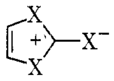
The reactions reported here provide an excellent opportunity to study the comparative reactivities and properties of sulfur and selenium in organic compounds. Furthermore, **1** and **4–8** are of interest as potential 6π-pseudo-aromatic systems in which each ring heteroatom contributes an electron pair as illustrated by the resonance structure **11**.[7] Synthetically, these compounds have gained attention as intermediates in the preparation of tetrathiofulvalene derivatives (**12**) which have recently been reported to form highly conducting charge-transfer salts.[8-11]



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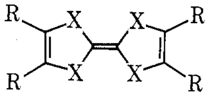

12

Experimental Section

General. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Molecular ion values (*m/e*) reported for compounds containing selenium are based on ^{80}Se. Some of the selenium compounds involved in the synthetic procedures described herein (*e.g.*, CSe_2 and H_2Se) are extremely toxic and difficult to control, and appropriate precautions should be exercised in handling such materials.

Reaction of Sodium Acetylide with Selenium and Carbon Disulfide. A 1-l., three-necked flask, equipped with an efficient mechanical stirrer, Dry Ice condenser, and gas inlet for acetylene was placed in a Dry Ice bath and 300 ml of ammonia added. While acetylene was being bubbled through the ammonia, 4.6 g of sodium (0.2 g-atom) was added in small portions. After the sodium had reacted, the Dry Ice bath was removed, and 200 ml of anhydrous ether and 15.8 g of powdered selenium (0.2 g-atom) were added with vigorous stirring. The ammonia was allowed to evaporate and 300 ml of acetonitrile added. Carbon disulfide (15.2 g, 0.2 mol) in 100 ml of ether was added dropwise over 1 hr. The reaction was stirred for 1 hr more, and acidified with 10% aqueous HCl. The mixture was then extracted several times with ether[12] and dried ($MgSO_4$) and the ether removed. The remaining tarry material was extracted with several portions of hot methylcyclohexane[13] from which crystallized 2.8 g of a yellow-orange solid. Column chromatography (3 ft, silica gel column, 5% $CHCl_3$ in CCl_4 eluent) on this material easily separated five products which were further purified either by recrystallization (hexane) or sublimation. Characterization of the products is based on their ir, nmr, and uv-visible spectra (see Table II), mass spectra, and elemental analyses[4] and they are the following. 1,3-Dithiole-2-thione (**1**): yellow solid; mp 49.5° (lit. 48.4°,[1] 50°[4]); *m/e* 13.4; 1,3-Thiaselenole-2-thione (**4**): yellow solid; mp 60.5°; *m/e* 182; 1,3-Dithiole-2-selone (**5**): orange solid; mp 59–60°; *m/e* 182; 1,3-Thiaselenole-2-selone (**6**): orange solid, mp 80–81°; *m/e* 230; 1,3-Diselenole-2-thione (**7**): yellow solid; mp 83–84°; *m/e* 230.

Reaction of Sodium Acetylide with Sulfur and Carbon Diselenide. The same experimental conditions as described above were followed. However, extreme care should be taken due to the high toxicity and foul smell of carbon diselenide.[14] On a 0.2 mol preparative scale, 1.5 g of a red solid was isolated from which were separated compounds **1** and **4–7** and also 1,3-diselenole-2-selone (**8**): red solid; mp 113.5–114°; *m/e* 278 (see Table II for ir, nmr, and uv–visible data).

Reaction of Sodium Acetylide with Selenium and Carbon Diselenide. The same experimental conditions as described above were followed to give **8** in yields varying from 10 to 25%.

Reaction of 1,3-Diselenole-2-selone (8) with P_4S_{10}. To 0.275 g of **8** (1 mmol) in 15 ml of benzene was added 1.0 g of P_4S_{10} (Pfaltz and Bauer) with stirring, and the solution was refluxed for 3 hr. Work-up consisted of filtering, adding ether, washing with $NaHCO_3$, and drying ($MgSO_4$). Evaporation of the ether gave a yellow-brown solid which was placed on a short silica gel column, and eluted with 5% $CHCl_3$ in CCl_4 to give a bright yellow solid identified as 1,3-diselenole-2-thione (**7**) in 25% yield.

