s), 0.8–2.8 (35 H, m), 2.76 (4α H) and 3.65 (4β H) (2 H, AB, J_{AB} = 19 Hz), 6.25 and 6.62 (2 H, AB, J_{AB} = 8 Hz), 7.54 (5 H, br s).

Anal. Calcd for $C_{35}H_{47}N_3O_3$: C, 75.37; H, 8.49. Found: C, 75.60; H, 8.64.

Cholesta-5,7-dien-3α-ol-4-Phenyl-1,2,4-triazoline-3,5-dione Adduct (7c). Ketone **7b** (3.0 g, 5.4 mmol) in MeOH (85 ml) and $CHCl_3$ (20 ml) was treated at room temperature with sodium borohydride (3 g, 0.12 mol) added over 40 min. After stirring for 2 h at room temperature, ether (400 ml) was added. The solution was washed with dilute HCl and saturated NaCl, dried (Na_2SO_4), and evaporated to a gum. The product was isolated by preparative TLC (EtOAc–hexane, 1:2) giving **7c**, 1.1 g, crystallized from MeOH as needles: mp 186–188 °C; $[\alpha]^{28}D$ −94° (*c* 1.0, $CHCl_3$); ν_{max} ($CHCl_3$) 3430 (br), 1750, 1690, 1420, 1395, 1167, 1152, 1085, 690 cm^{-1}; NMR ($CDCl_3$) δ 0.79 (3 H, s), 0.85–3.0 (37 H, m), 4.25 (1 H, m), 5.27 (1 H, br s, D_2O exchangeable), 6.23 and 6.49 (2 H, AB, J_{AB} = 8 Hz), 7.42 (5 H, br s).

Anal. Calcd for $C_{35}H_{49}N_3O_3$: C, 74.82; H, 8.83. Found: C, 75.10; H, 8.82.

Cholesta-5,7-dien-3α-ol (6b). 3-Epi adduct **7c** (553 mg, 1.02 mmol) in anhydrous THF (50 ml) was refluxed with $LiAlH_4$ (500 mg, 13.2 mmol) under N_2 in the dark for 11 h. After standing for 8 h at room temperature, the mixture was cooled in ice, and ethyl acetate (5 ml) was added dropwise followed by H_2O (1 ml) and ether (100 ml). The mixture was dried (Na_2SO_4), filtered, and evaporated to a semicrystalline residue. The major product was isolated by preparative TLC (ethyl acetate–hexane, 1:4, R_f 0.6) giving **6b**, 191 mg, as needles from MeOH: mp 128–130 °C; $[\alpha]^{30}D$ −51° (*c* 1.0, $CHCl_3$); ν_{max} ($CHCl_3$) 3620, 3450 (br), 1480, 1400, 1005 cm^{-1}; λ_{max} (EtOH) 252 nm (infl, ε 4260), 262 (infl, 7180), 269 (9550), 280 (10 500), 291 (6150); NMR ($CDCl_3$) δ 0.62 (3 H, s), 0.81 (3 H, s), 0.9–2.5 (35 H, m), 4.10 (1 H, dd, $J_1 = J_2$ = 3 Hz), 5.40 and 5.66 (2 H, AB, J_{AB} = 6 Hz, further coupled with *J* = 2 Hz).

Anal. Calcd for $C_{27}H_{44}O$: C, 84.56; H, 11.49. Found: C, 84.31; H, 11.53.

3-*epi*-Precholecalciferol (9). 3-*epi*-7-Dehydrocholesterol (**6b**, 191 mg) in ether (400 ml), in a quartz reaction vessel equipped with an inlet for rapid flushing with N_2, was irradiated for 30 min in a Rayonet RPR-100 reactor equipped with RPR-3000 Å lamps. The solution was then evaporated in vacuo at room temperature to an oil. The major product was isolated by preparative TLC (ethyl acetate–hexane, 1:9, R_f 0.5) giving 3-*epi*-precholecalciferol (**9**): 95 mg (glass); $[\alpha]^{28}D$ +34° (*c* 1.9, $CHCl_3$); ν_{max} ($CHCl_3$) 3620, 3450 (br), 1450, 1380, 1218, 1035 cm^{-1}; λ_{max} (EtOH) 260 nm (8200); NMR ($CDCl_3$) δ 0.71 (3 H, s), 0.84 (3 H, d, *J* = 6 Hz), 0.7–2.8 (34 H, m), 3.91 (1 H, m), 5.56 (1 H, br s), 5.71 and 6.03 (2 H, AB, J_{AB} = 12 Hz).

