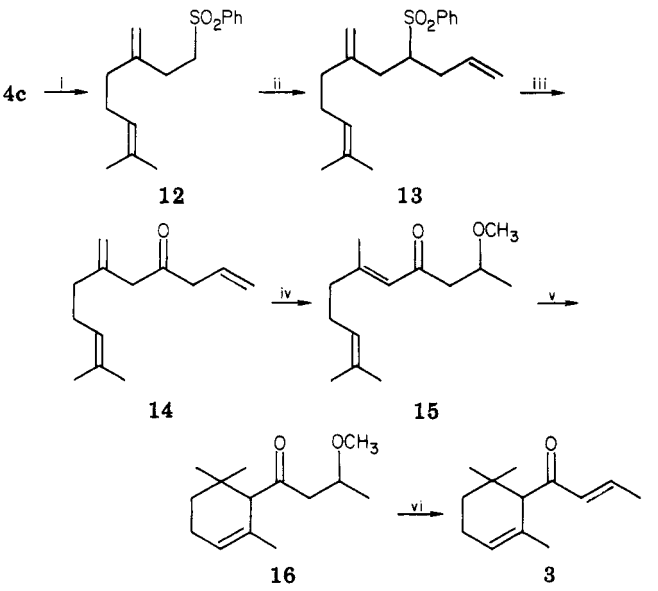
Preparation of 4c. To a stirred solution of the chlorosulfide **4b** (2.13 g, 10 mmol) in methanol (20 mL) was slowly added a mixed solution of selenium dioxide (2.55 g, 23 mmol) and 30% H_2O_2 (5 g, 44 mmol) in methanol (6 mL) at 0 °C. The reaction mixture was stirred at room temperature for 1 h and then poured into cold saturated sodium sulfite solution (100 mL) and extracted with benzene (100 mL). The extract was washed with water, dried ($MgSO_4$), and evaporated. Column chromatography of the residue (silica gel, 5:1 hexane–ether) gave the sulfone **4c** (1.91 g, 84%): IR 1648, 1595, 1445, 1300, 1140, 1080 cm^{-1}; NMR δ 2.50 (t, 2 H), 3.27 (t, 2 H, J = 7 Hz), 3.95 (s, 2 H), 4.90 (s, 1 H), 5.11 (s, 1 H), 7.17–7.97 (m, 5 H).

Preparation of 12. Prenylmagnesium chloride (15 mL, 12 mmol) was added over a period of 15 min to a stirred red brown mixture of the chloride **4c** (2.40 g, 9.42 mmol), cuprous iodide (179 mg, 0.94 mmol), and α,α'-dipyridyl (147 mg, 0.94 mmol) in THF (18 mL) at 0 °C. After being stirred at 0 °C for 15 min, the reaction mixture was poured into ice-cooled 1 N HCl and extracted with benzene (100 mL). The extract was successively washed with 1 N HCl, saturated sodium bicarbonate solution, and water, followed by drying ($MgSO_4$) and evaporation. The residual brown oil was purified by column chromatography (silica gel, 50:1 hexane–ethyl acetate) to give the sulfone **12** (1.73 g, 66%): IR 1640, 1440, 1300, 1140, 1080 cm^{-1}; NMR δ 1.54 (s, 3 H), 1.62 (s, 3 H), 1.95–2.12 (m, 4 H), 2.12–2.50 (m, 2 H), 2.95–3.30 (m, 2 H), 4.67 (br s, 2 H), 4.76–5.15 (m, 1 H), 7.30–7.80 (m, 5 H). Anal. Calcd for $C_{16}H_{22}O_2S$: C, 69.03; H, 7.97. Found: C, 68.79; H, 8.14.

Preparation of 13. To a solution of **12** (1.13 g, 4.08 mmol) in THF (20 mL) was added dropwise a hexane solution of n-BuLi (4.48 mmol) at −78 °C under a nitrogen atmosphere. The resulting wine-red solution was stirred at this temperature for 1 h, and then HMPA (0.85 mL, 4.89 mmol) and allyl bromide (0.42 mL, 4.90 mmol) were added. The reaction mixture was stirred at −78 °C for 1 h, then poured into ice water, and extracted with ether (100 mL). The organic layer was washed with water, dried ($MgSO_4$), and evaporated. Column chromatography (silica gel, 50:1 hexane–ether) of the residue gave the sulfone **13** (1.15 g, 88%): IR 1643, 1450, 1310, 1150, 1090, 1000, 900 cm^{-1}; NMR δ 1.53 (s, 3 H), 1.63 (s, 3 H), 1.73–2.03 (m, 4 H), 2.03–2.59 (m, 4 H), 2.83–3.28 (m, 1 H), 4.63–5.18 (m, 5 H), 5.38–6.12 (m, 1 H), 7.28–7.89 (m, 5 H).