Reaction of Sodium Methylacetylide with Selenium and Carbon Disulfide. The same experimental conditions as described above were followed to give, on a 0.2 mol preparative scale, 6.5 g of 5-methyl-1,3-thiaselenole-2-thione (**3**) (25% yield) as a yellow-orange solid: mp 34–35°; ir ($CDCl_3$) 1060 cm^{-1}; nmr (δ, rel to TMS, CCl_4) 2.28 (3 H, doublet), 7.20 (1 H, quartet), $J_{\text{allylic}} = 1.5$ Hz; *m/e* 196.

Reaction of Sodium Acetylide with Sulfur and Carbon Disulfide in the Presence of 8. The same experimental conditions as described above were followed on a 0.1 mol preparative scale, except that during the addition of carbon disulfide, **8** (0.1 g) was also added. High-pressure liquid chromatography revealed the presence of three products which were subsequently separated by column chromatography (5% $CHCl_3$ in CCl_4, silica gel) and identified by their ir and nmr spectra as **1** (~95% of product mixture), **4** (~4%), and **7** (~1%).

Acknowledgment. We thank D. Green for helpful discussions.

Registry No.—**1**, 930-35-8; **3**, 53555-43-4; **4**, 1120-65-6; **5**, 53555-44-5; **6**, 53555-45-6; **7**, 53555-46-7; **8**, 53555-47-8; sodium acetylide, 1066-26-8; selenium, 7782-49-2; carbon disulfide, 75-15-0; carbon diselenide, 506-80-9; sulfur, 7704-34-9; sodium methylacetylide, 10486-71-2.

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(12) Some difficulty was experienced in distinguishing the water–ether layer during the extraction step. An alternate work-up procedure has been developed by Dr. F. Wudl, Bell Laboratories, Murray Hill, N.J., which involves extraction of the acidified reaction mixture with a lighter-than-water liquid–liquid extractor, and extraction with hexane over a period of several hours.

(13) No rearrangement was observed upon refluxing **4** in methylcyclohexane for 1 day.

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A Simple Synthesis of γ-Bisabolene

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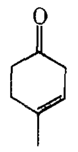
To pursue our research on the biosynthesis of marine natural products, we were obliged to synthesize γ-bisabolene. Our choice of synthetic strategies was limited because we required the capability of incorporating isotopic labels during the penultimate stages of the synthesis. We explored the only previous stereoselective synthesis of γ-bisabolene[1] but could not repeat a key reaction to our satisfaction. We have therefore devised a simple synthesis of γ-bisabolene based on the Claisen rearrangement. Hexadeuterio-γ-bisabolene was also prepared by this route.

4-Methyl-3-cyclohexen-1-one (**1**), prepared from *p*-cresol by the method of Braude and Webb,[2] was treated with



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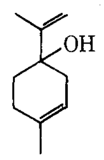

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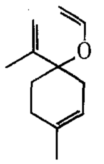

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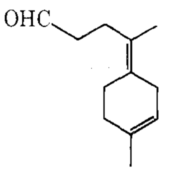
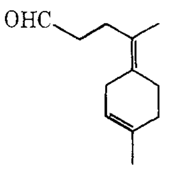


4a



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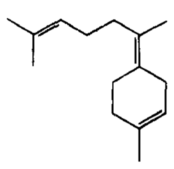
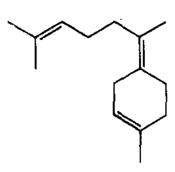


5a



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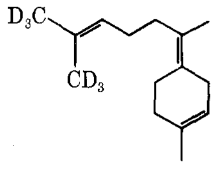
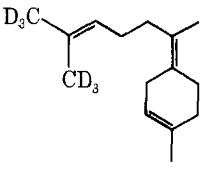
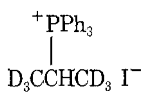