3-*epi*-Cholecalciferol (4). The 3-*epi*-precholecalciferol (93 mg) was refluxed for 3 h in benzene (20 ml) and MeOH (2 ml) under N_2 in the dark. The solution was evaporated in vacuo to a glass which was separated by preparative TLC (EtOAc–hexane, 1:9, R_f 0.4) giving **4**; 65 mg; $[\alpha]^{26}D$ −5.4° (*c* 2, $CHCl_3$); ν_{max} ($CHCl_3$) 3630, 3450 (br), 1480, 1450, 1395, 1050, 910 cm^{-1}; λ_{max} (EtOH) 264 nm (ε 17 000); NMR ($CDCl_3$) δ 0.55 (3 H, s), 0.87 (3 H, d, *J* = 6 Hz), 1.0–3.0 (33 H, m), 3.94 (1 H, m), 4.90 (1 H, d, *J* = 3 Hz), 5.12 (1 H, br s, $W_{1/2}$ = 5 Hz), 6.09 and 6.34 (2 H, AB, J_{AB} = 12 Hz).

5,6-*trans*-3-*epi*-Cholecalciferol (5). 3-*epi*-Cholecalciferol (**4**, 30 mg) in petroleum ether (bp 35–60 °C, 40 ml) was treated with a solution of iodine (1 mg) in petroleum ether (10 ml) for 2 h in "diffuse daylight"[7] (the flask was placed near a window on a bright, hazy day at noon). After evaporation of the solvent in vacuo, the product was separated by preparative TLC (ethyl acetate–hexane, 1:9) giving recovered **4** (15 mg) and the faster running **5** (10 mg), as a noncrystalline glass: $[\alpha]^{26}D$ +34° (*c* 1, $CHCl_3$); λ_{max} (EtOH) 272 nm (ε 22 000); NMR ($CDCl_3$) δ 0.54 (3 H, s), 0.8–3.3 (36 H, complex multiplet), 3.9 (1 H, broad m), 4.71 (1 H, br s), 5.00 (1 H, br s), 5.88 and 6.62 (2 H, AB, J_{AB} = 12 Hz).

Acknowledgment. This work was supported by Grant AM 17057 from the National Institute of Arthritis, Metabolism, and Digestive Diseases.

Registry No.—**4**, 57651-82-8; **5**, 57651-83-9; **6a**, 434-16-2; **6b**, 57651-84-0; **7a**, 57637-86-2; **7b**, 57637-87-3; **7c**, 57651-85-1; **9**, 57651-22-6; 4-phenyl-1,2,4-triazoline-3,5-dione, 15988-11-1.

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A Facile Synthesis of the Cyclohexyl Constituents of the Boll Weevil Sex Pheromone

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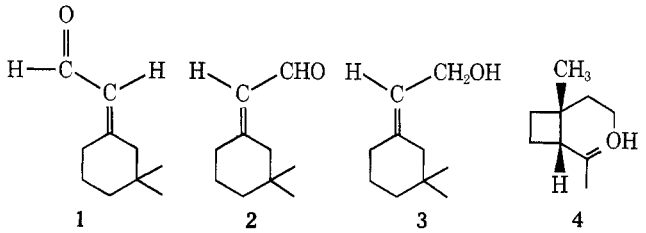
The four monoterpene compounds [(*E*)-3,3-dimethyl-$\Delta^{1,\alpha}$-cyclohexaneacetaldehyde (**1**), (*Z*)-3,3-dimethyl-$\Delta^{1,\alpha}$-cyclohexaneacetaldehyde (**2**), (*Z*)-3,3-dimethyl-$\Delta^{1,\beta}$-cyclohexaneethanol (**3**), and (+)-*cis*-2-isopropenyl-1-methylcyclobutaneethanol (**4**)] that comprise the pheromone of