Preparation of 14. To a stirred solution of LDA (6 mmol) in THF was added the sulfone **13** (318 mg, 1.0 mmol) in THF (5 mL), and the resulting dark yellow solution was stirred at −78 °C for 1 h. This solution was rapidly added to a stirred solution of MoOPH complex (1.30 g, 3.0 mmol) in THF (10 mL) at −78 °C, and stirring was continued at this temperature for 0.5 h. The reaction was quenched with saturated sodium sulfite solution (5 mL) and the mixture was stirred at 0 °C for 15 min, then poured into water, and extracted with ether (100 mL). The organic layer was successively washed with 1 N HCl and water, dried ($MgSO_4$), and evaporated. The residue was purified by column chromatography (silica gel, 50:1 hexane–ether) to give the ketone **14** (170 mg, 88%): IR 1720 cm^{-1}; NMR δ 1.58 (s, 3 H), 1.65 (s, 3 H), 1.85–2.20 (m, 4 H), 3.00 (s, 2 H), 3.05 (d, 2 H, J = 4 Hz), 4.65–5.15 (m, 5 H), 5.45–6.15 (m, 1 H).

Scheme II[a]



[a] (i) $(CH_3)_2C{=}CHCH_2MgCl$, CuI, α,α'-dipyridyl; (ii) n-BuLi, HMPA, $CH_2{=}CHCH_2Br$; (iii) LDA, MoOPH, (iv) MeONa–MeOH; (v) $SnCl_4$, CH_2Cl_2; (vi) catalyst p-TsOH, benzene.

Preparation of 15. To a sodium methoxide solution (5.94 mmol) in methanol (10 mL) was added dropwise the ketone **14** (380 mg, 1.98 mmol) in dry methanol (5 mL) at room temperature. After being stirred at this temperature for 1 h, the mixture was poured into water and extracted with ether (100 mL). The organic layer was washed with water, dried ($MgSO_4$), and evaporated. Column chromatographic purification (silica gel, 30:1 hexane–ether) gave the ketone **15** (167 mg, 62%): IR 1682, 1615 cm^{-1}; NMR δ 1.09 (d, 3 H), 1.58 (s, 3 H), 1.66 (s, 3 H), 1.83, 2.07 (s, 3 H), 2.00–2.60 (m, 6 H), 3.17 (s, 3 H), 3.32–3.92 (m, 1 H), 4.72–5.17 (m, 1 H), 5.88 (br s, 1 H).

Preparation of 16. To a solution of ketone **15** (80 mg, 0.36 mmol) in dichloromethane (5 mL) was added tin tetrachloride (0.4 mL, 3.42 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 30 h, then poured into ice water, and extracted with benzene (50 mL). The extract was washed with water and saturated sodium bicarbonate solution, dried ($MgSO_4$), and evaporated. The residue was purified by column chromatography (silica gel, 50:1 hexane–ether) to afford the ketone **16** (43 mg, 53%): IR 1710, 1660, 1440, 1360, 1130, 1080 cm^{-1}; NMR δ 0.86 0.90 (s, 6 H), 1.56 (br s, 3 H), 1.70–2.75 (m, 7 H), 3.18 (s, 3 H), 3.38–3.93 (m, 1 H), 5.30–5.55 (m, 1 H).

Preparation of 3. A mixed solution of the ketone **16** (40 mg, 0.18 mmol) and a catalytic amount of p-toluenesulfonic acid (ca. 1 mg) in benzene (10 mL) was heated under reflux for 2.5 h. The reaction mixture was washed with saturated sodium bicarbonate solution, dried ($MgSO_4$), and evaporated. The residual oil was subjected to column chromatography (silica gel, 80:1 hexane–ether) to afford α-damascone (**3**)[5] (34 mg, 99%): IR 1685, 1660, 1620, 1438, 1355, 1282, 1078, 970 cm^{-1}; NMR δ 0.76 (s, 3 H), 0.87 (s, 3 H), 1.00–1.40 (m, 2 H), 1.47 (s, 3 H), 1.60–2.25 (m, 2 H), 1.81 (d, 3 H, J = 7 Hz), 2.65 (br s, 1 H), 5.35–5.50 (m, 1 H), 6.04 (d, 1 H, J = 16 Hz), 6.62 (dq, 1 H, J = 16 Hz, 7 Hz).

Registry No. 1, 13066-51-8; 2, 41370-30-3; 3, 43052-87-5; 4a, 72445-15-9; 4b, 72445-16-0; 4c, 91112-21-9; 5, 78424-79-0; 6, 91112-18-4; 7, 78791-58-9; 8, 91112-23-1; 9, 91112-25-3; 10, 91112-26-4; 11, 91112-27-5; 12, 78424-72-3; 13, 78424-74-5; 14, 91112-19-5; 15, 57524-03-5; 16, 91112-20-8; prenyl chloride, 503-60-6.