6a



6b



$\mathrm{D_3C}\overset{{}^{+}\mathrm{PPh_3}}{\overset{|}{\mathrm{C}}}\mathrm{HCD_3\ I^-}$

7

isopropenylmagnesium bromide in tetrahydrofuran solution at 0° to obtain the allylic alcohol (**2**) in 43% yield. The use of isopropenyllithium in this reaction caused the formation of 4-methyl-2-cyclohexen-1-one, which then underwent various side reactions. The alcohol **2** was converted into the corresponding vinyl ether **3** in 74% yield using the mercuric acetate catalyzed transetherification reaction.[3] Pyrolysis of the allyl vinyl ether **3** resulted in an almost quantitative conversion to the aldehyde **4** *via* the Claisen rearrangement.

Since the mercuric acetate catalyzed transetherification reaction was not reproducible, we investigated the possibility of combining the transetherification and pyrolysis reactions in order to remove the allyl vinyl ether **3** as it was formed and drive the transetherification reaction to completion. Acid catalyzed transetherification reactions[4] gave poor yields of the aldehyde **4** since the product underwent further reactions. The best conditions we found for this sequence involved heating the allylic alcohol **2** with 10 equiv of ethyl vinyl ether in the presence of 1 equiv of mercuric acetate and 2 equivalents of anhydrous sodium acetate under an argon atmosphere in a sealed tube at 100° for 16 hr.[5] Under these conditions an 81% yield of the aldehyde **4** was isolated after distillation. A Wittig reaction between the aldehyde **4** and isopropyltriphenylphosphonium ylide gave γ-bisabolene (**5**) in 45% yield.

The existence of two geometrical isomers of γ-bisabolene (**5a** and **5b**) has generally been ignored by previous investigators. The two γ-bisabolenes, isomeric about the tetrasubstituted olefinic bond, may be designated as (*E*)-γ-bisabolene (**5a**) and (*Z*)-γ-bisabolene (**5b**). The formation of both aldehydes **4a** and **4b** is a predictable outcome of the Claisen rearrangement. Thus our synthetic γ-bisabolene (**5**) was a mixture of both geometrical isomers in the ratio 60:40. The (*E*)- and (*Z*)-γ-bisabolenes may be separated by vpc on a 6-ft column of 2% Carbowax 20M or by spinning-band distillation. We have not found any spectral feature which permitted a structural assignment of the two stereoisomers.

The hexadeuterio-γ-bisabolenes (**6a** and **6b**) were prepared by the reaction of the aldehyde **4** with hexadeuterioisopropyltriphenylphosphonium ylide (**7**), which was, in turn, prepared from hexadeuterioisopropyl alcohol *via* hexadeuterioisopropyl iodide.[6] Only two peaks in the mass spectrum of hexadeuterio-γ-bisabolene (M^+ 210, $C_5H_3D_6$ 75) differ from those of γ-bisabolene (M^+ 204, C_5H_9 69) but this difference is sufficient to allow the detection of unlabeled γ-bisabolene in a hexadeuterio-γ-bisabolene carrier,[7] permitting its use in biosynthetic studies.

Experimental Section

Nmr spectra were obtained on Varian HR-220, T-60, or EM-360 spectrometers; infrared spectra on a Perkin-Elmer 700 spectrometer. Boiling points are uncorrected. Gas chromatographic analyses were performed on a Hewlett-Packard 402 instrument.

4-Methylcyclohex-3-enone (1) (The method of Braude and Webb[2]). A solution of redistilled *p*-methoxytoluene (61 g, 0.5 mol) in anhydrous ethyl ether (300 ml) was added to liquid ammonia (800 ml). After 15 min, small pieces of lithium wire (13.2 g, 1.9 equiv) were added over a 30-min period. Stirring was continued for 15 min, then ethanol (96.5 g, 2.1 mol) was added dropwise. Following addition of alcohol, the blue color disappeared and the ammonia was allowed to evaporate overnight. Ice (375 g) was added to residue, followed by a little water. The mixture was extracted with ether. The combined ether extracts were washed with water and concentrated to approximately 200 ml. The ether layer was stirred overnight with aqueous 2*M* oxalic acid (200 ml). The ether layer was separated, washed successively with sodium bicarbonate and water, dried over sodium sulfate, and distilled to obtain 4-methyl-3-cyclohexenone as a clear oil: bp 70–73° (20 mm), lit[2] bp 74° (17 mm); yield 49.6 g (89%); ir (film) 1720, 785 cm^{-1}; nmr (CCl_4) δ 1.80 (s, 3 H), 2.42 (s, 4 H, broad), 2.73 (s, 2 H, broad), 5.21 (t, 1 H).