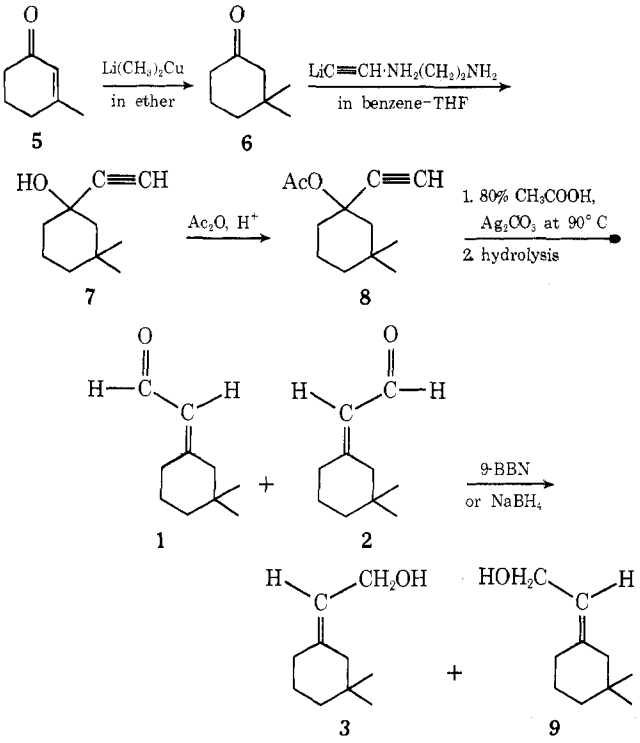


1 2 3 4

male boll weevil *Anthonomus grandis* Boheman were identified and first synthesized by Tumlinson et al.[1] These sex attractants are currently of considerable interest since they may provide a generally nontoxic method of surveying and controlling boll weevil population.[1] The growing concern over the environmental pollution and ecological imbalance caused by insecticides has further stimulated interest in this area. The commercial importance of these sex attractants prompted us to develop an efficient, high-yield synthesis of these compounds.[2,3] This paper describes a facile route from commercially available 3-methyl-2-cyclohexenone to the *E* and *Z* aldehyde components (**1** and **2**) in 80% overall yield. Separation of the aldehyde mixture,[4] followed by reduction of aldehyde **2** with $NaBH_4$ or 9-BBN, affords a route to the component *Z* alcohol (**3**) in an essentially quantitative yield. Scheme I outlines the synthesis of sex pheromone components **1**, **2**, and **3**.

The known 3,3-dimethylcyclohexanone (**6**), the same intermediate utilized in the previous syntheses,[1,2] was prepared from commercially available 3-methyl-2-cyclohexenone (**5**) by conjugate addition of lithium dimethylcopper in 98% yield.[5] Addition of lithium acetylide–ethylenedi-

Scheme I



amine complex[6] in benzene and THF to **6** afforded, in a yield of 96%, 1-ethynyl-3,3-dimethylcyclohexanol (**7**). A study was subsequently undertaken to determine the stereoselectively of a Meyer–Schuster type rearrangement of compound **7**. The latter was converted into the corresponding acetate **8** by treating with acetic anhydride in the presence of catalytic amounts of phosphoric acid for 12–15 h at room temperature or refluxing with acetic anhydride and pyridine under a nitrogen atmosphere for 2.5 h in 85–90% yield. Compound **8** was refluxed at 90°C with 80% acetic acid, sodium carbonate, and catalytic amounts of silver carbonate[7,8] under an argon atmosphere for 1.5 h. The resulting mixture was hydrolyzed to give the desired aldehydes **1** and **2** in a 47:53 mixture[9] in 88–90% yield. Compound **8** showed very little stereoselectivity in a Meyer–Schuster type rearrangement. Aldehydes **1** and **2** can also be synthesized directly from compound **7** in a yield of 85% without isolating the intermediate compound **8**. This route provided aldehydes **1** and **2** in an overall yield[10] of 82% from 3,3-dimethylcyclohexanone (**6**). A mixture of aldehydes **1** and **2** was reduced with $NaBH_4$ *or* 9-BBN[11] to give the corresponding mixture of *Z* alcohol (**3**) and its *E* isomer (**9**) in quantitative yield.