An Intramolecular Acetylene Transfer between Anthracene and 5,6,7,8-Tetrafluorobenzobarrelene. A Novel Synthesis of Janusene and Dibenzobarrelene

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Janusene **3** has been constructed via the [4 + 2]-cycloaddition of dibenzobarrelene **2** to anthracene.[1] Until recently, dibenzobarrelene has been prepared in modest yields by various methods, including addition of acetylene to anthracene at elevated temperature and pressure.[2]

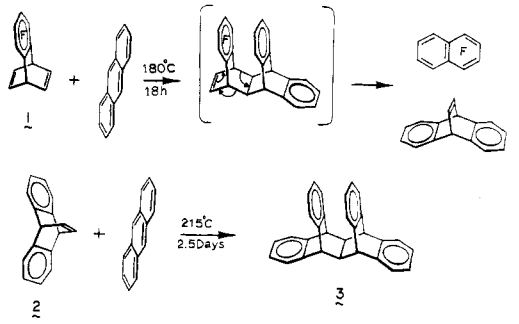
Disadvantages of direct addition of acetylene have stimulated the development of a number of acetylene equivalents.[3-5] The synthons thus far studied are dienophiles activated by electron-withdrawing groups which must be removed in a subsequent step. The conditions and reagents necessary for the removal of the activating moieties often limit the scope, result in undesirable byproducts, and reduce yields. The optimal acetylenic equivalent should consist of a dienophile which undergoes facile addition as well as subsequent regeneration of the olefinic group. Although phenyl vinyl sulfoxide meets both requirements, the byproduct is the undesirable phenylsulfenic acid.[3] The less reactive *trans*-1-(phenylsulfonyl)-2-(trimethylsilyl)ethylene obviates the latter problem but requires a two-step process[4] as does (*Z*)- and (*E*)-1,2-bis(phenylsulfonyl)ethylenes.[5]

We perceived that an efficient "one-pot" procedure could be accomplished by an addition–reversion sequence resulting in a relatively inert aromatic system. A precedent is the reaction of 5,6,7,8-tetrafluorobenzobarrelene and phenyl azide,[6] in which the monoadduct spontaneously cycloreverts to 1,2,3,4-tetrafluoronaphthalene and 1-phenyltriazole.

In this paper, we report the use of 5,6,7,8-tetrafluorobenzobarrelene (**1**) as the reactive acetylene transfer agent, with 1,2,3,4-tetrafluoronaphthalene as the latent leaving group to provide a vastly improved avenue to dibenzobarrelene and janusene (Scheme I).

In these reactions, readily available or easily prepared starting materials were employed. Unlike the laborious synthesis of barrelene[7] or benzobarrelene,[8] 5,6,7,8-tetrafluorobenzobarrelene was obtained directly from tetrafluorobenzyne and benzene,[9,10] in 48–55% yields.

Scheme I



Dibenzobarrelene was prepared in 91% yield by heating at 180 °C for 18 h an equimolar mixture of 5,6,7,8-tetrafluorobenzobarrelene and anthracene. The companion product 1,2,3,4-tetrafluoronaphthalene was isolated in 84% yield.

Janusene was obtained similarly, in 74% yield, by simply doubling the number of equivalents of anthracene relative to 5,6,7,8-tetrafluorobenzobarrelene and increasing the temperature to 215 °C, with a reaction period of 2.5 days.

Experimental Section

Melting points (uncorrected) were carried out on a Melt-Temp capillary apparatus. The infrared spectra in KBr were recorded on a Pye-Unicam 3-300 spectrophotometer. ^1H NMR spectra were determined at 60 MHz on a Varian T-60 spectrometer. ^{13}C NMR spectra were recorded on a Varian CFT-20 spectrometer at 20 MHz in $CDCl_3$. Chemical shifts were reported in parts per million relative to tetramethylsilane in solution.

Tetrafluorobenzyne was generated from pentafluorobenzene (PCR) and *n*-BuLi (2.5 M in hexanes) purchased from Aldrich. The anthracene was purchased from Eastman and used without further purification.

9,10-Dihydro-9,10-ethenoanthracene (Dibenzobarrelene). 5,6,7,8-Tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene (274 mg, 1.21 mmol) (5,6,7,8-tetrafluorobenzobarrelene), prepared by the procedure of Callander,[10] was placed in a 1-mL ampule along with anthracene (210 mg, 1.18 mmol) and hydroquinone (10 mg). The ampule was sealed under dry N_2 and placed in a tube furnace. The reaction was conducted in a melt at 180 °C for 18 h. The resulting pale yellow glassy material was dissolved in dichloromethane, filtered through activated charcoal, and fractionally sublimed. 1,2,3,4-Tetrafluoronaphthalene (206 mg, 103 mmol, 84%) was recovered first (room temperature, 0.1 mmHg), followed by dibenzobarrelene[11] (225 mg, 1.09 mmol, 91%) (60 °C, 0.1 mmHg) [mp 117–118 °C (lit.[11] mp 118–119 °C)].

5,5a,6,11,11a,12-Hexahydro-5,12:6,11-di-*o*-benzenonaphthacene (Janusene). Janusene was prepared by placing 5,6,7,8-tetrafluorobenzobarrelene[10] (220 mg, 0.97 mmol), anthracene (345 mg, 1.90 mmol), and hydroquinone (15 mg) in a 1-mL ampule under purified N_2. The contents were heated in a tube furnace at 215 °C for a period of 2.5 days. The light brown

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