4-Isopropenyl-4-hydroxy-1-methylcyclohexene (2). Magnesium metal shavings (3.645 g, 0.15 g-atom) were placed in a 250-ml 3-neck round-bottom flask equipped with a reflux condenser, a mechanical stirrer, and an additional funnel. The system was flushed with nitrogen for 15 min before addition of tetrahydrofuran (5 ml). A small volume of 2-bromopropene was added to the stirred solution. Glass chips were placed in the flask to help initiate the reaction. Once the reaction had started, the remainder of the bromide (18.1 g, 0.15 mol) in tetrahydrofuran solution (50 ml) was added. The reaction mixture was kept at <20° throughout addition. After approximately 1 hr, the brown solution was cooled to 0° with an ice-salt bath and the cyclohexenyl ketone (11.0 g, 0.1 mol) was added dropwise. The temperature was kept below 5° throughout addition. The reaction mixture was stirred for 3 hr at room temperature. The solution was poured into ice-cold ammonium chloride solution and extracted with ether. The extracts were combined and dried over anhydrous sodium sulfate and distilled to give 4-isopropenyl-4-hydroxy-1-methylcyclohexene: bp 85° (1 mm); yield 6.5 g (43%); ir (film) 3450, 1650, 1450, 1380, 910 cm^{-1}; nmr (CCl_4) δ 1.71 (s, 3 H), 1.80 (s, 3 H), 2.42 (s, 1 H), 4.72 (s, 1 H), 4.95 (s, 1 H), 5.25 (t, broad, 1 H); high resolution mass spectrum M^+ 152.1200, $C_{10}H_{16}O$ requires 152.1201.

4-Isopropenyl-1-methyl-1-cyclohexen-4-yl Vinyl Ether (3) (*cf.* Church, *et al.*[3]). 4-Isopropenyl-4-hydroxy-1-methylcyclohexene (**2**, 3.450 g, 22.6 mmol), mercuric acetate (7.20 g, 22.6.6 mmol, freshly recrystallized from ethanol containing a trace of acetic acid), and ethyl vinyl ether (200 ml, freshly distilled from sodium metal) were boiled under reflux for 48 hr under a nitrogen atmosphere. The mixture was cooled, glacial acetic acid (0.5 ml) was added, and the mixture was again stirred for 24 hr at room temperature. An equal volume of petroleum ether (30–60°) was added and the solution was washed with 5% potassium hydroxide solution (2 × 200 ml) and water (200 ml), then dried over anhydrous potassium carbonate. The petroleum-ether mixture was evaporated to a small volume (10 ml) which was placed on a 1 × 2 in. column of neutral alumina. Elution with petroleum ether (150 ml) afforded 4-isopropenyl-1-methyl-1-cyclohexen-4-yl vinyl ether: yield 2.96 g (74%); ir (film) 1635, 1185 cm^{-1}; nmr (CCl_4) δ 1.69 (s, 3 H), 1.75 (s, 3 H), 1.90 (s, broad, 4 H), 2.21 (multiplet 2 H), 3.89 (d, 1 H, J = 4 Hz), 4.25 (d, 1 H, J = 4 Hz), 4.90 (s, 2 H), 5.20 (t, 1 H), 6.08 (double doublet 1 H, J = 14, 4 Hz).