Experimental Section

Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, Ga. Infrared (ir) spectra were determined as film with a Perkin-Elmer Model 257 G spectrometer. Mass spectra were taken with a Hewlett-Packard 5930 quadrupole mass spectrometer operating with an ionization energy of 70 eV. NMR spectra were taken in deuteriochloroform with a Varian T-60 spectrometer. Tetramethylsilane was used as an internal standard. Bulb-to-bulb evaporative distillation was carried out using Buchi Kugelrohrofen.

3,3-Dimethylcyclohexanone (6). To a cold (0°C) solution of lithium dimethylcuprate, prepared from 9.0 g (47 mmol) of copper(I) iodide and 111 mmol of methyllithium in 145 ml of ether, was added dropwise with stirring over a 20-min period a solution of 5.00 g (45.5 mmol) of redistilled 3-methyl-2-cyclohexenone (**5**), bp 84–85°C (13 mm). During the addition some methylcopper separated from the reaction mixture as a yellow precipitate. The resulting mixture was stirred at room temperature for 20 min and then poured into an aqueous solution (pH ~8) of ammonium chloride and ammonia. The combined ether phase and extracts were washed with brine, dried with anhydrous $MgSO_4$, and concentrated in vacuo to give 5.55 g (98%) of 3,3-dimethylcyclohexanone (**6**): bp 58–60°C (15 mm); ν_{max} (film) 1725 cm^{-1}; NMR δ 0.95 (s, 6 H, geminal CH_3) and 2.06 [s, 2 H, $-COCH_2C(CH_3)_2$].

1-Ethynyl-3,3-dimethylcyclohexanol (7). Lithium acetylide–ethylenediamine (1.1 g, 11 mmol) was placed in the nitrogen-flushed reactor, followed by 10 ml of dry benzene and tetrahydrofuran (50:50 mixture). Stirring was started, the mixture was warmed to 35°C, and 1.26 g (10 mmol) of ketone (**6**) was added dropwise over a period of 5 min, while maintaining temperature at 35°C by cooling. This mixture was stirred for 2 h at room temperature. Water (10 ml) was added slowly to hydrolyze the mixture after which it was brought to gentle reflux and held for 15 min. The organic layer was separated, dried with anhydrous $MgSO_4$, and concentrated in vacuo to give 1.46 g (96%) of 1-ethynyl-3,3-dimethylcyclohexanol (**7**): ν_{max} (film) 3415, 3310 and 2350 cm^{-1} (–C≡CH, very weak); NMR[12] ($CDCl_3$) δ 0.98 and 1.00 (two singlets for geminal methyl group), 1.70 [s, 2 H, $RR'C-CH_2C(CH_3)_2$], 2.30 (s, 1 H, –OH), and 2.48 (s, 1 H, –C≡CH).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.60. Found: C, 79.08; H, 10.57.

Acetylation of 1-Ethynyl-3,3-dimethylcyclohexanol (7). To a solution of 1-ethynyl-3,3-dimethylcyclohexanol (**7**, 500 mg) in 3 ml of acetic anhydride, a few drops of phosphoric acid (catalytic amount) were added. After a few minutes the solution became warm and turned light pink in color. The resulting mixture was allowed to stand for 12–15 h at room temperature, and then extracted with petroleum ether. The extract was washed with water and dried over $MgSO_4$. On removal of the solvent, an oily acetate (**8**) was obtained in 90% yield: ν_{max} 3280, 2100 (very weak), 1750 cm^{-1}; NMR ($CDCl_3$) δ 0.98 and 1.00 (two singlets for geminal methyl group), 2.04 (s, 3 H, $-OCOCH_3$), 2.60 (s, 1 H, –C≡CH).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.18; H, 9.34. Found: C, 73.98; H, 9.26.