4-Methyl-1-(1′-propanalethylidene)-3-cyclohexene (4a, 4b). 4-Isopropenyl-1-methylcyclohex-1-en-4-yl vinyl ether (2.96 g, 16 mmol) was dissolved in dry toluene (10 ml) and heated at 110° for 2 hr, after which thin layer chromatography showed disappearance of the vinyl ether. Kugelrohr distillation of the product gave the pure aldehyde, 4-methyl-1-(1′-propanalethylidene)-3-cyclohexene:

bp 96° (0.1 mm); yield 2.53 g (86%); ir (film) 2740, 1725, 740 cm^{-1}; nmr (CCl_4) δ 1.65 (s, 6 H), 2.39 (s, 4 H, broad), 2.68 (3, 2 H), 5.28 (t, 1 H), 9.70 (d, 1 H); high resolution mass spectrum M^+ 178.1359, $C_{12}H_{18}O$ requires 178.1358. The aldehyde consisted of a 41:59 ratio of stereoisomers as determined by vpc (1% OV-1).

4-Methyl-1-(1′-propanalethylidene)-3-cyclohexene (4a, 4b). Alternate Method. 4-Isopropenyl-4-hydroxy-1-methylcyclohex-1-ene 2 (2.50 g, 22 mmol), ethyl vinyl ether (10 ml, 180 mm), mercuric acetate (6.39 g, 20 mmol) and anhydrous sodium acetate (2.46 g, 30 mmol) were sealed in a thick glass ampule under an argon atmosphere. The mixture was heated to 100° for 15 hr. The mixture was then cooled, petroleum ether (30–60°) (50 ml) was added, and the solution was washed with 5% potassium hydroxide solution (2 × 100 ml) followed by water (2 × 100 ml). The organic phase was separated and dried over anhydrous sodium carbonate and solvent evaporated. Short-path distillation of the oily residue yielded a clear sweet-smelling oil, 4-methyl-1-(1′-propanalethylidene)-3-cyclohexene, identical with the material synthesized in the two-step procedure: yield 2.10 g (82%).

γ-Bisabolene (5a, 5b). A 100-ml round-bottom 3-neck flask equipped with a magnetic stirrer, a reflux condenser, and a rubber septum was flushed with nitrogen to ensure dryness. Isopropyltriphenylphosphonium iodide[8] (669.3 mg, 1.55 mmol) was added. Dry tetrahydrofuran (5 ml) was added, and the solution was cooled to 0°. *n*-Butyllithium (0.68 ml, 1.50 mmol, 2*M*) was added dropwise to obtain an intense-red-colored solution which was stirred at 0° for 30 min. A solution of the aldehyde (267 mg, 150 mmol) in tetrahydrofuran was added. The solution was stirred at 40° for 30 min, then at room temperature for 3 hr. The mixture was poured onto ice-water and extracted with petroleum ether (30–60°). The hydrocarbon layer was washed several times with water and dried over sodium sulfate. The solvent was evaporated, yielding a clear oil (200 mg). The oil was purified by preparative thin layer chromatography on silica gel PF-254 to obtain a hydrocarbon whose spectral properties were identical to those of a commercial sample of γ-bisabolene[9]: yield 150 mg (49%); ir (CCl_4) 1680, 1460, 1380, 1240, 1180, 1160, 1120, 940 cm^{-1}; nmr (CCl_4) δ 1.56 (s, 3 H), 1.62 (s, 9 H), 2.01 (s, 6 H), 2.23 (m, 2 H), 2.68 (s, 2 H), 5.10 (t, 1 H), 5.27 (2, 1 H); high resolution mass spectrum M^+ 204.1884, $C_{15}H_{24}$ requires 204.1878. The synthetic mixture consisted of a 60:40 mixture of stereoisomers, as determined by vpc on 1% OV-1. The spectral data were in close agreement with published values.[10]

1,1,1,3,3,3-Hexadeuterio-2-propyltriphenylphosphonium Iodide (7). A solution of acetone-d_6 (20 g, 0.31 mol) in anhydrous ether (25 ml) was added dropwise to a cooled slurry of lithium aluminum hydride (6.07 g, 0.16 mol) in anhydrous ether (75 ml) and the mixture was stirred for 30 min at 0°. Dropwise addition of water (5 ml) was followed by dropwise addition of 15% sodium hydroxide solution (6 ml) and finally water (18 ml). A granular precipitate was removed by filtration and the ether extract dried over sodium sulfate.

The dried solution was added to a stirred solution of *o*-phenylene phosphochlorite (50.4 g, 0.29 mol) and dry pyridine (22.9 g, 0.29 mol) in ether (400 ml) at 0°. The mixture was allowed to stand for 18 hr at 25°. Pyridine hydrochloride was removed by filtration and the solvent evaporated *in vacuo* to yield an oil. Distillation of the oil gave hexadeuterioisopropyl-*o*-phenylene phosphite: yield 45 g (77%); bp 54° (1 mm); ir (film) 3100, 2250, 1600 cm^{-1}; nmr (CCl_4) δ 4.17 (d, 1 H), 7.08 (s, 4 H); high resolution mass spectrum M^+ 204.0825, $C_9H_5D_6O_3P$ requires 204.0822.

Iodine (50.4 g, 0.1 mol) was added to a solution of the phosphite (20.4 g, 0.1 mol) in dichloromethane (400 ml). The solution was stirred for 15 hr at 25° and then extracted with 5% sodium hydroxide solution (400 ml), 5% sodium bisulfite solution (200 ml), and saturated sodium chloride solution (200 ml). The dichloromethane layer was dried over anhydrous sodium sulfate and the solvent then carefully distilled at atmospheric pressure. The residue was distilled to obtain hexadeuterioisopropyl iodide: yield 13.9 g (79%); bp 88°; ir (film) 2950, 2250 cm^{-1}; nmr (CCl_4) δ 4.23 (s, 1 H). This material rapidly decomposes and was used without further purification.

The iodide (13.9 g, 79 mmol) and triphenylphosphine (20.43 g, 78 mmol) were heated together to 100°. The melt was stirred for 15 hr at 100° using an efficient reflux condenser to prevent loss of the iodide. The salt was allowed to cool and washed with petroleum ether. The crude product was recrystallized from ethanol (100%) to obtain white crystals of hexadeuterioisopropyltriphenylphosphonium iodide: yield 15.1 g (45%); mp >200° dec; nmr ($CDCl_3$) δ 4.95 (d, 1 H), 7.40 (s, 5 H), 7.85 (s, 10 H).

Hexadeuterio-γ-bisabolene (6). A 2.2 *M* solution of *n*-butyllithium in hexane (2.88 ml, 6.36 mmol) was added to a stirred solution of hexadeuterioisopropyltriphenylphosphonium iodide (2.80 g, 6.40 mmol) in tetrahydrofuran (25 ml) under an argon atmosphere at 0°. After stirring for 30 min at 0°, a solution of the aldehyde (1.13 g, 6.36 mmol) in tetrahydrofuran (20 ml) was added. The reaction was worked up according to the procedure for γ-bisabolene to obtain hexadeuterio-γ-bisabolene as a clear oil: yield 547 mg (41%); high resolution mass spectrum M^+ 210.2255 $C_{15}H_{18}D_6$ requires 210.2254.

Acknowledgments. This research was supported by a training grant (GM-01045-11) from the National Institutes of Health and by unrestricted grants from Abbott Laboratories and Hoffmann-La Roche.

Registry No.—**1**, 5259-65-4; **2**, 3419-02-1; **3**, 53586-54-2; **4a**, 53585-11-8; **4b**, 53585-12-9; **5a**, 53585-13-0; **5b**, 13062-00-5; **6a**, 53585-14-1; **6b**, 53586-55-3; **7**, 1787-43-5; 2-bromopropene, 557-93-7; acetone-d_6, 666-52-4; *o*-phenylene phosphochlorite, 1499-17-8; hexadeuterioisopropyl-*o*-phenylene phosphite, 53535-10-7; hexadeuterioisopropyl iodide, 39091-64-0; triphenylphosphine, 603-35-0.

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