Aldehydes 1 and 2. To acetate **8** (970 mg) dissolved in 3 ml of 80% acetic acid were added 50 mg of sodium carbonate and 20 mg of silver carbonate. The reaction mixture was refluxed at 90°C under an argon atmosphere for 1.5 h. After cooling the resulting mixture was poured into ice water (10 ml), and the mixture was extracted with methylene chloride. The combined extracts were washed with water, 5% aqueous $NaHCO_3$, and water, dried ($MgSO_4$), and evaporated to give 669 mg (88%) of a mixture of aldehydes **1** and **2**, showing properties consistent with those reported by Tumlinson:[1] ν_{max} (film) 1680 and 1640 cm^{-1}; NMR ($CDCl_3$) peaks at δ 0.90 (s, 6 H, geminal CH_3), 2.00 (s, 2 H, CH_2 trans to aldehyde group), 5.74 (d, 1 H, –C=CH–), 10.02 (d, 1 H, –CHO) were assigned to **1**, while those at δ 0.95 (s, 6 H, geminal CH_3), 2.40 (s, 2 H, CH_2 cis to aldehyde group), 5.88 (d, 1 H, –C=CH–), and 9.98 (d, 1 H, –CHO) were assigned to **2**. Aldehydes **1** and **2** were identical with authentic samples.[10]

Alcohols 3 and 9. To a solution of 100 mg of the mixture of aldehydes **1** and **2** in absolute ethanol (6 ml), 50 mg of $NaBH_4$ was added. The reaction mixture was stirred for 1 h at room temperature. The resulting mixture was hydrolyzed with water and extracted three times with methylene chloride. The combined extracts were washed with water, dried over anhydrous $MgSO_4$, and evaporated in vacuo to give alcohols **3** and **9** in a quantitative yield. The spectral properties of **3** and **9** were consistent with those reported by Tumlinson and co-workers.[1]

Registry No.—**1**, 26532-25-2; **2**, 26532-24-1; **3**, 26532-23-0; **5**, 1193-18-6; **6**, 2979-19-3; **7**, 57559-98-5; **8**, 57559-99-6; **9**, 30346-27-1.

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Synthesis of 4-Cyano-4′-halobiphenyls

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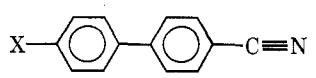
As part of a study of intermolecular halogen–cyanide interactions in the solid state it was desired to prepare very pure samples of the 4-cyano-4′-halobiphenyls. Pummerer and Seligsberger[1] have previously reported the synthesis of Ia and Niwa[2] has reported the synthesis of Ib and Ic. We



Ia, X = I
b, X = Br
c, X = Cl

wish to report the synthesis of these compounds by a different and very simple route involving the displacement of halogen with CuCN in refluxing dimethylformamide[3] (for the iodide and bromide) and *N*-methylpyrrolidone[4] (for the chloride).

For the synthesis of Ia and Ib the reaction was run with 1 equiv of CuCN per mole of the dihalogenated biphenyl. The reaction mixture was very conveniently separated by preparative thin layer chromatography. In a few runs the main components of the reaction mixture were isolated and were approximately those expected for a statistical reaction. An attempt was made to run the displacement reaction on 4,4′-dichlorobiphenyl in refluxing dimethylformamide but even at long reaction times no product could be detected. Use of the higher boiling solvent *N*-methylpyrrolidone, an excess of CuCN, and long reflux times were necessary for a successful synthesis of Ic.

Experimental Section

Melting points were determined on a Mel-Temp apparatus and are uncorrected. Laser Raman spectra were obtained with a Jeol Model JRS-S1 spectrometer equipped with an argon ion laser. Preparative thin layer chromatography was done on silica gel G PF-254 (E. Merck) using benzene as developer. Compounds were detected using an ultraviolet lamp and products extracted with methanol–chloroform (1:19). Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

4-Cyano-4′-iodobiphenyl (Ia). 4,4′-Diiodobiphenyl (0.50 g, 1.2 mmol), cuprous cyanide (0.11 g, 1.2 mmol), and 15 ml of dimethylformamide were placed in a 50-ml round-bottomed flask and refluxed for 2.5 hr. After cooling, 35 ml of ferric chloride solution (200 g of hydrated $FeCl_3$ and 50 ml of concentrated HCl in 300 ml of water) was added to the reaction vessel. The resulting mixture was heated at 60–70 °C for 20 min. The dimethylformamide–ferric chloride mixture was extracted three times with approximately 20 ml of toluene. The reddish toluene layer was then extracted with 50 ml of 10% HCl, 20 ml of water, and 50 ml of 5% NaOH. The toluene layer was dried over $MgSO_4$ and filtered. The toluene was evaporated at reduced pressure and the residue fractionated by preparative thin layer chromatography. The desired product has R_f 0.51 in benzene. The crude product was sublimed at 135 °C (1 mm), affording 4-cyano-4′-iodobiphenyl (160 mg, 42%). An analytical sample recrystallized from absolute ethanol melted at 179.5–181.5 °C (lit.[1] 166 °C), laser Raman (crystal) 2225 cm^{-1} (–C≡N).

Anal. Calcd for $C_{13}H_8NI$: C, 51.17; H, 2.64; N, 4.59; I, 41.59. Found: C, 51.05; H, 2.59; N, 4.58; I, 41.65.

4-Bromo-4′-cyanobiphenyl (Ib). The procedure was identical with one used for the iodo compound, except that 4,4′-dibromobiphenyl (0.50 g, 1.6 mmol) and cuprous cyanide (0.14 g, 1.6 mmol) were refluxed in dimethylformamide for 4.0 h. The R_f of 4-bromo-4′-cyanobiphenyl is 0.50 in benzene. The crude product was sublimed at approximately 120 °C (1 mm), producing 4-bromo-4′-cyanobiphenyl (210 mg, 50%). A sample recrystallized from absolute ethanol had mp 153.5–155 °C (lit.[2] 144 °C), laser Raman (crystal) 2225 cm^{-1} (–C≡N). An analysis of this compound was not performed. Its identity has been confirmed unambiguously by a complete x-ray analysis.[5]

4-Chloro-4′-cyanobiphenyl (Ic). The procedure used was similar to the one used for the iodo compound, except that 4,4′-dichlorobiphenyl (0.50 g, 2.2 mmol) and cuprous cyanide (0.40 g, 4.46 mmol) were refluxed for 93.0 h in *N*-methylpyrrolidone. The R_f of the product is 0.48 in benzene. The crude product was sublimed at about 105 °C (1 mm), affording 4-chloro-4′-cyanobiphenyl (110 mg, 23%). An analytical sample recrystallized from absolute ethanol melted at 133–133.5 °C (lit.[2] 129–130°C), laser Raman (crystal) 2225 cm^{-1} (–C≡N).

Anal. Calcd for $C_{13}H_8NCl$: C, 73.07; H, 3.77; N, 6.56; Cl, 16.60. Found: C, 73.24; H, 3.78; N, 6.45; Cl, 16.40.

Acknowledgment. We thank Professor Stuart Fenton for the laser Raman spectra and Professor Doyle Britton for his continued interest in this work.

Registry No.—Ia, 57774-34-2; Ib, 57774-35-3; Ic, 57774-36-4; cuprous cyanide, 544-92-3; 4,4′-diiodobiphenyl, 3001-15-8; ; 4,4′-dibromobiphenyl, 92-86-4; 4,4′-dichlorobiphenyl, 2050-68-2.

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A Convenient Synthesis of Labile Optically Active Secondary Alkyl Bromides from Chiral Alcohols

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Recent interest and reports[1-3] concerning the synthesis of optically active secondary alkyl halides prompts this disclosure of our experience in the area and of a convenient preparative procedure for active bromides, including those which are prone toward racemization.

Conceivably, one of the simplest approaches to the preparation of active halides involves treatment of the corresponding chiral alcohol with a phosphorus trihalide as in eq 1–4. Unfortunately, in practice this method has met with considerable difficulty primarily because the reactions represented by eq 3 and 4 are slow and have afforded halides of much lower optical purity.[1,4-6] To alleviate this problem, HX is commonly swept out (CO_2 or N_2) which essentially eliminates the last two steps (eq 3 and 4).

This produces product of high optical purity but the resulting low yields (i.e., 23% 2-bromooctane from 2-octanol)[1,7] severely limit the usefulness of the procedure, espe-